Impurity Conduction in Silicon*

R. K. Ray and H. Y. Fan
Purdue University, Lafayette, Indiana
(Received September 23, 1960)

Impurity conduction at low temperature was investigated for various p- and n-type silicon samples. Emphasis was placed on the study of samples of low impurity concentration where the conduction is attributed to charge exchange between impurity centers which are partially ionized by some compensating impurity. A new method was used to determine the compensation. Donors were added to p-type samples by heat treatment. From changes in the room temperature resistivity and the Hall coefficient in the deionization range, the added compensation and the original compensation were determined. The measurement of various samples gave the dependence of the activation energy of conduction on impurity concentration and degree of compensation. The activation energy was much larger for the Ga- and Al-doped samples than for the B-doped samples of comparable impurity concentration. However, it was found that the high activation energies may be the result of ion-pairing between gallium or aluminum atoms and the compensating impurity in the sample. The conductivities of the various samples may be correlated by an expression of conductivity which involves the impurity concentration and the radius of impurity wave function. The results are discussed in the light of current theories of impurity conduction.

I. INTRODUCTION

THE resistivity and Hall coefficient of silicon exhibit the characteristics of impurity conduction at sufficiently low temperature.[1-3] The Hall coefficient passes through a maximum and the resistivity increases more slowly with decreasing temperature, corresponding to an activation energy which is much lower than the ionization energy of the impurity. These phenomena are indicative of impurity conduction which has been observed in various semiconductors.[4] The most extensive investigations have been made in the case of germanium,[5-10] in which the impurity conduction was first discovered by Hung and Gliessman.[5] Measurements on samples of a wide range of impurity concentration[7,9] suggest that different conduction processes may be distinguished.

At high impurity concentration, the conduction may be explained in terms of an impurity band formed as a result of the overlapping of the wave functions of neighboring impurity atoms.[5,11-14] Carriers in this band may give conduction. The presence of compensating impurities is not necessary. At low impurity concentration, overlapping of the wave functions is not sufficient to form a band. The carriers are localized on the isolated impurity atoms at low temperature. Conduction is not possible in a set of weakly interacting impurities which are all neutral. However, any compensating impurity that is present ionizes some of the majority impurity atoms. Charge exchange between the neutral and the ionized centers becomes possible, giving rise to conduction. Thus an ionized center may be considered as having a carrier for impurity conduction. Atoms of the compensating impurity are permanently ionized and do not actually take part in the conduction, but their presence is essential.

At Purdue, the concept of two different types of impurity conduction evolved in the course of experimental investigation made on germanium.[5,7] The concept has been used also in various treatments of the problem by different authors, including Gudden and Schottky,[15] Schottky,[16] Conwell,[17] Aigrain,[18] and Mott.[19] A clear contrast between the effects of added compensation on the different types of impurity conduction was shown experimentally by Fritzsche[9] in the case of germanium. For silicon, such investigation was made by using deuteron irradiation to introduce controlled amount of compensation.[20] These results seem to be consistent with the concept.

The conduction at low impurity concentration is pictured as the jumping of carriers among majority impurity centers. The simplest mechanism is resonance jumping. However, such mechanism cannot account for the existence of an activation energy. The most satisfactory explanation of the activation energy seems

* This work was supported by a Signal Corps Contract.
[1] F. J. Morin and J. P. Maita, Phys. Rev. 94, 1525 (1954).
[2] R. O. Carlson, Phys. Rev. 100, 1075 (1955).
[3] G. A. Swartz, Bull. Am. Phys. Soc. 2, 134 (1957); J. Phys. Chem. Solids, 12, 245 (1960).
[4] For list of references see V. A. Johnson and K. Lark-Horovitz, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.
[5] C. S. Hung and J. R. Gliessman, Phys. Rev. 79, 726 (1950); Phys. Rev. 96, 1226 (1954). See also: C. S. Hung, Phys. Rev. 79, 727 (1950).
[6] H. Fritzsche and K. Lark-Horovitz, Physica XX, 834 (1954).
[7] H. Fritzsche, Phys. Rev. 99, 406 (1955).
[8] S. H. Koenig and G. R. Gunther-Mohr, J. Phys. Chem. Solids 2, 268 (1957).
[9] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958); see also: H. Fritzsche and K. Lark-Horovitz, Phys. Rev. 113, 999 (1959).
[10] J. S. Blakemore, Phil. Mag. 4, 560 (1959); A. L. McWhorter, Lincoln Laboratory, Massachusetts Institute of Technology, Solid State Quarterly Report, April–June, 1958 (unpublished).
[11] G. Busch and H. Labhart, Helv. Phys. Acta 19, 463 (1946).
[12] H. M. James and A. S. Ginzbarg, J. Phys. Chem. 57, 840 (1953).
[13] C. Erginsoy, Phys. Rev. 80, 1104 (1950); Phys. Rev. 88, 893 (1952).
[14] X. Baltensperger, Phil. Mag. 44, 1355 (1953).

[15] B. Gudden and W. Schottky, Z. tech. Physik 16, 323 (1935).
[16] W. Schottky, Manuscript of Zurich Seminar, 1955 (unpublished).
[17] E. M. Conwell, Phys. Rev. 103, 51 (1956).
[18] P. Aigrain, Physica 20, 978 (1954).
[19] N. F. Mott, Can. J. Phys. 34, 1356 (1956).
[20] T. A. Longo, R. K. Ray, and K. Lark-Horovitz, J. Phys. Chem. Solids 8, 259 (1959).

to be that advanced by Mott.[19] The activation energy is attributed to the Coulomb attraction between the charged atoms of minority impurity and the carriers of impurity conduction. The Coulomb field of the charged minority atoms makes the majority impurity sites nonequivalent. This tends to inhibit resonance jumping of carriers.[21,19,16] Theoretical treatments based on phonon-assisted jumping have been given recently by several authors.[22-24]

Whatever the process, the motion of charge carriers from one impurity atom to the next will be determined by the overlap of the wave functions of adjacent centers which depends critically on the spacing between the majority impurity atoms and the radius of the wave functions of the impurity atom. In silicon, various impurities have appreciably different ionization energies[25] with corresponding differences in the spread of the wave function. Measurement of samples with different impurities in various concentrations should provide information of interest.

Reported in the following are the results of investigations made on p-type silicon doped with B, Al, or Ga and n-type samples doped with Sb or As. The work emphasizes the low range of impurity concentration which is more susceptible to theoretical treatment. The amount of compensating impurity, which is important for the conduction in this range, is determined for the p-type samples by a heat treatment method. In Ga- or Al-doped samples, evidence of ion-pairing between the acceptor impurity and the compensating impurity has been found. The effects of various factors on the conductivity and its temperature dependence are studied, and the interpretation of the results is discussed.

II. EXPERIMENTAL TECHNIQUE

Silicon single crystals used in these measurements were supplied by P. Klose of this laboratory, W. Adcock of Texas Instruments, B. Jacobs of Sperry Rand Corporation, and W. Spitzer of Bell Telephone Laboratories. The crystals were pulled from starting material of high purity with the addition of the specified doping impurity. The samples were cut with their large areas transverse to the concentration gradient, in order to minimize nonuniformity. Most of the samples were about $0.1\times0.4\times1.5$ cm^3 in dimension. The samples surfaces were ground with a mixture of number 600 carborundum powder with glycerine or water on a smooth, flat glass plate, etched with CP4 solution, and rinsed with distilled water. The homogeneity of each sample was checked by careful probing. Electrical

[21] H. M. James, Purdue University, Quarterly Report, October–December, 1956 (unpublished).
[22] W. D. Twose, thesis, Cambridge University, 1959 (unpublished).
[23] T. Kasuya and S. Koide, J. Phys. Soc. Japan 13, 1287 (1958).
[24] A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).
[25] W. Kohn, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.
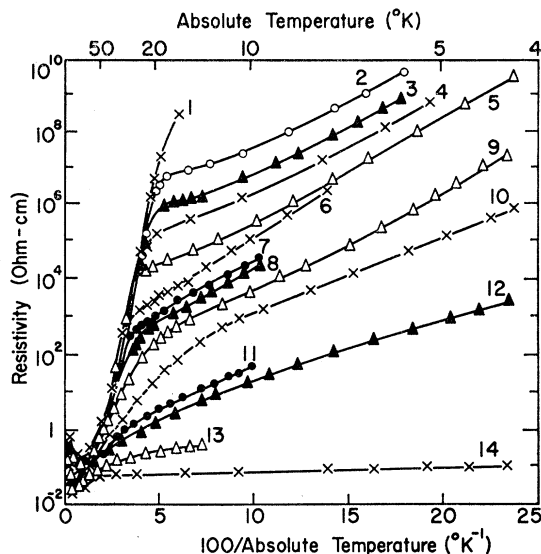
FIG. 1. Resistivity of B-doped silicon (p type) as a function of $1/T$. For data on samples 1–6 see Table I. Samples 7–14 have carrier concentrations at room temperature: 6.9, 8.9, 17.5, 18.6, 21.8, 25.4, 34.0, 41.3 in 10^{17} cm^{-3}, respectively.

contacts were soldered by using indium metal as solder without any flux. Each electrical contact was checked and rectifying barriers which were sometimes present could be broken down by sparking through the contact with a Tesla coil.

The low-temperature cryostat employed for these measurements was of the usual type, using helium exchange gas and a heater coil to regulate the temperatures of the sample. A potentiometer circuit was used for measuring the voltages. For higher resistance range, a vibrating reed electrometer was used as the null detector. In the measurements, the electric field applied to the sample was kept below 1 volt/cm. The samples were found to be Ohmic at such low fields. The Hall coefficient was usually measured with a magnetic field of 7000 gauss.

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show the temperature dependence of the resistivity and the Hall coefficient of silicon samples doped with various concentrations of boron ranging from 5×10^{16} to 5×10^{18} cm^{-3}. The transition to impurity conduction occurs at lower temperature and higher resistivity for smaller impurity concentration. The lowest impurity concentration that can be used is limited by the resistivity measurement. For the samples of low impurity concentration, the Hall coefficient in the impurity conduction region drops rapidly with decreasing temperature and becomes difficult to measure. Investigations gave no indication that it became large again at still lower temperatures. The behavior of n-type samples is qualitatively similar as shown by Figs. 3 and 4 for antimony-doped and arsenic-doped samples.
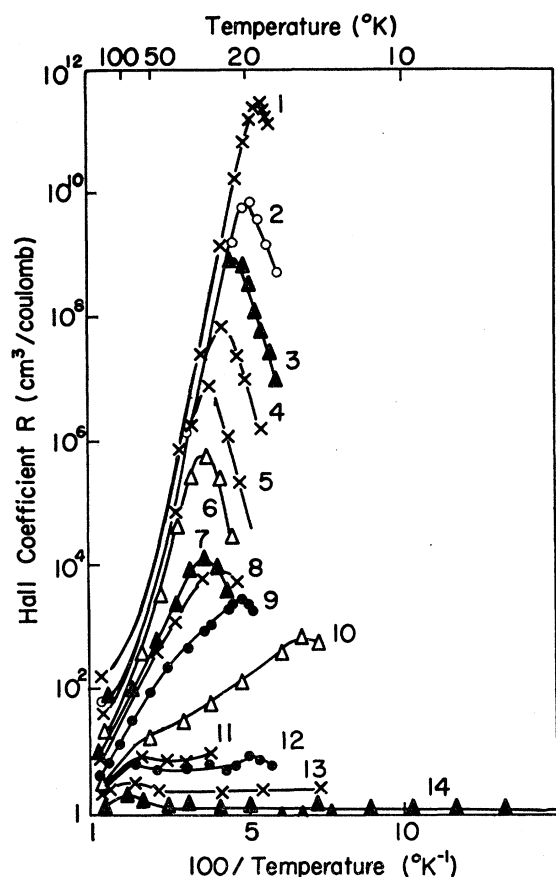
Fig. 2. Hall coefficient of B-doped silicon (p type) as a function of $1/T$. For sample data see Table I.

In impurity conduction, the average distance between impurities, R, as compared to the Bohr radius, a, of an isolated impurity is of great importance. When the ratio (R/a) is large the interaction between impurity atoms will be small. The resistivity behavior of samples with low boron concentrations, samples 1 to 6, is characterized by exponential dependence on $1/T$, involving two activation energies. The larger energy, E_1, is the ordinary ionization energy of the impurity atom, and the other, E_3, is much smaller and will be referred to as the activation energy of impurity conduction. The value of E_3 increases with increasing impurity concentration for samples in this range. The range of low impurity concentration may be approximately specified by $R/a > 6$. This condition corresponds to a maximum impurity concentration of $\sim 5 \times 10^{17}$ cm^{-3} for boron and $\sim 2 \times 10^{18}$ cm^{-3} for gallium. With higher impurity concentration, the resistivity and Hall coefficient show more complicated behavior in the intermediate concentration range as shown by the curves 9, 10, 11, 12 for the samples having boron concentrations of the order of 10^{18} cm^{-3}. For the samples of still higher impurity concentration, e.g., samples 13 and 14, the Hall coefficient shows a small peak and

remains nearly constant at low temperature. It seems that the conduction in such samples may be discussed on the basis of energy bands formed from the impurity states. More detailed discussions have been given previously.[20] We are concerned here primarily with samples in the low-concentration range. Measurements have also been made on Ga-doped and Al-doped samples of this low-concentration range; the resistivity and Hall coefficient curves are shown in Figs. 5 to 8. Some relevant data for the samples studied are listed in Table I.

Major Impurity Concentration

The samples are not in the exhaustion range at room temperature. The difference between the carrier concentration and the majority impurity concentration is considerable, being larger than a factor of two in some cases. The majority impurity concentration has to be calculated from the carrier concentration by using the dissociation equation:

$$\frac{n(N_1+n)}{(N-N_1-n)} = \frac{2}{g}\left(\frac{2\pi m^*kT}{h^2}\right)^{\frac{3}{2}} \exp(-E_i/kT)$$

$$= \frac{N_d}{g} \exp(-E_i/kT), \tag{1}$$

where N and N_1 are the majority and minority impurity concentrations, N_d is the density of states of the energy band in question, n is the free carrier concentration at temperature T, m^* is the effective density-of-state mass, g is the degeneracy of the ground-state energy level, and E_i is the ionization energy of the majority

TABLE I. Impurity concentration and activation energy in silicon samples with "low" impurity concentration.

Impurity	Sample Number	E_i 10^{-2} ev	n 10^{17} cm^{-3}	N 10^{17} cm^{-3}	E_3 10^{-3} ev
B	1 (B-172)	4.50	0.42	0.460	···
	2 (B-977)	3.71	0.79	0.894	5.0
	3 (B-171)	3.89	0.92	1.07	5.2
	4 (B-5)	3.88	1.32	1.62	5.5
	5 (B-4)	3.62	1.69	2.14	5.5
	6 (B-3)	2.68	3.31	4.54	6.7
Al	29	5.1	1.21	1.62	4.8
	27	5.1	2.09	3.30	6.8
	25	5.1	2.72	4.77	9.5
	26	5.1	2.98	5.44	10.6
	24	5.1	3.12	5.82	11.1
	23	5.1	4.14	8.88	11.1
Ga	10/78	4.96	2.40	3.95	20.4
	2	4.46	4.43	8.74	20.4
	62/78	3.5	8.57	19.8	16.0
Sb	-1 (T-15)	3.6	0.58	0.59	4.8
	-2 (T-14)	3.6	0.76	0.78	6.8
	-3 (C2Q9)	2.2	1.68	1.73	5.7
	-4 (IQ9)	2.2	3.03	3.18	5.7
As	-11 (Q-6-2)	5.3	0.627	0.65	···
	-12 Q-6(4+2)	4.5	1.38	1.46	5.8

impurity. Values of $m^* = 0.58m$ for holes and $m^* = 1.08m$ for electrons were taken. For the acceptors and donors, $g = 4$ and $g = 2$, respectively,[25] have been used.

The ionization energy E_i is determined from the Hall coefficient data in the freeze-out temperature range, according to the expression:

$$n = \left[\frac{N - N_1}{N_1}\right]\left[\frac{N_d}{g}\right] \exp(-E_i/kT). \qquad (2)$$

The values obtained are given in Table I. They are lower than quoted values of ionization energy for the impurities. This is consistent with the effect of high concentration on the ionization energy as found in electrical and optical studies.[26,27] The compensation is low in these samples, (N_1/N) being of the order of a few percent. Neglecting N_1 compared to n, the majority impurity concentration N is calculated by using (1) with the value E_i and the value of n obtained from the room temperature Hall coefficient. Due to the presence of large amounts of neutral and ionized impurities, the ratio of Hall mobility to drift mobility is difficult to
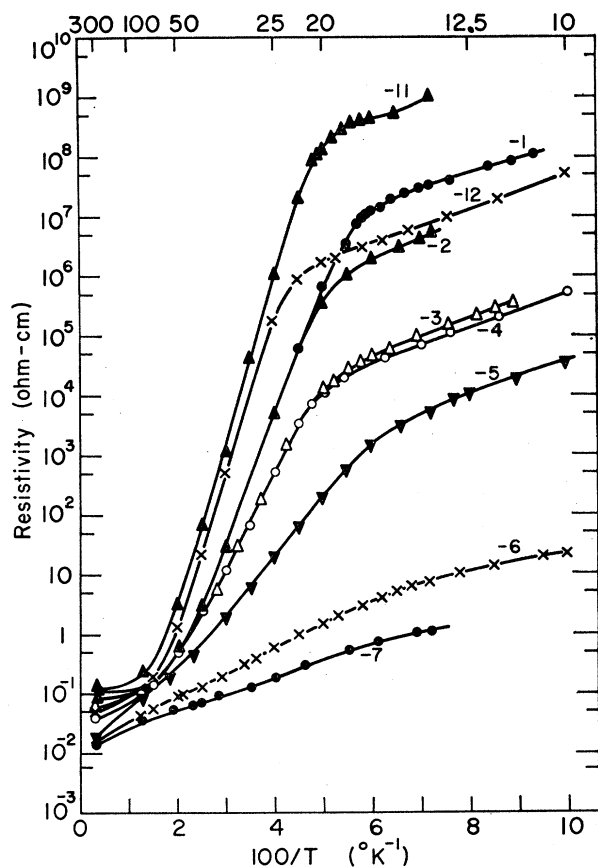

FIG. 3. Resistivity of Sb- and As-doped silicon (n type) as a function of $1/T$.

[26] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).
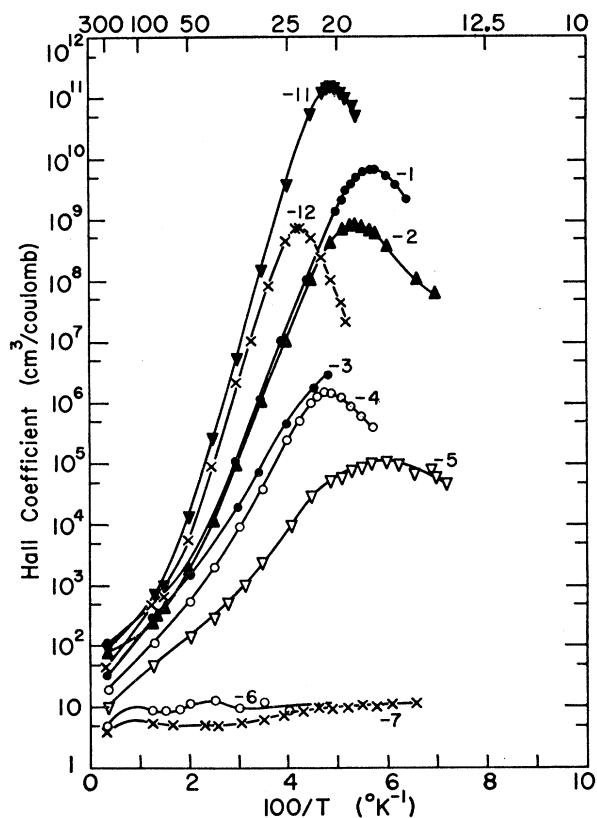[27] R. Newman, Phys. Rev. **103**, 103 (1956).

FIG. 4. Hall coefficient of Sb- and As-doped silicon (n type) as a function of $1/T$.

estimate accurately. For simplicity, the relation $R_H = 1/en$ is used uniformly.

Activation Energy

We have seen that impurity conduction in the low impurity concentration samples may be characterized by a single activation energy, E_3. According to Mott, the activation energy arises from the Coulomb interaction between ionized majority impurity and oppositely charged centers of minority impurity. The activation energy would be expected, therefore, to be independent of the nature of the majority impurity. The values of E_3 given in Table I for the samples are plotted in Fig. 9 as a function of the concentration, N, of majority impurity. A considerable variation is seen. The binding energy depends on the concentrations of majority and minority impurities. A simple consideration leads to the relation (14), given in Sec. IV, which can be written as

$$E_B = 2.18 \times 10^{-3}(N/10^{15})^{\frac{1}{3}}[1 - 2(N_1/N)^{\frac{1}{3}}] \text{ ev}. \qquad (3)$$

The solid line represents the theoretical relation for negligible compensation. The B- and Al-doped samples fall below the solid line. Qualitatively, at least, this could be attributed to the presence of compensation.

However, the values of E_3 for the two Ga-doped samples seem to be too high; one of them lies above the solid line and the other falls so close to the solid line as to imply an unreasonably low compensation. According to (3), E_B is very sensitive to the compensation; almost 50% reduction of E_B would result from one percent compensation. It is therefore important to determine the compensation reliably.

Determination of Compensation

The concentration of compensating impurity is usually determined by using either the temperature dependence of carrier concentration in the freeze-out region or the magnitude of ionized impurity scattering.[28] Unfortunately, these methods cannot be relied upon to give better than an order of magnitude estimate in these heavily doped samples. In the case of very low compensation, the methods are entirely inadequate. The following method has been found to give a reliable estimate for the p-type samples.

It is known that donor centers can be introduced in silicon by heat treatment at $\sim$450°C.[29,30] The method
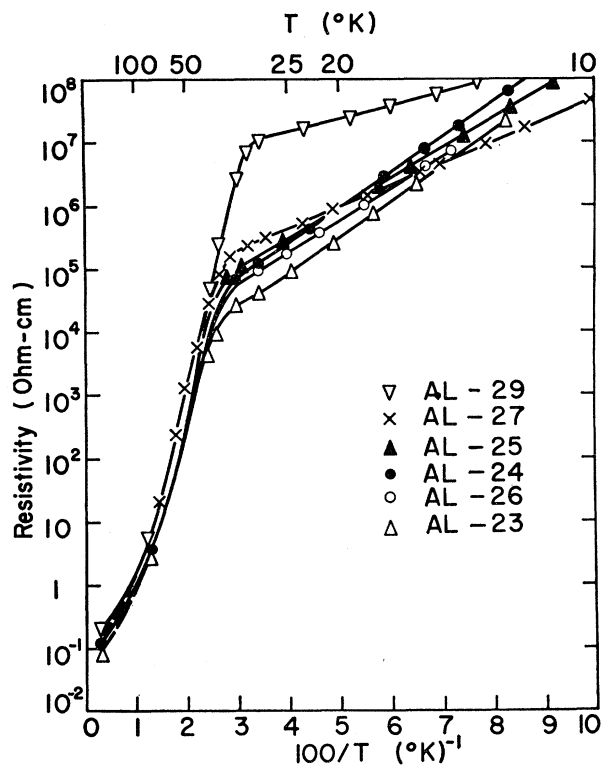
FIG. 5. Resistivity of Al-doped silicon (p type) as a function of $1/T$.

[28] H. Brooks, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, New York, 1956), Vol. 7, p. 87.
[29] C. S. Fuller and R. A. Logan, J. Appl. Phys. 28, 1427 (1957); C. S. Fuller, J. A. Ditzenberger, N. B. Hannay, and E. Buehler, Phys. Rev. 96, 833 (1954).
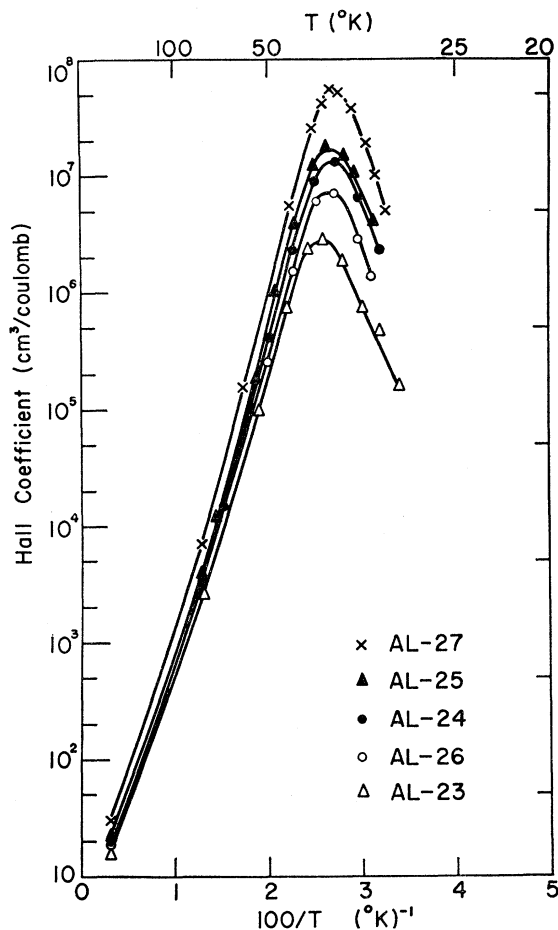[30] W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. 112, 1546 (1958).

FIG. 6. Hall coefficient of Al-doped silicon (p type) as a function of $1/T$.

was used to add small amounts of compensation in the p-type specimens. The added compensation ΔN_D was kept between 1–5% of the majority impurity concentration, N_A. Equation (1), with n replaced by p, may be written as

$$N_D = \left[\frac{GN_A}{G+p}\right] - p,\qquad(4)$$

where

$$G = (N_d/g)\exp(-E_i/kT).\qquad(5)$$

If the added compensation is kept low, the ionization energy and, therefore, G will not be changed appreciably. We have then:

$$\frac{\Delta N_D}{N_A} = -\Delta p\left[\frac{1}{N_A} + \frac{G}{(G+p)(G+p+\Delta p)}\right].\qquad(6)$$

In principle, Δp and hence ΔN_D can be obtained from the change in Hall coefficient. Ordinarily, for a set of two fixed Hall leads, the relative accuracy of the Hall measurement is good. But for heat treatment we need to remove the leads from the sample and put them back
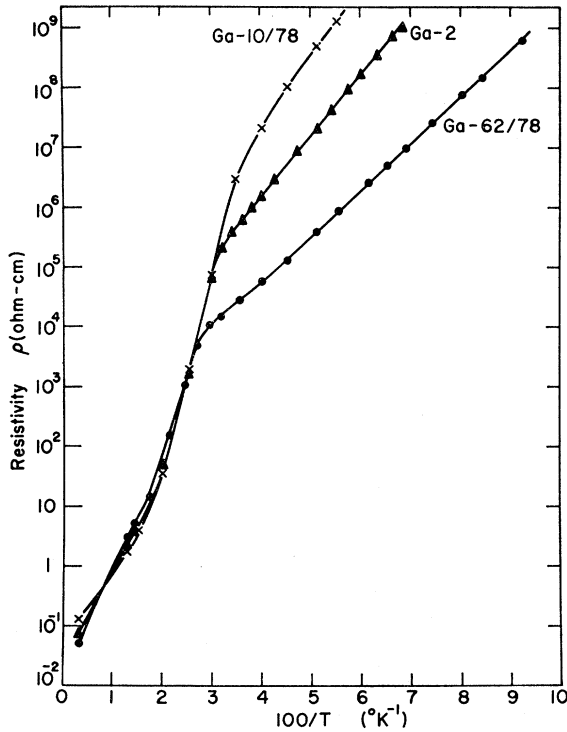
FIG. 7. Resistivity of Ga-doped silicon (p type)
as a function of $1/T$.

The mobility as determined by ionized impurity scattering could be calculated by using the Brooks-Herring formula.[28] However, we find in agreement with other workers that μ_I calculated from this formula is about an order of magnitude higher than that required to account for the measured mobility. Therefore, an estimate of the mobility term in (7) will be made by using the experimental data. Figure 10 shows $1/\mu$ and $1/\mu_I = (1/\mu - 1/\mu_L)$ plotted against the room temperature carrier concentration, which is closely equal to the concentration N_I of ionized impurity, for several samples in the range of interest. The value of μ_L is taken to be 500 cm^2/volt-sec. It is seen that, for this range, $1/\mu_I$ varies nearly linearly with N_I:

$$(1/\mu_I) \sim (7.2 \times 10^{-21} \text{ volt-sec-cm})(\Delta N_I \text{ cm}^{-3})$$
$$= K\Delta N_I, \quad (10)$$

where the numerical factor, K, is obtained from the slope of the straight line drawn for $1/\mu_I$. It should be noted that (10) applies only for the limited range, as is evident from the fact that the straight line does not extrapolate to the origin.

The additional ionized impurity, ΔN_I, introduced by the heat treatment is approximately equal to the change of carrier concentration. Actually, there is some

again after heat treatment. In this procedure small changes in Hall coefficient can no longer be measured reliably, as even two pairs of adjacent leads in a sample often show $\sim$1-2% difference between their Hall data. Therefore, the change in resistivity at room temperature was used instead of the change in Hall coefficient for the determination of Δp.

In using the resistivity to determine Δp, we have taken into account the fact that not only the carrier concentration but also the mobility may be affected by the heat treatment. For a small addition of compensation, we may write

$$\frac{-\Delta\rho}{\rho} \simeq \frac{\Delta\sigma}{\sigma} = \frac{\Delta p}{p} + \frac{\Delta\mu}{\mu} \simeq \frac{\Delta p}{p} - \frac{\Delta(1/\mu)}{(1/\mu)}. \quad (7)$$

The reciprocal mobility can be expressed as

$$\frac{1}{\mu} = \frac{1}{F}\left[\frac{1}{\mu_L} + \frac{1}{\mu_I} + \frac{1}{\mu_N}\right], \quad (8)$$

where μ_L, μ_I, μ_N are the mobilities given by the lattice, ionized impurity, and neutral impurity scatterings individually. F is a constant which depends on the relative importance of these mechanisms. It is difficult to estimate the value of F accurately. For an approximate estimate, it is sufficient to take $F=1$. Also, the scattering by neutral impurity will be neglected. Then:

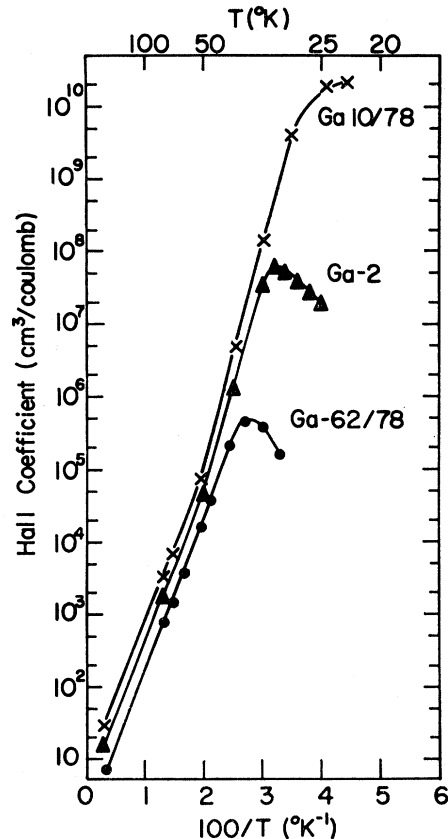$$\Delta(1/\mu) \sim \Delta(1/\mu_I). \quad (9)$$

FIG. 8. Hall coefficient of Ga-doped silicon (p type)
as a function of $1/T$.

TABLE II. Summary of heat treatment and estimated compensation.

Sample	R_H cm³ coul⁻¹	ρ ohm cm	$\Delta N_D/N_A$ %	$R'_H/R_H = N_D'/N_D$	N_D/N_A %	E_3 10^{-3} ev
B-977	79.1	0.302			1.4	5.0
a	81.0	0.318	4.2	4		4.5
B-171R	70.6	0.287			3.4	5.2
a	70.8	0.293	1.7	1.5		5.1
B-5	47.7	0.200			3.0	5.5
a	47.9	0.205	2.0	1.7		5.0
Al-25	22.7	0.111			8.2(?)	9.5
a	23.8	0.122	8.2	2.0		6.5
Al-24	20.1	0.109			6(?)	11.1
a	21.65	0.116	6	2.0		6.7
Ga-10/78	26.9	0.127			0.11	20.4
a	26.05	0.129	1.4	14		7.5
Ga-2	14.55	0.0776			0.13	20.4
a	14.1	0.0782	0.5	5		12
Ga-5[a]	11.93	0.0705				14.2
Ga 2-2	18.9	0.0948	(Li 13%)			8.9
Ga 60/78	9.97	0.0646	(Li 14%)			9.3

[a] Heat treatment.

change also in the ionized majority impurity which is normally not completely ionized. The effect of this is, however, small. Thus we get

$$-\Delta\rho/\rho \simeq (\Delta p/p) - K(-\Delta p)\mu = (\Delta p/p)[1 + K p \mu]. \quad (11)$$

For the three heat-treated samples, the values of $K p \mu$ vary from 0.15 to 0.23. Since the second term is small compared to the first, the approximations made in estimating it will not give rise to serious error.

In the freeze-out range, the carrier concentration is given by (2), with n replaced by p. No appreciable change of slope of the log p versus $1/T$ curve was produced by the heat treatment used, indicating that E_i remained actually unchanged. The ratio of compensations before and after the heat treatment can therefore be calculated from the Hall coefficients at any given temperature, according to

$$N_D'/N_D \simeq p/p' = R'_H/R_H, \quad (12)$$

which follows from (2) under the condition that N_D and N_D' are much smaller than N_A. Having determined N_D'/N_D and $\Delta N_D/N_A$, the initial compensation N_D can be obtained from

$$N_D/N_A = (\Delta N_D/N_A)[N_D'/N_D - 1]^{-1}. \quad (13)$$

The values of $\Delta N_D/N_A$, N_D'/N_D, and N_D obtained by using the heat treatment method are given for several samples in Table II.

Ion Pairing

The estimated compensations fall in the range 1.4–3.4% for the B-doped samples, 0.1–0.2% for the Ga-doped samples, and 6–10% for the Al-doped samples. The reported values of segregation coefficient of B,

Ga, and Al in silicon are 0.9, 0.01, and 0.004, respectively.[31] When a crystal is doped with an impurity of a small segregation coefficient, it should be in general more difficult to avoid spurious impurities, some of which may well be donors. Therefore we would not expect the Ga-doped samples to have the lowest compensation.

The addition of compensation changes the activation energy, as is seen in Table II. The Ga-doped samples had initially $E_3 \gtrsim 20 \times 10^{-3}$ ev, much higher than is expected according to (3). Addition of <1% compensation reduced E_3 by nearly 50% (Ga-2), making it close to the expected value. The addition of compensation does not have such a big effect on E_3 in the B- and Al-doped samples. These observations indicate that there was in the Ga-doped samples, some pairing between the compensating donors and Ga. A well-known case of ion pairing in silicon is that of Li donor with acceptor impurities.[32] Pairing of a donor and an acceptor effectively removes from the energy gap the levels associated with the impurity atoms.[33,34] As a result, an apparently small compensation will be observed. The compensating impurity atoms which are not so closely paired will still be closer to the majority impurity atoms than in a random distribution. Thus, a higher activation energy for impurity conduction may be expected.

Interaction between impurities raises a problem in the use of heat treatment for the determination of compensation in the case of Al-doped samples. It is

[31] J. A. Burton, Physica 20, 845 (1954).
[32] C. S. Fuller, Chem. Revs. 59, 65 (1959).
[33] H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech J. 35, 535 (1956).
[34] N. B. Hannay, editor, Semiconductors (Reinhold Publishing Corporation, New York, 1959), pp. 214, 217.

known that heat treatment below 500°C produces donors and that the process is influenced by the interaction with Al acceptors.[35] In the dissociation Eq. (1), N_1 should now be replaced by N_{Du}, the concentration of unpaired compensating impurity, and N should be replaced by $(N_A - N_{Dp})$, N_{Dp} being the concentration of paired compensating impurity. Equation (12) for the deionization range applies then to the unpaired compensation: N_{Du}'/N_{Du}. On the other hand, the samples at room temperature are not too far from exhaustion and the changes in carrier concentration and resistivity give approximately the total additional compensations $(\Delta N_{Du} + \Delta N_{Dp})$. Therefore, it is not possible to determine either N_{Du} or N_{Dp} by combining the room temperature data and the data for the deionization range.

If the existence of ΔN_{Dp} is neglected, the combination of deionization range and room temperature data would give a value for N_{Du} which is too high. Thus, we deduce $N_{Du}/N_A = 6\%$ for sample Al-24 and $N_{Du}/N_A = 8\%$ for sample Al-25. Table II shows that these samples have $E_3 = 9.5 \times 10^{-3}$ ev and $E_3 = 11.1 \times 10^{-3}$ ev, respectively. These values are much higher than the value $E_3 = 5.5 \times 10^{-3}$ ev for the B-doped sample B-5 which
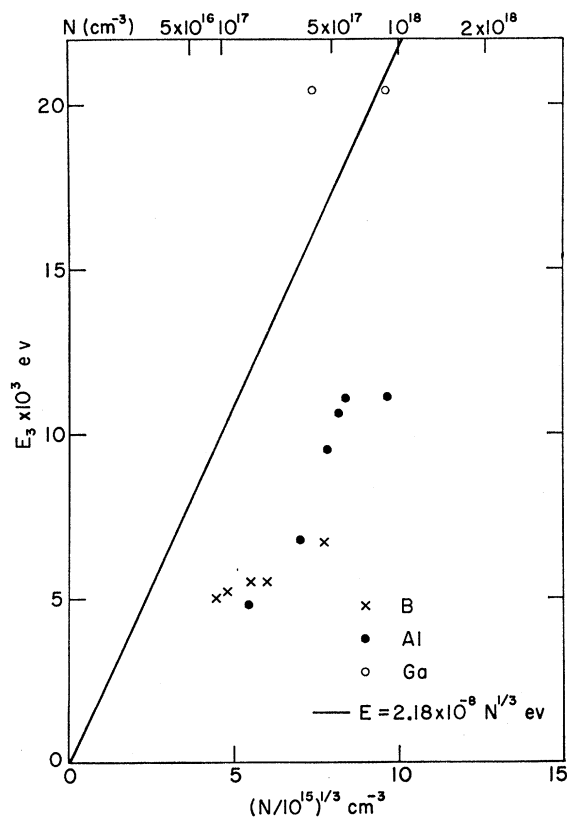

FIG. 10. $1/\mu$ and $1/\mu_I$ vs N_I at room temperature for B-doped silicon samples.

FIG. 9. Activation energy, E_3, vs majority impurity concentration for B-, Al-, and Ga-doped silicon samples.

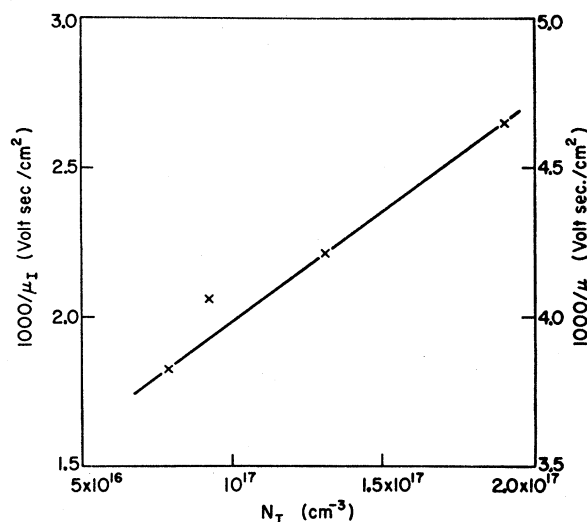[35] C. S. Fuller and F. H. Doleiden, J. Appl. Phys. 29, 1264 (1958).

has a comparable majority impurity concentration and 3% compensation. This indicates that N_{Du} in the Al-doped samples is considerably smaller than the values estimated by overlooking ion-pairing of the added donors with aluminum. Furthermore, the values E_3 of the Al-doped samples are close to the value $E_3 = 12 \times 10^{-3}$ ev for Ga-2 which had a very low unpaired compensation to begin with and $\sim 0.5\%$ compensation added by heat treatment. It appears then that N_{Du} in the Al-doped samples was only $\lesssim 1\%$. We note that Al has a much smaller segregation coefficient[31] than B and would not be expected to give a small compensation. We suspect, therefore, that there was also some ion-pairing between the original compensating donors and Al-acceptors.

Li Diffusion

In the above discussion, it has been assumed that atoms of the compensating impurity which are ion-paired with the majority impurity atoms do not have the effect of reducing the activation energy as those which are randomly distributed. In order to test the assumption, measurements were made on Ga-doped samples into which Li was diffused since it has been shown that Li has definitely the tendency of ion-pairing with the acceptor impurities. The two Ga-doped samples, 10/78 and Ga-2, from nearby sections of the same crystal had initially $E_3 > 20 \times 10^{-3}$ ev. Addition of less than 2% and 1% compensation by heat treatment at 450°C reduced the activation energy to $E_3 = 7.5 \times 10^{-3}$ and 12×10^{-3} ev, respectively. Shown in Fig. 11 are the resistivity curves for sample Ga-2 before and after the heat treatment and for sample Ga-10/78 after the heat treatment. From the region of the crystal in between these two samples, a sample Ga2-2 was
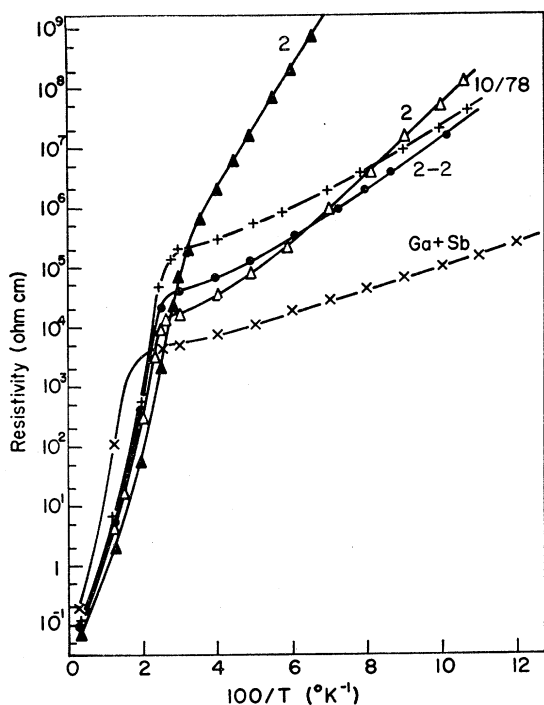
FIG. 11. Resistivity of Ga-doped silicon samples as a function of $1/T$. Curves are shown for sample 2 before and after heat treatment, for sample 10/78 after heat treatment, for sample 2-2 after Li diffusion, and for the Sb compensated sample.

chosen. Li was diffused in[36] at 450°C. From the change of room temperature resistivity, it was estimated that $N_{Li}\sim13\%$ of the gallium concentration. The value of E_3 was reduced to 8.9×10^{-3} ev as shown by the curve 2-2. This reduction can be attributed to the effect of heat treatment alone. Thus the large amount of Li introduced did not produce a large effect on E_3. In contrast to this experiment, another Ga-doped sample was measured in which Sb was added during crystal growth. The Ga concentration was comparable to that of Ga2-2. The compensation was estimated from the mobility data to be ~15–20% of the gallium. This sample had a much lower activation energy, 3.4×10^{-3} ev as shown in Fig. 11. This result is consistent with the fact that Sb does not have a strong tendency of ion-pairing with Ga.[34]

IV. DISCUSSION OF RESULTS

Survey of the Theories

The conduction in the range of impurity concentration is explained on the basis of charge exchange between neutral and ionized majority impurities. The ionized impurity atoms can be considered as occupied by carriers of the impurity conduction, and they exist because of the presence of compensating impurities. It was first suggested by Mott,[19] that the Coulomb inter-

action between the carriers and the oppositely charged compensating impurities tends to trap the carriers near the atoms of compensating impurity, thus giving rise to the observed activation energy, E_3, for conduction. In the case of a single compensating impurity atom, the carrier would have a binding energy, $E_B=e^2/Kr_1$, where r_1 is the distance between the compensating impurity and the nearest majority impurity atom. With more than one compensating atom in a random distribution of majority impurity, it seems reasonable to use the statistical average of the nearest distance for r_1. When the compensation is very small, the average distance between a minority impurity atom and the nearest majority impurity atom is the same as the average distance between two majority atoms; then $r_1=0.88(3/4\pi N)^{\frac{1}{3}}$, where N is the concentration of the majority impurity. Furthermore, each carrier experiences the Coulomb attraction of all the ionized compensating atoms and the repulsion of all the other carriers. Thus E_B should depend on the concentration of compensating impurity. A rough estimate may be obtained using the simple picture that the semiconductor is divided into spheres each containing a minority impurity atom at its center and, on the average, one carrier or unoccupied majority site.[37] The binding energy is taken to be the difference in potential energy between a trap site nearest to the minority impurity atom and a site at the boundary of the sphere, i.e.,

$$E_B=\frac{e^2}{K}\left[\frac{1}{r_1}-\frac{2}{r_2}\right], \tag{14}$$

where r_2 is the average spacing between compensating impurities. Such an expression gives an order of magnitude for E_B comparable with the observed E_3.

We consider now the conduction process in more detail. In general, the probability of a transition of charge carriers from occupied to unoccupied impurity atoms, is controlled by the small but finite overlap of the wave functions of neighboring impurity atoms. This problem has been treated by Conwell[17] on the basis of resonance jumping of the electron in a hydrogen molecule ion in a medium of dielectric constant K. A diffusion coefficient is obtained as $D=\nu d^2$, where ν and d are, respectively, the frequency and average distance of a jump. The mobility is then obtained by using the relationship $\mu=De/kT$; giving

$$\mu=\frac{8e}{kT}\frac{E_i}{h}\frac{1}{Na}\exp(-d/a), \tag{15}$$

where d is taken to be $2r_s=2(3/4\pi N)^{\frac{1}{3}}$. The activation energy is unaccounted for, in such a model.

Using the simple assumption that there are on the average r sites with binding energy E_B around each

[36] H. Reiss and C. S. Fuller, J. Metals 12, 276 (1956).

[37] P. J. Price, IBM J. Research Develop. 2, 123 (1958); also reference 8.

compensating impurity atom and that all the other sites are free, Price obtained the concentration of free carriers to be[37]

$$n = \left[\frac{N_1 N}{r} \exp(-E_B/kT) \right]^{\frac{1}{2}}, \quad (16)$$

at low temperatures. These above expressions for μ and n, taken together in a simple theoretical estimate of the conductivity, give:

$$\sigma = ne\mu = 4 \left(\frac{N_1}{N} \right)^{\frac{1}{2}} \frac{e^4}{kT} \frac{1}{hKa^2} \exp\left[-\left(\frac{E_B}{2kT} + \frac{2r_s}{a} \right) \right], \quad (17)$$

for $r=1$, and this has been used by Koenig and Gunther-Mohr[8] and by Blakemore[10] for the analysis of their data. The activation energy E_3 corresponds then to $\frac{1}{2}E_B$.

With the use of the observed activation energy, (17) gives estimates of conductivity which are of the same order of magnitude as that observed. For example, the calculated value of the resistivity at 10°K is $\sim 9 \times 10^5$ ohm cm for sample B-5. The observed resistivity is 1.5×10^6 ohm cm. In the calculation, the value used for a was 13 A which was estimated from the ionization energy according to the simple hydrogenic model. The calculated conductivity is very sensitive, however, to the value of $2r_s$ which represents the jumping distance d. It is not clear that, in a random distribution of impurity atoms, the appropriate value of d is $2r_s$, and the order of magnitude agreement cannot therefore be taken too seriously.

Basically, the treatment in terms of resonance jumping faces serious objection. The concept used in the treatment is that of successive independent jumps between adjacent impurity atoms, which leads to a random-walk diffusion process. James[21] pointed out that resonance exchange leads to coherent scattering in which the mean free path is quite different from the distance between adjacent centers. Also, the motion from center to center cannot be regarded as an effective jumping frequency of a random walk process. In the resonance exchange treatment, the impurity centers are treated as equivalent sites. Schottky[16] pointed out that a difference in the crystal deformation around an ionized and a neutral center may give rise to a potential difference. Fluctuation of the energy levels of the impurities due to lattice vibration will then be important for the resonance exchange, as discussed by James.[21] A more important cause for the nonequivalence of the centers is the potential variation produced by the charged impurity centers which is the basis for the binding energy, E_B, discussed above.[19] The problem of carrier jumping between nonequivalent centers with the help of lattice vibration has been treated theoretically by Twose and Mott[22] and by Kasuya and Koide.[23] Twose and Mott calculated the rate of transitions between adjacent centers i and j in which the electron energy changes by $|E_i - E_j|$. Mobility is calculated by con-
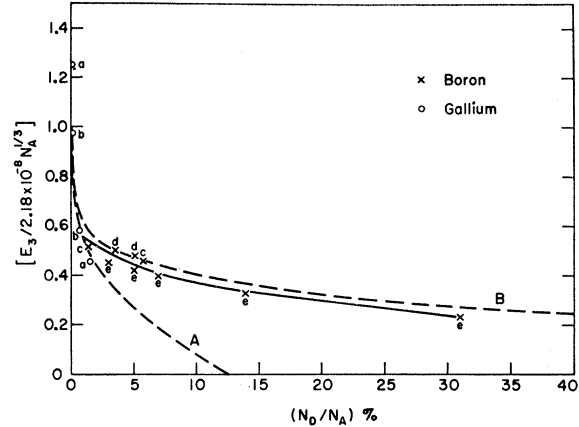

FIG. 12. Activation energy, E_3, normalized with respect to impurity concentration, N_A, as a function of compensation for B- and Ga-doped silicon samples. The letters a, b, c, d, and e correspond to samples Ga-10/78, GA-2, B-977, B-171, and B-5, respectively.

sidering the transitions between the "free" sites for which $|E_i - E_j|$ is small, $<kT$. The mobility turns out then to be independent of temperature:

$$\mu \propto J^2 = \left[\frac{1}{3}(R/a)^2 + (R/a) + 1 \right]^2 \exp(-2R/a), \quad (18)$$

where R, the average center separation, is taken to be r_s. In this picture, the activation energy, E_3, of the conductivity, would be associated with the temperature variation of the number of carriers on the free sites.

The division of majority impurity into free and trapping sites is arbitrary and unrealistic. Kasuya and Koide treated the problem of phonon-assisted jumping without making this division but introduced a number of simplifications. The conductivity was also found to be proportional to J^2. In addition to an exponential dependence on $1/T$, the expression for conductivity involves also a factor T^4. Recently, Miller and Abrahams[24] extended the treatment using the approach of Kasuya and Koide. They found an exponential dependence on $1/T$ for the conductivity with an activation energy which decreases with increasing compensation, reaching a minimum at $\sim 50\%$ compensation. Some additional temperature dependence enters through a factor representing the effect of the excited states of the impurity atom. Beside affecting the activation energy, the concentration of impurity influences the conductivity predominantly through an exponential factor:

$$\sigma \propto \exp[-1.09(r_s/a)^{\frac{1}{3}}]. \quad (19)$$

which is to be compared with the $\exp(-2r_s/a)$ dependence of (18). It should be emphasized that the random distribution of impurity atoms makes a rigorous treatment of the problem extremely difficult. All the treatments available so far, involve drastic simplifications.
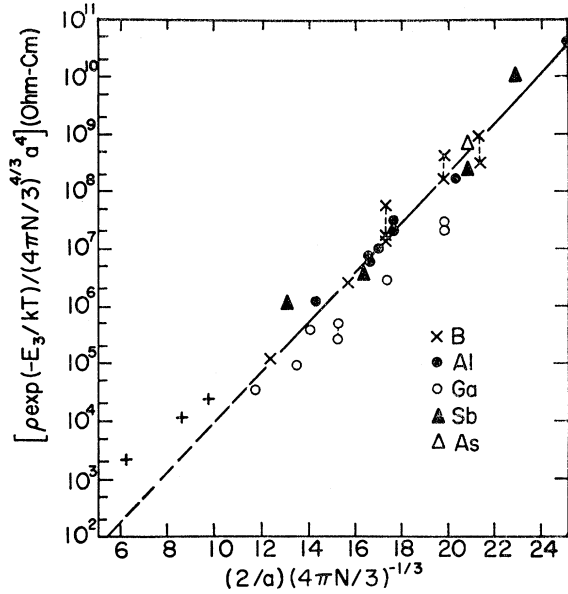
FIG. 13. Dependence of resistivity on impurity concentration for various silicon samples doped with different impurities. Points corresponding to the sample after heat treatments are connected with dashed lines.

Interpretation of Experimental Results

Since the theory is still in the stage of development, quantitative interpretation of the experimental results in terms of a theory is premature. We shall attempt to deduce from the experimental results the effects of some of the important parameters.

Consider first the effects of the majority impurity concentration, N, and the compensation, N_1/N, on the activation energy, E_3. We assume that E_3 can be expressed as

$$E_3 = f(N_1/N) N^{\frac{1}{3}}, \qquad (20)$$

where $f(N_1/N)$ is some function of the compensation. The expression is consistent with the simple formula (3) as well as the theory of Miller and Abrahams.[24] Figure 12 shows the plot of $(E_3/N^{\frac{1}{3}})$ against (N_1/N) for the B- and Ga-doped samples, for which (N_1/N) has been determined from heat treatment. The samples included had N varying from 8.94×10^{16} to 8.74×10^{17} cm^{-3}. The points seem to follow a smooth curve, indicating that the expression (20) is essentially correct. The curve varies slowly at large compensation. The dashed curves, A and B, represent, respectively, the simple formula (3) and the variation of E_3 with N_D/N_A according to Miller and Abrahams. Curve A is seen to decrease too fast as N_1 increases. But, curve B is fairly close to the experimental data for high compensation.

The theoretical curves rise steeply for N_1 below 1%. Unfortunately, reliable estimates of compensation is difficult for this range. Also, samples with such low compensation are not readily available. In the Ga-doped samples, the original compensation before the heat

treatment is estimated to be quite low, ∼0.1%, but ion-pairing of compensating impurities is suspected. For instance, the point corresponding to the data of sample Ga-10/78 lies even higher than the maximum expected value of 1, for the theoretical plots.

Besides an exponential factor involving the activation energy, we expect the conductivity to be proportional to the square of the exchange integral, J^2, which is a determining factor for the frequency of jumping. Furthermore, we might expect the conductivity to be proportional to the concentration of compensating impurity, the presence of which is instrumental in producing the conduction. However, this simple argument is questionable. For example, the statistical analysis of Price[37] based on an approximate model, predicts a proportionality factor of $(N_1)^{\frac{1}{3}}$ instead of N_1, and, according to Miller and Abrahams,[24] N_1 affects the conductivity only through E_3. We shall try to fit the results with the simple expression:

$$\sigma \propto J^2 \exp(-E_3/kT). \qquad (21)$$

$|J|^2$ is given by (18), in which the parameter R will be taken as

$$R = C r_s = C (4\pi N/3)^{-\frac{1}{3}}, \qquad (22)$$

where C is a constant. For all our samples, $a/R \ll 1$, and we can write

$$\rho \exp(-E_3/kT) \propto J^{-2} \sim \left(\frac{a}{C r_s}\right)^4 \exp\left(C\frac{2r_s}{a}\right). \qquad (23)$$

Figure 13 shows the semilogarithmic plot of $\rho \exp(-E_3/kT)(r_s/a)^4$ versus $2r_s/a$ for the samples measured. The values of $\rho \exp(-E_3/kT)$ were obtained by extrapolating the straight portions of the experimental curves, $\ln\rho$ vs $1/T$, to $1/T = 0$. The value of a used in each case is obtained from the ionization energy of the majority impurity according to the simple hydrogenic approximation: 13 A for B, 9.0 A for Al, 8.5 A for Ga, and 14 A for Sb. The straight line is drawn with a slope of one. The samples cover impurity concentrations ranging from 0.59 to 19.8×10^{17} cm^{-3}, excluding the last three points for B on the left. The points seem to group around the straight line. The last three points on the left are for B-doped samples which are outside of the low impurity concentration range, and progressive deviation from the straight line is seen. The data for the Ga-doped samples appear to be lower. It is possible that a slightly larger value of a should be taken for gallium. On the whole, the results indicate that (21) is a reasonable approximation.

The theoretical treatment of Miller and Abrahams[24] gives a different dependence for the resistivity on R/a:

$$\rho \propto \frac{r_s}{a}\left[1 + 18.2\left(\frac{a}{r_s}\right)^{\frac{3}{2}}\right] \exp[1.09(r_s/a)^{\frac{1}{3}}]. \qquad (24)$$

The data do not agree with an expression of this form if the value of a is estimated according to the hydro-

genic model. It is possible to fit the data reasonably with this expression by using values of a about twice as large: 22 A for B, 19 A for Al, and 24 A for Sb. It seems that the value estimated according to the hydrogenic model should be close to the proper value to be used. Kohn[25] has shown that the ground state wave function for acceptors in germanium can be represented by two terms, each of which has the form $\exp(-r/a)$. The calculated values of a are 43.3 A and 33.8 A. The larger

value is close to the estimate 42 A given by the hydrogenic model for a typical ionization energy of 0.0108 ev. Thus, it appears that the form (21) is to be preferred.

ACKNOWLEDGMENT

Nuclear Magnetic Resonance in Superconducting Tin*

G. M. ANDROES AND W. D. KNIGHT
Department of Physics, University of California, Berkeley, California
(Received September 19, 1960)

The nuclear magnetic resonance (NMR) is investigated in small particles ($\sim$100 A diam) of β tin between 1.5 and 4.2°K, and in magnetic fields between 1.2 and 8.8 kilogauss. The critical temperature and critical field are 3.71°K and 25 kilogauss, respectively. The effective penetration depth for the superconducting particles is estimated to be 1500 A. The resonance linewidth is 0.34% of the magnetic field, and it is independent of temperature. With respect to α tin, the NMR shift for β tin is 0.77% in the normal state; it approaches 0.59% in the superconductor as $T \rightarrow 0$. (The largest known chemical shift is only 0.17%.) The variation with magnetic field is less than 0.03%. One may conclude that the electronic spin susceptibility in the superconducting particles at absolute zero is approximately three quarters of the normal value. The result for 1000 A particles, though less accurate, is substantially the same.

I. INTRODUCTION

THE feature which makes nuclear magnetic resonance (NMR) attractive as a method for studying solids is that the nuclear resonance frequency is quite sensitive to the local fields at the position of the nucleus. A principal source of local fields is the hyperfine interaction between electrons and nucleus which may be quite strong in a metal. The average local field, which is proportional to the polarization of the conduction electron spins, shifts the resonance line; fluctuations in the local field allow for the relaxation of the nuclear spins toward their equilibrium distribution. Moreover, the resonance line is broadened if the several nuclei are not found in a homogeneous magnetic field.

Because of the very local nature of the hyperfine interaction, we should expect the data to be useful in constructing a microscopic model of a metal. In particular, the method has considerable significance for a microscopic theory of superconductivity, which must consider electron spin polarization and density of states at the Fermi surface, since the resonance line shift and the nuclear spin relaxation time are measures of these quantities.

Although it was realized some time ago[1] that the

nuclear resonance could provide unique information about superconductors, the attainment of experimental results was delayed by several difficult problems, principal among which was the fabrication of a specimen. This must consist of a dispersion of colloidal metallic particles or of a stack of thin films; the particle diameter or film thickness to be much less than the penetration depth; and the aggregate to contain one gram or more of the desired material. It is well known that the critical fields are high and that the internal fields are quite homogeneous in small specimens. Both of these conditions must be met for nuclear magnetic resonance (NMR), and, although the making of colloids and films is easy enough, it has been a major effort to concentrate a sufficient quantity of finely-divided material for the resonance experiments.

There are many methods for preparing the sample—ultrasonic disintegration, chemical reduction, electrolytic deposition, photochemical reduction, evaporation into an inert gas or liquid, and evaporation onto a solid surface—from among which we have chosen the last as being most generally applicable to all metals, most reproducible, and most capable of yielding a sample containing pieces of uniform size. We have been able to make multiple films, alternate layers of which are collections of quite uniformly-sized platelets of tin.

Tin is a good candidate for the investigation, since

[1] W. D. Knight, *Advances in Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 2, pp. 93–136. A preliminary account of the present work may be found in Phys. Rev. Letters 2, 386 (1959).