

## Approximations for the ac Impurity Hopping Conduction

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A previous approximation of the ac impurity hopping conduction in the high-temperature, low-concentration limit is extended to low temperatures and to highly compensated material. Only the real part of the conductivity is considered, and random distribution is assumed. The lengths  $r_D \equiv r_{\text{maj}} = (4\pi N_D/3)^{-1/3}$ ,  $r_T = e^2/4\pi\kappa kT$  ( $\kappa$  is the dielectric constant) and  $r_\omega$  are defined for the sake of simple expressions. The latter is a distance characteristic of the frequency, proportional to the radius  $a$  of the localized impurity state and only weakly dependent on other parameters. All the expressions for  $\sigma$ , written as functions of these variables, are explicitly proportional to  $a$ , to the imaginary conductivity  $\kappa\omega$ , and for low compensations, to  $N_A = N_{\text{min}}$ . In addition to the distribution of spacings between impurities already considered in the high-temperature limit, the distribution in energies is now taken into account. The low-temperature treatment holds in the region where  $\sigma$  can be expanded in  $r_D/r_T$  and  $r_\omega/r_T$ . Due to the existence of a zero-order term,  $\sigma$  is almost independent of temperature at very low temperatures. At extremely low temperatures, however, where  $kT$  is much smaller than the resonance energy for a separation  $r_\omega$ ,  $\sigma$  is proportional to the temperature. The low-compensation and high-compensation results are basically identical at high temperatures. At very low temperatures, they differ mainly in the concentration dependence. At intermediate temperatures, the high-compensation case is expected to interpolate smoothly between the two temperature extremes; the low-compensation case is not. For both cases, the frequency dependence at very low temperatures is slightly more pronounced than at high temperatures, as is borne out by experiments. The following additional results are of interest for low compensation. At very low temperatures, the previously reported experimental result, that  $\sigma$  is practically independent of  $N_D$ , is accounted for. The magnitudes of the calculated and measured conductivities are in very satisfactory agreement, particularly when compensated for the experimentally found  $N_A^{0.86}$  dependence. It is shown that the results are valid up to much higher concentrations than the previous high-temperature treatment. At higher temperatures, the situation is less satisfactory. A tendency for pairing and an alteration of the radii  $a$  from those calculated by Miller and Abraham is necessary to get reasonable agreement. The radii have to be altered so as to make  $a_P/a_{A_s} = 1.14$  instead of 1.05. To test the validity of the previously described model at intermediate temperatures, similarity relations based on statistical equivalence are developed. Comparison with data again necessitates the assumption  $a_P/a_{A_s} = 1.14$ . The results on the heavy compensation cannot be evaluated because of lack of experimental data.

### INTRODUCTION

EXPERIMENTS that had been performed on the low-temperature conductivity of silicon<sup>1</sup> and germanium<sup>2</sup> in periodic fields support the Mott-Conwell<sup>3,4</sup> model of the hopping conduction, inasmuch as the results can be sensibly explained<sup>1</sup> by the use of this model. The experiments were, however, analyzed only in the higher temperature regions. While many features of the experiments could be theoretically reproduced (the dependences of the conductivity on frequency and majority and minority concentrations, and its order of magnitude at high temperatures), others remained unexplained. This includes the somewhat surprising independence of the conductivity on majority concentration at the lowest temperatures and the temperature dependence itself. In fact, in the region where the treatment of Ref. 1 should be valid, the conductivity is expected to be a decreasing function of the temperature. In practice, however, such a region was never reached. This work attempts to extend the analysis of Ref. 1 to low temperatures.

The Mott-Conwell model for impurity conduction is based on a situation where all the extrinsic carriers are in localized states around impurities. The model allows for electrical transport by permitting the carriers to tunnel from a state localized around one impurity to a state localized around another, if the latter is vacant due to compensation. With such a model, there must be a difference between a steady conduction and a conduction in periodic fields. This is because a polarization current will exist<sup>1,5,6</sup> when all impurities are not equivalent. The degree by which the impurities differ, therefore, will influence the behavior of the ac conductivity and must be an important feature of this investigation. There are two reasons why the impurities are not equivalent: variations in the distances from other impurities, and in the energy. The latter is a variation in Coulombic energy due to variations of distance from ionized impurities. The knowledge of the distributions of both the energies and the spacings between majority impurities is essential, therefore, for the treatment. Those distributions depend on how the impurities distribute themselves in the crystal. A random distribution shall be assumed in this treatment.

For sufficiently high frequencies, contributions to the

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

<sup>2</sup> S. Golin, *Bull. Am. Phys. Soc.* **8**, 225 (1963). After finishing this manuscript a more recent treatment by Dr. Golin [*Phys. Rev.* **132**, 178 (1963)] came to our attention which is similar to the very-low-temperature approximation of this paper.

<sup>3</sup> N. F. Mott, *Can. J. Phys.* **34**, 1356 (1956).

<sup>4</sup> E. M. Conwell, *Phys. Rev.* **103**, 51 (1956).

<sup>5</sup> M. Pollak, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 86.

<sup>6</sup> G. L. Sewell, *Phys. Rev.* **129**, 597 (1963).

conductivity from multiple hops can be neglected<sup>1</sup> and only hops between pairs of impurities have to be considered. The high-frequency assumption imposes an upper limit on the concentration. It will be shown here that at low temperatures this limit is much higher than at the high temperatures treated in Ref. 1. If, in addition to the high-frequency approximation, it may be assumed that at the site of any pair the periodic field produced by all other pairs can be neglected, the total conductivity becomes a superposition of the conductivities of all pairs. This assumption is made to avoid undue complications despite some indications from Golin's experiments<sup>2,7</sup> that it is not necessarily justified for germanium. We then may write

$$\begin{aligned}\sigma(\omega) &= \Sigma \sigma(\mathbf{r}, \Delta E, \omega) n(\mathbf{r}, \Delta E) \\ &= n \int \sigma(\mathbf{r}, \Delta E, \omega) d\mathbf{p}(\mathbf{r}, \Delta E). \quad (1a)\end{aligned}$$

A pair is specified by the spatial separation  $\mathbf{r}$  and energy separation  $\Delta E$  between the impurities that form it. The number of pairs at some value of the two variables is  $n(\mathbf{r}, \Delta E)$ . This number may be replaced by the total number of carriers times the differential probability that a pair has the energy separation  $\Delta E \pm \frac{1}{2} d\Delta E$  and spatial separation  $\mathbf{r} \pm \frac{1}{2} d\mathbf{r}$ . It turns out that the ac conductivity is a selective function of both variables. Pairs are selected which have an energy separation smaller than  $kT$  and some very specific spatial separation.<sup>8</sup> The analysis of Ref. 1, while taking account of the spatial distribution, assumed  $kT > \Delta E$  for most pairs. The energy distribution thus was ignored. It is the purpose of this work to incorporate the energy distribution in the analysis and to obtain results valid also for lower temperatures. The results are compared with experimental results reported in Ref. 1. We note, in passing, that Golin<sup>2</sup> took an opposite approach in his work on  $p$ -type germanium, in trying to extract the distribution in energy separations from the experimental results.

The expression for  $\sigma(\mathbf{r}, \Delta E, \omega)$  has been derived in Ref. 1. An equation is thus obtained which was the basis for most of this treatment and is copied here for convenience

$$\begin{aligned}d\sigma(\mathbf{r}, \Delta E, \omega) &= \frac{1}{12} d\mathbf{p}(\mathbf{r}, \Delta E) N_A r^2 \cosh^{-2}(\Delta E/2kT) \\ &\quad \times \omega(\omega^{-1}\tau^{-1} + \omega\tau)^{-1} e^2/kT. \quad (1)\end{aligned}$$

The various symbols are all explained in Ref. 1. The symbol  $\sigma$  will be used to denote  $\text{Re}\sigma$ , because only the real part will be considered here. The notation  $N_D \equiv N_{\text{maj}}$ ,  $N_A \equiv N_{\text{min}}$  is used in this report without committing it to  $n$ -type material.

The temperature dependence enters, apart from the already established  $1/T$  dependence, in three ways:

explicitly through the  $\cosh^{-2}$  factor, through the temperature dependence of  $\tau$ , as given by Eq. (13a) in Ref. 1, and finally by the possibility that  $d\mathbf{p}$  in Eq. (1) may depend explicitly on temperature. The latter will take place in lightly compensated material ( $N_{\text{maj}}/N_{\text{min}} \gg 1$ ); that is, in cases where many majority atoms have other majority atoms between them and the nearest minority atom. In such cases, the probability that a pair of impurities is occupied by a carrier depends on the temperature. Because of this and other differences between the light and heavy compensation cases, the two shall be treated separately.

In order to be able to separate the different effects that may be relevant to the conductivity of hopping, the low-compensation régime shall be further divided into different temperature regions. The very low-temperature region lends itself more easily to good approximations. While the high-temperature approximation assumed that all equally spaced pairs contribute equally to the conductivity, the very-low-temperature approximation forbids any pairs to contribute, except those which coincide in energy within  $kT$ . This allows for a relatively simple and accurate treatment because the distribution in energy is almost constant within a small  $kT$ . In addition the conditions necessary for this approximation are readily realizable, at least for silicon, and indeed, the calculated and the measured values and functional dependences of the conductivity agree very well at the very low temperatures, as already was briefly reported.<sup>9</sup>

At higher temperatures the analytical treatment becomes more difficult. The contribution of the pairs with equal spacing but different energy separations cannot be represented either by a perfectly flat function of the energy separation, as it can at high temperatures, nor by an extremely selective function of energy separation, as is the case at very low temperatures. Instead, a more complicated function of energy has to be integrated over the distribution in energy separation. The result is given by an expansion in the reduced energy separation. The first term must express the behavior at the very low temperatures. The rest is considered as one of three effects characteristic of higher temperatures. The other two considered here are the variation with temperature of the relative occupation by a carrier of pairs with different energy separations, and the possibility that deep lying pairs which cannot contribute at very low temperatures may start contributing at high temperatures. It turns out that none of the three effects is capable to account for experimental results. Only the last effect lends a functional dependence to the conductivity, which is consistent with experimental results. However, the magnitude falls considerably short of the experimental one. To decide whether this failure is due to inadequate analysis, or to an inadequacy of the model at temperatures above the

<sup>7</sup> S. Golin (private communication).

<sup>8</sup> The latter is true only for the real part of the conductivity, which shall be the exclusive subject of this work.

<sup>9</sup> M. Pollak, Bull. Am. Phys. Soc. 8, 53 (1963).

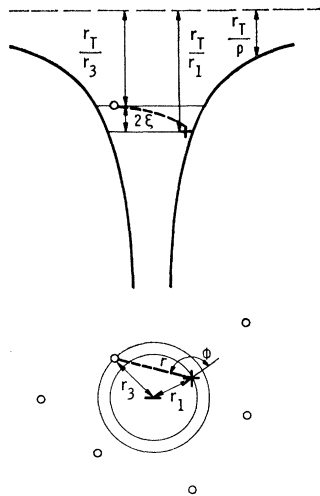


FIG. 1. A schematic representation of the Mott-Conwell model in the neighborhood of the compensating impurity. The bottom part represents several majority atoms (circled) randomly positioned around the ionized minority impurity (minus sign). At very low temperatures, the majority which is at the nearest distance ( $r_1$ ) from the minority impurity is also ionized (plus sign). The dashed line represents a hop between it and another majority impurity a distance  $r$  away. The top part of the figure represents the Coulombic interaction between the two ionized impurities on a reduced energy scale. The symbols have the following meanings:  $r_T \equiv e^2/4\pi\kappa kT$ ;  $2\xi$  is the reduced energy separating the impurities involved in the hop;  $\rho$  is the distance from the minority impurity. The circles on the bottom part of the picture are equipotentials.

very low ones, relations are derived between conductivities valid under certain similarity conditions. While these relations do not allow one to predict the conductivity from basic principles as a full theory would, one can predict on their basis the behavior of the conductivity of one sample from the measured behavior of the conductivity of another sample. A failure of such a prediction should be interpreted as an incompleteness of the model used, if the impurities are known to be distributed at random.

#### LIGHTLY COMPENSATED MATERIAL

The model that shall be used for the light compensation is presented in Fig. 1. The potential fluctuations responsible for the hopping model are produced by the ionized impurities. For low compensations, this effect can be adequately described by using the (mobile) majority ion to be in the Coulombic field of the nearest (immobile) minority ion, as shown in Fig. 1. Fields from other minority ions shall be much smaller because of larger distances and a large degree of cancellation from their associated majority ions.

To avoid the necessity for simultaneous treatments of all the temperature effects, the explicit dependence of  $dp$  on temperature shall at first be ignored. This approximation is satisfactory at the very low temperatures when the majority atom which is nearest to the minority has, except for occasional hops, a probability of almost unity to be ionized. Treating first the very

low temperature region also allows the use of other approximations which are not valid for the higher temperatures.

#### A. Very Low Temperatures

*Normal Effects.* The treatment here varies from the treatment of Ref. 1 in the following two ways. The "hopping time" is left to depend on  $\Delta E/T$ , and the expression is integrated over the distribution of  $\Delta E$  and  $r$ . The latter is the distance between the two impurities exchanging the state of ionization. The energy separation between two majority atoms is a function of the distances that separate them from the nearest minority atom. Eq. (1) will be rewritten to contain these separations as variables instead of the energy separation. For consistency with Ref. 1, rationalized units are used here.

$$\Delta E/kT = (1/r_1 - 1/r_3)e^2/4\pi\kappa kT = (1/r_1 - 1/r_3)r_T, \quad (2)$$

where

$$r_3 = (r_1^2 + r^2 + 2r_1r \cos \varphi)^{1/2}; \quad (2a)$$

the significance of the angle  $\varphi$  is apparent from Fig. 1. The distance  $r_T$ , as defined in Eq. (2), is plotted in Fig. 2.

It will be convenient for what follows to express the factor  $e^2/kT$ , that appears in Eq. (1), as  $4\pi\kappa r_T$ . The differential probability  $dp$  can be written as follows:

$$dp(r, \Delta E) \rightarrow dp(r_1, r | \varphi) dp(r_1 | r) dp(r_1). \quad (3)$$

Here  $dp(r_1)$  is the probability of finding a minority atom and the majority atom nearest to it separated by  $r_1 \pm \frac{1}{2}dr_1$ ,  $dp(r_1 | r)$  is the conditional probability of finding a majority atom a distance  $r \pm \frac{1}{2}dr$  from the majority that is at  $r_1$ ;  $dp(r_1, r | \varphi)$  is the conditional probability that, if two atoms are thus located, the relevant angle will have the value  $\varphi$  within  $\frac{1}{2}d\varphi$ . If no forces act between the minority and majority impurities during the preparation of the material,  $dp(r_1 | r)$  shall be independent of  $r_1$  (as assumed in the following).<sup>10</sup> If, how-

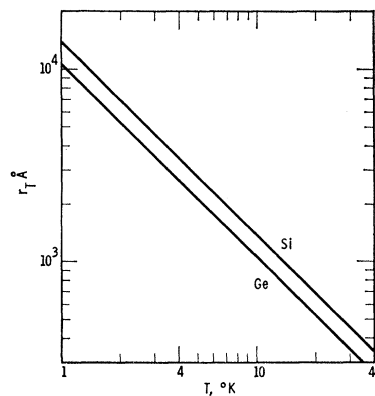


FIG. 2. A plot of the distance  $r_T \equiv e^2/4\pi\kappa kT$  versus temperature, for silicon and germanium.

<sup>10</sup> The assumption that the atom at  $r_1$  is a nearest neighbor to the minority atom makes a certain volume inaccessible to other majority atoms. The effect of this on  $dp(r_1 | r)$  is neglected.

ever, such forces exist, as is the case in silicon or germanium where the majority impurity is obtained by diffusion of lithium, this is no longer true. As experiments demonstrate,<sup>11</sup> interesting differences are observable between such a case and a random distribution. In the following we shall always assume random distributions.

$$dp(r_1) = \nu_1 4\pi r_1^2 N_D \exp(-4\pi r_1^3 N_D/3) dr_1 \\ \equiv \nu_1 3r_1^2 r_D^{-3} \exp(-r_1/r_D)^3 dr_1, \quad (3a)$$

$$dp(r_1|r) = dp(r) = \nu_1 3r^2 r_D^{-3} \exp(-r/r_D)^3 dr, \quad (3b)$$

$$dp(r_1, r|\varphi) = \nu \sin\varphi d\varphi, \quad (3c)$$

where  $\nu$  are normalization factors. Inserting this into Eq. (1) and integrating,

$$\sigma(\omega) = \int \sigma(r, \Delta E, \omega) dr d\Delta E = \int \sigma(r, r_1, \varphi, \omega) dr_1 dr d\varphi \\ = \int \frac{1}{2} \nu_1 \frac{3r_1^2}{r_D^3} \exp\left(-\frac{r_1}{r_D}\right)^3 \nu_1 \frac{3r^2}{r_D^3} \exp\left(-\frac{r}{r_D}\right)^3 \\ \times \nu \sin\varphi N_A 4\pi r r_T r^2 \cosh^{-2}\left[r_T \left(\frac{1}{r_1} - \frac{1}{r_3}\right)\right] \\ \times \frac{\omega}{\omega\tau + (\omega\tau)^{-1}} dr_1 dr d\varphi. \quad (4)$$

The integration limits for  $r_1$  and  $r$  are from zero to infinity. This makes  $\nu_1 = 1$ . Some care is required in determining the integration limits for  $\varphi$  because it is easy to violate the assumption that  $r_1$  is the distance from the minority to the nearest majority atom, with the result that the assumed distribution function for  $r_1$  would no longer be valid. A limit has to be imposed on  $\varphi$  from Eq. (2a), so as to make  $r_3 \geq r_1$ . This leaves  $\nu$  undetermined for the time being. The quantity  $\nu$  is, of course, defined by  $\nu^{-1} = \int \sin\varphi d\varphi$ , where the limits are the same as in the main integral.

To simplify the integration, a procedure similar to that employed in Ref. 1 is used here. It makes use of the fact that  $\tau$  depends exponentially on  $r$ . This causes  $[\omega\tau + (\omega\tau)^{-1}]^{-1}$  to be a strongly peaked function of  $r$ . The contribution to the conductivity thus comes from a very small region of  $r$ . If  $r < r_D$  the other dependences on  $r$  are much slower and may be assumed to have a constant value. The condition  $r < r_D$  is always imposed, except where explicitly stated otherwise (for reasons see Appendix of Ref. 1). Hence the integration over  $r$  of Eq. (4) is as follows:

$$\sigma(\omega) = \int_0^\infty F(r, \omega) [\omega\tau(r) + \omega^{-1}\tau^{-1}(r)]^{-1} dr \\ \cong F(r_\omega, \omega) \int_0^\infty (\omega\tau + \omega^{-1}\tau^{-1})^{-1} dr = \frac{1}{4}\pi a F(r_\omega, \omega),$$

<sup>11</sup> M. Pollak and D. H. Watt (to be published); M. Pollak, Bull. Am. Phys. Soc. **8**, 485 (1963).

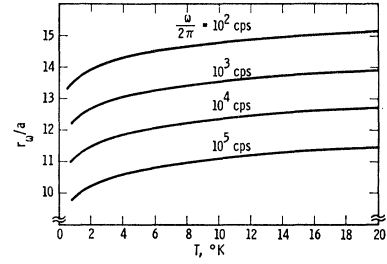


FIG. 3. A plot of the hopping distance selected at frequency  $\omega, r_\omega$ , versus temperature. The quantity  $r_\omega$  is plotted in units of  $a$ .

where  $r_\omega$  is the  $r$  where  $(\omega\tau + \omega^{-1}\tau^{-1})^{-1}$  has a maximum. It is the same quantity as  $r_{\max}$  in Ref. 1. The symbol  $r_\omega$  is used here to indicate that it is responsible for a frequency dependence.  $r_\omega$ , apart from being frequency-dependent, is also temperature-dependent, although the latter had been suppressed in Ref. 1. Applying the formula of Miller and Abrahams<sup>12</sup> to silicon,<sup>1</sup> and including the fact that in the range of interest  $r_\omega \approx 10a$  (see Ref. 1), one obtains for  $r_\omega$  ( $T$  in  $^\circ\text{K}$  and  $\omega$  in cps),

$$r_\omega/a = 16.3 + 0.53 \ln(T/\omega) + 0.53 \ln(\xi/\tanh\xi), \quad (5)$$

where

$$\xi = \Delta E/2kT. \quad (5a)$$

The dependence of  $r_\omega$  on  $\xi$  is trivial since we can say, in anticipation, that the contribution to the conductivity will come from pairs with  $\Delta E$  not larger than  $kT$ , i.e., where  $\xi/\tanh\xi$  is almost unity, independent of  $\xi$ . The dependence of the logarithm is, of course, much smaller yet. We may therefore express  $r_\omega$  as

$$r_\omega = [16.3 + 0.53 \ln(T/\omega)]a. \quad (6)$$

The ratio of  $r_\omega/a$  is plotted in Fig. 3.

This accomplishes the integration over  $r$ , with the result that in Eq. (4) every  $r$  has to be replaced by  $r_\omega$ , and  $[(\omega\tau)^{-1} + \omega\tau]^{-1} dr$  by  $\frac{1}{4}\pi a$ . This is equivalent to replacing  $[(\omega\tau)^{-1} + \omega\tau]^{-1}$  by  $\frac{1}{4}\pi a \delta(r - r_\omega)$ :

$$\sigma(\omega) = \frac{3}{4}\pi^2 N_A r_D^{-6} r_T r_\omega^4 \kappa \omega a \\ \times \int r_1^2 \exp(-r_1/r_D)^3 \cosh^{-2}\left[\frac{1}{2}r_T(r_1^{-1} - r_3^{-1})\right] \\ \times \nu \sin\varphi dr_1 d\varphi. \quad (7)$$

To simplify the expression, we shall make the following substitutions:

$$r_1 = x_1^{-1}; \quad dr_1 = -x_1^{-2} dx_1; \\ r_3 = x_3^{-1}; \quad \text{and from Eq. (2a)} \quad \sin\varphi d\varphi = x_3^{-3} x_1 r_\omega^{-1} dx_3; \quad (8)$$

$$\sigma(\omega) = \frac{3}{4}\pi^2 N_A r_D^{-6} r_T r_\omega^4 \kappa \omega a \int -x_1^{-3} \exp(-x_1 r_D)^{-3} \\ \times \cosh^{-2}\left[\frac{1}{2}r_T(x_1 - x_3)\right] \nu x_3^{-3} dx_1 dx_3; \quad (9)$$

$$\nu^{-1} = \int \sin\varphi d\varphi = x_1 r_\omega^{-1} \int x_3^{-3} dx_3. \quad (10)$$

<sup>12</sup> A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

The new variables,  $x_1$  and  $x_3$ , are proportional to the energy on the impurities located at  $r_1$  and at  $r_3$ , respectively, measured with respect to infinity.  $x_1$  is proportional to what one may call the "ionization energy." The range of integration over  $x_1$  is from infinity to zero (corresponding to zero to infinity for  $r_1$ ) and for  $x_3$  such as to leave  $r_3 \geq r_1$ . The minimum value that  $r_3$  can obtain is  $|r_\omega - r_1|$ . This happens when  $\varphi = 180^\circ$ . If this value should be smaller than  $r_1$ ,  $\varphi$  has to be cut off

before it reaches  $180^\circ$  in such a way as to forbid  $r_3$  to be smaller than  $r_1$ . In this case, the lower limit for  $r_3$  will be  $r_1$ . If  $|r_\omega - r_1|$  is not smaller than  $r_1$ , no restriction has to be imposed on  $\varphi$ . The limit on  $r_3$  then is  $|r_\omega - r_1|$ . The upper limit is  $r_\omega + r_1$  for both cases. The boundary between the two cases is determined by  $r_1 = \frac{1}{2}r_\omega$ . The situation is illustrated in Fig. 4.

With the insertion of the limits as described above, the conductivity becomes

$$\sigma(\omega) = \frac{3}{4}\pi^2 N_A r_D^{-6} r_T r_\omega^3 a \kappa \omega \left[ \int_{\infty}^{2/r_\omega} x_1^{-3} \exp(-x_1 r_D)^{-3} \nu_a \int_{(r_\omega+r_1)^{-1}}^{(r_\omega-r_1)^{-1}} x_3^{-3} \cosh^{-2}[\frac{1}{2}r_T(x_1-x_3)] dx_3 dx_1 + \int_{2/r_\omega}^0 x_1^{-3} \exp(-x_1 r_D)^{-3} \nu_b \int_{(r_\omega+r_1)^{-1}}^{r_1^{-1}} x_3^{-3} \cosh^{-2}[\frac{1}{2}r_T(x_1-x_3)] dx_3 dx_1 \right]. \quad (11)$$

With the aid of Eq. (10)  $\nu_a = \frac{1}{2}$  and  $\nu_b = (1 + \frac{1}{2}r_\omega x_1)^{-1}$ . We now replace the quantity  $\frac{1}{2}r_T(x_1-x_3)$  by  $\xi$  in such a way that  $x_1$  (i.e.,  $r_1$ ) remains constant.

$$\frac{1}{2}r_T(x_1-x_3) = \xi; \quad dx_3 = -2r_T^{-1}d\xi. \quad (12)$$

The meaning of the new variable  $\xi$ , is the energy difference  $\Delta E$  normalized to  $2kT$ , and is, therefore, consistent with the notation used previously in Eq. (5).

The first integral in Eq. (11) represents the contribution to the conductivity from those configurations in which a majority atom can be found at a smaller distance from a minority than  $\frac{1}{2}r_\omega$ ; the second integral is the contribution from the other configurations. Applying the limits of  $x_3$  to the variable  $\xi$ , we notice that  $\xi$

does not approach zero in the first integral. As large contributions to conductivity come only from small  $\xi$  (because of the  $\cosh^{-2}$  factor), the first integral shall not contribute appreciably to the conductivity. Moreover, with the condition  $r_\omega < r_D$  which was imposed so far on the whole treatment, it can be shown that the number of configurations with  $r_1 < \frac{1}{2}r_\omega$  can be only a few percent. It is therefore legitimate to neglect the first integral in Eq. (11) and we obtain

$$\sigma(\omega) = 1.5\pi^2 N_A r_D^{-6} r_\omega^3 a \kappa \omega \times \int_{2/r_\omega}^0 x_1^{-3} (1 + \frac{1}{2}r_\omega x_1)^{-1} \exp(-x_1 r_D)^{-3} \times \int_0^{r_T/2r_1(1+r_1r_\omega^{-1})} (x_1 - 2r_T^{-1}\xi)^{-3} \cosh^{-2}\xi d\xi dx_1. \quad (13)$$

Remembering that  $x_1$  is proportional to the "ionization energy," it is legitimate to neglect  $2r_T^{-1}\xi$  as compared to  $x_1$ . The validity of this approximation is experimentally verified by the fact that the dc conductivity is orders of magnitude smaller than the ac conductivity. This is particularly true at very low temperatures. With this approximation,

$$\sigma(\omega) = 1.5\pi^2 N_A r_D^{-6} r_\omega^3 a \kappa \omega \times \int_{2/r_\omega}^0 x_1^{-6} (1 + \frac{1}{2}r_\omega x_1)^{-1} \exp(-x_1 r_D)^{-3} \times \tanh[r_T/2r_1(1+r_1r_\omega^{-1})] dx_1. \quad (14)$$

At low temperatures the argument of  $\tanh$  becomes very large because  $r_T$  is inversely proportional to temperature and  $r_1$  is almost never larger than  $r_D$  [see, e.g., Eq. (3a)]. As a practical example, consider measurements at  $1^\circ\text{K}$  on silicon samples at frequencies and concentrations similar to those in Ref. 1. With the pessi-

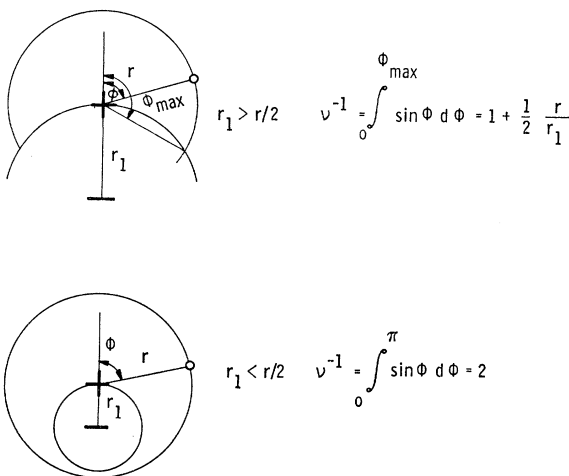


FIG. 4. A diagram explaining the limits of integration and the normalization integral for the cases where the nearest majority to minority impurity distance  $r_1$ , is larger (top) or smaller (bottom) than half the hopping distance. For the top configuration, the angle  $\varphi$  cannot be arbitrary. For  $\varphi > \varphi_{\max}$ , the circle impurity would be closer to the minority impurity than the + impurity. This is contrary to assumption.

TABLE I. Comparison of the calculated and measured conductivities at very low temperatures.

Sample No.	$10^{15}N_A \text{ cm}^{-3}$	$10^8 a \text{ cm}$	$10^8 r_\omega \text{ cm}$ 1 kc, 1.1°K	$10^8 r_D \text{ cm}$	$\alpha$	$\alpha^{1/3}I(\alpha)$	$10^{11} \sigma_{\text{calc.}}$ 1 kc, 1.1°K	$10^{11} \sigma_{\text{meas.}}$ 1 kc, 1.1°K
9	0.8	21.1	266	257	0.139	0.28	2.14	2.3
12	0.8	21.1	266	130	1.06	0.33	2.5	2.5
16	1.3	20.0	247	275	0.091	0.26	2.75	2.0
17	2.6	20.0	247	275	0.091	0.26	5.5	3.5
18	6.2	21.1	266	218	0.233	0.31	18.3	12.6
19	6.6	20.0	247	218	0.181	0.30	16.0	8.0
20	4.9	20.0	247	241	0.143	0.29	11.5	5.8
21	2.1	20.0	247	241	0.143	0.29	4.9	3.1
22	0.62	20.0	247	312	0.062	0.25	1.2	1.1
23	1.2	20.0	247	303	0.068	0.25	2.4	1.3
24	12.0	21.1	266	180	0.405	0.33	38.0	22.0
32	1.1	22.0	272	257	0.149	0.29	3.5	2.5
36	5.2	22.0	272	250	0.162	0.30	16.9	10.1
37	5.2	22.0	272	175	0.465	0.34	19.0	13.3

mistic assumption  $r_1=r_D$ , the argument of tanh is about 20. Obviously, under these conditions, the tanh can be replaced by unity. To perform the remaining integration, we substitute

$$x_1=r_D^{-1}Z^{-1/3}, \quad dx_1=\frac{1}{3}r_D^{-1}Z^{-4/3}dZ, \quad (15)$$

and obtain

$$\sigma(\omega)=\pi^2 N_A r_\omega^2 a \kappa \omega \alpha^{1/3} \int_\alpha^\infty Z(Z^{1/3}+\alpha^{1/3})^{-1} e^{-Z} dZ; \quad (16)$$

$$\alpha^{1/3}=r_\omega/2r_D.$$

The integral  $I$  can be approximated for moderate  $\alpha$  ( $r_\omega \sim r_D$ ) and for small  $\alpha$  ( $r_\omega \ll r_D$ ). In the first case,

$$I \approx r_D/r_\omega = \frac{1}{2}\alpha^{-1/3}; \quad (17a)$$

in the second,

$$I \approx 1. \quad (17b)$$

For intermediate cases, a numerical calculation was performed. The plot of  $\alpha^{1/3}I$  versus  $\alpha$  which was obtained is shown in Fig. 5. Note that  $\alpha$  is proportional to the majority concentration. A rather simple expression can be obtained if one defines a "concentration"  $N_\omega$ , related to  $r_\omega$  as  $N_D$  is to  $r_D$ . For moderate  $r_\omega/2r_D$  (moderate majority concentration),

$$\sigma(\omega) \approx \frac{3}{8}\pi(N_A/N_\omega)(a/r_\omega)\kappa\omega; \quad (18a)$$

and for small  $r_\omega/2r_D$  (small majority concentration),

$$\sigma(\omega) \approx \frac{3}{8}\pi(N_A/N_\omega)(N_D/N_\omega)^{1/3}(a/r_\omega)\kappa\omega. \quad (18b)$$

These are rather interesting relationships between the low-temperature conductivity and the imaginary conductivity of the host material  $\kappa\omega$ , i.e., for the loss factor  $\tan\delta = \text{Re}\sigma(\omega)/[\text{Im}\sigma(\omega)+\kappa\omega] \approx \sigma(\omega)/\kappa\omega$ . The factor  $a/r_\omega$  is approximately 0.1 and is given more exactly by Eq. (6) or Fig. 3. It does not depend either directly on the host material, or on the type of impurity. The "concentration"  $N_\omega$  for Si at low temperatures is  $\sim 10^{16}$ . For samples described in Ref. 1, where most samples have  $N_A \sim 10^{15}$ , the conductivity should be of the order of one percent of  $\omega\kappa$ . This, indeed, is the correct order

of magnitude. Table I presents a more complete comparison between the theoretical and the experimental magnitudes. It utilizes Eq. (16), together with the numerical calculation plotted in Fig. 5, for the calculated values of the conductivity. The sample numbers in the first column correspond to those used in Ref. 1. The two last columns of the table compare the calculated and measured conductivities at  $10^3$  cps and  $1.1^\circ\text{K}$  in units of  $\Omega^{-1} \text{ cm}^{-1}$ . The agreement tends to become worse with larger minority concentration. This can be at least partially attributed to the observed dependence of the conductivity on the minority concentration. It was stated in Ref. 1 that  $\sigma$  at low temperatures is proportional to  $N_A^{0.85}$  rather than to  $N_A$ , as assumed in calculating results. Hence, at large values of  $N_A$ ,  $\sigma_{\text{meas.}}$  seems to fall short of  $\sigma_{\text{calc.}}$ .

The concentration dependence is given explicitly in Eqs. (18a) and (18b). At "moderate" majority concentrations, the conductivity is independent of the majority concentration, while at low concentrations it is proportional to  $N_D^{1/3}$ . While the approximation for moderate concentrations is only a rough one, the numerical evaluation of Eq. (16) also shows that  $\sigma$  tends to be independent of  $N_D$  for "moderate" concentrations. This is demonstrated by Fig. 5, where the ordinate is proportional to the conductivity and the abscissa to  $N_D$ . The seventh column of Table I, which

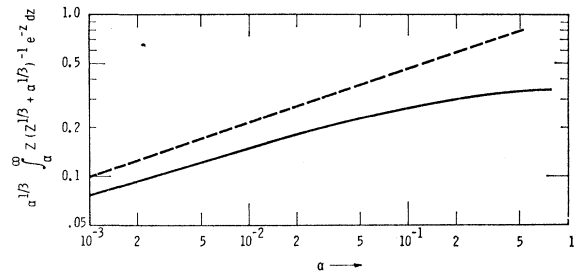


FIG. 5. A plot of  $\alpha^{1/3}I(\alpha)$  versus  $\alpha$ . The function  $\alpha^{1/3}I(\alpha)$  is proportional to the conductivity while  $\alpha$  is proportional to the majority impurity concentration. The dashed line is a plot of  $\alpha^{1/3}$ .

contains the entire dependence of the conductivity on the majority concentration, also demonstrates the lack of sensitivity of  $\sigma$  on  $\alpha$ , i.e., on the majority concentration. This bears directly on one of the problems posed in Ref. 1, which stated that  $\sigma$  is observed to be independent of  $N_D$  at low temperatures. It was hypothesized that this resulted from possible attractions of the majority atoms to the minority atoms during crystallization. It is demonstrated here that such an independence should exist in a completely random arrangement of impurities (i.e., no correlation between the position of minority atoms and majority atoms), as long as  $N_D$  becomes comparable to  $N_\omega$ . This happens to be true for all samples of Ref. 1 (except, perhaps, samples 25 and 26, which were doped by irradiation and as such did not yield interpretable results). It would be of interest to measure samples with low  $N_D$  to see whether  $\sigma$  tends to follow an  $N_D^{1/3}$  dependence for low concentrations. Unfortunately, for such concentrations, the conductivity at very low temperatures becomes too small to be accurately measured.

It is worth noting that some detailed features of the experimental and theoretical investigation seem to agree at least qualitatively. In Fig. 6(a) of Ref. 1, one observed that the lack of dependence of  $\sigma$  of  $N_D$  at low temperatures is more pronounced at low frequencies than it is at higher frequencies. As  $r_\omega$  decreases with increasing frequency,  $r_\omega/r_D$  is larger at low frequencies, and therefore, closer to the range of validity of Eq. (18a) than at high frequencies. From Fig. 7 of Ref. 1, and unpublished data for higher frequencies for samples represented in Fig. 7, the same results are apparent.

The frequency dependence (apart from the explicit proportionality with  $\omega$ ) is contained in  $a/r_\omega$  and in  $N_\omega$ . As  $N_\omega$  is proportional to  $r_\omega^{-3}$ , the implicit frequency dependence should be as of  $r_\omega^2$  at moderate concentrations, and as of  $r_\omega^3$  at low concentrations. In the frequency range  $10^2$ – $10^5$  cps, the dependence of  $r_\omega$  on  $\omega$  can be well described as being proportional to  $\omega^{-0.05}$ . The frequency dependence of the conductivity at very low temperatures should be between  $\omega^{0.85}$  and  $\omega^{0.9}$ ; the former term is approached by lightly doped material, the latter by more heavily doped material. These trends, for the lightly and heavily doped materials, are again visible in Fig. 6(a) of Ref. 1, and are actually a direct consequence of the previous remark made about Fig. 6(a).

To compare the frequency dependence at very low temperatures with that at high temperatures, we observe in Eq. (15) of Ref. 1, that  $\sigma$  at high temperatures is proportional to  $r_\omega^4$  [remembering that the factor  $(14.8 - \frac{1}{2} \ln \omega)$  is actually  $r_\omega/a$ ]. The frequency dependence, therefore, should be somewhat more pronounced at very low temperatures than it is at high temperatures. That this trend is obeyed in practice can be verified from Fig. 3 in Ref. 1, and plots made in a similar fashion from data on the other lightly compensated samples described in Ref. 1.

There is no explicit temperature dependence at the very low temperatures; the only variation with temperature is due to the variation of  $r_\omega$ . Equation (6) shows that the dependence on temperature should be the same as on  $\omega^{-1}$ . The very-low-temperature behavior of the conductivity should, therefore, be between  $T^{0.1}$  and  $T^{0.15}$ .

*Extremely Low Temperatures.* It is surprising that the hopping conductivity, a phonon-induced process, approaches a finite value at very low temperatures when the slight temperature dependence of  $r_\omega$  is disregarded. At extremely low temperatures it is, indeed, incorrect for the following reason. In Ref. 1, the expression for  $\sigma$  was derived from the basic Eqs. (7)–(9). At extremely low temperatures the contributions to the conductivity, as represented by this expression for  $\sigma$ , come from pairs with extremely small  $\Delta E$ . For such pairs, however, Eq. (9) of Ref. 1 is invalid. It assumes that an electron is located either on one or on the other of the impurity atoms, and that, therefore, the phonons in affecting a transition between states, transport the full charge of the electron from one atom to another. The actual transitions, however, occur between states as described by Eq. (II-3) or, approximately, by Eq. (II-9) of Ref. 12. The transition, accordingly, will be complete only when the resonance energy  $W$  is much smaller than  $\Delta E$  (denoted  $\Delta$  in Ref. 12). The validity of the above results therefore will apply only to situations where very little contribution comes from transitions with  $\Delta E \sim W$ . Lowering the temperature, a point has to be reached ultimately when this is no longer true. To determine this temperature we notice from Eq. (1) that the  $\cosh^{-2}$  factor permits only such pairs to contribute to  $\sigma$  whose  $\Delta E$  is of the order of  $kT$  or smaller. Therefore, it is required for the validity of this treatment that  $kT$  be larger than  $W$ . The latter has been calculated in Ref. 12. As we are interested primarily in silicon, we shall apply Eq. (II-19) of Ref. 12 to that material.

$$W = 0.27(R/a)^{3/4} e^{-R/a6} \times 10^{-2} [\text{eV}]. \quad (19)$$

$R$  is the distance between the two atoms and therefore should be appropriately replaced by  $r_\omega$ . As  $r_\omega/a \approx 10$ ,  $W \approx 0.1^\circ\text{K}$ . It is therefore safe to apply the foregoing to all the measurements of Ref. 1.

To derive the behavior of the conductivity at extremely low temperatures, i.e., where  $W > kT$ , we make use of the equation preceding Eq. (II-4) in Ref. 12. We can derive from this equation the transfer of charge occurring with a transition of an electron. (It should be noted that such a procedure is valid only for the real part of the conductivity. The imaginary part of the conductivity will probably get its major contribution from the polarization of the wave functions rather than from phonon-induced transitions.) For  $W \gg \Delta$ , the transfer of charge is  $\frac{1}{2} e S \Delta E / W$ ,  $S$  being defined by Eq. (II-7) of Ref. 12. In this range, therefore, the right-hand side of Eq. (9) of Ref. 1, and consequently the

right-hand sides of the various equations for  $\sigma$  of this paper,<sup>8</sup> have to be reduced by the factor  $\frac{1}{2}\Delta E/W$ . Equation (13) thus becomes

$$\begin{aligned} \sigma(\omega) &= \frac{3}{4}\pi^2 N_A r_D^{-6} r_\omega^3 a_{\kappa\omega} S k T / W \\ &\times \int_{2/r_\omega}^0 x_1^{-3} (1 + \frac{1}{2} r_\omega x_1)^{-1} \exp(-x_1 r_D)^{-3} \\ &\times \int_0^{r_T/2r_1(1+r_1 r_\omega^{-1})} (x_1 - 2r_T^{-1}\xi)^{-3} \xi \cosh^{-2}\xi d\xi dx_1. \quad (20) \end{aligned}$$

Equation (20) reveals without actual integration, that the conductivity at extremely low temperatures is explicitly proportional to the temperature (apart from the temperature dependence implicit in  $r_\omega$ ) and goes to zero at 0°K.

*High Impurity Concentrations.* The condition  $r_D > r_\omega$  was imposed till now to guarantee that hops of length  $r_\omega$  occur by a direct transition without an easily accessible impurity in-between posing as an intermediate state. This is why the distribution in Eq. (3b) includes a factor  $\exp(-r/r_D)^3$ . The factor is the probability that no impurity atom exists in the volume, where it could thus effect the hopping rate between the atoms separated by  $r_\omega$ . The argument of the exponential is equal to this volume (approx.  $\frac{4}{3}\pi r^3$ ), times the probability  $N_D$  that an atom exists in this volume. The condition  $r_\omega < r_D$  makes it possible to approximate the exponential

by unity. At very low temperatures, most of the volume is inaccessible to a carrier because of energy considerations. Only a slice of the volume, the thickness of which is  $kT$ , is of concern. The volume from which an impurity has to be excluded is, therefore, considerably reduced. The reduction factor can be shown to be approximately  $r_D^2/r_T$ . The factor  $\exp(-r/r_D)^3$  should be replaced by  $\exp(-r^2/r_T r_D)$ , and the condition  $r_\omega < r_D$  by  $r_\omega < (r_T r_D)^{1/2}$ . To determine the permissible concentration, use can be made of Figs. 2 and 3. At 20°K, e.g.,  $r_T/r_\omega$  is found to be approximately 2.5. At 20°K, therefore, the concentration can be  $(2.5)^3 \approx 16$  times higher than the original restriction allowed. The factor is, of course, even larger for lower temperatures.

To treat the higher concentrations, one has to go back to Eq. (11) where the first integral has been neglected for the low concentration case. It expresses the part of the conductivity due to the configurations of the type which is illustrated in the lower half of Fig. 4. As one increases the concentration, configurations of this kind become more numerous and, therefore, may contribute appreciably to the conductivity at high enough concentrations. The rest of the contribution still comes from the second integral, and hence shall remain as given by Eq. (16). Using Eq. (12) and neglecting again  $2r_T^{-1}\xi$  with respect to  $x_1$  and replacing the upper limit of  $\xi$  by  $\infty$ , one can write for the first integral of Eq. (11)

$$\begin{aligned} 2r_T^{-1} \int_{r_\omega/2}^0 r_1^4 \exp(-r_1/r_D)^{3\frac{1}{2}} \int_{r_T(r_\omega-2r_1)/2r_1(r_\omega-r_1)}^\infty \cosh^{-2}\xi d\xi dr_1 &= 2r_T^{-1} \int_{r_\omega/2}^0 r_1^4 \exp(-r_1/r_D)^3 \\ &\times \{1 + \exp[r_T(r_\omega-2r_1)/r_1(r_\omega-r_1)]\}^{-1} dr_1. \quad (21) \end{aligned}$$

Because of the range of integration, the argument of the exponential function inside the braces can acquire only positive values. The value of the braces, therefore, will be always smaller than unity. In fact, an appreciable contribution to the integral can be expected only from a region where the argument is not larger than unity. For low temperature this happens where  $r_1 > \frac{1}{2}r_\omega(1-r_\omega/r_T)$ . As the upper limit on  $r_1$  is  $\frac{1}{2}r_\omega$ , most of the contribution to the integral shall be from a region  $\frac{1}{2}r_\omega \cdot r_\omega/r_T$  wide, around  $\frac{1}{2}r_\omega$ . For very small temperatures the region becomes very small. Unless the other exponential in Eq. (21) varies rapidly near  $\frac{1}{2}r_\omega$  (i.e.,  $\frac{1}{2}r_\omega \sim r_D$ ), we can approximate the integral by assigning the value  $\frac{1}{2}r_\omega$  to  $r_1$  in the rest of the integrand. Thus we obtain

$$\begin{aligned} 2r_T^{-1} \int_{r_\omega/2}^0 &\approx (\frac{1}{2}r_\omega)^4 \\ &\times \exp(-\frac{1}{2}r_\omega/r_D)^3 r_\omega^2 r_T^{-2} \int_0^\infty (1 + \exp Z)^{-1} dZ \\ &= (\ln 2/16) (r_\omega^6/r_T^2) \exp(-\frac{1}{2}r_\omega/r_D)^3, \end{aligned}$$

where

$$Z = r_T(r_\omega - 2r_1)/r_\omega^2. \quad (22)$$

The exponential function can be approximated by 1 where the argument is smaller than 1, and by 0 elsewhere. This part of the conductivity makes a contribution only at concentrations below those given by the condition  $r_D = \frac{1}{2}r_\omega$  (for *n*-type silicon this is several times  $10^{17}$  cm<sup>-3</sup>). For such a condition, the total conductivity becomes

$$\begin{aligned} \sigma(\omega) &= \frac{3}{4}\pi^2 (N_A/N_\omega) (a/r_\omega) \\ &\times \kappa\omega [\alpha^{1/3}I + 0.014(N_D/N_\omega)^2 (r_\omega/r_T)]. \quad (23) \end{aligned}$$

The quantity  $\alpha^{1/3}I$  is defined in Eq. (16). Figure 5 shows that for  $r_D = \frac{1}{2}r_\omega$  (i.e.,  $\alpha=1$ ) the expression  $\alpha^{1/3}I$  is approximately equal to 0.3. At such a concentration,  $(N_D/N_\omega)^2 = 64$ . The second term is then equal to  $0.9r_\omega/r_T$ . Since at very low temperatures  $r_\omega \ll r_T$ , we conclude that in this region the configurations with  $r_D < \frac{1}{2}r_\omega$  do not contribute appreciably to the conductivity even at high concentrations.



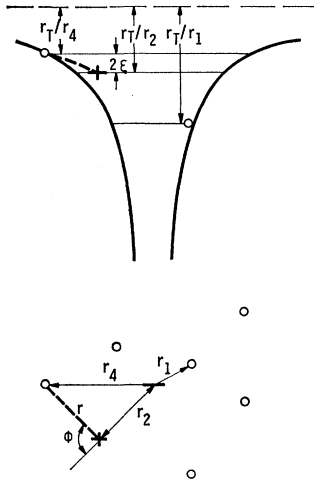


FIG. 6. The Conwell-Mott model for the treatment at higher temperatures. The figure is similar to Fig. 1, but involves impurities more distant from the minority impurity.

### B. Low Temperatures

This is the region where we must take account of contributions from pairs in which the ionized majority atom is not the nearest one to a minority atom. At such temperatures hopping may occur in regions higher up the potential well. The characteristics of the pairs formed from atoms that are at different energies in the well may be different. Therefore,  $d\rho(r, \Delta E)$  of Eq. (1) now depends on temperature. Specifically, the distribution of  $\Delta E$  depends on the position in the well (and thus on  $T$ ), because of the decreasing steepness of the potential with increasing height. The distribution of  $r$ , on the other hand, is unaffected by the temperature, as long as random distribution of impurities exists. In addition to the treatment of the effect just mentioned, we have to revise some of the approximations used in the previous section.

The model for this temperature range is shown in Fig. 6. The difference between this situation and that in the last section is that here the charge carrier may hop further away from the minority atom. Accordingly, the contributions from the various pairs have to be taken into account according to the fraction of the time that the carrier spends in them. This amounts to calculating the sum of the probabilities for the two members

of the pair to be occupied by a carrier

$$p_0 = \{ \exp[-r_T(r_1^{-1} - r_2^{-1})] + \exp[-r_T(r_1^{-1} - r_4^{-1})] \} / \sum_i \exp[-r_T(r_1^{-1} - r_i^{-1})]. \quad (24)$$

The sum is over all the majority atoms surrounding one minority atom. In a rigorous procedure, all possible arrangements of majority atoms surrounding a minority atom would have to be considered and weighed according to their probability of occurrence. For simplicity we shall replace the sum in Eq. (24) by

$$\int \exp[-r_T(-r_1^{-1} - \rho^{-1})] p(\rho) d\rho,$$

where  $p(\rho)$  is the probability density of finding a majority atom at the position  $\rho$ .

The probability  $d\rho(r, \Delta E)$  must also be modified to include all three atoms that are of importance as shown in Fig. 6:

$$d\rho(r, \Delta E) \rightarrow p_0 d\rho(r_1) d\rho(r_1 | r_2) \times d\rho(r_1, r_2 | r) d\rho(r_1, r_2, r | \varphi). \quad (25)$$

The meaning of the various differential probabilities is analogous to those in Eq. (3). Thus  $d\rho(r_1)$  is given by Eq. (3a),  $d\rho(r_1, r_2 | r)$  by Eq. (3b), and  $d\rho(r_1, r_2, r | \varphi)$  by Eq. (3c). The direct application of Eq. (3c) may be questioned because of the problems of the range of integration over the variable  $\varphi$  and of the normalization. The procedure can, however, be applied in exactly the same manner. When  $r_2$  is sufficiently close to  $r_1$ , the limited range of  $\varphi$  will again prevent the violation of the assumption that the nearest neighbor to the minority impurity lies at  $r_1$ . Where such a danger does not exist, the prescribed procedure will prevent us from counting the same pairs twice. There is no analogy in Eq. (3) to  $d\rho(r_1 | r_2)$ . This is the probability of finding a majority atom at the distance  $(r_2 \pm \frac{1}{2} dr_2)$  from the minority atom. Since random distribution is assumed,

$$d\rho(r_1 | r_2) = 3r_D^{-3} r_2^2 dr_2. \quad (26)$$

We now combine Eqs. (1) and (25) and integrate over  $r$ . This is done in the same way as in the last section; namely, by replacing  $[(\omega\tau)^{-1} + \omega\tau]^{-1}$  by  $\frac{1}{4}\pi a\delta(r - r_\omega)$ . The result may be written

$$\begin{aligned} \sigma(\omega) = & \frac{3}{4}\pi^2 N_A r_D^{-6} r_T r_\omega^3 a \kappa \omega \int_0^\infty r_1^2 \exp(-r_1/r_D)^3 \nu_3 \exp(-r_T/r_1) \\ & \times \int_{r_1}^{r_A} \{ [r_2^{-1} \delta(r_1 - r_2) + 3r_D^{-3} r_2] \exp r_T/r_2 + 3r_D^{-3} r_2 \exp[(r_T/r_2) - 2\xi] \} \nu \int_{(r_2+r_\omega)^{-1}}^{r_2^{-1}} x_4^{-3} \cosh^{-2} \xi dx_4 dr_2 dr_1. \quad (27) \end{aligned}$$

The two terms in the braces correspond, respectively, to the two terms in Eq. (24). The first term includes a delta function because of the assumption that a majority atom exists at  $r_1$ . The second term does not in-

clude it because the nearest neighbor can only be the low-energy member of a pair. The symbol  $\nu_3$  represents a normalization factor, from the denominator of Eq. (24). In accordance with the remark following that

equation, it may be written

$$\nu_3^{-1} = \exp(-r_T/r_1) \int_{r_1}^{r_A} [\delta(r_1-r_2) + 3r_D^{-3}r_2^2] \times \exp(r_T/r_2) dr_2. \quad (28)$$

The upper limit  $r_A$  in Eqs. (27) and (28) is defined as  $[(4/3)\pi N_A]^{-1/3}$ , but its magnitude is unimportant provided it is small enough that the integrand is cut off before it starts to increase at very large values of  $r_A$ . To facilitate computation, Eq. (27) is written in the following way:

$$\begin{aligned} \sigma(\omega) &= \frac{3}{4}\pi^2 N_A r_D^{-6} r_T r_\omega^3 a k \omega \\ &\times \int_{\alpha}^{\infty} x_1^{-3} \exp(-x_1 r_D) \frac{\nu I_0 + 3r_D^{-3} I_1}{1 + 3r_D^{-3} I_1} dx_1, \\ I_0 &= \int_{(r_1+r_\omega)^{-1}}^{r_1^{-1}} x_4^{-3} \cosh^{-2} \xi dx_4, \\ I_1^1 &= \exp(-r_T x_1) \int_{r_A^{-1}}^{r_1^{-1}} x_2^{-4} \exp(r_T x_2) dx_2, \\ I_1 &= x_1^{-1} \exp(-r_T x_1) \int_{r_A^{-1}}^{r_1^{-1}} x_2^{-3} \exp(r_T x_2) \nu I_2 dx_2, \\ I_2 &= 4 \int_{(r_1+r_\omega)^{-1}}^{r_2^{-1}} x_4^{-3} (1 + \exp 2\xi)^{-1} dx_4. \end{aligned} \quad (29)$$

By writing  $r_T(x_1-x_2) = \eta$ , and  $r_T(x_2-x_4) = 2\xi$ , we can rewrite Eq. (29) as

$$\begin{aligned} I_0 &= 2r_T^{-1} \int_0^{r_T/2r_1(1+r_1r_\omega^{-1})} (x_1 - 2r_T^{-1}\xi)^{-3} \cosh^{-2} \xi d\xi, \\ I_1^1 &= r_T^{-1} \int_0^{r_T(r_A^{-1}+r_1^{-1})} (x_1 - \eta r_T^{-1})^{-4} \exp(-\eta) d\eta, \\ I_1 &= x_1^{-1} r_T^{-1} \int_0^{r_T(r_A^{-1}+r_1^{-1})} (x_1 - \eta r_T^{-1})^{-3} \exp(-\eta) \nu I_2 d\eta, \\ I_2 &= 4r_T^{-1} \int_0^{r_T/r_2(1+r_2r_\omega^{-1})} (x_2 - 2\xi r_T^{-1})^{-3} \\ &\quad \times (1 + \exp 2\xi)^{-1} d(2\xi). \end{aligned} \quad (29a)$$

The integral  $I_0$  is the same as the one that appears in Eq. (13). If the second term in the numerator and denominator of the first of Eqs. (29) can be neglected, Eq. (29) becomes identical with Eq. (16). It will be shown that these terms can be neglected at sufficiently low temperatures. All the integrals in Eq. (29a) have an upper limit proportional to  $r_T$ , say  $r_T/r_0$ . For large  $r_T$  (low temperatures), the difference between the integrals integrated to their proper limit, and similar integrals integrated to infinity, is of the order  $\exp(-r_T/r_0)$ .

This difference is negligible because terms varying as various powers of  $r_T^{-1}$  are more important than the exponential at sufficiently low temperatures. The low temperature approximation, therefore, consists of extending the integration to infinity, and expanding the parentheses that contain  $r_T$  in the four integrals of Eq. (29a) in powers of  $r_T^{-1}$ . The result is

$$\begin{aligned} I_0 &= 2r_T^{-1} x_1^{-3} [1 + 6(\ln 2) x_1^{-1} r_T^{-1} + 12\zeta(2) x_1^{-2} r_T^{-2} + \dots], \\ I_1^1 &= r_T^{-1} x_1^{-4} (1 + 4x_1^{-1} r_T^{-1} + 20x_1^{-2} r_T^{-2} + \dots), \\ I_1 &= 4r_T^{-2} x_1^{-7} \gamma \{ \ln 2 + [6 \ln 2 + \frac{3}{2}\zeta(2)] x_1^{-1} r_T^{-1} \\ &\quad + \frac{1}{2} (\ln 2) r_\omega \nu r_T^{-1} + \dots \}. \end{aligned} \quad (29b)$$

Here  $\zeta$  is the Riemann's zeta function, and  $\gamma = (1 + \frac{1}{2} r_\omega / r_T)^{-1}$ . Approximating  $(1 + 3r_D^{-3} I_1^1)^{-1}$  in Eq. (29) by  $1 - 3r_D^{-3} I_1^1 + \dots$ , we finally obtain for the conductivity, to second order in  $r_T^{-1}$ ,

$$\begin{aligned} \sigma(\omega) &= \frac{1}{2}\pi^2 N_A r_D^{-1} r_\omega^3 a k \omega [I_{3,1} + (4.0I_{4,1} + 1.0I_{7,1}) r_D / r_T \\ &\quad + (20I_{5,1} + 20I_{8,1}) r_D^2 / r_T^2 + 1.4I_{7,2} r_D r_\omega / r_T^2], \end{aligned} \quad (30)$$

with

$$I_{j,k} = \int_{\alpha}^{\infty} Z^{j/3} (Z^{1/3} + \alpha^{1/3})^{-k} e^{-Z} dZ.$$

The leading term of Eq. (30) is identical with Eq. (16). The terms  $I_{3,1}$ ,  $I_{4,1}$ ,  $I_{5,1}$  are due to the expansion of  $I_0$  only, and therefore, represent the conductivities of pairs in which the nearest neighbor to the minority is a member of the pair. The revision of the approximations used in the last section, therefore, becomes important before the occupation of higher lying impurities does. The actual importance of either effect is, however, doubtful. Equation (30) reveals that increasing powers of  $r_D$  are involved as a consequence of, and together with, increasing powers of  $r_T^{-1}$ . Therefore, the successive terms of the expansion become relatively more important for larger  $r_D$ , i.e., for smaller concentrations. This would make the temperature dependence more pronounced for smaller concentrations. There is, at present, no experimental evidence for such behavior. Although only a few experiments have been performed to date, they all indicate that, throughout the temperature range, the temperature dependence becomes more pronounced when the majority concentration is increased (see Figs. 6 and 7, Ref. 1). Such behavior is more reminiscent of the functional dependences of the second term of Eq. (23). We shall now examine whether the effects represented by that term can explain the observed behavior in a better way than the foregoing treatment. The approximations used to derive Eq. (23) must now be changed so that they will be valid at higher temperatures. Specifically, none of the integrand in Eq. (21) can be taken out of the integral sign. The other approximations, i.e., the replacement of the upper limit by infinity, approximating  $r_1(r_\omega - r_1)$  by  $(r_\omega/2)^2$ , and neglecting  $2r_T\xi$  with respect to  $x$ , will be used again. The expression  $\exp(-r_1/r_D)^3$  can be approxi-

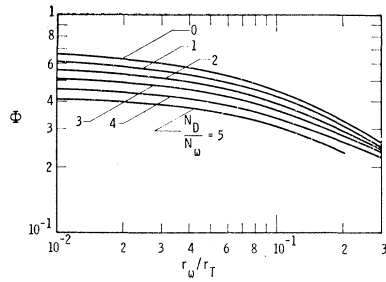


FIG. 7. A plot of the polynomial  $\Phi$  of Eq. (31) versus the ratio  $r_\omega/r_T$  with  $N_D/N_\omega$  as a parameter.

mated by  $(1 - 0.63r_1^3/r_D^3)$ . This is a good approximation for  $r_1 \leq r_D$ . As the range of integration over  $r_1$  is from 0 to  $\frac{1}{2}r_\omega$ , and  $\frac{1}{2}r_\omega$  is assumed to be less than  $r_D$ , the last approximation holds well. Using the substitution defined by Eq. (22), and replacing the upper limit of  $Z$  by infinity, we obtain for the first integral of Eq. (11)

$$r_\omega^6 \Phi / 32r_T,$$

where

$$\begin{aligned} \Phi = & \{ (0.692 - 0.0548N_D/N_\omega) - (3.26 - 0.452N_D/N_\omega) \\ & \times (r_\omega/r_T) + (10.83 - 2.97N_D/N_\omega)(r_\omega/r_T)^2 \\ & - (22.8 - 15.7N_D/N_\omega)(r_\omega/r_T)^3 + (23.3 - 64.2N_D/N_\omega) \\ & \times (r_\omega/r_T)^4 + 195N_D/N_\omega(r_\omega/r_T)^5 - 393N_D/N_\omega(r_\omega/r_T)^6 \\ & + 398N_D/N_\omega(r_\omega/r_T)^7 \}. \end{aligned} \quad (31)$$

This expression is not an expansion, but a complete polynomial.  $\Phi$  is plotted in Fig. 7 as a function of  $r_\omega/r_T$  for several values of  $N_D/N_\omega$ .

The total conductivity may be written

$$\begin{aligned} \sigma = & \frac{3}{4}\pi(N_A/N_\omega)(a/r_\omega)\kappa\omega \\ & \times [\alpha^{1/3}I(\alpha) + (3/128)(N_D/N_\omega)^2(r_\omega/r_T)\Phi]. \end{aligned} \quad (32)$$

The first term in the square brackets represents the conductivity due to those configurations where the majority impurity, which is a nearest neighbor to the minority impurity, can have an equienergetic majority atom at the distance  $r_\omega$ . The second term represents the conductivity of those where it cannot. As one expects, for  $N_D/N_\omega \rightarrow 0$  and  $r_\omega/r_T \rightarrow 0$ ,  $\Phi$  approaches  $\ln 2$ , and Eq. (32) reduces to Eq. (23). Functionally, Eq. (32) has a desirable behavior. The conductivity increases at higher temperatures; the increase being more pronounced for higher impurity concentrations or for larger Bohr radii. (This appears to be the case in Fig. 4 of Ref. 1, for example.) When the second term is significant, the frequency dependence decreases. This occurs because the second term is proportional to  $\omega r_\omega^9$ , i.e., to  $\omega^{0.55}$ . The experimental data for the samples with higher impurity concentration show a power lower than 0.8 at higher temperatures. Unfortunately Eq. (32) cannot quantitatively explain the experimental data at temperatures above the very low temperature region. For example, the second term of Eq. (32) for sample 9, at 10°K and 100 cps is about  $1.6 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$ . This is much too small to account for the departure of the experimental conductivity from Eq. (23) at

that temperature. It is possible to increase the importance of the second term by assuming a tendency for pairing. Such a tendency would bring the nearest-neighbor impurities of opposite kind closer than when randomly distributed, and thus increase the number of configurations represented by the second term. Nevertheless, even if the pairing is large enough that the second term dominates the conductivity, Eq. (32) does not agree with the observations if the numbers for  $a$  quoted by Miller and Abraham<sup>12</sup> are assumed to be correct. This is most readily demonstrated by trying to account for the behavior illustrated in Fig. 11 of Ref. 1. The conductivity of two samples with the same concentration, but a different kind of donor (i.e., with a different  $a$ ) are plotted there. The conductivities at higher temperatures differ for the two samples by a factor of approximately 3. This difference is larger than can be accounted for with Eq. (32), using the Bohr radii from Miller and Abraham<sup>12</sup>; i.e., a difference of about 5% between  $a$  for arsenic and for phosphorous in silicon. At a given frequency the value of  $r_\omega/a$  does not depend on the kind of donor. Therefore the second term of Eq. (32) is proportional to  $a^{10}$ . Hence the observed difference between the conductivities of samples 18 and 19 should be no greater than  $(1.05)^{10} = 1.6$ , i.e., 60%. To give agreement between the data and Eq. (32), the difference between the radii  $a$  must be 14%. A 14% difference, incidentally, would also give reasonable agreement at low temperatures, where the dependence on  $a$  should be approximately  $a^3$  [see Eq. (18a) or Eq. (42b)]. The frequency dependence at higher temperatures is also similar to that of the second term of Eq. (32). For example, at 10°K and around  $10^9$  cps, the experimentally observed dependence is  $\omega^{0.58}$ . Unfortunately, evaluation of Eq. (32) for sample 18

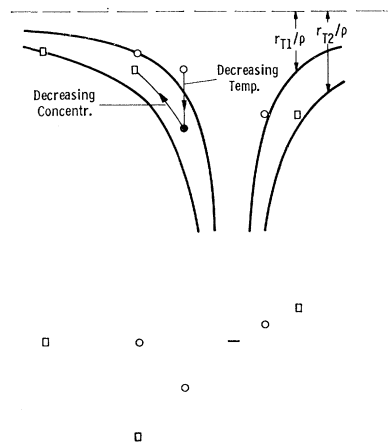


FIG. 8. An illustration of the similarity conditions. The circles represent conditions similar to those in Fig. 2. The squares represent a statistically equivalent situation with a concentration decreased by a factor 2<sup>3</sup>. If the temperature is also decreased by a factor of 2, as indicated on the top part of the figure, the corresponding impurities of the two systems are seen to have the same reduced energy.

at 10°K and 10<sup>3</sup> cps shows that the first term is ten times as large as the second.

It must be concluded that, in contrast to the very-low-temperature region, the behavior of the ac conductivity at the higher temperatures is not understood in detail. This may be due either to the analytical difficulties that exist in this range and the consequential crudeness of the approximations, or to a failure of the model itself. In an attempt to decide which of the two is the case, we develop some similarity relations in the following section. As indicated in the introduction, they do not yield the complete functional dependence of  $\sigma$  on the temperature, frequency, concentration, and kind of donor, but rather relate the dependence on one to the dependence on the others. Their value is in their generality. If a clear violation of the similarity relations is observed, a modification of the model is necessary.

### C. Similarity Relations

The basic considerations that lead to the similarity relations are illustrated in Fig. 8, where part of the con-

figuration from Fig. 6 is shown again as open circles. Two transformations are performed on the configuration. In one, the distance of each atom from the minority is increased by a factor of 2. In the other, the value of  $r_T/r_i$  is increased by a factor of 2. The results of the two operations are represented by squares and a full circle. The second operation corresponds to a decrease in temperature by a factor of 2. The first transformation may be interpreted as a decrease in concentration by a factor of 8 ( $N_{D1}/N_{D2}=[r_{D2}/r_{D1}]^3=2^3$ ). For such a ratio of concentrations, the configurations represented by the circles and by the squares will be equally likely to occur and hence equally represented in an ensemble.<sup>13</sup> From the top part of Fig. 8, one may observe that corresponding items of the two configurations possess the same normalized energies. Therefore, the occupation probability of the corresponding atoms will be identical for the two cases. Thus one can establish a one-to-one statistical correspondence between the two cases.

We are interested in finding the ratio  $s$  of the conductivities of the two situations with identical  $r_D/r_T$ . The ratio  $s$  can be expressed as

$$s = \frac{\sigma(r_{D2}, r_{T2}, \omega_2)}{\sigma(r_{D1}, r_{T1}, \omega_1)} = \frac{N_{A2} \int dp(r_2, \Delta E_2) n r_{T1} \cosh^{-2}(\xi_2) r_2^2 \omega_2 [\omega_2 \tau_2 + \omega_2^{-1} \tau_2^{-1}]^{-1}}{N_{A1} \int dp(r_1, \Delta E_1) r_{T1} \cosh^{-2}(\xi_1) r_1^2 \omega_1 [\omega_1 \tau_1 + \omega_1^{-1} \tau_1^{-1}]^{-1}}, \quad (33a)$$

where

$$r_{D2}/r_{D1} = r_{T2}/r_{T1} = n. \quad (33b)$$

Equation (33a) is obtained by using Eq. (1). The differential probability  $dp(r_i, \Delta E_i)$  can be written

$$dp(r_i, \Delta E_i) = p(\Delta E_i/kT, r/r_{Di}) d(r/r_{Di}) d(\Delta E_i/kT), \quad (34)$$

because every configuration in one system is brought into a configuration in the other system with the same  $\Delta E/kT$  and  $r/r_D$ . The functions  $[\omega_i \tau_i + \omega_i^{-1} \tau_i^{-1}]^{-1}$  are again replaced by  $\frac{1}{4} \pi a \delta(r - r_{\omega i})$ . The  $\delta$  functions may be written

$$\delta(r - r_{\omega i}) = r_D^{-1} \delta(r/r_D - r_{\omega i}/r_D).$$

Choosing  $r_{\omega 1}$  and  $r_{\omega 2}$  such that  $r_{\omega 1}/r_{D1} = r_{\omega 2}/r_{D2}$  and integrating over  $r$ , we find

$$s = \frac{N_{A2} p(\xi, r_{\omega}/r_D) n r_{T1}^2 n^2 r_{\omega 2}^2 n^{-1} r_{D1}^{-1} \omega_2}{N_{A1} p(\xi, r_{\omega}/r_D) r_{T1} r_{\omega 1}^2 r_{D1}^{-1} \omega_1} = \frac{N_{A2}}{N_{A1}} \frac{\omega_2}{\omega_1} n^2. \quad (35)$$

This ratio relates conductivities at frequencies corresponding to different  $r_{\omega}$ , such that  $r_{\omega 2} = n r_{\omega 1}$ . Using Eq. (6) we obtain the following relationship between  $\omega_1$  and  $\omega_2$ :

$$\omega_2 = n^{-1} \omega_1^n e^{(1-n)r_{\omega}/a} = n^{-1} \omega_1^n T_1^{(1-n)} e^{30.8(1-n)}. \quad (36)$$

The similarity relations imply that if some material, with a majority impurity concentration given by  $r_{D1}$  and minority concentration  $N_{A1}$ , exhibits a conductivity  $\sigma_1$  at a temperature  $T_1$  and frequency  $\omega_1$ , then a material with concentrations given by  $n r_{D1}$  and  $N_{A2}$  must have a conductivity  $(N_{A2}/N_{A1}) \sigma_1 n^2 (\omega_2/\omega_1)$ , at a temperature  $T_2 = T_1/n$  and frequency  $\omega_2$  given by Eq. (36).

Measurements of Ref. 1 are evaluated, utilizing these relations, in the following way. The temperature dependence of the conductivity  $\sigma_1(T_1)$  is plotted for a sample at a frequency  $\omega_1$ . Another sample, with the same type of donor, is selected. The value of  $n$  is determined from the ratio of the majority impurity concentrations. From this, and the values of  $\omega_1$  and  $T_1$ , the frequencies  $\omega_2$ , and temperatures  $T_2$  are chosen from the similarity conditions  $r_{\omega 2} = n r_{\omega 1}$ , and  $r_{T2} = n r_{T1}$ . The conductivity  $\sigma_2$  is determined at these values of temperature and frequency by interpolating or extrapolating the

<sup>13</sup> Actually, in order that the relation between the configurations hold exactly as stated above, the minority concentration must undergo the same transformation as the majority concentration (particularly for more heavily compensated materials). However, this is of no practical importance if the functional dependence on  $N_A$  can be accounted for separately ( $\sigma \propto N_A$ ).

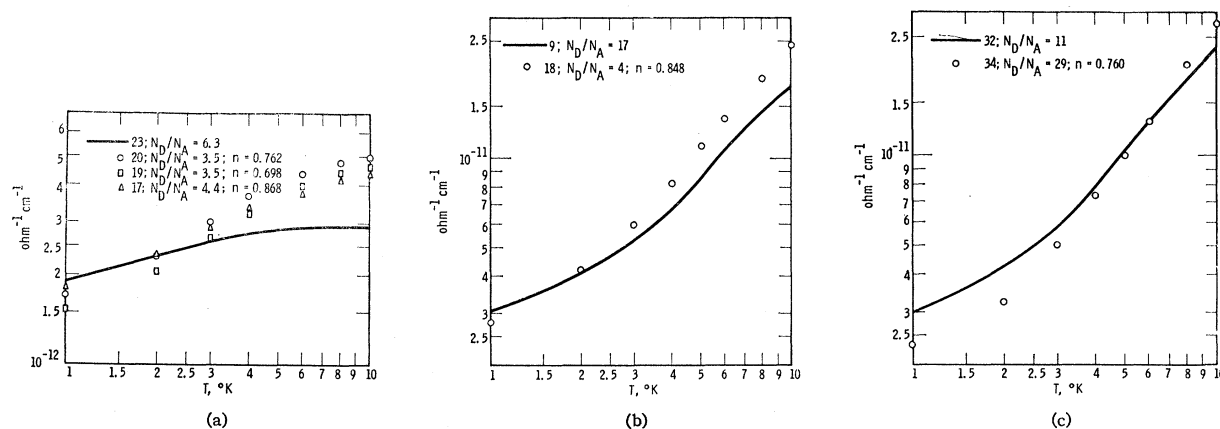


FIG. 9. The application of the similarity relations to experimental results of Ref. 1 for samples with (a) arsenic, (b) phosphorus, and (c) antimony donors. The plots are of  $\sigma(N_{D1}, T_1, \omega_1)$  (solid lines) and of  $[\sigma(n^{-2}N_{D1}, n^{-1}T_1, \omega_2)/n^2](\omega_1/\omega_2)(N_{A1}/N_{A2})^{0.85}$  (points), plotted versus the temperature  $T_1$ . The frequency  $\omega_1$  was chosen to be  $2\pi 10^2$  cps,  $\omega_2$  is calculated from Eq. (36) to satisfy the similarity conditions.

measured data. The quantity  $\sigma_2 n^{-2}(\omega_1/\omega_2)(N_{A1}/N_{A2})^{0.85}$  is then calculated and plotted as a function of the temperature  $T_1$ . Note that the experimental dependence on the minority concentration is used. If the experimentally observed behavior obeys the similarity relations, the two plots will be identical. Plots of this type are shown in Fig. 9 for arsenic-phosphorous- and antimony-doped samples. Except for sample 23, the results are within 20%. Apart from some scatter, there is a trend for the more heavily doped samples to lie below the less heavily doped ones at low temperatures, and above them at high temperatures. The discrepancy at low temperature can be traced to a somewhat puzzling, relatively rapid decrease of the conductivity with temperature at high frequencies and very low temperatures. (This trend may be seen in most plots of  $\sigma$  versus  $T$  in Ref. 1.) This is quite out of line with the similarity relations. It could perhaps be the beginning of the effect described preceding Eq. (20). The discrepancy at low temperatures is minimized in Fig. 9 by obtaining the values of  $\sigma$  at high frequencies and very low temperatures by extrapolation above  $10^4$  cps, rather than by interpolation between  $10^4$  and  $10^5$  cps. The remaining discrepancy may be the result of the assumption that the dependence on minority impurity is known separately and does not have to be included in the similarity conditions. This assumption is not completely justified, as the observed  $N_A^{0.85}$  dependence demonstrates. It is, moreover, not clear that this dependence is followed above the very-low-temperature region. In fact, the agreement between theory and experiment shown on Fig. 9 can be greatly improved at the high temperature end by assuming a proportionality with  $N_A$ . If the dependence on  $N_A$  cannot be separated, Eq. (35) is valid only under the additional condition of constant compensation,  $N_{A1}/N_{D1} = N_{A2}/N_{D2}$ . The compensation, unfortunately, is not adjustable for given samples the way  $r_\omega$  and  $r_T$  are. An

extensive comparison, therefore, is not possible. Only two of the comparable samples of Fig. 9 have the same compensation (19 and 20). Those, indeed, are very close to each other in their behavior, apart from a constant displacement of 10%. This may not be significant, as the measurements of Ref. 1 were not intended for such detailed interpretation.

The foregoing treatment can be used only for comparison of materials with the same kind of impurity. However, it is easy to incorporate a variation of  $a$  and thus to extend the similarity relations to cover materials with different donors. The changes required in the preceding treatment are the following: The right-hand side of Eq. (35) has to be multiplied by  $a_2/a_1$ . In the exponents of Eq. (36), every  $n$  has to be multiplied by  $a_1/a_2$ ; the  $n^{-1}$  appearing as a factor in that equation, however, remains unchanged and so does the relation between  $T_1$  and  $T_2$ .

Samples 18 and 19 have been evaluated accordingly. The result is shown in Fig. 10. When the values for  $a_{As}$  and  $a_P$  calculated by Miller and Abraham<sup>12</sup> are used, the discrepancy between the observed conductivities and the similarity relations is pronounced. The two can be brought into very good agreement, if one assumes  $a_P/a_{As} = 1.14$ . Notice that this result agrees very well with the one quoted towards the end of the last section.

We conclude that the comparison of the similarity relations with the somewhat limited data presently available does not seem to call for a modification of the model for impurity conduction, but perhaps a modification of the available numbers for the Bohr radii.

The above relations, while quite general, are not very convenient for use because measurements at different frequencies are necessary to test the validity of the relations. It would be preferable to use, instead of the ratio  $s$  defined by Eq. (31), a ratio of conductivities at the same frequency. This can be obtained formally as

follows:

$$s' \equiv \frac{\sigma(\omega_1, r_{D2}, r_{T2})}{\sigma(\omega_1, r_{D1}, r_{T1})} = \frac{\sigma(\omega_1, r_{D2}, r_{T2})}{\sigma(\omega_2, r_{D2}, r_{T2})} \cdot \frac{\sigma(\omega_2, r_{D2}, r_{T2})}{\sigma(\omega_1, r_{D1}, r_{T1})} \equiv s'' \cdot s. \quad (37)$$

The coefficient  $s''$  is essentially the frequency dependence, as it is the ratio of conductivities of the same material (same  $r_D$ ), at the same temperature, and at different frequencies. Unfortunately, no general expression for  $s''$  is available; therefore the experimental situation cannot be alleviated. However, one may make use of the theoretical frequency dependences obtained thus far to test whether the various theoretical expressions for the conductivity are consistent with the similarity relations. For cases so far treated analytically, one may write  $s''$  as follows:

$$s'' = (\omega_1/\omega_2)(r_{\omega 1}/r_{\omega 2})^p, \quad (38)$$

where  $p=4$  for high temperatures (Ref. 1),  $p=3$  for very low temperatures and low concentrations [Eq. (18b)],  $p=2$  for very low temperatures and moderate concentrations [Eq. (18a)], and  $p=9$  for the second term at intermediate temperatures [Eq. (32)]. To facilitate the desired comparison, Eqs. (35) and (38) are written (excluding the  $N_A$  dependence),

$$\sigma(\omega_2, r_{D2}, r_{T2})/r_{\omega 2}^2 \omega_2 = \sigma(\omega_1, r_{D1}, r_{T1})/r_{\omega 1}^2 \omega_1, \quad (35a)$$

$$\sigma(\omega_2, r_{D2}, r_{T2})/r_{\omega 2}^p \omega_2 = \sigma(\omega_1, r_{D2}, r_{T2})/r_{\omega 1}^p \omega_1. \quad (38a)$$

Equation (35a) means that, under conditions of constant  $r_D/r_{\omega}$ , and constant  $r_T/r_{\omega}$ , the expression  $\sigma/\omega r_{\omega}^2$  is constant. In other words,

$$\sigma = r_{\omega}^2 \omega F(r_D/r_{\omega}, r_T/r_{\omega}), \quad (35b)$$

where  $F$  is some function of  $r_D/r_{\omega}$  and  $r_T/r_{\omega}$  only. Similarly, from Eq. (38a), we may write

$$\sigma = r_{\omega}^p \omega \Phi(r_D, r_T), \quad (38b)$$

and, from Eqs. (35b) and (38b),

$$F(r_D/r_{\omega}, r_T/r_{\omega}) \equiv r_{\omega}^{p-2} \Phi(r_D, r_T). \quad (39)$$

The following form is consistent with Eq. (39):

$$F(r_D/r_{\omega}, r_T/r_{\omega}) = \sum_K C_K (r_D/r_{\omega})^K (r_T/r_{\omega})^{2-p-K}. \quad (40)$$

In certain cases, Eq. (40) is a necessary condition for Eq. (39) to be satisfied, and in every case, it is a sufficient condition. Inserting Eq. (40) into Eq. (35b), we find

$$\sigma = \sum_K C_K \omega r_{\omega}^p r_D^K r_T^{2-p-K}. \quad (41)$$

We rewrite the derived expressions as follows. The high-temperature approximation [Eq. (15) of Ref. 1] gives

$$\sigma = \frac{1}{4} \pi^2 N_A a \kappa \omega r_{\omega}^4 r_D^{-3} r_T. \quad (42a)$$

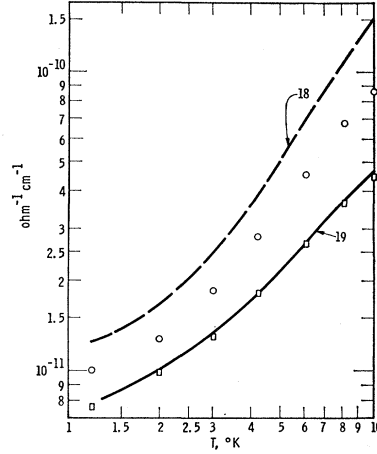


FIG. 10. The application of the similarity relations to samples with different kinds of donors. Sample 18 is phosphorus doped and sample 19 is arsenic doped with the same concentration (therefore,  $T_1 = T_2$ ). The minority concentrations are also very close. The lines are plots of the conductivities of both samples at 100 cps. The points are plots of  $\sigma_2(a_2/a_1)(\omega_1/\omega_2)(N_{A1}/N_{A2})$ , the subscripts 2 refer to the phosphorus doped sample, 1 to the arsenic doped. The circles correspond to  $a_2/a_1 = 1.05$ , the squares to  $a_2/a_1 = 1.14$ . The frequency  $\omega_1$  is  $2\pi \cdot 10^2$  cps while  $\omega_2$  is adjusted to satisfy the similarity conditions.

The very-low-temperature, moderate-concentration approximation [Eq. (18a)] yields

$$\sigma = \frac{1}{2} \pi^2 N_A a \kappa \omega r_{\omega}^2. \quad (42b)$$

The very-low-temperature, low-concentration approximation [Eq. (18b)] gives

$$\sigma = \frac{1}{2} \pi^2 N_A a \kappa \omega r_{\omega}^3 r_D^{-1}, \quad (42c)$$

and the term which may contribute at intermediate temperatures [second term in Eq. (32)] becomes

$$\sigma = (3/128) \pi^2 N_A a \kappa \omega$$

$$\times \sum_{i=0}^2 (\alpha_i r_{\omega}^{9+i} r_D^{-9} r_T^{-1-i} - \beta_i r_{\omega}^{12+i} r_D^{-9} r_T^{-1-i}), \quad (42d)$$

where  $\alpha_i$  and  $\beta_i$  are given in Eq. (31).

It can be verified by inspection that Eqs. (42a) through (42d) are consistent with Eq. (40). All of the approximations to the ac conductivity which we have obtained, therefore, are consistent with the similarity relations.

#### HEAVILY COMPENSATED MATERIAL

In this regime, two of the assumptions made previously have to be examined. (1) For heavily compensated material, the Boltzmann equation, as it appears in Eq. (5) of Ref. 1 [and on which Eq. (1) of this work is based], does not describe accurately the distribution. The reasons are pointed out in the remark following Eq. (5) of Ref. 1. (2) The assumption that  $\Delta E$  can be derived from the nearest minority impurity only is

valid only for low compensation. Actually, for high compensation, there is no single nearest minority impurity. Therefore, the potential from a large number of impurities has to be considered. Moreover, some ionized majority impurities will be at a distance comparable with that of the nearby minority impurity atoms.

The form of the Boltzmann equation appropriate for the heavy compensation case in the pair approximation is<sup>14</sup>

$$\dot{f}_1 = w_{21}f_2(1-f_{21}) - w_{12}f_1(1-f_{12}). \quad (43)$$

Here  $f_1$  and  $f_2$  are the occupation probabilities of impurity No. 1 and impurity No. 2 of the pair, respectively, and  $f_{12}$  signifies the conditional probability that atom 2 is occupied if atom 1 is occupied.

If the occupation of atom 1 and atom 2 are independent events (that is, if  $f_{ij} = f_j$ ), Eq. (43) will be representative of a Fermi-Dirac distribution

$$\dot{f}_1 = w_{21}f_2(1-f_1) - w_{12}f_1(1-f_2). \quad (43a)$$

If, on the other hand, the occupation of one atom implies the nonoccupation of the other (i.e.,  $f_{ij} = 0$  as in the case of low compensation), then Eq. (43) becomes

$$\dot{f}_1 = w_{21}f_2 - w_{12}f_1. \quad (43b)$$

This equation represents a Boltzmann distribution. To make Eq. (43) compatible with the condition  $f_{ij} = 0$ , an impurity will be called occupied by a carrier either if it is ionized and  $N_D/N_A < 0.5$ , or if it is neutral and  $N_D/N_A > 0.5$ . This is analogous to transport by holes or electrons (respectively, for  $n$ -type material). In view of the above, the number of carriers  $N_c$  is defined in the following way:  $N_c = N_A$  for  $N_D/N_A < 0.5$  and  $N_c = N_D - N_A$ , otherwise. Equations (43a) and (43b) are limiting cases of Eq. (43).

Writing  $f_i = f_{i0} + \Delta f_i$  with  $\Delta f/f \ll 1$  and expanding to first order in  $\Delta f$ , and hence to first order in the electric field, we obtain from Eq. (43a)

$$\dot{f}_1 = \Delta \dot{f}_1 = w_{21}f_{20}f_{10} - w_{12}f_{10}f_{20} - \Delta f_1[(f_{20} + f_{10}^-)w_{21} + (f_{10} + f_{20}^-)w_{12}], \quad (43c)$$

and from Eq. (43b)

$$\dot{f}_1 = \Delta \dot{f}_1 = w_{21}f_{20} - w_{12}f_{10} - \Delta f_1(w_{21} + w_{12}). \quad (43d)$$

The symbol  $f_i^-$  is defined as  $(1-f_i)$ . Again, use has been made of the assumption that only hopping in pairs contributes significantly to the conductivity. This assumption is equivalent to the condition  $\Delta f_1 = -\Delta f_2$ . The last two equations are of the same general form; namely,  $f = A - \Delta f \tau^{-1}$  and hence the conductivity in both cases also has the same form, i.e.,  $d\sigma(\omega) = F(A) \times \omega(\omega\tau + \omega^{-1}\tau^{-1})^{-1}dn$  ( $dn$  is the number of like pairs in an appropriate ensemble). The coefficient multiplying

$\Delta f$  in Eqs. (43c) and (43d) is the inverse of the relaxation time, and hence determines the frequency dependence of the conductivity. It can be shown that the rate of relaxation associated with Eq. (43c) is always longer than the rate associated with Eq. (43d). The physical reason for this is that in the Boltzmann case every pair which has a carrier can contribute to the relaxation, while in the Fermi-Dirac case some pairs may possess two carriers and hence cannot contribute to the relaxation. The coefficient  $F(A)$  is also different for the Boltzmann and for the Fermi-Dirac cases. We have to conclude that the question of what correlation exists between the occupancies of two neighboring impurities has some bearing upon the conductivity. However, we shall neglect the effects of any tendency towards a Fermi-Dirac distribution for the following reasons. For cases of very high compensation where  $N_D/N_A$  is almost unity,  $f_{ij}$  in Eq. (43) is very small and Eq. (43b), and hence (43d), become very good approximations. (In other words, very few pairs will be doubly occupied.) To decide whether the Boltzmann approximation is justifiable in cases of not so large compensation, we compare the energy that is involved in repelling a charge at one site of a pair by a charge at the other site with the energy difference between a site and the "would be" Fermi level. While the latter quantity is typically of the order of the Coulombic energy at average impurity spacings, the former is approximately the Coulombic energy of pairs with a spacing  $r_\omega$ , i.e., smaller than the average spacing. This means that the Boltzmann approximation should be a good one for most cases. Accordingly, we shall use Eq. (1) also for the high-compensation region.

Concerning the second point raised in the beginning of this section, we shall use an approximation for finding the distribution of  $\Delta E$ , which may be somewhat crude, but which will help us to obtain an idea about the behavior of the conductivity in this region. The treatment will employ a result derived by Born which gives the distribution of the electric field due to a random distribution of monopoles.<sup>15</sup> As long as there is no spatial correlation between the positive and the negative charges, the distribution of the electric field will be the same as if all charges were of one kind. This is so for the following reason: a configuration of positive charges will produce at any point a field identical to the field which would be produced by a configuration of negative charges with all coordinates centrally inverted through the point. If two such configurations have the same probability of occurrence, the sign of the charges does not affect the distribution. Consider now, that both kinds of monopoles exist. For a given arrangement of the positive charges, two centrally inverted configurations of the negative charges will be equivalent if no correlation exists between the positive and negative charges. In such a case, therefore, the negative charges

<sup>14</sup> Some confusion exists with respect to the notation  $w_{ij}$ . In this paper it will represent the hopping rate from impurity  $i$  to impurity  $j$ , although in Ref. 1 this hopping rate was annotated by  $w_{ji}$ .

<sup>15</sup> Max Born, *Optik* (Springer-Verlag, Berlin, 1933), pp. 444-455

can be replaced by positive charges and we are left with  $2N_A - 1 \approx 2N_A$  charges of one type only. The correlation between the position of the charges of the two kinds will decrease as the degree of compensation is increased, and for large compensations we shall assume that the correlation is unimportant.

We shall also assume that  $\Delta E = \epsilon_r r$  ( $\epsilon$  is the electric field), i.e., the field is constant over the distance  $r$ . This assumption is justified for the purpose of obtaining semiquantitative results, since the distances  $r$  that are of concern are smaller than the average distance. In order to use Born's result, we have to convert the distribution in  $\epsilon$  to a distribution in  $\epsilon_r$ . The conversion is readily achieved with the result:

$$W(\epsilon_r) = (\epsilon_0/\pi) \int_{\epsilon_r}^{\infty} \int_0^{\infty} x \sin(2x) e^{-(\epsilon_0 x)^{2/3}} dx d\epsilon, \quad (44)$$

where  $\epsilon_0 = 4.14eN_A^{2/3}/4\pi\kappa$ .

The integrand is not absolutely convergent and hence the order of integration has to be preserved. Unfortunately, the first integration cannot be performed in a closed form. It is, however, bounded by the expressions  $\int_0^{\infty} x \sin(\epsilon x) e^{-(\epsilon_0 x)^{2/3}} dx$  and  $\int_0^{\infty} x \sin(\epsilon x) e^{-\epsilon_0 x} dx$ , i.e., by  $\pi^{1/2} \epsilon \exp[-(\epsilon/2\epsilon_0)^2]/4\epsilon_0^3$  and  $2\epsilon_0\epsilon/(\epsilon_0^2 + \epsilon^2)^2$ . The second integration of these functions yields

$$W'(\epsilon_r) = 2\pi^{1/2} \exp[-(\epsilon_r/2\epsilon_0)^2] \\ \text{and } W''(\epsilon_r) = \epsilon_0^2/(\epsilon_0^2 + \epsilon_r^2).$$

The two functions are similar in that they vary slowly for  $\epsilon_r \ll \epsilon_0$  and fall off rapidly to very small values for  $\epsilon_r > \epsilon_0$ . The function  $W(\epsilon_r)$  must behave similarly.

To obtain the conductivity, we use Eq. (1) and write

$$dp(r, \Delta E) = dp(r) dp(r|\Delta E), \quad (45)$$

where

$$dp(r|\Delta E) = W(\Delta E/er) d(\Delta E/er) \\ = [W(\Delta E/er)/er] d\Delta E \quad (45a)$$

and  $dp(r)$  is given by Eq. (3b).

Combining Eq. (1), Eq. (3b) and Eq. (45), we obtain

$$\sigma(\omega) = \pi r_T \kappa \omega N_C r_D^{-3} \int r^3 \cosh^{-2}(\Delta E/2kT) W(\Delta E/er) \\ \times (\omega\tau + \omega^{-1}\tau^{-1})^{-1} dr d\Delta E.$$

Using the previous procedure to integrate over  $r$ , we find

$$\sigma(\omega) = \frac{1}{4}\pi^2 a r_T \omega N_C r_D^{-3} r_\omega^3 \\ \times \int \cosh^{-2}(\Delta E/2kT) W(\Delta E/er_\omega) d(\Delta E). \quad (45b)$$

To elucidate how the conductivity depends on the variables, we observe that the integrand in Eq. (45b) consists of a multiplication of two functions, both of which are slowly varying for small  $\Delta E$  and become very small for large  $\Delta E$ . For the  $\cosh^{-2}$  function, around the

region of rapid decrease is  $\Delta E \approx 2kT \equiv \Delta E'$ , and for the  $W$  function around  $\Delta E \approx 4e^2 r N_A^{2/3}/4\pi\kappa \equiv \Delta E''$ . If  $\Delta E' < \Delta E''$ , the  $\cosh^{-2}$  function will dominate the integrand (case *a*) and if  $\Delta E'' < \Delta E'$ , the  $W$  function will dominate it (case *b*). If we insert some typical values for silicon, say  $r = 200 \text{ \AA}$ , we obtain for  $N_A = 10^{14} \text{ cm}^{-3}$ ,  $\Delta E''/k \cong 2^\circ\text{K}$ ; for  $N_A = 10^{15}$ ,  $\Delta E''/k = 10^\circ\text{K}$ ; for  $N_A = 10^{16}$ ,  $\Delta E''/k = 50^\circ\text{K}$ . Case *a* will apply for temperatures much lower than these, and case *b* for temperatures much higher. Obviously, the latter is observable only for very pure material. To obtain the dependences on the various variables, we have to normalize  $W(\epsilon_r)$  properly, i.e., we require  $\int_{-\infty}^{+\infty} W(\epsilon_r) d\epsilon_r = 1$ . For that purpose we replace  $W(\epsilon_r)$  by a step function, finite between  $-\epsilon_0$  and  $+\epsilon_0$  and 0 elsewhere. The normalization then is

$$\int W(\epsilon) d\epsilon = 2\epsilon_0\nu = 1, \quad \nu = 1/(2\epsilon_0) \cong 1.5\kappa/(eN_A^{2/3}).$$

While this factor is only approximate, the functional dependence itself is probably quite accurate. With this, the conductivity for the low-temperature case is

$$\sigma(\omega) = C(N_C/N_A)(N_D/N_\omega)(a/r_A)\kappa\omega, \quad (46a)$$

and for the high-temperature case

$$\sigma(\omega) = C'(N_C/N_\omega)(N_D/N_\omega)(r_T/r_\omega)(a/r_\omega)\kappa\omega, \quad (46b)$$

where the  $C$ 's are numerical constants.

The result for the high-temperature region turns out to be identical with the result for the similar region for the light-compensation case (with  $N_C$  replacing  $N_A$ ). This, of course, is as it should be, as the distribution in  $\Delta E$  is neglected in this region.

The low-temperature region has again a somewhat enhanced frequency dependence ( $\sigma \propto \omega^{0.85}$ ) and no explicit temperature dependence. The dependence on the majority concentration is much more pronounced here than in the low-compensation case. The physical reason for this is that an increase in the majority concentration does not push the distribution of  $\Delta E$  toward large values, as it does in the low-compensation case.

It is expected that the transition between the explicit  $T^0$  and  $T^{-1}$  dependences in the intermediate temperature range is a smooth one in distinction to the low compensation case, where  $\sigma$  is expected to reveal an explicit increase with temperature in the intermediate temperature region.

Unfortunately, no experiments with heavily compensated materials are available, and thus the results of the last section cannot be tested at the present.

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