

Study of Impurity Distributions (Mainly Lithium in Silicon) Using ac Hopping Conduction

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The results of previous studies on ac impurity conduction are applied in an attempt to study the distribution of impurities when this is not random. The present study applies mostly to the distribution of lithium in silicon, but a few other situations are also examined. A possibility is presented, on a theoretical basis, to determine experimentally the complete distribution function of the distances between minority impurities and their nearest-neighbor majority impurities. It is found, however, that the experimental methods which are required must be more sensitive than methods thus far employed. A less quantitative method for determining the distribution is also proposed. It utilizes previously derived similarity relations which make it possible to compare experimental results on one sample with results on another where the distribution is known to be random. The latter have been reported in the literature by S. Golin. This method is used successfully in the present paper. The following cases are examined: (1) All the impurities are added to the melt before crystallization. (2) Acceptors are added to the melt, but the donors (lithium) are diffused into the crystallized material at 400°C. All the data, except for Golin's samples which serve as the standard, refer to silicon. The experimental data for the first category are taken from the literature. For the second category they are reported in this paper. The results are as follows: Materials where all the impurities were introduced before crystallization indicate that the distribution of impurities is random, or very close to it. In lithium-doped samples, the randomness of the distribution depends on various conditions. A dramatic difference between oxygen-poor and oxygen-rich samples is observed. Oxygen-rich samples, *n*- or *p*-type, always exhibit a random distribution. This indicates that oxygen inhibits the mobility of lithium. In oxygen-poor samples, *n*- and *p*-type, the distribution depends on the temperature from which the samples were quenched. When this temperature is in excess of 200°C, the distribution is again random, or very close to it. For lower temperatures, the distribution deviates from random. To explain the results, one has to assume either pairs with relatively large separations compared to those occurring in the theory of Reiss, Fuller, and Morin, or with traps of the nature described by Tanaka and Fan. The latter is found to be the likely explanation. The distance of closest approach between the lithium and boron atoms in silicon is calculated to be $2.87 \pm 0.03 \text{ \AA}$, in good agreement with Morin's results on aluminum and lithium.

I. INTRODUCTION

IN some recent studies of the ac impurity conduction in the hopping regime,¹⁻⁵ it was found that most experimental observations can be well explained by the use of the Conwell-Mott model^{6,7} for the hopping conduction. It is thus believed that the ac conduction is sufficiently well understood to attempt the use of some of its more detailed features for other investigations. This report tries to use such features to study the way that impurities distribute themselves in the crystals. Forces which exist among the ionized impurities may tend to affect their distribution. In such a case, it will generally differ from a random distribution. The degree to which deviations from a random distribution exist may depend on the material, the kind of impurities, and the way in which the material is prepared. A clear case where such deviations exist is the case of lithium donors in germanium and silicon, which are known to pair with acceptors. The frequency dependence of the hopping conductivity is closely associated with the distribution of the electrically active impurities in the host material. A case of particular interest is one where

the conductivity can be deduced from pairs of impurities. This is because under such conditions the theory is easy to handle. Furthermore, at very low temperatures, this condition is fulfilled, in most cases.³ The important features of the distribution, when the pair treatment is valid, are the spatial and potential separations of the various pairs. The potential separation is due to the Coulombic energy of ionized impurities (majority and minority) and is thus itself determined by the spacing between impurities. A particularly simple case to treat is that of small compensation, where it can be assumed that the potential of the majority impurities is due to the nearest minority impurity only. Low compensation and the pair approximation are assumed throughout this report, except when explicitly mentioned otherwise. The distributions of importance are those of the separation between two majority impurities and of the separation between a majority impurity and a minority impurity. Suitable measurements of the conductivity should therefore be a means to elucidate the distribution of majority atoms both in relation to each other and in relation to the minority impurity atoms.

At high temperatures the energy separation becomes unimportant.¹ The conductivity is thus determined by the spatial distribution of majority impurity atoms, irrespective of their position relative to the minority impurity atoms. Unfortunately, such a temperature range is never reached in practice,¹⁻⁴ and hence the

¹ M. Pollak and T. H. Geballe, *Phys. Rev.* **122**, 1742 (1961).

² S. Golin, *Phys. Rev.* **132**, 178 (1963).

³ M. Pollak, *Phys. Rev.* **133**, A564 (1964).

⁴ S. Tanaka and H. Y. Fan, *Phys. Rev.* **132**, 1516 (1963).

⁵ M. Pollak, *Phys. Rev.* **138**, A1822 (1965).

⁶ N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956).

⁷ E. M. Conwell, *Phys. Rev.* **103**, 51 (1956).

utilization of this regime is not possible. The very low-temperature range is much more readily realizable. There all the conductivity may be attributed to hops which start or end at the majority impurity atom which is nearest to a minority impurity atom. Such a situation exists in *p*-type germanium throughout the investigated temperature range² and in *n*-type and *p*-type silicon at the low-temperature end of the range which was investigated.^{3,4}

The various data presented here and elsewhere^{1,4} are analyzed in two ways. The first method utilizes measurements of σ as a function of temperature and frequency to determine how close the distribution of impurities is to a random one. The data obtained by Golin² on materials in which the distribution of impurities is known to be random serves as the basis of comparison. In order to enable comparison with Golin's results, the data to be compared are transformed by means of certain similarity relations.³ The degree of variance between the results of the transformation and Golin's data indicates how far the distribution is from random.

The second method utilizes the very low temperature data and a theory based on the Mott-Conwell^{6,7} model. The distribution of separations between minority impurity atoms and their nearest-neighbor majority atoms (r_1) can be fully deduced under certain conditions. This is true for a certain range of distances which depends on the frequency range of the measurements.

The first method yields less information than the second method, but it is not subject to any detailed assumptions and generally requires less accurate measurements.

Experimental results are evaluated for various ways of doping germanium and silicon and for various kinds of impurities. Data obtained on silicon doped with lithium under various conditions are also reported.

II. METHODS OF ANALYSIS

a. Comparative Analysis

This analysis compares ac conductivity measurements on materials having an unknown distribution of impurities with similar measurements on materials where the distribution of impurities is known to be random, as is, e.g., the case for the material measured by Golin. Golin's samples were doped by irradiation with thermal neutrons and therefore may be assumed to have a random distribution of impurities. The impurity concentration and the compensation ratio are also well known for these samples. Furthermore, the experimental results for Golin's sample A correspond closely to theoretical predictions (see Fig. 9, Ref. 2). For these reasons, Golin's measurements are used here as the standard for comparison. The comparison of the various materials investigated in this work with Golin's sample A is made by using the similarity relations reported in Ref. 3. The similarity relations were derived under the assumptions that the Mott-Conwell model is

valid and that a random distribution of impurities exists. One must remember, however, in view of Ref. 5, that some care is required to ascertain that only single hops are of importance. Otherwise, the similarity relations are not perfectly obeyed even under the above conditions. The similarity relations give the ratio of conductivities of different materials when certain conditions relating temperatures and frequencies are fulfilled. This makes it possible to transform a set of measurements⁸ $\sigma(T, \omega)$ for one material with a random distribution into a set which must be valid for another material. The transformation depends, of course, on the impurity concentration, type of impurity, and host material. In Ref. 3, the similarity relations and conditions are given in such a way that they relate only samples of the same material. This has to be extended to enable a comparison between different materials if we wish to use Golin's results on germanium also for silicon. This generalization is possible because the quantity r_ω/a of Ref. 3 (r_{\max}/a in Refs. 1 and 2) is extremely insensitive to various quantities of the host materials, e.g., velocity of sound, deformation potential, etc. Thus, for example, at 1°K, 10⁴ cps, the value of r_ω/a is 14.2 in germanium² and 14.4 in silicon.³ The temperature and frequency dependences of r_ω/a are the same for different materials. We make use of the fact that r_ω/a is almost the same for silicon and germanium and assume that it is identical in both cases. With this, the similarity relations and conditions given in Ref. 3 are generalized as follows:

$$\frac{\sigma_2}{\sigma_1} \equiv s = \frac{N_{A2}}{N_{A1}} \frac{\omega_2 a_2}{\omega_1 a_1} n^2, \quad (1)$$

where

$$\begin{aligned} n &= (N_{D1}/N_{D2})^{1/3}, \\ T_2 &= (\kappa_1/\kappa_2) T_1 n^{-1}, \\ \omega_2 &= n^{-1} e^{20.8(1-na_1/a_2)} T_1^{(1-na_1/a_2)} \omega_1^{na_1/a_2} \kappa_1/\kappa_2. \end{aligned} \quad (2)$$

Equation (1) is the similarity relation obeyed under the similarity conditions given in Eq. (2).

The subscripts *A* and *D* are assigned to minority and majority impurities, respectively, regardless of whether they apply to *n*- or *p*-type material. The subscripts 1 and 2 refer to the two materials to be compared. (Subscript 1 will refer usually to Golin's sample A.) The symbols used in Eqs. (1) and (2) are consistent with those used in Ref. 3.

The factor N_{A2}/N_{A1} has not been incorporated in the derivation of the similarity relations. It was assumed that the dependence on the minority impurity concentration can be taken into account separately, since the conductivity should be proportional to N_A . Experimental results on *n*-type silicon were reported to follow a proportionality¹ with $N_A^{0.85}$ rather than with N_A . In view of this, N_{A2}/N_{A1} in Eq. (1) will be replaced by $(N_{A2}/N_{A1})^{0.85}$ for such materials.

⁸ Unless otherwise stated, σ will refer to the real part of the conductivity only.

b. Basic Analysis

This analysis utilizes ac conductivity measurements at very low temperatures and theoretical results similar to those obtained in Ref. 3 for very low temperatures. However, we leave unspecified the distributions of impurities which in Ref. 3 [Eqs. (3a), (3b), (3c)] were assumed to be random. Equation (3a) represents the distribution of distances r_1 between minority and nearest-neighbor majority impurities, while Eqs. (3b) and (3c) refer to the distribution of distances r_3 among the majority impurities. As was pointed out in the Introduction, the latter could be determined from high-temperature measurements. However, such a range is not practically realizable. Hence the distribution of distances r_3 between majority impurities is assumed to be random. This is justified because forces which are responsible for altering the distribution from a random one influence much more strongly the distances between a minority atom and its nearest-neighbor majority atom than they influence the distance between two majority atoms. This becomes clear when one considers the extreme case of pairing and lack of pairing. In the latter case, the distribution is, of course, random. In the first case, the majority atom which pairs with the minority atom almost cancels the Coulombic field so that other majority atoms are not subjected to the Coulombic force of the minority atom. More specific reasons may justify the assumption in some cases. A relevant case is that of *p*-type, lithium-doped samples where the majority atoms distributed themselves before pairing forces existed. In any case, the assumption may be tested from the very low temperature data itself by comparing the real and the imaginary parts of the conductivity. While the real part of the conductivity of pairs with a hopping time τ is proportional to $(\omega^{-1}\tau^{-1} + \omega\tau)^{-1}$, the imaginary part is proportional to $(1 + \omega^2\tau^2)^{-1}$. Since τ is essentially an exponential function of the distance between the majority impurity atoms, the first function resembles a δ function, finite only around $r - r_\omega$, while the second function resembles a step function equal to unity for $0 < r < r_\omega$ and zero elsewhere. Therefore the real part measures the number of majority atom pairs of the size r_ω , while the imaginary part is a measure of the number of pairs of the size r_ω or less. The relation between the two thus is given by the distribution of distances between majority atoms. It is easy to show that $\text{Re}\sigma/\text{Im}\sigma = 1.25\pi a/r_\omega$ for a random distribution and generally will be different for an altered distribution. It therefore provides a test for the above assumption.

The conductivity for the pair model is given in general terms by Eq. (1a) of Ref. 3. When the variable ΔE is replaced by the variable r_1 and all other integrations are performed, this equation can be written for very low temperatures:

$$\sigma(\omega) = \int \sigma(r_1, \omega) p(r_1) dr_1. \quad (3)$$

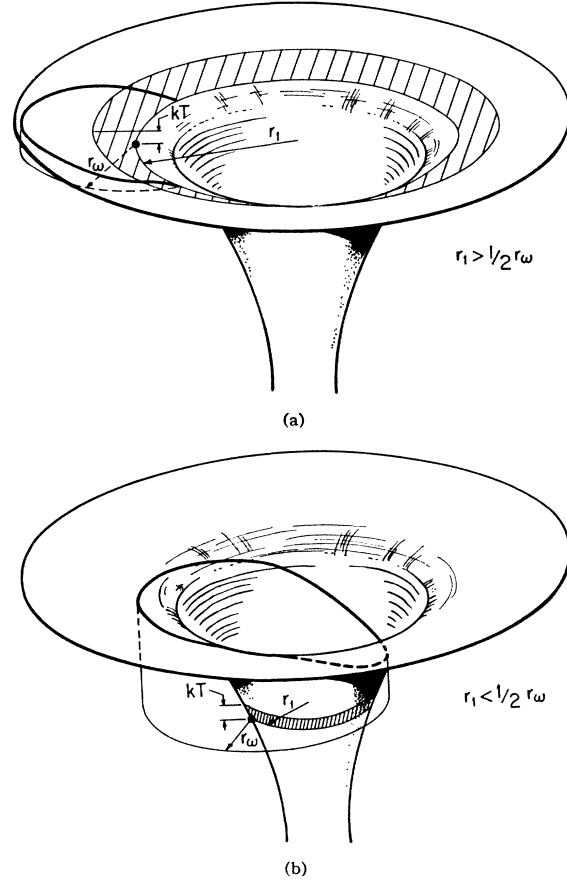


FIG. 1. The figure demonstrates that configurations of impurities in which the separation r_1 between the minority impurity and its nearest majority impurity is smaller than a certain value cannot contribute to the ac conductivity. For such a case, it is impossible that a majority impurity has simultaneously a spatial separation very nearly r_ω from the impurity at r_1 and an energy separation less than kT from that impurity. The first condition is represented by the heavy curve on the Coulomb energy surface. The curve is an intersection of the surface with a cylinder of radius r_ω centered around the impurity at r_1 . The second condition is represented by the shaded bands on the energy surface. In (a), where $r_1 > \frac{1}{2}r_\omega$, there is a common domain for both conditions, and thus an impurity lying in that domain will fulfill both conditions simultaneously. Such a configuration would contribute to the conductivity. In (b), where $r_1 < \frac{1}{2}r_\omega$, there is no common domain to the two conditions and thus no contribution to the conductivity can come from such a configuration.

Here $\sigma(r_1, \omega)$ is the conductivity of a proper ensemble of pairs, all of which have the separation r_1 between a minority and its nearest-neighbor majority impurity. A pair can contribute to the conductivity only if it has a spatial separation r_ω and an energy separation not much larger than kT . For some values of r_1 , it is impossible to fulfill both of these conditions. This is demonstrated in Fig. 1, which illustrates that the possibility to fulfill both conditions exists only for $r_1 > \frac{1}{2}r_\omega - \Delta r$. The magnitude of Δr is $(r_\omega/r_T)^{\frac{1}{2}}r_\omega$. At 1°K, the factor r_ω/r_T is typically 0.02. Thus, at very low temperatures, $\sigma(r_1, \omega)$ has a steep rise at $r_1 = \frac{1}{2}r_\omega$, and suppresses a part of $p(r_1)$ in the expression for the conductivity, as is indicated in

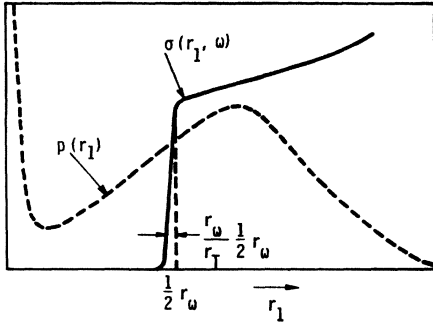


FIG. 2. A graphical representation of Eq. (3). The conductivity $\sigma(\omega)$ is the area under a curve which results from the multiplication of the two curves in the figure. The one represents the distribution of distances r_1 , the other the conductivity at the frequency ω , of an ensemble of configurations which are characterized by the distance r_1 . The reason for the steep slope of the latter curve at the point $r_1 = \frac{1}{2}r_\omega$ is explained by Fig. 1.

Fig. 2. By changing the frequency, and thus r_ω , the steep part of $\sigma(r_1, \omega)$ changes position, and the distribution can be evaluated from the observations of changes of the conductivity. Specifically, if $p(r_1)$ is left undetermined in the very low temperature treatment of Ref. 3, the conductivity is

$$\sigma(\omega) = \frac{1}{2}\pi^2 N_A N_D r_\omega^3 a \kappa \omega \int_{\frac{1}{2}r_\omega}^{\infty} p(r_1) r_1^2 dr_1. \quad (4)$$

The factor $(1 + \frac{1}{2}r_\omega/r_1)^{-1}$ which appears in the equivalent expressions of Ref. 3 is missing here. The omission is the result of eliminating the approximation described in footnote 10 of Ref. 3. When this is done, the factor $(1 + \frac{1}{2}r_\omega/r_1)^{-1}$ is replaced by a factor much closer to unity. If, using Eq. (4), one takes the derivative $\sigma(\omega)/(\omega r_\omega^3)$ with respect to r_ω , the following expression is valid:

$$p(\frac{1}{2}r_\omega) = \frac{3}{\pi^2 N_A N_D a \kappa r_\omega^2} \frac{d}{dr_\omega} \left(\frac{\sigma}{\omega r_\omega^3} \right), \quad (5)$$

where $p(\frac{1}{2}r_\omega) = p(r_1)$ at $r_1 = \frac{1}{2}r_\omega$. The following procedure will thus determine the distribution $p(r_1)$. The experimental value of σ/ω is divided by r_ω^3 and the result plotted against r_ω . The latter may be determined for each ω with the aid of Ref. 3, using either Eq. (6) or Fig. 3. The value of the slope is measured for various values of r_ω . This, divided by $\frac{1}{2}\pi^2 N_A N_D a \kappa r_\omega^2$ is the value of the properly normalized distribution function at $r_1 = \frac{1}{2}r_\omega$. This procedure is, of course, limited to the range of $r_1 = \frac{1}{2}r_\omega$ given by the frequency range in which σ was measured. Thus the frequency range 10^2 – 10^5 cps in p -doped silicon corresponds to a range r_1 of 110–160 Å in which the distribution can be examined. It is clear that a large frequency range must be available for an extensive examination of the impurity distribution. Furthermore, since it is the very low temperature conductivity which is of interest, the resistivities are

very high. Therefore, it is difficult to obtain a measurement which is sufficiently accurate to determine $d\sigma/dr_\omega$.

III. RESULTS

The following cases are evaluated: measurements on germanium described in Ref. 2; measurements on silicon described in Ref. 1; and measurements on lithium-doped silicon which will be described in this report. The measurements on germanium will serve primarily as a reference for the comparative analysis. The basic analysis cannot be applied to them, because the lowest temperature at which conductivity was measured, i.e., 1.2°K, is not sufficiently low for the purpose.

a. Silicon; Impurities Added to the Melt

This section utilizes data from Ref. 1 which were prepared either by method (1) or (2) as described in that report. The material is n -type silicon with arsenic, phosphorus, or antimony added to the melt from which the crystal was pulled.

1. Comparative Analysis

Results of conductivity measurements on some of the samples of Ref. 1 are compared via the similarity relations [Eqs. (1) and (2)] with Golin's² conductivity measurements on his sample A. The curve for 10^3 cps in Fig. 4 of Ref. 2 is used to represent sample A. The procedure for comparison is as follows: The value of n is determined from the majority impurity concentrations of sample A and the sample under consideration (sample X). For the temperature T_1 corresponding to each experimental point on the curve representing sample A, the temperature T_2 is found using the first of Eqs. (2). The frequency ω_2 is calculated for each point from the second of Eqs. (2) using 10^3 cps for ω_1 . The conductivity σ_2 of sample X is determined for the frequency ω_2 and the temperature T_2 . This is done by interpolation (extrapolation was necessary in one case) between measured experimental points. The value of $\sigma_2(\omega_2, T_2)$ is divided by the value of s , as calculated from Eq. (1). In accordance with previous remarks, $(N_{A2}/N_{A1})^{0.85}$ is used instead of N_{A2}/N_{A1} in Eq. (1). The value of σ_2/s is compared with σ_1 . If the distribution of impurities in sample X is random, the two must coincide.

The following numbers are used in the calculation: $\kappa_1 = 16$, $\kappa_2 = 12$, $a_1 = 74$ Å, $a_{2As} = 20$ Å, $a_{2P} = a_{2Sb} = 22.8$ Å. The value for a_1 is from Ref. 2; the value of a_{2As} from calculations by Miller and Abrahams⁹; and the values of a_{2P} and a_{2Sb} are from the result³ $a_{2P}/a_{2As} = 1.14$ and¹⁰ $a_{2P}/a_{2Sb} = 1.00$. Results of the comparison are

⁹ A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

¹⁰ M. Pollak and T. H. Geballe (unpublished).

shown in Fig. 3 for an antimony-doped, a phosphorus-doped, and an arsenic-doped sample. The last is in very good coincidence with sample A, while the other two agree well in magnitude, but the functional dependence on temperature is not exact. The existing differences can perhaps be attributed to the somewhat unrealistic implicit assumption that the wave functions of the various ground states differ only by their radius and are otherwise identical. A more likely reason is that multiple hops may begin to contribute to the conductivity⁶ in the phosphorus- and antimony-doped samples. The slight differences thus are not necessarily an indication of lack of randomness.

2. Basic Analysis

The attempt to utilize Eq. (5), together with measurements of conductivity at very low temperatures to determine the distribution function of distances between

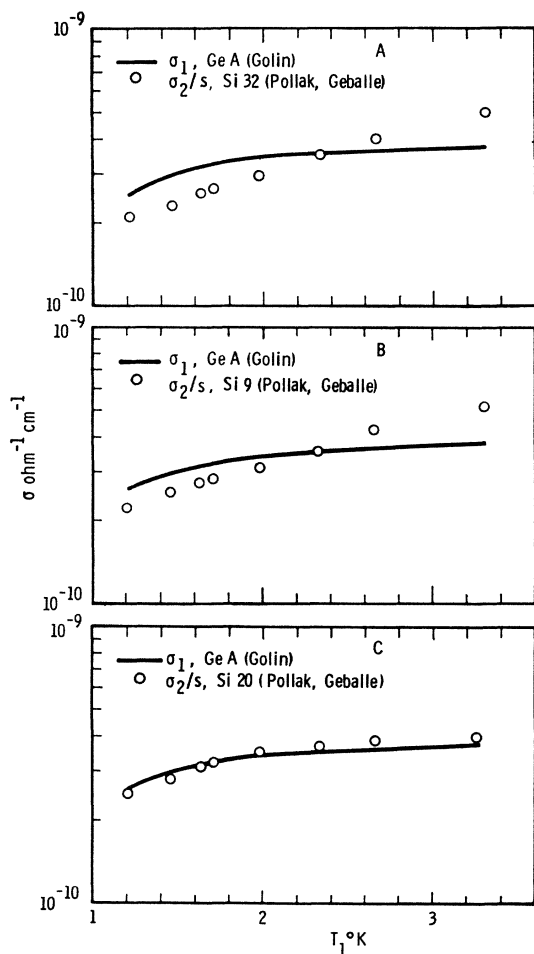


FIG. 3. Results of the application of similarity relations for a comparison of data reported in Ref. 1 with Golin's data on Sample A (Ref. 2). (a) A comparison of an antimony-doped sample, (b) phosphorus-doped, and (c) arsenic-doped. For a detailed description of the samples see Ref. 1.

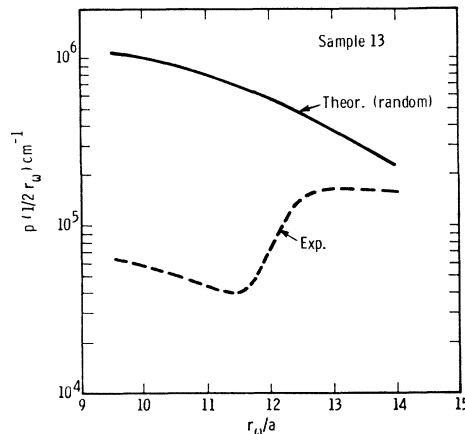


FIG. 4. Results of an attempt to obtain the distribution of r_1 in Sample 13 of Ref. 1 by the method of basic analysis described in the text. The upper curve is theoretical and corresponds to a random distribution. The lower curve is the application of Eq. (5) to data obtained from ac conductivity measurements.

minority and nearest-neighbor majority impurities, i.e., $p(r_1)$, was not successful. This is demonstrated in Fig. 4 for sample 13 of Ref. 1. The upper curve is the theoretical distribution function when a random distribution is assumed; the lower curve is the result of applying Eq. (5) to the conductivity measured at 1.2°K between 30 and 2×10^5 cps at approximately 1-octave intervals. It is obvious that the difference between the two curves is too large to be attributable to an actual deviation from a random distribution. It is probable that both experimental difficulties and an imperfect understanding of the hopping conductivity are responsible for this failure. It must be realized that the attempted analysis is based on much finer details of the conductivity behavior than previous work had utilized.¹⁻⁴ It is possible, therefore, that details of the wave functions which had been ignored in the past are of sufficient importance to make themselves demonstrable here. On the other hand, the experimental situation under the present conditions also is not very good. The function $\sigma(\omega)/r_w^3\omega$ is a slowly varying function of r_w . Thus the measured derivative with respect to r_w , which is the crucial term in determining the distribution, may well be dominated by the inaccuracies in measuring $\sigma(\omega)$ at various ω rather than by the actual value of the derivative. It is therefore concluded that a more accurate experimental arrangement is required, preferably one that would directly measure the quantity $d\sigma(\omega)/d\omega$.

b. Silicon—Acceptors Added to the Melt, Li Donors by Diffusion

The case of lithium-diffused donors is very suitable for this study, since the distribution r_1 of distances between a minority impurity and the majority impurity nearest to it is known to differ from a random one due to

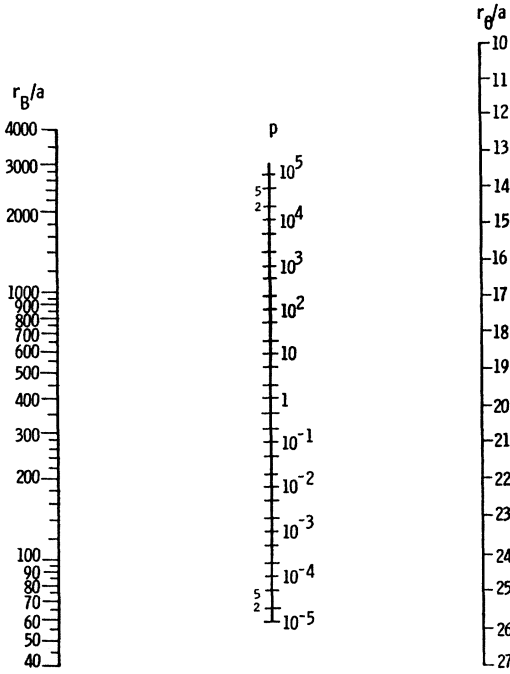


FIG. 5. A nomogram for evaluating the distance of closest approach α between a lithium atom and a minority impurity. The values of r_B and r_Θ are calculated from Eq. (7) (replacing the subscript D for B) and Eq. (8), respectively; r_B is related to the acceptor concentration and r_Θ to the temperature characteristic of the lithium distribution. The value of ρ is related to the pairing by Eq. (10), and can be obtained from conductivity measurements as suggested in the text relevant to Table II. When these values are known, a line is drawn through the appropriate point of the central column. The line must be drawn, by trial and error, at such an angle that the values intersected in the right and left columns yield a consistent value for α .

the process of pairing.¹¹⁻¹⁴ The paper by Reiss, Fuller, and Morin¹¹ includes a rather detailed treatment of the pairing phenomenon. Rewriting Eq. (7.11) from that work in the present notation, the equilibrium distribution of the quantity r_1 at temperature Θ is given by

$$\rho(r_1) = \nu 4\pi r_1^2 N_D \exp(r_\Theta/r_1) \exp(-r_1/r_D)^3, \quad (6)$$

where ν is a normalization factor,

$$r_D = (4\pi N_D/3)^{-1/3}, \quad (7)$$

and r_Θ is defined in analogy to r_T as

$$r_\Theta = e^2/4\pi\kappa k\Theta. \quad (8)$$

In the following, Θ refers to the temperature from which the samples were quenched and T to the temperature at which ac conductivity measurements were taken. Figure 2 of Ref. 3 can be used for a quick determination of r_Θ , allowing for order-of-magnitude changes. Equations

¹¹ H. Reiss, C. S. Fuller, and F. J. Morin, *Bell System Tech. J.* **35**, 535 (1956).

¹² E. M. Pell and F. S. Ham, *J. Appl. Phys.* **32**, 1052 (1961).

¹³ J. P. Maita, *J. Phys. Chem. Solids* **4**, 68 (1958).

¹⁴ E. M. Pell, *Symposium on Solid State Physics and Electronics and Telecommunications* (Academic Press Inc., New York, 1960), Vol. I.

tion (8) and corresponding equations in Refs. 11, 12, and 13 differ by a factor 4π . This merely reflects the use of different units. The general shape of the distribution of Eq. (6) is shown by the dashed line in Fig. 2. Unfortunately, we cannot employ the basic method proposed in Sec. II to evaluate how well the distribution given by Eq. (6) actually is obeyed. As was already pointed out, the accuracy of our measurements is too poor to allow us to predict a random distribution of impurities. With respect to the present problem, the situation is made worse since the pairing process is bound to decrease the conductivity. We shall, however, make use of the comparative method to bring out some qualitative features of the problem. The important feature of the distribution, as given by Eq. (6), is the possibility of separating the curve into two distinct regions according to whether $r_1 < \frac{1}{2}r_\Theta$ (left-hand side of the minimum) or $r_1 > \frac{1}{2}r_\Theta$ (right-hand side of the minimum). In the former region, the distribution is governed predominantly by the factor $\exp(r_\Theta/r)$, i.e., by the pairing forces. In the latter, the distribution is very close to random, except for the constant ν . This constant arises for the following reason. In a random distribution, $\nu = 1$, but when pairing occurs, an appreciable area from beneath the distribution is shifted to the left of $\frac{1}{2}r_\Theta$. Since the total area must stay normalized to unity, the area to the right of $\frac{1}{2}r_\Theta$ must decrease appropriately. Therefore, one may think of a fraction of ν of atoms as being randomly distributed, while the rest are paired. The latter will not contribute to the ac conductivity, since they all are much below the cutoff at $\sigma(r_1, \omega)$, even at temperatures around 15°K (see Fig. 2). If the distribution given by Eq. (6) is correct, the samples therefore should behave exactly like samples which have a random distribution, except that the conductivity will be caused by $N_A - P$ carriers instead of by N_A carriers. (As in the notation of Ref. 11, P is the number of pairs per cm³.) Reference 11 provides a method of evaluating P . This is based on the possibility to achieve a good approximation of Eq. (6) by neglecting the term $\exp(-r/r_D)^3$. We shall follow this procedure and obtain in this way

$$P/N_A = 1 - \left(1 - \int_2^{r_\Theta/\alpha} \zeta^{-4} e^\zeta d\zeta / \int_{r_\Theta/r_B}^{r_\Theta/\alpha} \zeta^{-4} e^\zeta d\zeta \right)^t, \quad (9)$$

where ζ stands for r_Θ/r , α stands for the distance of nearest approach between a lithium and a boron atom, and r_B is defined in analogy with Eq. (7) for the acceptor concentration. (Therefore, for p -type material, $r_B \equiv r_D$.) For n -type material, t in Eq. (9) is equal to N_D/N_A ; for p -type material, $t=1$. The dominant contributions to the integral come from regions near the limits, because $r_\Theta/\alpha \gg 1$ and $r_\Theta/r_B \ll 1$. Thus it is possible to approximate the integrals as follows:

$$P/N_A \sim 1 - \{ 1 + [\frac{1}{3}(r_\Theta/\alpha)(r_B/\alpha)^3 e^{-r_\Theta/\alpha}]^{-1} \}^{-t} \\ \equiv 1 - (p^{-1} + 1)^{-t}, \quad (10)$$

where $p = \frac{1}{3}(r_{\Theta}/\alpha)(r_B/\alpha)^3 e^{-r_{\Theta}/\alpha}$. Thus for $p \gg 1$, tp^{-1} is approximately the probability that a minority impurity is paired; for $p \ll 1$, p' is approximately the probability that a minority impurity is not paired. A convenient nomogram which relates p to r_{Θ} , r_B , and α is given in Fig. 5.

1. Description of Samples and of Their Preparation

The measurements were performed primarily on the samples described in Table I. The geometry of the samples was similar to the one described in Ref. 1. All the samples were cut from singly doped (boron) crystals before Li was diffused into them. Samples *L5* and *L56* were cut from pulled crystals; *L45*, *L50*, and *L55* were cut from crystals obtained by the floating-zone method. The lithium was diffused by immersing the samples into a tin-lithium alloy at approximately 400°C for a period of 15 h and subsequently quenching in liquid nitrogen, where they were also stored.¹⁵ The samples listed in Table I are representative of the following categories: In *L5*, lithium is the majority impurity, and the sample has a high oxygen concentration; *L45* has lithium again as a majority impurity, but the sample has a small oxygen concentration; in *L50* and *L55*, lithium is the minority impurity and the oxygen concentration is low; *L56* has also lithium as a minority impurity and the oxygen concentration is high. Since the lithium was diffused at a temperature close to that at which thermal donors are created in samples with a high oxygen content, a control sample was used with *L56*. The control sample was kept at the high temperature together with *L56* but outside the tin-lithium bath. The Hall effect measured on the control sample after heating was identical with the Hall effect before heating. This indicates that thermal donors were not created in significant amounts. The use of a control sample with *L5* was not necessary, because thermal donors would not affect the sample as much.

The boron concentration was determined by room-temperature Hall-effect measurements before the lithium was diffused into the samples. The Hall effect was also measured after diffusion to determine the lithium concentration. These measurements were performed directly on the disk-shaped samples utilizing

the method described by Van der Pauw.¹⁶ Small electrodes were gold plated both for the Hall voltage and the current, and pressure contacts were made to those. Reproducibility was better than 1%. Measurements of the ac conductivity were performed after the samples were brought to a series of different temperatures between 0 and 300°C and quenched in liquid nitrogen. The samples were kept at the various elevated temperatures long enough for the lithium atoms to redistribute themselves around the minority impurity, but not long enough to allow for the formation of noticeable layers of depletion. To ascertain this, the measurement of the room-temperature Hall effect was repeated after the whole series of experiments was finished on a sample. In addition, the ac conductivity measurements at low temperatures were repeated for the room-temperature distribution. Comparison of the measurements before and after the sample was subjected to the various heat treatments indicated that no noticeable depletion of lithium occurred during the whole series of experiments.

2. Results on Oxygen-Poor Samples

In these samples which were obtained from crystals grown by the floating-zone method, and which thus contained very little oxygen, there was found a common characteristic that the conductivity was markedly dependent on the temperature Θ . This is illustrated in Figs. 6 and 7, where the measured conductivities are plotted for samples *L45* and *L50*, both quenched from 200°C and from 23°C. For a comparison with a random distribution, the similarity relations are applied to these data. Sample 20 is used again for the reference sample. Figures 8 and 9 show the result of the similarity transformation for various temperatures Θ . The following values were used for the similarity transformation. For sample *L45*: $n=1.065$, $\kappa_1:\kappa_2=1.00$, $a_1:a_2=0.738$. For sample *L50*: $n=0.750$, $\kappa_1:\kappa_2=1.00$, $a_1:a_2=1.00$. The subscripts 2 refer to the lithium doped samples, the subscript 1 to sample 20. The values of n are calculated from the majority concentrations. The value of a for boron is assumed to be equal to that of arsenic on the basis of Tanaka and Fan's work.⁴ The value for a for lithium is calculated from ionization energies and from Kohn's relation between ionization energies and radii of localized wave functions.¹⁷ The conductivity at 10^5 cps is used for sample 20. The following ranges are then implied by the similarity conditions: The range of T_2 for sample *L45* is from 1.2°K to 11.3°K, and the frequency is around 1.5×10^4 cps. For sample *L50*, T_2 ranges from 1.8°K to 18°K, and the frequency is around 4×10^5 cps. The measurements thus had to be extrapolated above 10^5 cps for the latter sample.

The result shows that, for large Θ , the distribution of r_1 is close to random for both samples, as expected.

TABLE I. Specifications of the lithium-doped samples treated in this article.

Sample No.	Boron conc.	Lithium conc.	Crystal growth	Type
<i>L5</i>	1.4×10^{15}	8.1×10^{15}	pulled	n
<i>L45</i>	1.2×10^{15}	1.4×10^{16}	floating zone	n
<i>L50</i>	4.1×10^{16}	9.3×10^{15}	floating zone	p
<i>L56</i>	2.14×10^{16}	1.2×10^{15}	pulled	p
<i>L55</i>	8.2×10^{15}	2.0×10^{15}	floating zone	p

¹⁵ At this point, the authors would like to express their thanks to Dr. C. S. Fuller for his generous advice about the technique of lithium doping.

¹⁶ L. J. Van der Pauw, Philips Res. Rept. 13, 1 (1958).

¹⁷ W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

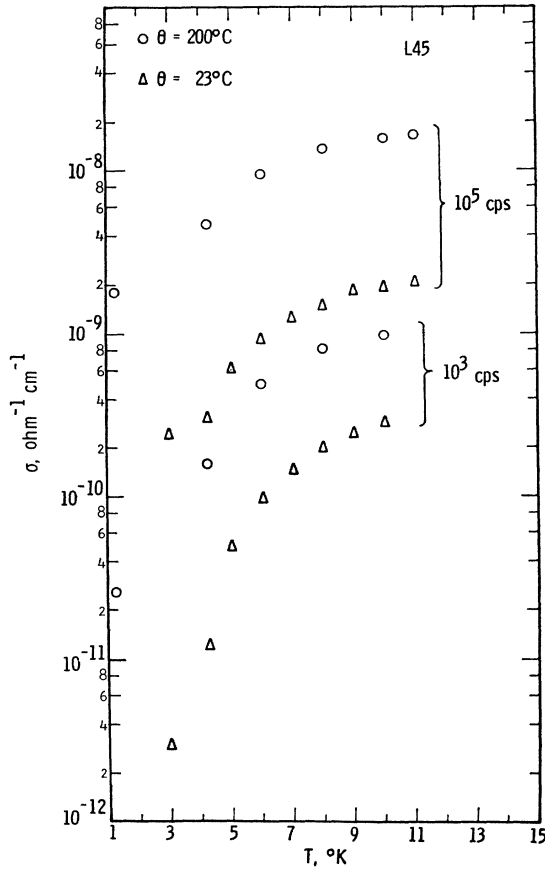


FIG. 6. Conductivity of sample L45 measured for $\Theta = 23^\circ\text{C}$ and $\Theta = 200^\circ\text{C}$. To preserve the clarity of the figure, the conductivities are plotted only for 10^3 cps and for 10^5 cps.

While the strong variation in conductivity with the temperature Θ is, by itself, consistent with the pairing phenomenon, the details of Figs. 6, 7, 8, and 9 do not seem to support Eq. (6). To be consistent with the theoretical distribution of Eq. (6), the curves of $\ln\sigma$ for a given frequency and different Θ would have to be parallel. This again reflects the fact that apart from a constant factor, Eq. (6) represents a random distribution for $r_1 > \frac{1}{2}r_\Theta$. The distribution for $r_1 < \frac{1}{2}r_\Theta$ is not random, but in our frequency range this regime of r_1 is too small to contribute to the conductivity. This is demonstrated by the following figures: At $\Theta = 300^\circ\text{K}$, $\frac{1}{2}r_\Theta \approx 25 \text{ \AA}$, while $\frac{1}{2}r_\omega(1 - r_\omega/r_T) = 70 \text{ \AA}$ when $r_\omega = 200 \text{ \AA}$ and $r_T = 600 \text{ \AA}$. The last two figures are appropriate for the highest temperature T of our experiments. The quantity $\frac{1}{2}r_\omega(1 - r_\omega/r_T)$ represents the value of r_1 below which $\sigma(r_1, \omega)$ vanishes (see Fig. 2). It is possible, therefore, to disregard all the paired atoms when evaluating the ac hopping conductivity and to assume $N_A - P$ randomly distributed minority, and $N_D - P$ randomly distributed majority, impurity atoms. For lightly compensated material, $N_D - P \sim N_D$. The conductivity of a sample described by Eq. (6) is related to a

sample without pairing by a constant factor, because the conductivity is known to be proportional to N_A (or $N_A^{0.85}$). Thus, on the basis of Eq. (6), it is difficult to explain that $\sigma(\Theta)/\sigma(\Theta' < \Theta)$ is larger for small T than it is for large T . Neither can this observation be accounted for by a nonrandom distribution of r_3 , since the same effect occurs also in L50. The distribution of r_3 in the latter is guaranteed to be at least as close to random as it is in sample 20. The reason for this is that the boron atoms, which constitute the majority impurity in sample L50, were not subjected to pairing forces during their distribution in the crystal. Two possible explanations for this inconsistency must be considered: The first is simply to conclude that Eq. (6) does not describe in detail the lithium-doped samples. The experimental results then would indicate that an appreciable fraction of the pairs is larger than Eq. (6) suggests. If a large number of pairs is approximately of the size $\frac{1}{2}r_\omega$, then the increasing T will cause an increase in the conductivity because of the contribution from pairs inside the broadening region between $\frac{1}{2}r_\omega$ and $\frac{1}{2}r_\omega(1 - r_\omega/r_T)$. This explanation is not compelling, however. It is possible that the relatively rapid increase of σ with T for the measurements at low Θ comes from traps with a sufficiently small activation energy to be observable in the relevant regime of T . Such traps would

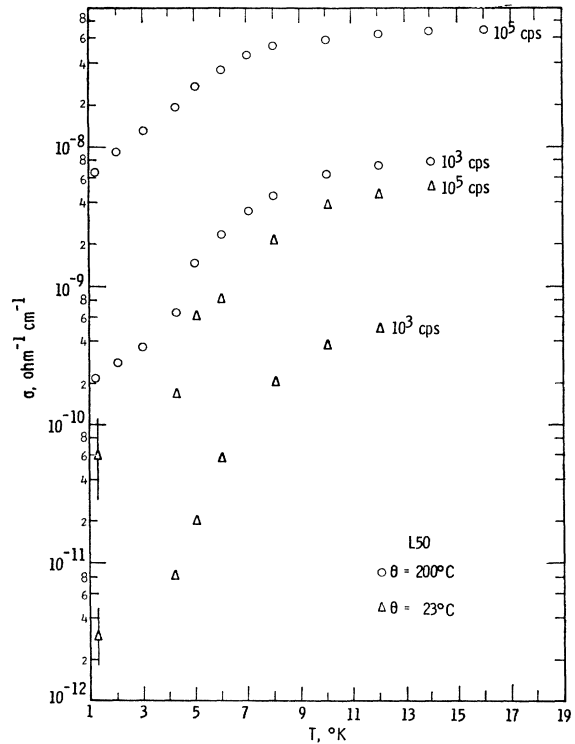


FIG. 7. Conductivity of sample L50 for $\Theta = 23^\circ\text{C}$ and for $\Theta = 200^\circ\text{C}$. As in Fig. 6, only the conductivities at 10^3 cps and 10^5 cps are shown. The vertical lines through the points at $\Theta = 23^\circ\text{C}$ and $T = 1.2^\circ\text{K}$ indicate a considerable uncertainty for these measurements.

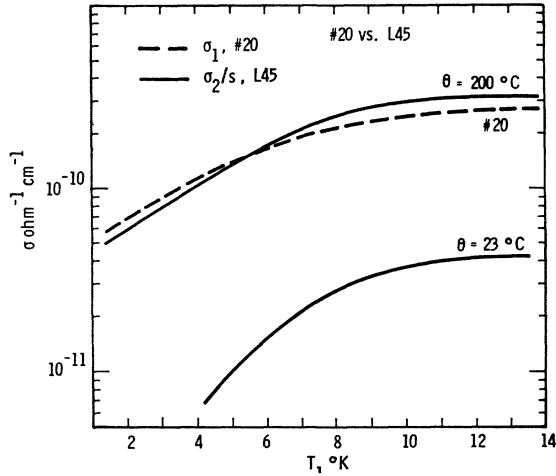


FIG. 8. Comparison of sample L45 with Sample 20 of Ref. 1, using the similarity relations. The comparison is done for $\theta = 23^\circ\text{C}$ and $\theta = 200^\circ\text{C}$.

consist of majority atoms which may be far removed from the minority impurities but which have, for some reason, an energy below that of the nearest neighbor of the minority impurity. One reason for such a trap to exist was suggested by Tanaka and Fan⁴; another is associated with pairs. The Tanaka-Fan traps are created by the resonance energy between two majority atoms. If these happen to be sufficiently close together, the resonance energy is large enough to suppress one of the states below the energy at the nearest neighbor to the minority atom. The dipole traps are created when a majority atom is near enough to an acceptor-donor pair. It then must be in the proper position so that the dipole potential suppresses its state below that of the nearest neighbor to an unpaired minority impurity. The following is an evaluation of the possibility that the two types of traps could be responsible for the observations.

The conductivity $\sigma(r_1, \omega)$ in Eq. (3) must be modified by a certain factor. In deriving the expression for $\sigma(\omega)$, it was assumed that in every configuration with one minority impurity atom, the charge carrier is situated predominantly at the majority impurity, which is at the distance r_1 from the minority impurity. Since this is not the case when traps are present, the conductivity must be reduced accordingly. The reduction factor thus must include the probability that a trap exists in a configuration characterized by r_1 and the probability for thermal activation from this trap. When traps occur with high probability, there may be several per configuration, but account of the lowest one only is taken. This is a good approximation and keeps the analysis simple. To be consistent with this approximation, it is essential to ignore the formation of levels similar to the traps above the energy of the state of r_1 . The reason for this is that other states exist above the state of r_1 , namely those which contribute to the hopping

conduction. Taking account of the traps is accomplished by replacing $\sigma(r_1, \omega)$ in Eq. (3) by $\sigma'(r_1, \omega)$, where

$$\sigma'(r_1, \omega) = \sigma(r_1, \omega) \int_0^\infty f(x) d\mathcal{P}(r). \quad (11)$$

In Eq. (11), x is the reduced energy of the trap, i.e., $\Delta E/kT$; r is a parameter characterizing the trap, and is a single-valued function of x ; $f(x)$ is the probability for thermal activation, and $d\mathcal{P}(r)$ is the probability that the lowest trap in a configuration with r_1 will be characterized by r . In view of the foregoing remarks, the function $f(x)$ has the following form:

$$\begin{aligned} f(x) &= (e^x + 1)^{-1}, & \text{for } x > 0; \\ f(x) &= 1, & \text{for } x < 0. \end{aligned} \quad (12)$$

The expression for $d\mathcal{P}(r)$ and the connection between r and x depends on the type of trap. For the Tanaka-Fan traps,

$$\begin{aligned} d\mathcal{P}(r) &= 3 \frac{N_D - P}{N_A - P} \left(\frac{r}{r_D} \right)^2 \\ &\times \exp\left(-\frac{N_D - P}{N_A - P} \frac{r^3}{r_D^3} \right) d\left(\frac{r}{r_D} \right) \equiv e^{-z} dz, \end{aligned} \quad (13)$$

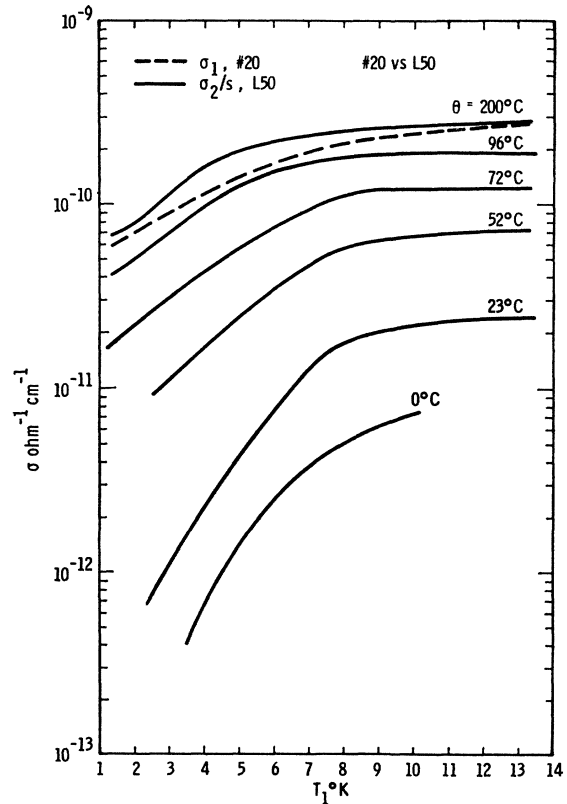


FIG. 9. Comparison of sample L50 with sample 20 of Ref. 1, using the similarity relations. The comparison is done for several values of θ between 0°C and 200°C .

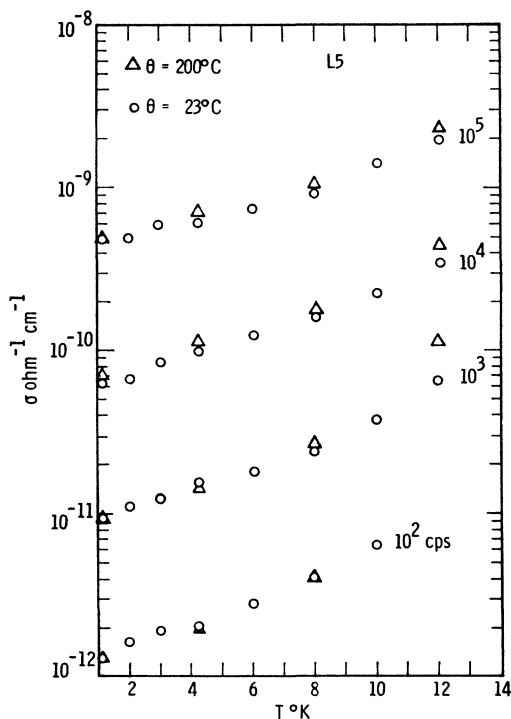


FIG. 10. Conductivity of sample L5 at 10^2 , 10^3 , 10^4 , and 10^5 cps and for $\Theta=23^\circ\text{C}$ and $\Theta=200^\circ\text{C}$.

where the parameter r represents the distance between two majority atoms, and⁴

$$x = \frac{4}{3} (r_T/r_1) \left[\frac{r_1/a}{r_D/a} (r/a) e^{-r/a} - 1 \right] \\ = \frac{4}{3} (r_T/r_1) \left[\frac{r_1/a}{r_D/a} (r_D^*/r_A^*) z^{1/3} \right. \\ \left. \times \exp(-r_D^2 z^{1/3}/ar_A) - 1 \right], \quad (14)$$

where $(r_D^*/r_A^*)^3 = (N_A - P)(N_D - P)$.

The integral in Eq. (11) may be evaluated by partial integration:

$$I \equiv \int_0^\infty f(x) e^{-z} dz = e^{-z} f(x) \Big|_{r=0}^\infty - \int_{r=0}^\infty e^{-z} df(x).$$

Equation (14) suggests that the resonance energy tends to zero as r tends to zero. This is, however, an artifact. When eliminated, the first term of the right-hand side of the last equation becomes zero. The form of $df(x)$ is as follows:

$$df(x) = [df(x)/dx] dx = \left[\frac{1}{2} \delta(x) + f_1(x) \right] dx, \\ f_1(x) = \frac{1}{4} \cosh^{-2} \frac{1}{2} x, \quad \text{for } x > 0, \\ f_1(x) = 0, \quad \text{for } x < 0.$$

The following approximate expression for z in terms of x is obtained from Eq. (13):

$$z \sim (1.6a/r_D)^3 (1 - 1.41r_1x/r_T) (N_D - P)/(N_A - P).$$

The integral I can now be approximately evaluated:

$$I = \left(1 + 10 \frac{a^3 N_D - P r_1}{r_D^3 N_A - P r_T} \right) \exp \left(- \frac{(3.6a)^3 N_D - P}{r_D^3 N_A - P} \right) \\ = \left(1 + 0.22z_0 \frac{r_1}{r_T} \right) e^{-z_0}. \quad (15)$$

The approximation $\exp(0.63z_0r_1x/r_T) \sim 1 + 0.63z_0r_1x/r_T$ has been used here. It is a good approximation as long as z_0 is not considerably larger than unity. This condition is obeyed unless there is a very high degree of pairing and low compensation [i.e., $(N_D - P)/(N_A - P) < 30$]. If this happens, the temperature dependence cannot be expected to follow Eq. (15) at high temperatures (small r_1/r_T). It is not difficult to incorporate Eq. (15) into Eq. (3) and integrate over r_1 . However, one can evaluate the effect of traps directly from Eq. (15). The traps will be effective to the degree that the value of the exponential function is different from unity. For sample L50, at $\Theta=23^\circ\text{C}$, for example, $(N_D - P)/(N_A - P) = 44$, $a/r_D = 0.10$. Hence the argument of the exponential function is -2 , and its value 0.14. This is the proper magnitude to explain the observed lack of parallelism between the curves for $\Theta=23^\circ\text{C}$ and $\Theta=200^\circ\text{C}$ in Fig. 9. Quantitatively, the temperature

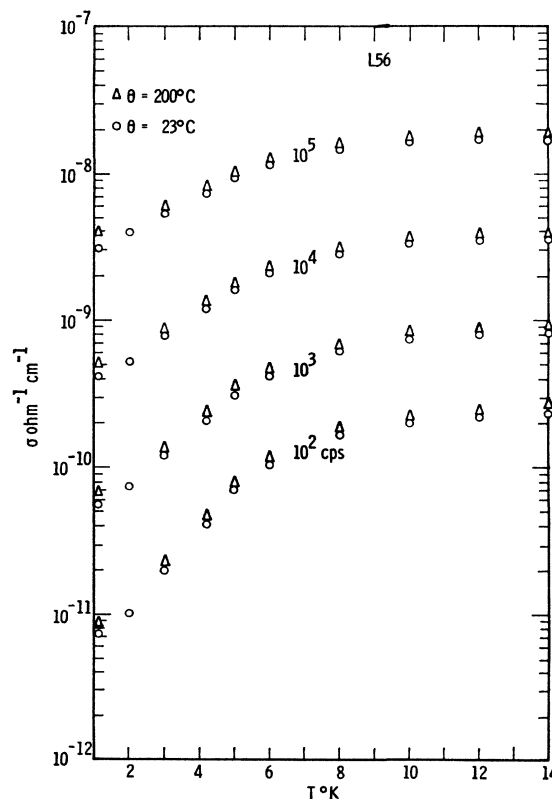


FIG. 11. Conductivity of sample L56 at 10^2 , 10^3 , 10^4 , and 10^5 cps and for $\Theta=23^\circ\text{C}$ and $\Theta=200^\circ\text{C}$.

TABLE II. The distance of shortest approach α between the lithium atoms and the acceptors obtained from various samples at various temperatures Θ .

Sample No.	$\theta^\circ\text{C}$	r_θ	$\sigma_\theta/\sigma_{200}$	N/P	p	α
L50	23	47	0.10	1.110	0.110	2.90
	52	43	0.245	1.325	0.325	2.84
	72	40.3	0.407	1.668	0.665	2.85
	96	32.7	0.665	2.98	1.98	2.86
L45	23	47	0.131	1.150	5.00	2.90
L55	23	47	0.401	1.67	0.666	2.90
	50	43	0.65	2.86	1.85	2.88

dependence of the experimental data appears to be too strong. Qualitatively, however, the temperature dependence, insofar as it is stronger at low T and weakens at high T , is in agreement with the theory. The possibility that the discussed behavior is caused by Tanaka-Fan traps is, therefore, not excluded.

For the dipole traps,

$$d\phi(r) = -\frac{3P}{8N_A r_D^2} \frac{r^2}{r_D^3} \exp\left(-\frac{1P}{8N_A r_D^3} \frac{r^3}{r_D}\right) d\left(\frac{r}{r_D}\right) \equiv e^{-z'} dz' \quad (13a)$$

and

$$x = (r_T/r_1) \left[(r_1/r_D) (l/r_D) (P/4N_A z')^{2/3} - 1 \right]. \quad (14a)$$

The expression (13a) is an approximate one. It assumes that the area of an equipotential surface which cuts the axis of the dipole at the distance r from the dipole is $\frac{1}{2}\pi r^2$. In Eq. (14a), l refers to the size of the dipole. Employing an approximation similar to that described for Eq. (15), one obtains for the dipole traps

$$I = \left[1 + \frac{1}{36} \left(\frac{r_1}{r_D} \frac{l}{r_D} \right)^{3/2} \frac{P}{N_A r_T} \right] \times \exp \left[-\frac{1P}{8N_A} \left(\frac{r_1}{r_D} \frac{l}{r_D} \right)^{3/2} \right]. \quad (15a)$$

It is easy to see from Eq. (15a) that dipole traps cannot account for a noticeable reduction of conductivity for the samples treated in this paper.

It is interesting to evaluate the smallest pair size α (a in Refs. 11-14). If traps are the correct explanation for the observed behavior, then at high T the various measurements should provide a consistent value for α . In evaluating this number, it is assumed that there is no pairing at $\Theta=200^\circ\text{C}$. This is borne out experimentally by the fact that measurements for $\Theta=300^\circ\text{C}$ are identical with those for $\Theta=200^\circ\text{C}$. The value of α is then evaluated as follows: From the measurements at various temperatures Θ and at large T , the degree of pairing is obtained using

$$1 - P/N_A = \sigma_\Theta/\sigma_{200}.$$

The value of p is then calculated using Eq. (10). Finally, the value of α is found by aid of Fig. 5. The

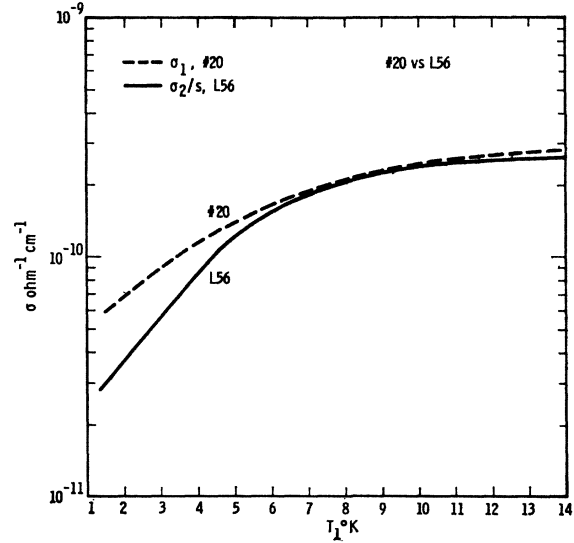


FIG. 12. Comparison of sample L56 with sample 20 of Ref. 1, using the similarity relations.

results are shown in Table II for five samples. It is quite clear from the Table II that the values are consistent with each other and compare very reasonably with Maita's results for lithium-aluminum pairs in silicon. This would strongly favor the explanation that the observed temperature dependence is caused by traps and that the distribution predicted by Eq. (6) is essentially correct, at least in the region $r_1 > \frac{1}{2}r_\omega$. This conclusion constitutes stronger experimental support for the theory of pairing¹¹ than was obtained by previous experiments. The latter were capable only of determining how many acceptor-lithium pairs from a given total were smaller than a certain value. Another advantage of the method discussed here for the studying of pairing is its suitability also for materials with low compensation.

3. Results on Oxygen-Rich Samples

The oxygen-rich samples were prepared from ingots obtained by the Czochralski method. Thus the oxygen concentration is of the order 10^{18} cm^{-3} . These samples are represented in this report by sample L5 (n -type) and sample L56 (p -type). The experimental results on these samples are plotted in Figs. 10 and 11. The striking feature of the results is the lack of dependence of σ on the temperature Θ . This is particularly well demonstrated by Fig. 11. In this figure, the points representative of $\Theta=20^\circ\text{C}$ were measured after leaving the sample at that temperature for 60 h. They also lie on exactly the same curve (within experimental error) as the points measured for the same Θ after an exposure of several minutes to that temperature. It is apparent that the mobility of the lithium atoms is practically destroyed by the presence of oxygen, as has been indeed stated by Pell and Ham.¹² The distribution of the atoms

thus must correspond to the temperature at which the lithium was diffused into the silicon, that is, to very high values of Θ . This conclusion is supported by Fig. 12. The latter gives the result of comparing this sample with sample 20 by means of the similarity relations. Although the agreement is not very good at low temperatures T , the two curves are close enough to indicate an almost random distribution. The disagreement at low T may, in this case, well be due to the Tanaka-Fan traps, since sample *L56* has very low compensation.

Note added in proof. After submitting the article for publication, a previous work by E. M. Pell on lithium-

boron ion pairing in silicon [J. Appl. Phys. **31**, 1675 (1960)] was brought to our attention. The comparison between his result on the pair size, 2.5–2.7 Å, and ours of 2.87 Å is quite satisfactory.

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Generalized Master Equation for Arbitrary Initial States

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Exact generalized master equations, for both quantum and classical systems, are derived for completely arbitrary initial states (arbitrary initial "correlations") in the form of a "density expansion." This result is a generalization of a previous equation which was restricted to initially "uncorrelated" states.

I. INTRODUCTION

IN a previous article¹ (hereafter referred to as I) an exact equation for the evolution of the density matrix of a quantum-mechanical system (generalized master equation) was derived as a "formal" expansion in powers of the density—for density matrices which are initially diagonal.

It is the purpose of the present article to extend that result to completely arbitrary initial states (arbitrary initial density matrices). We shall thus derive a master equation, for both quantum and classical systems, which is exact for *arbitrary initial states* (at all times) and which is expressed as a "formal" expansion in the density.

The comparable master equations of Prigogine and Resibois,² Van Hove,³ Zwanzig,⁴ Peterson,⁵ and Janner,⁶ on the other hand, are expressed as formal expansions in the interaction potential whereas Swenson's⁷ equation is expressed as an expansion in the two-body scattering matrix.

The present article is a continuation of I, to which the reader is referred for definitions and nomenclature.

II. QUANTUM MASTER EQUATION FOR ARBITRARY INITIAL STATES

We begin with Eq. (43) of I which is valid for arbitrary initial states of the system [arbitrary $\rho(0)$]. The problem now, as in I, is to obtain an expression for $\mathbf{O}_D g_N \rho(0)$ in terms of $\rho_D(t)$ which, when substituted into Eq. (43), yields a closed equation for $\rho_D(t)$ (master equation). This was done in Appendix D of I for initially diagonal density matrices (initially independent of particle configurations in momentum representation) by setting $\mathbf{O}_D g_0(E) \rho(0) [= g_0(E) \mathbf{O}_D \rho(0)]$ equal to zero. To obtain an expression for $\mathbf{O}_D g_N \rho(0)$ which is valid for arbitrary initial states we need only add $g_0(E) \mathbf{O}_D \rho(0)$ to the right-hand side of Eqs. (D1) and (D3) of I. If we then follow the remaining steps of Appendix D and keep all terms which appear postmultiplied by $g_0(E) \mathbf{O}_D \rho(0)$ we eventually obtain, in place of (D10),

$$\begin{aligned} \mathbf{O}_D g_N(E) \rho(0) &= {}^{nmc} \left\{ \sum_{k=1}^{\infty} (\mathbf{O}_D T g_0^{-1})^k \right\} D g_N(E) \rho(0) \\ &\quad + {}^{nmc} \left\{ \sum_{k=0}^{\infty} (\mathbf{O}_D T g_0^{-1})^k \right\} g_0(E) \mathbf{O}_D \rho(0) \\ &= {}^{nmc} \left\{ \mathbf{O}_D T g_0^{-1} (1 - \mathbf{O}_D T g_0^{-1})^{-1} \right\} D g_N(E) \rho(0) \\ &\quad + {}^{nmc} \left\{ (1 - \mathbf{O}_D T g_0^{-1})^{-1} \right\} g_0(E) \mathbf{O}_D \rho(0). \quad (1) \end{aligned}$$

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