discrepancy would be quite as large as that required here. Thus, at the moment, no resolution of the question can be advanced.

From the temperature dependence of the dHvA oscillations, the effective mass of the associated carriers can be determined readily. Thus, at a fixed field H, the couple acting on the sample can be written

$$C = \alpha T e^{-(2\pi^2 kT/\beta H)} , \qquad (3)$$

where α is a constant, $\beta = (e\hbar/m^*c)$ and it is assumed that $(2\pi^2 kT/\beta H) \gg 1$. From (3) it follows that a semilog of C/T versus T is a straight line of slope $-2\pi^2 k/\beta H$, thus giving m^*. Such a plot, for an [001] suspension with $H \| [110]$, is given in Fig. 8. The resulting effective mass of the associated β arm is $(m^*/m_0) = 0.19$, which is to be compared with the single OPW value of 0.11. As noted previously, such a discrepancy has been noted in many metals, most notably aluminum.[1,10] No satisfactory explanation of this disagreement has yet been advanced. Attempts to obtain effective mass data with $H \| [100]$ were not successful, due to the difficulty of obtaining an oscillatory behavior free from beats.

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[10] T. W. Moore and F. W. Spong, Phys. Rev. 125, 846 (1962).

The low-frequency oscillations observed in the present data are similar to those found by Gunnerson[11] in aluminum. It is probable that they arise from extremal areas around the ends of the arms α, β. An exact calculation of these areas is of course very difficult, since they are very sensitive to the effective lattice potential. It seems clear, however, that for $H \| [100]$, quite complicated orbits would be involved, since they correspond to junctions of four arms. This probably accounts for the rather unusual cusps in the angular variation of $f(1/H)$ shown in Fig. 7(b).

V. CONCLUSION

Low-field de Haas–van Alphen data for indium have been obtained up to fields of 18 kG. The resulting extremal areas are in qualitative agreement with the third-zone surface of the single OPW model. For certain field orientations the amplitude is much less than would be expected; a possible explanation of this effect is considered.

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[11] E. M. Gunnerson, Phil. Trans. Roy. Soc. (London) A249, 299 (1957).

Impurity Conduction in p-Type Silicon at Microwave Frequencies*

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The microwave conductivity of boron-doped silicon was studied at low temperature at $\sim$9000 Mc/sec. Samples measured had boron concentrations ranging from 6.7×10^{15} to 1.6×10^{17} cm^{-3}. In the impurity conduction range, the microwave conductivity varied much more slowly than the dc conductivity, becoming orders of magnitude larger in comparison at 4.2°K. Calculations based on the hopping model give microwave conductivity of the right order of magnitude as measured. However, pronounced nonohmic behavior was observed in samples of impurity concentrations less than $\sim$10^{16} cm^{-3}, and the measured temperature dependence of conductivity for the samples of high-impurity concentrations was too strong. These observations cannot be accounted for by the hopping model. It is shown that the nonohmic behavior may be attributed to the direct absorption of microwave power for which phonon interaction is not the essential part of the process. The strong temperature dependence is explained on the basis of carrier trapping by closely spaced impurity centers. Some measurements were made at lower frequencies. The results are consistent with the interpretation.

I. INTRODUCTION

MICROWAVE conductivity in semiconductors has been measured for the purpose of determining the effective mass and relaxation time of carriers,[1,2] polarizability of neutral impurities,[2] and density of in-

jected carriers.[3] In these measurements, samples of low resistivities were used. The work presented here deals with impurity conduction at microwave frequencies. Boron-doped p-type silicon has been studied using samples with impurity concentrations less than 2×10^{17} cm^{-3}.

Impurity conduction under dc conditions has been investigated by many authors[4] for various semiconductors. At low-impurity concentrations, the conduction

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[1] T. S. Benedict and W. Shockley, Phys. Rev. 89, 1152 (1953); Y. Klinger, *ibid.* 92, 509 (1953).

[2] F. A. D'Altroy and H. Y. Fan, Phys. Rev. 94, 1415 (1954).

[3] A. F. Gibson and J. W. Granville, J. Electron. 2, 259 (1956).

[4] For bibliography see Ref. 6.

process can be described as hopping of electrons or holes from one impurity to another, the hopping being made possible by phonon interaction.[5] This description is applicable for low-impurity concentrations, less than 5×10^{17} cm^{-3} for boron doped p-type silicon.[6] Ac impurity conduction has been studied by Pollak and Geballe[7] for n-type silicon in the frequency range 10^2–10^5 cps. They found the ac conductivity much larger than the dc conductivity, and were able to interpret the results using the hopping model. Our studies made in the microwave-frequency range showed that the hopping model alone is inadequate to account for all the observations. The results led us to introduce additional mechanisms into consideration. For comparison, some measurements were made also at lower frequencies.

II. EXPERIMENTAL PROCEDURE

Measurements were made at frequencies ~ 9000 Mc/sec. In the temperature range of the experiment, the resistivity of the samples varied from 10^4 to 10^5 Ω cm, which is unusually large for accurate microwave measurements. The following method was used successfully. The sample in the form of a circular disk was placed at the center of a cylindrical cavity of the same cross section. The thickness of the samples was limited to 2 mm in order to avoid possible nonuniformity; larger thicknesses were used for some dielectric-constant measurements. The rest of the cavity was filled with two pieces of neutron-bombarded silicon, one on either side of the sample. The neutron-bombarded silicon had negligible conductivity at low temperatures, but its dielectric constant was very nearly the same as that of the samples. This arrangement simplified the field pattern in the cavity and improved the accuracy of the measurement. The cavity was operated in the TE_{011} mode. The conductivity and dielectric constant of the sample were obtained from the measured Q factor of
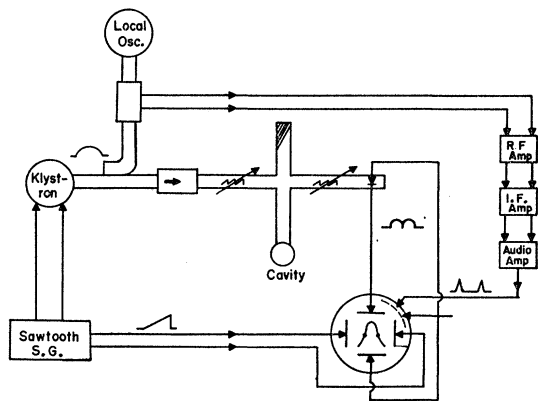

FIG. 1. Diagram of measurement circuit.

[5] N. F. Mott, Can. J. Phys. 34, 1356 (1956).
[6] K. R. Ray and H. Y. Fan, Phys. Rev. 121, 768 (1961).
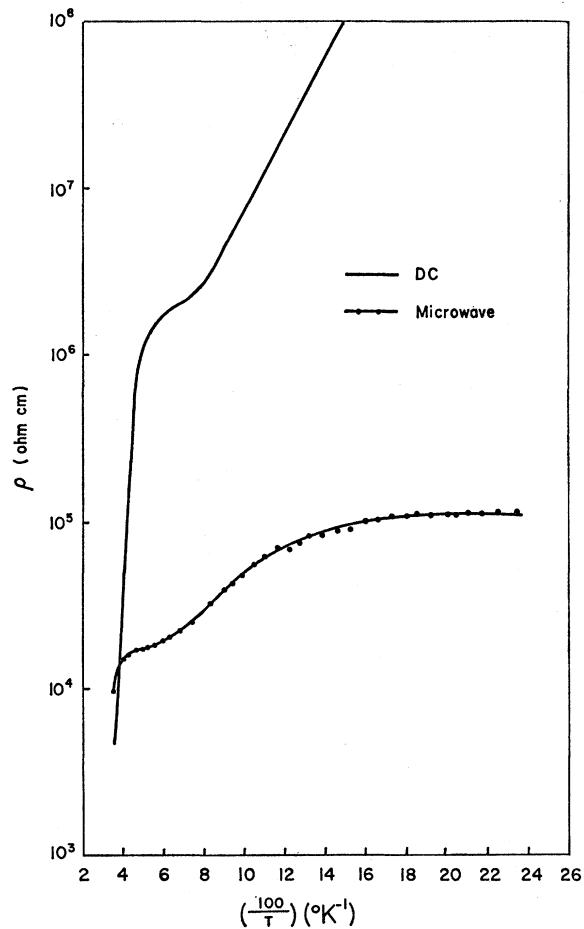[7] M. Pollak and T. H. Geballe, Phys. Rev. 122, 1742 (1961).

FIG. 2. Comparison of dc and microwave conductivities. Reciprocal conductivity, $\rho = 1/\sigma$, is plotted.

the cavity and the resonance frequency. The method of calculation is briefly outlined in the Appendix.

A good fit was kept between the cavity and the silicon pieces filling it. The cavity was made of cold rolled steel to keep down thermal contraction upon cooling. A heater of nichrome wire wound on the cavity and a brass can around the cavity which can be evacuated or filled with exchange gas allowed measurements to be made at liquid helium and higher temperatures. The block diagram of the circuit used is shown in Fig. 1. The resonance frequency and the Q factor of the cavity can be determined from the measured frequency of the local oscillator and the setting of the tuned radio frequency amplifier.

III. EXPERIMENTAL RESULTS

Single-crystal samples of boron-doped silicon were measured. The impurity concentration of the samples is given in Table I. Some of the samples were subjected to one or more heat treatments at 450°C in vacuum, for the purpose of studying the effect of minority impurity

Sample No.	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8
$N_{maj}(10^{15}\,cm^{-3})$	162	107	89.4	46.0	15	14	11	6.7

concentration. Such heat treatments of silicon are known to introduce donors. Figure 2 shows, for comparison, the dc and microwave resistivities measured on two separate samples cut adjacently from an ingot. At the high-temperature end, the microwave and dc resistivities merge, both being determined by free carrier conduction. With decreasing temperature, the two curves separate rather abruptly, differing by orders of magnitude. The comparison shows clearly the effect of greatly increased impurity conduction at high frequencies.

Nonohmic behavior was observed which was more pronounced the lower the impurity concentration of
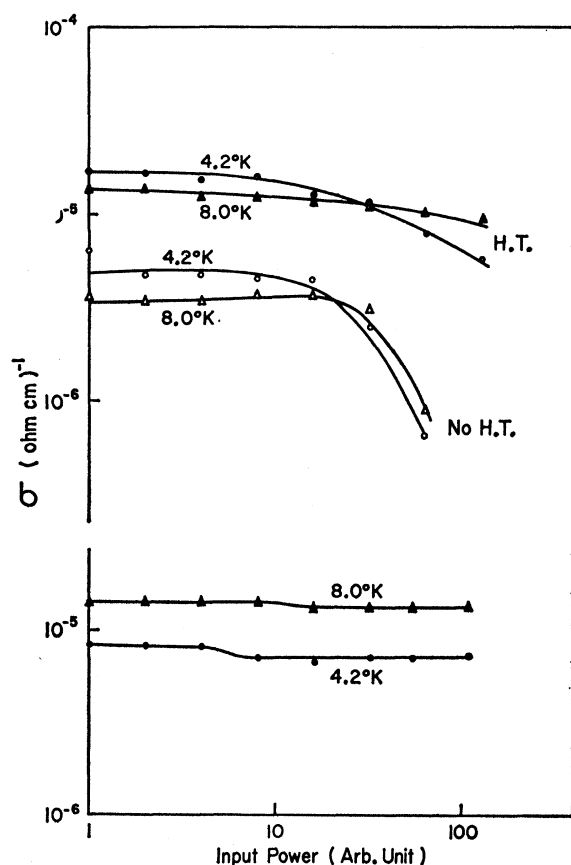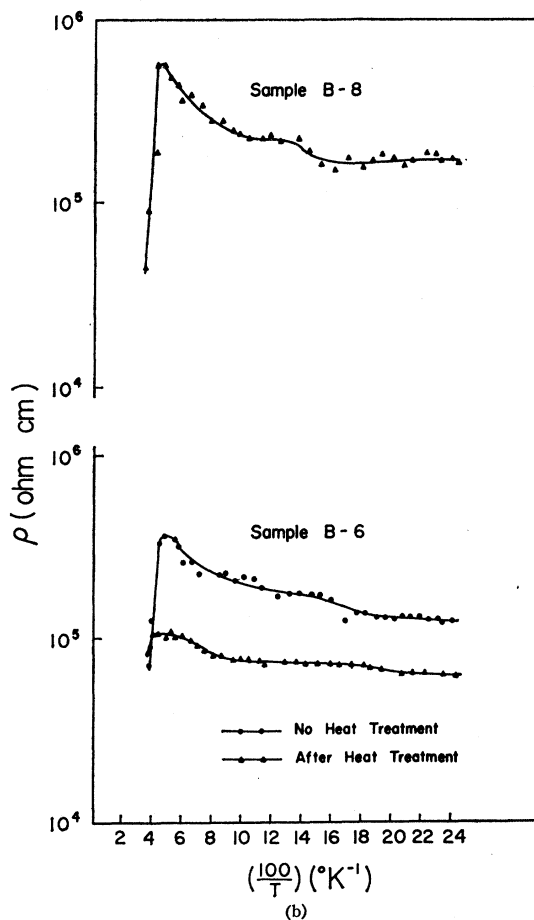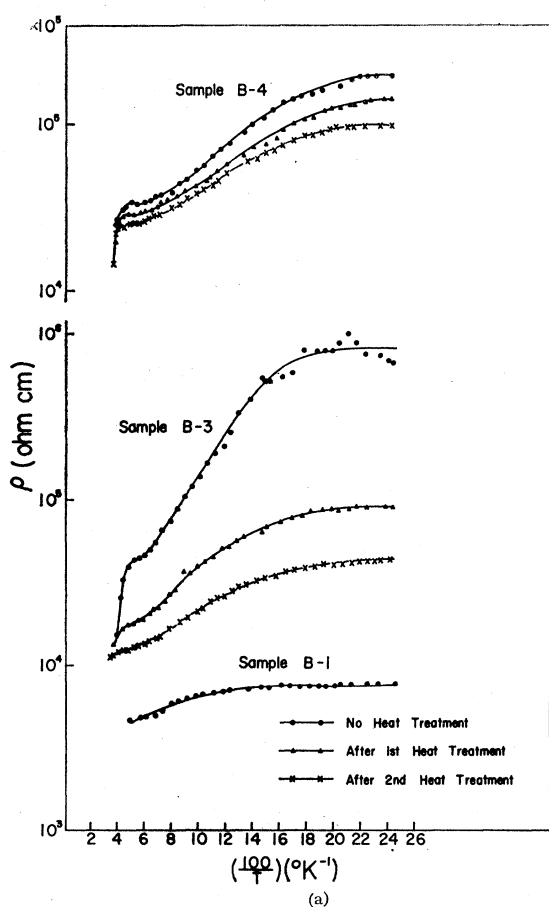

FIG. 3. Dependence of conductivity on microwave power showing marked nonohmic behavior of sample B-6 (upper part of the figure). The two curves in lower part are for sample B-2. Smallest power input into the cavity corresponds to ~16 μW.

the sample. Figure 3 shows the conductivity as a function of microwave power for two samples. It is seen that the nonohmic effect is not appreciable for sample B-2 but is quite large for sample B-6. The effect is larger at lower temperature and is reduced by heat treatment or increase of compensation. In making these measurements, the power to the microwave detector was kept constant by a calibrated attenuator while the power input to the cavity was varied. Thus, the results could not be affected by possible nonlinear response of the detector. The nonohmic behavior observed could not be attributed to such effects as carrier injection or multiplication. It appears to be the true property of impurity conduction.

The temperature dependence of the measured conductivity can be seen in Fig. 4 where resistivity is plotted as a function of reciprocal temperature. The microwave power, about 16 μW, used in these measurements was sufficiently low to avoid the complication of the nonohmic effect which also depended on temperature. The temperature dependence is generally much weaker than that of dc conductivity. It is interesting to note that the resistivity of the samples (B-1 to B-4) of high-impurity concentrations increased with decreasing temperature, whereas it decreased with decreasing temperature in the samples (B-5 to B-8) of low-impurity concentrations. The results obtained with heat treatments indicated that the conductivity increased with increase of compensation. The temperature dependence appears to have been affected by the heat treatments also.

The dielectric constants of all the samples were almost the same as that of very pure crystals, for which the value of 11.5 was measured by the cavity method. With the experimental accuracy of the method, it is difficult to compare the magnitudes of dielectric constant for different samples. It was possible to detect a relative variation with temperature for a given sample from the small change of the resonance frequency of the cavity. The frequency shift, Δf, obtained by subtracting the resonance frequency of cavity with pure silicon from the resonance frequency with sample inserted, is shown in Fig. 5 for sample B-2. The difference in dielectric constant, $\Delta\epsilon$, between the sample and pure silicon is calculated according to (3A); only the variation is significant. To check the reliability of the measurement, two samples of different thicknesses and cut from the same ingot were measured. The measured variations with temperature were similar for the two samples and the variation for the thicker sample was correspondingly larger. Measurements were also made on sample B-3; the frequency variation became large after the sample was heat treated. The results show that the dielectric constant decreased with increasing $1/T$. We note that the conductivity of these samples also decreased with increasing $1/T$ (see Fig. 4 for sample B-3). For the samples of small impurity concentrations, no frequency variation was detectable.

FIGS. 4(a) and 4(b). Temperature dependence of microwave conductivity.

IV. DISCUSSIONS

As explained in the preceding section, the microwave conductivity of p-type silicon is higher than the dc conductivity by several orders of magnitude in the temperature range of impurity conduction. The dc impurity conduction in p-type silicon was investigated by Ray and Fan[6] in detail. They showed that the hopping model of charge exchange between neutral and ionized impurity centers may be applied for impurity concentrations less than 5×10^{17} cm^{-3}. In this model, the ionized impurity atoms can be regarded as occupied by carriers of the conduction which arise from the presence of compensating impurities. The atoms of compensating impurity and the carriers of conduction are oppositely charged. Mott[5] suggested that the activation energy for dc impurity conduction arises from the coulomb attraction which tends to trap the carriers near the atoms of compensating impurity. The problem has since been treated theoretically along this line by several authors. Most of the treatments assumed that the carrier hopping between impurity centers is assisted by phonons.

Under ac field, hopping motion of the carriers could give rise to in-phase as well as out-of-phase current.

Since the motion is oscillatory, conduction does not depend on having the carriers completely overcome the attraction of the compensating centers. Thus, ac conduction need not have the activation energy of dc
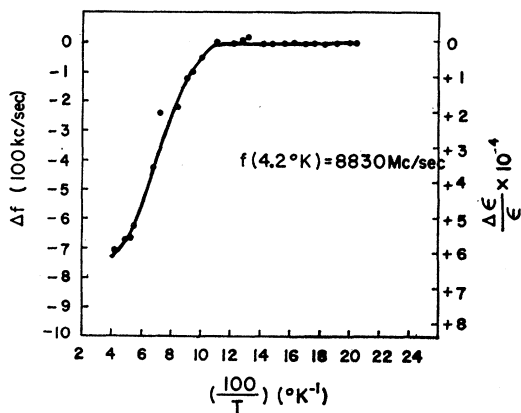

FIG. 5. Temperature shift of the resonance frequency of the cavity containing sample B-2. The calculated variation of the dielectric constant of the sample is given by the scale on the right-hand side.

conduction. Pollak and Geballe[7] investigated the ac impurity conduction of *n*-type silicon in the audiofrequency range and interpreted their experimental results by applying the hopping model to the ac case. Our work extends the study of ac impurity conduction to microwave frequencies. The nonohmic behavior observed under certain conditions indicated that straight extension of the hopping model used for dc conduction may not be adequate. We shall first attempt to interpret the experimental results on the basis of the simple hopping model, then discuss the possibilities of another supplementary model.

A. Hopping Model

The samples used in our experiments were not strongly compensated, the concentration of minority impurity was less than 10% of the majority impurity concentration in all cases. For weak compensation, we may divide the volume of the crystal into cells, each centered around a charged minority impurity. Each cell contains a carrier which hops among the majority centers, with the center closest to the minority center having the highest probability of carrier occupation. At low compensation, we may consider the carrier motion in each cell as unaffected by the motion of the carriers in other cells. The problem of tracking the carrier hopping among randomly distributed majority centers in a cell is still very complicated. Pollak and Geballe greatly simplified the problem by considering a pair of centers at a time. The starting point is the problem of a carrier hopping back and forth between two centers. It seems that the method is justified if each carrier is situated on one particular site most of the time. The average distance between a compensating impurity atom and the nearest majority center is $0.893(\frac{4}{3}\pi N)^{-1/3}$, where N is the concentration of majority impurity. The attractive potential for a carrier at such distance is

$$E=\frac{1}{0.893}\frac{e^2}{\epsilon}\left(\frac{4\pi}{3}N\right)^{1/3}\sim 4.6\times 10^{-3}\text{ eV},$$

for the lowest N of the samples used. The average distance of the next nearest center is larger by a factor of $\frac{4}{3}$, corresponding to a potential $\frac{3}{4}E$. Thus, the carrier may be expected to be on the nearest center most of the time, if

$$kT<\tfrac{1}{4}E\sim 14^\circ\text{K}.$$

The above consideration is very rough and can only be used for an estimate of order of magnitude. With a temperature range of interest $T<20^\circ$K, it seems reasonable to adopt the pair approach for the simplification. We shall try first to apply the hopping model as was done by Pollak and Geballe.

Consider a carrier hopping between two centers. The frequency of phonon-assisted hopping may be represented by the expression:

$$\nu_{12}=F_{12}(T,\Delta V_{12},r)e^{-2r/a},\qquad (3)$$

where ν_{12} is the jump frequency from center 1 to center 2, F_{12} is a function of the temperature, T, the potential difference, ΔV_{12}, and the distance, r, between the centers, and a is the effective Bohr radius of the carrier wave function. When electric field is applied, the balance of occupation probabilities of the carrier on the two centers is disturbed and the rate of the change of the occupation probabilities is given by

$$-df_1/dt=f_1\nu_{12}-f_2\nu_{21},$$
$$-df_2/dt=f_2\nu_{21}-f_1\nu_{12},$$

with

$$f_1+f_2=1.\qquad (4)$$

Under an applied ac field, the solution leads to a conductance of the pair of centers:

$$\sigma_{\text{pair}}=i\omega\left(\frac{f_{10}a_1-f_{20}a_2}{\nu_{12}(0)+\nu_{21}(0)+i\omega}\right)(\cos^2\phi)er,\qquad (5)$$

where f_0 and $\nu(0)$ denote the values of f and ν under thermal equilibrium, respectively. The quantities a_1 and a_2 are defined by

$$\Delta\nu_{12}=a_1\cos\phi Ee^{i\omega t},\quad \Delta\nu_{21}=a_2\cos\phi Ee^{i\omega t},\qquad (6)$$

where E and ω are, respectively, the amplitude and the angular frequency of the applied electric field, and ϕ is the angle between the electric field and the line joining the centers r_{12}. The same expression (6) was obtained by Pollak and Geballe. The quantities a_1 and a_2 are determined by the function $F(T,\Delta V,r)$. Kasuya and Koide,[8] Abraham and Miller,[9] and Mott and Twose[10] made the analysis of phonon-assisted hopping frequency. Taking Miller and Abraham's expression, we have

$$\nu_{12}(0)=\nu(0)\frac{Se^{-S}}{\sinh S},\quad \nu_{21}(0)=\nu(0)\frac{Se^S}{\sinh S},$$

$$\nu(0)=2\left(\frac{E_1^2}{\pi\rho_0 v^5\hbar^4}\right)kT\left(\frac{2}{3}\frac{e^2}{\epsilon a^2}\right)^2 r^2 e^{-2r/a},\qquad (7)$$

where $S=|\Delta V/2kT|$, E_1 is the deformation potential, a is the effective Bohr radius, v is the sound velocity, ρ_0 and ϵ are the density and dielectric constant of the crystal, respectively. Under applied electric field, we have $S=(\Delta V+Er\cos\phi)/2kT$. The expression (6) is obtained by differentiating ν_{12} and ν_{21} with respect to E, implying that the effect of E is small. This should be valid for electric fields as high as 100 V/cm, which is higher than the fields used in our measurements. Using (7) and (6) we get from (5)

$$\sigma_{\text{pair}}=\left(\frac{1}{2\cosh S}\right)^2(i\omega)\left(\frac{\nu_{12}(0)+\nu_{21}(0)}{\nu_{12}(0)+\nu_{21}(0)+i\omega}\right)$$
$$\times\left(\frac{e^2 r^2}{kT}\right)\cos^2\phi.\qquad (8)$$

[8] T. Kasuya and S. Koide, J. Phys. Soc. Japan 13, 1287 (1958).
[9] A. Miller and E. Abraham, Phys. Rev. 120, 745 (1960).
[10] N. F. Mott and W. D. Twose, Advan. Phys. 10, 107 (1961).

Averaging $\cos^2\phi$ over all directions we get a factor of $\frac{1}{3}$. Thus, the real and imaginary parts of the pair conductance are

$$\sigma_{\text{pair}}(\text{Re})=\frac{1}{12}\left(\frac{1}{\cosh S}\right)^2 \frac{\omega^2[\nu_{12}(0)+\nu_{21}(0)]}{[\nu_{12}(0)+\nu_{21}(0)]^2+\omega^2}\frac{e^2r^2}{kT},$$

$$\sigma_{\text{pair}}(\text{Im})=\frac{1}{12}\left(\frac{1}{\cosh S}\right)^2 \frac{\omega[\nu_{12}(0)+\nu_{21}(0)]^2}{[\nu_{12}(0)+\nu_{21}(0)]^2+\omega^2}\frac{e^2r^2}{kT}. \quad (9)$$

In the following, only the real part of conductance will be considered, since the measurements of the imaginary part were not as accurate.

In order to obtain the conductance of the crystal, we have to average the pair conductance with respect to r and ΔV. The integrations involved cannot be carried out to give closed expressions. We shall simplify the result by making use of the fact that the conductance has a sharp maximum with respect to r, due to the the fact that $\nu_{12}(0)+\nu_{21}(0)$ is very sensitive to r. For given ω and S, the maximum of the real part of conductance corresponds to

$$\omega=\frac{1}{1-2a/r}[\nu_{12}(0)+\nu_{21}(0)]=cS\coth S\frac{r^2}{1-2a/r}e^{-2r/a},$$

where c is a constant and $S\coth S$ gives the effect of ΔV. For $\Delta V=0$, $S\coth S=1$. Using the value $E_1=10$ eV and the value $a=13$ Å estimated from the ionization energy of boron impurity, we get $r/a=6$ and $r\sim 80$ Å. The conductance falls off sharply as r departs from the optimum value. The half-width Δr, corresponding to $\frac{1}{2}$ maximum conductance, is about 14 Å. On account of the exponential term, $\exp(-2r/a)$, the values of the optimum r and the half-width Δr are not sensitive to S. The value of $S\coth S$ is close to unity for $S<1$ and becomes nearly equal to S for large values of S. For values of S up to $S=10$, the optimum value of r varies from 1 to 1.2 times the value for $S=0$. On the ground that the peak of conductance is sharp and insensitive to ΔV, we shall approximate the summation of conductance over pairs of various separations by the product of peak conductance and the number of pairs falling within Δr of the optimum separation, Δr being of the order of the half-width.

Let the majority center nearest to an atom of compensating impurity be at a distance R, and let r be the optimum hopping distance corresponding to the applied frequency. The volume of the thin ring $BCDE$ in Fig. 6 is

$$\Delta v=2\pi r^2\cos\theta d\theta(\Delta r). \quad (10)$$

The probability of finding another center in this ring is

$$P=N_{\text{maj}}(\Delta v). \quad (11)$$

The potential difference between these two majority centers is

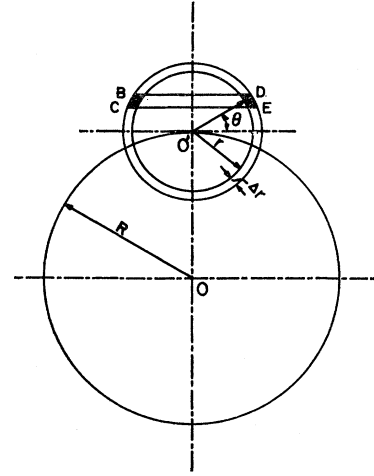$$\Delta V=\frac{e}{\epsilon}\left[\frac{1}{R}-\frac{1}{(R^2+r^2+2Rr\sin\theta)^{1/2}}\right]. \quad (12)$$

FIG. 6. Schematic diagram for the calculation of the unit cell conductance. The position of the minority center is indicated by point O, and the position of the nearest majority center is indicated by point O'.

The conductance of the cell is

$$\sigma_{\text{cell}}=\frac{1}{24}\frac{e^2r^2}{kT}\omega\int_{\theta_1}^{\theta_2}2\pi N_{\text{maj}}r^2(\Delta r)\cos\theta\left(\frac{1}{\cosh S}\right)^2 d\theta. \quad (13)$$

For integration over θ, we make the approximation

$$\left(\frac{1}{\cosh S}\right)^2\sim 1-\frac{\Delta V}{4kT}$$

$$=1-\alpha\left[1-\frac{1}{(1+\beta^2+2\beta\sin\theta)^{1/2}}\right], \quad (14)$$

where

$$\alpha=(1/4kT)(e^2/\epsilon R), \quad \beta=r/R. \quad (15)$$

The lower limit of this integral is given by[11]

$$\sin\theta_1=-r/2R=-\tfrac{1}{2}\beta. \quad (16)$$

For the upper limit, we take the condition

$$1-\Delta V/4kT\geq 0.$$

When the condition is satisfied at $\theta<\frac{1}{2}\pi$, the upper limit is

$$\sin\theta=\frac{1}{2\beta}\left[\left(\frac{\alpha}{\alpha-1}\right)^2-(1+\beta^2)\right], \quad (17)$$

giving

$$\int_{\theta_1}^{\theta_2}\cos\theta\left(\frac{1}{\cosh S}\right)^2 d\theta=\frac{1}{2\beta}\left(\frac{1}{\alpha-1}\right)=g_1(R,r,T). \quad (18)$$

If the condition is satisfied for the whole range of θ, the upper limit is given by $\sin\theta_2=1$, and we get

$$\int\cos\theta\left(\frac{1}{\cosh S}\right)^2 d\theta=1+\tfrac{1}{2}\beta(1-\alpha)=g_2(R,r,T). \quad (19)$$

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[11] For $\beta>2$, the lower limit is given by $\sin\theta=-1$. The maximum value of β is restricted by the upper limit of integration. According to (17), $(1/2\beta)\{[\alpha/(\alpha-1)]^2-(1+\beta^2)\}\geq-1$, which leads to $\beta\leq(2\alpha-1)/(\alpha-1)$. For the estimated value of $r=80$ Å, we get $\alpha>87/T$ which gives $\beta\leq 2.3$ at 20°K and $\beta\leq 2.04$ at 4.2°K. Calculations show that the contribution to conductivity from cells with $\beta>2$ is negligible.
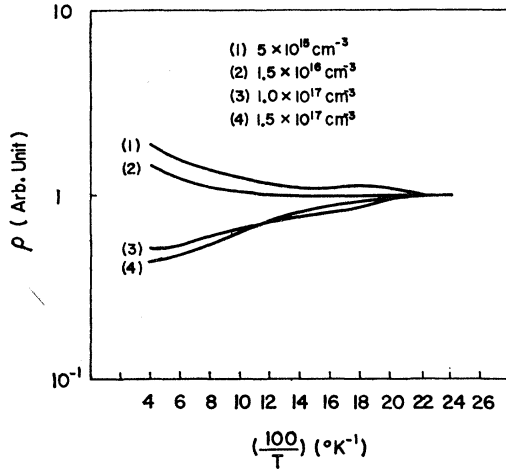
FIG. 7. Temperature depencence of microwave conductivity calculated from (22) for various concentrations of majority impurity. The curves are normalized to the conductivity at 4.2°K.

The division between the two cases is given by

$$\alpha = (1+\beta)/\beta. \qquad (20)$$

The expression (18) applies for large α and (19) applies for small α.

Different cells have various values of R. For a random distribution, the probability for the nearest majority center to be found within the range R to $R+dR$ is

$$G(R)dR = 4\pi R^2 N_{maj} \exp(-\tfrac{4}{3}\pi N_{maj}R^3)dR. \qquad (21)$$

Therefore, the conductivity of the crystal per unit volume is given by

$$\sigma = \sigma_1 + \sigma_2,$$

$$\sigma_1 = \frac{\pi^2}{2}\omega r^4(\Delta r)\left(\frac{e^2}{kT}\right)N_{min}N_{maj}{}^2$$

$$\times \int_0^{R'} g_1 R^2 \exp(-\tfrac{4}{3}\pi N_{maj}R^3)dR,$$

$$\qquad\qquad (22)$$

$$\sigma_2 = \frac{\pi^2}{2}\omega r^4(\Delta r)\left(\frac{e^2}{kT}\right)N_{min}N_{maj}{}^2$$

$$\times \int_{R'}^{R''} g_2 R^2 \exp(-\tfrac{4}{3}\pi N_{maj}R^3)dR,$$

where R' is the radius corresponding to the critical condition (20) and R'' is the radius of the unit cell. When $R' > R''$, R' is replaced by R'' and the second term is not needed; such cases occur at low temperature.

The magnitude of conductivity given by expression (22) is very sensitive to the value of the effective Bohr radius, a, which is contained in the exponential factor of the hopping frequency. If the value $a = 13$ Å, estimated from the ionization energy of boron impurity

on the basis of simple hydrogenic model, is used, the calculated conductivity comes out too low by about a factor of 10 as compared to the experimental data. For example, the conductivity calculated for the frequency 9000 Mc/sec is 6×10^{-7} $(\Omega\ cm)^{-1}$ for a crystal with $N_{maj} = 10^{16}$ cm^{-3} and $\epsilon = 5\%$, at 20°K. This value is seen to be too low compared with the data shown in Fig. 4(b). Similar situation was found in the studies of dc impurity conduction in p-type germanium[12] and silicon.[6] The magnitude of conductivity given by (22) would be in agreement with the experimental data if a large value, $a \sim 20$ Å, is used. In fact, the calculation of Schechter[13] gives an effective Bohr radius of 17 Å for acceptor state in silicon. It seems, therefore, that the formula gives the correct order of magnitude.

The calculated variation of conductivity with temperature is shown in Fig. 7 for various concentrations of majority impurity. The resistivity decreases with decreasing temperature for low-impurity concentration, and increases with decreasing temperature for high-impurity concentration. The behavior agrees qualita-
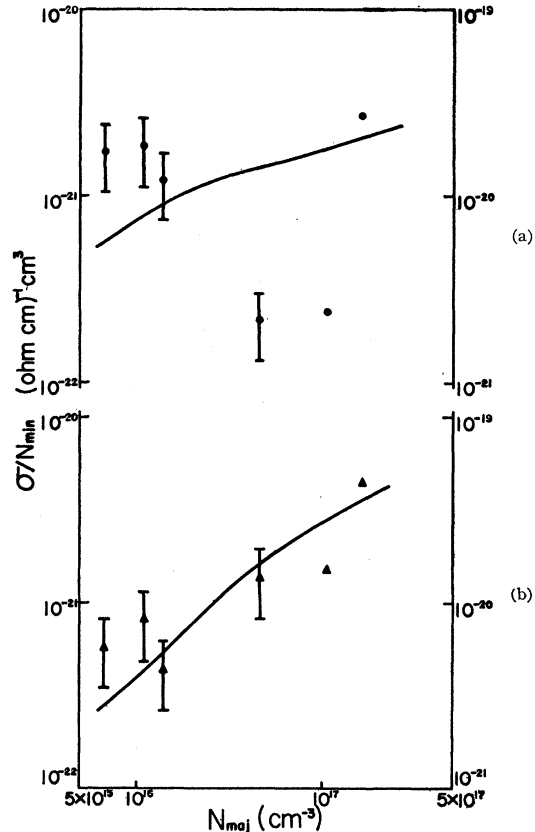

FIG. 8. Dependence of unit-cell conductance on the concentration of majority impurity for two different temperatures, (a) 4.2°K and (b) 20°K. The curves are calculated with scale given on the right-hand side. The points are experimental results with scale given on the left.

[12] H. Fritsche and M. Cuevas, Phys. Rev. 119, 1238 (1960).
[13] D. Schechter, J. Phys. Chem. Solids 23, 237 (1962).

tively with the data shown in Fig. 4. However, the temperature dependence calculated for high-impurity concentration is not nearly as strong as that observed experimentally (see Fig. 4). The curves in Fig. 8(a) and 8(b) show the dependence of calculated conductivity on impurity concentration for two different temperatures. The conductance does not increase in proportion to the concentration, N_{maj}, of the majority impurity, more so at higher concentrations. This behavior results from the fact that the potential difference which tends to prevent the hopping between a pair of centers increases, on the average, with N_{maj}. The curve for the higher temperature is steeper as the effect of potential difference on hopping is weaker at higher temperature. The experimental data are shown by the points. There is reasonable agreement at the higher temperature, 20°K, but, the experimental data for 4.2°K, Fig. 8(a), exhibit a pronounced minimum around the concentration of 10^{17} cm^{-3} which cannot be accounted for by the theoretical formula. Finally, the nonohmic behavior observed, which is pronounced in the purer samples, cannot be explained. Nonlinear behavior may be expected at large electric fields when the relationship (6) is no longer valid. On this basis, it is estimated that non-ohmic behavior should set in at fields over 100 V/cm, whereas sample B-8 at 4.2°K showed nonohmic behavior at fields less than 5 V/cm. To summarize, three aspects of the experimental results cannot be explained: (1) the nonohmic behavior of the purer samples. (2) the strong temperature dependence of the impure samples. (3) the minimum in the low-temperature conductivity as a function of the concentration of majority impurity.

B. Direct Absorption

We shall now consider a different process of power absorption that contributes to conductivity. In the hopping model for dc conduction, the hopping of a carrier between two centers corresponds to the transition between two states of the system of two charged centers with one carrier. In the model, the two centers are considered to be at points of different potential, the potential difference being larger than the "resonance energy." Under such conditions, there are approximately two states corresponding to carrier orbitals, each concentrated around one or the other center, and the transition between the two states corresponds to carrier hopping from one center to the other. A transition is produced by interaction with a phonon and the energy required is supplied by the phonon. The effect of an applied field is treated as changing the potential difference between the two centers, thus affecting the transitions or hoppings. In the case of ac applied field, it is possible for the transitions to be produced solely by interaction with the photons without phonon participation, provided the system has the suitable energy-level separation. The effect of phonon interaction may be regarded as broadening the energy

level. This description is appropriate if the frequency of phonon-induced transitions is small compared to the phonon frequency.

Consider first two centers at the same potential, sharing one carrier. We have a molecule ion. In the hydrogenic approximation, the energy difference between the bonding and antibonding states is given by

$$\Delta E = 2W = \frac{2e^2}{er}e^{-r/a}\left[\frac{2}{3}\left(\frac{r}{a}\right)^2 - 1\right] \sim \frac{4e^2}{3er}\left(\frac{r}{a}\right)^2 e^{-r/a},$$

$$\text{for } r \gg a. \quad (23)$$

Taking $a = 13$ Å as the Bohr radius for boron impurity, we get $r \sim 130$ Å for $2W$ to be equal to microwave quantum, $\hbar\omega$, at 9000 Mc/sec. For comparison, we note that the average distance between nearest neighbor centers is ~ 300 Å in the purest sample and ~ 100 Å in the most impure sample used in the experiments. The energy difference ΔE will generally be larger for the same r if there is a potential difference ΔV between the positions of the two centers. Therefore, r should be larger in order for ΔE to be equal to $\hbar\omega$. Thus, direct absorption arises from pairs with $r > 130$ Å. The pairs with small values of r, $r \sim 130$ Å, are the most efficient for absorption, having large transition probabilities. Such pairs have $\Delta V < W$ and may be referred to as molecule ions. For the hopping model, we have estimated that the significant values of r are ~ 80 Å which corresponds to a hopping frequency $\nu = \frac{1}{2}\omega$. Since the hopping frequency is very sensitive to r, it will be much smaller than ω or $\Delta E/\hbar$ for the pairs giving direct absorption. It is, therefore, sensible to regard the effect of phonon interaction as level broadening which is related to the relaxation of the excited state.

A detailed treatment involving direct absorption will be reported in another publication. For the present, we shall confine the discussion to the qualitative effect of the direct absorption process. We have seen that the relaxation for this process is much weaker than for the hopping process. On the other hand, the transition probability is strong for direct excitation. Therefore, conductivity due to direct absorption saturates more easily. The saturation behavior of conductivity in the pure samples can be attributed to this effect. In the more impure samples, the average distance between majority centers becomes comparable to the separation suitable for direct absorption. The simple consideration of a pair of centers is not applicable and the effect of direct transition is difficult to assess. We shall not attempt to discuss at present the lack of saturation in such samples.

C. Molecule-Ion Traps

We turn now to the remaining unexplained observations, i.e., the strong temperature dependence of conductivity of impure samples and the minimum in the low-temperature conductivity as a function of impurity concentration. These phenomena may be attributed to

the presence of traps for carriers. When a carrier is shared by a pair of centers, the energy is lowered by the resonance energy, W, with the carrier in a bonding orbital of the molecule ion. In a random distribution of impurity, pairs of centers may be found which have exceptionally small r and large W, acting as traps for carriers. The trapping energy is given by

$$E_t = V_n - (V_m - W), \qquad (24)$$

where V_m is the potential at the molecule ion and V_n is the potential at the center where the carrier would be located in the absence of the trap. The probability of finding a trap within a range of R to $R+\Delta R$ from a minority center increases as R^2. For simplicity, we take for V_m the potential at the boundary of the cell around the minority impurity, and we take V_n to be the potential at the center nearest to the minority impurity. Thus,

$$E_t = W - (e^2/\epsilon)(1/R_1 - 1/R_c), \qquad (25)$$

where R_1 is the distance of the nearest center and R_c is the radius of the cell boundary. The average W for pairs with $E_t > 0$ is

$$\langle W \rangle = \int_0^{r_0} W 4\pi r^2 dr \Big/ \int_0^{r_0} 4\pi r^2 dr, \qquad (26)$$

where r_0 corresponds to $E_t = 0$ and W is given by (23). The number of traps per cell is

$$N_t = (1/c)\tfrac{4}{3}\pi r_0^3 N_{maj}, \qquad (27)$$

where $c = N_{min}/N_{maj}$ is the compensation. For a sample with $N_{maj} = 10^{17}$ cm^{-3} and $c = 3\%$, we get by using (23), (26), (27): $R_0 \sim 52$ Å, $\langle E_t \rangle \sim 6 \times 10^{-3}$ eV, and $N_t \sim 1.6$ per cell, assuming a value $a = 13$ Å. The number of traps decreases with decreasing N_{maj}. For samples with $N_{maj} < 10^{16}$, the number becomes negligibly small.

The above estimate shows that molecule-ion traps may be present in appreciable amount in our impure samples. These molecule ions have considerably smaller r than the optimum separation of ~ 80 Å for hopping conduction, and their excitation energy, $\Delta E = 2W \gg \hbar\omega$, is too large for direct absorption. The trapped carriers may be considered then as ineffective for conduction. As a result, the conductivity will have a component which requires thermal activation, thus giving rise to a strong temperature dependence. With an average number N_t of traps per cell, the probability of finding a cell with no traps is given by $\exp(-N_t)$. For the cells with one or more traps, we shall take for simplicity $[1 + (N_t/N_c)\exp(E_t/kT)]^{-1}$ as the average probability for the carrier to be free of the traps. The conductivity may then be written as

$$\sigma = N_{min}\sigma_c\{(1 - e^{-N_t})[1 + (N_t/N_c)e^{E_t/kT}]^{-1} + e^{-N_t}\}, \qquad (28)$$

where σ_c is the normal conductance of a cell which is given mainly by the hopping process in the case of

impure samples. We get two components of conductivity one of which has only the weak temperature dependence of σ_c while the other component may show strong temperature variation depending on E_t.

Figure 4(a) shows that the conductivities of samples B-3 and B-4 approached constant values at low temperature which we take as the temperature-insensitive component. The increase of conductivity resulting from the heat treatments was apparently caused by the introduction of additional donors, i.e., by the increase of N_{min}. The difference $\sigma(T) - \sigma(4.2°K)$ is plotted in Fig. 9 for sample B-3. It is interpreted as the component of conductivity which requires thermal activation. The slope of the sample before heat treatment corresponds to $E_t = 2.5 \times 10^{-3}$ eV, which is reasonable in the light of the estimates made above. The slope was slightly affected by the heat treatments as it might be expected. Reasonable values of E_t are obtained also from the results for samples B-2 and B-4. However, sample B-1 appears to be an exceptional case. Its conductivity plotted in Fig. 4(a) does not show appreciable trapping effect. The reason for this is not yet clear.

Finally, the anomalous behavior of the conductivity as a function of impurity concentration, found at 4.2°K but not at 20°K (Fig. 8), can be understood qualitatively as a result of the trapping effect. Trapping becomes fully effective at the lower temperature. In the samples of low-impurity concentrations, the amount of traps is negligible according to the estimates of N_t made previously. With increasing impurity concentration, the amount of traps becomes appreciable and the conduc-
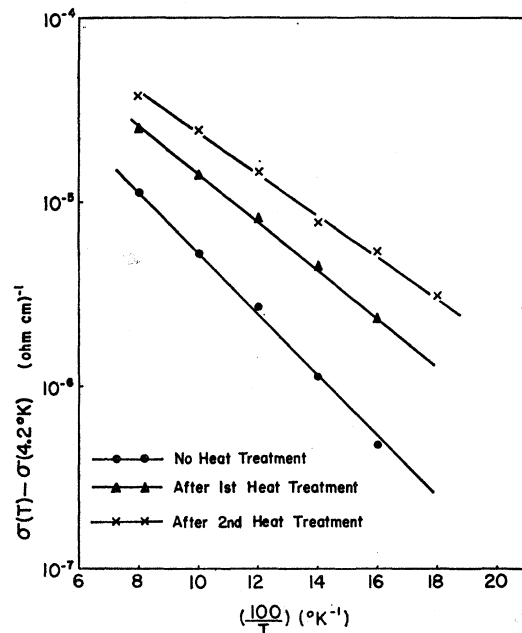

FIG. 9. The difference between the conductivity at temperature T and the conductivity at 4.2°K plotted against $1/T$ for sample B-3.

(a)

FIG. 11. Temperature dependence of $\sigma(T) - \sigma(4.2°K)$ for two different frequencies. Sample B-4.
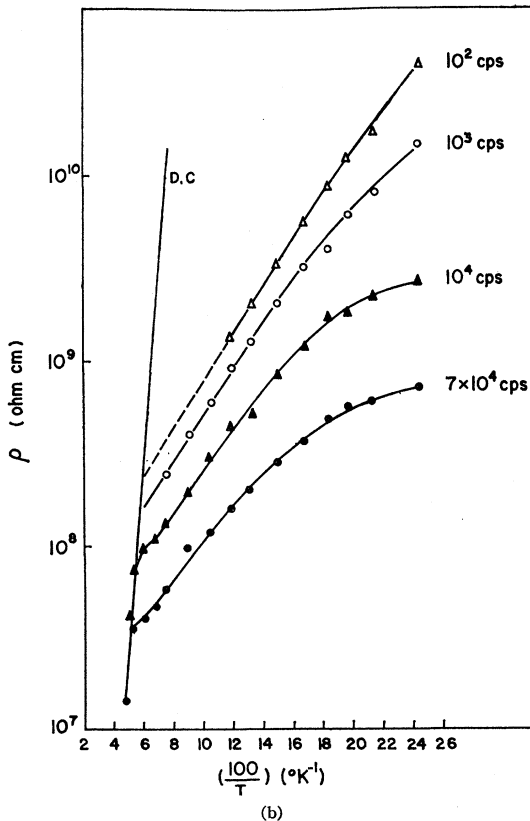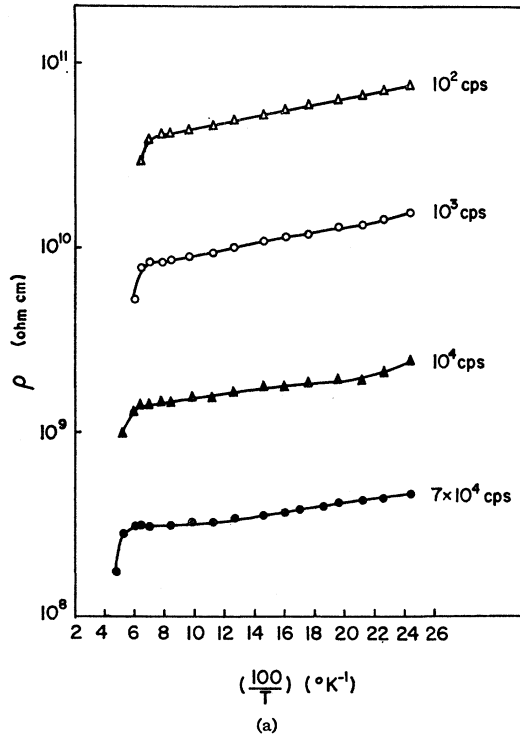

(b)

FIG. 10(a). Temperature dependence of conductivity at low frequencies, for sample B-5. (b) Temperature dependence of conductivity at low frequencies, for sample B-4.
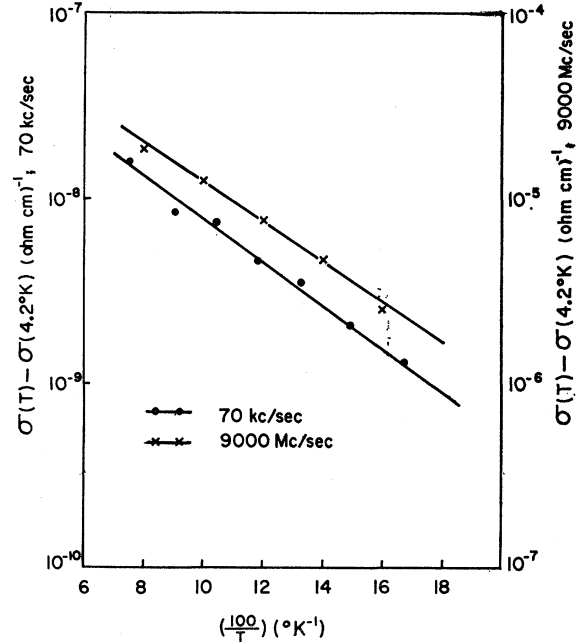
tivity drops. The point for the highest concentration represents sample B-1. As pointed above, it is not clear why this sample showed very little trapping effect.

D. Low-Frequency Conduction

Consider the influence of the two effects, direct absorption and carrier traps, at lower frequencies. With smaller $\hbar\omega$, larger r is required for direct absorption. The transition probability will be smaller and the effect of direct absorption will be reduced. On the other hand, the effect of the traps should be substantially independent of frequency.

Some measurements were made in the frequency range 10^2 to 10^5 cps, the same range used by Pollak and Geballe in their study of n-type samples. The results for samples B-4 and B-5 are shown in Fig. 10. Nonohmic behavior of conductivity was not detectable which is consistent with negligible direct absorption. The curves for sample B-5 show slight increase with $1/T$, while the resistivity of this sample decreased slightly with $1/T$ at the microwave frequency. This difference can be understood on the basis that the optimum hopping distance is larger at low frequencies. In contrast to B-5, the curves for sample B-4 vary much more strongly with temperature, which is consistent with the strong temperature dependence also at microwave frequency [Fig. 4(a)] and indicates the presence of trapping effect. Figure 11 shows the plot of $\sigma(T) - \sigma(4.2°K)$ for 70 kcps and the microwave frequency. It is seen that the curves have about the same slope corresponding to a trapping energy of $\sim 2 \times 10^{-3}$ eV.

V. SUMMARY

The results on the microwave conductivity of boron-doped samples can be interpreted by taking into account the direct absorption process and the carrier trapping effect, in addition to the hopping model. The nonohmic behavior of conductivity observed at low temperature in the samples of low-impurity concentrations may be expected from the direct absorption process. The strong increase of resistivity with decreasing temperature observed in the samples of high-impurity concentrations is explained as the effect of carriers trapping. The low-frequency measurements show that the trapping effect does persist at low frequencies.

ACKNOWLEDGMENTS

APPENDIX: CALCULATION OF CONDUCTIVITY AND DIELECTRIC CONSTANT

The cylindrical cavity is filled with the sample of thickness l sandwiched between two pieces of high resistivity, neutron bombarded silicon each of thickness d. The dielectric constant of the sample is very nearly the same as that of the high-resistivity silicon, and l is small compared to $2d$. The cavity is operated in the TE_{011} mode. It can be readily shown that at resonance we have

$$\frac{1}{\gamma_1}\tanh\gamma_1 d = \frac{1}{\gamma_2}\coth\gamma_2\frac{l}{2}, \qquad (A1)$$

where γ denotes propagation constant, and the subscripts 1 and 2 refer to the high resistivity silicon and the sample, respectively. The propagation constant is given by

$$\gamma = \alpha + i\beta = [-(\omega^2\epsilon\mu - k^2) + i\omega\sigma]^{1/2}, \qquad (A2)$$

where ϵ, σ, and μ are the dielectric constant, conductivity, and magnetic permeability, respectively, and $k = 3.832/a$, a being the radius of the cavity. The effect of the small conductivities of the sample and the neutron-bombarded silicon is negligible, and (A1) may be reduced to

$$\frac{1}{\beta_1}\tan\beta_1 d = \frac{1}{\beta_2}\cot\beta_2\frac{l}{2}. \qquad (A3)$$

This equation can be used to calculate the dielectric constant, ϵ_2, of the sample, taking ϵ_1 of the neutron-bombarded silicon as known.

Since the power loss due to the small conductivities of the silicon pieces is very small, the electric field in the cavity may be expressed approximately by

$$E(r,z) = E(r)\sin\beta z, \qquad (A4)$$

with

$$\beta = \frac{\pi}{2d+l} \approx \beta_1 \approx \beta_2. \qquad (A5)$$

The energy stored in the cavity is given by

$$W_s = \frac{\epsilon_1}{4}(l+2d)\int_s E^2(r)ds. \qquad (A6)$$

The power absorbed in the sample is

$$W_l = \frac{\sigma_2}{2}\int_d^{d+l}\int_s E^2(r)\sin^2\beta z\,ds\,dz$$

$$= \frac{\sigma_2}{2}\left[\frac{l}{2} + \frac{2d+l}{2\pi}\sin\left(\frac{\pi l}{2d+l}\right)\right]\int_s E^2(r)ds. \qquad (A7)$$

The Q factor of the cavity due to the loss in the sample is, therefore,

$$Q_s = \frac{\omega\epsilon_1}{\sigma_2}\left\{(2d+l)\Big/\left[l + \frac{2d+l}{\pi}\sin\left(\frac{\pi l}{2d+l}\right)\right]\right\}. \qquad (A8)$$

This expression is used for the calculation of the conductivity, σ_2, of the sample. Experimentally, the Q factor is measured with the sample in place, Q, and with the cavity filled entirely with neutron-bombarded silicon, Q_0. The value of Q_s is then obtained from

$$1/Q_s = 1/Q - 1/Q_0. \qquad (A9)$$

With the cavity used, the value $Q_0 = 8820$ was obtained which remained the same throughout the temperature range of the experiment.

The cavity method used has a high sensitivity for conductivity measurement, conductivity as low as 2×10^{-6} (Ω cm)$^{-1}$ can be measured. Also, the electric-field strength can be calculated simply and accurately for a given power input. The intimate contact of the sample with the bombarded silicon and cavity helps to prevent the heating up of the sample by the absorption of microwave powers.