magnetic scattering. We consider the resistivity as a sum of the residual resistivity ($\rho_{\rm res}$), the magnetic contribution ($\rho_{\rm mag}$), and the phonon contribution ($\rho_{\rm ph}$).

We assume that by extrapolating the linear high-temperature part of the resistivity curve back to zero degrees K we eliminate $\rho_{\rm ph}$. The resistivity intercepts thus obtained are shown as $\rho_{\rm ext}$ in Table II. Also shown in Table II are the $\rho_{\rm res}$ and the $\rho_{\rm mag}$. The latter are obtained by subtracting the $\rho_{\rm res}$ from the $\rho_{\rm ext}$. This method is somewhat simpler than the method used by Anderson and Legvold[26] and follows the free electron model.[27] The two methods yield about the same results.

In Fig. 9 we have plotted the $\rho_{\rm mag}$ contributions as functions of two different parameters. The $S(S+1)$ parameter is the one used by Anderson and Legvold[26] and the parameter $[(J+1)/J]S^2$ has been suggested by Brout and Suhl.[28]

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Impurity Conduction at Low Concentrations*†

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The conductivity of an n-type semiconductor has been calculated in the region of low-temperature T and low impurity concentration n_D. The model is that of phonon-induced electron hopping from donor site to donor site where a fraction K of the sites is vacant due to compensation. To first order in the electric field, the solution to the steady-state and current equations is shown to be equivalent to the solution of a linear resistance network. The network resistance is evaluated and the result shows that the T dependence of the resistivity is $\rho \propto \exp(\epsilon_3/kT)$. For small K, $\epsilon_3=(e^2/\kappa_0)(4\pi n_D/3)^{1/3}(1-1.35K^{1/3})$, where κ_0 is the dielectric constant. At higher K, ϵ_3 and ρ attain a minimum near $K=0.5$. The dependence on n_D is extracted; the agreement of the latter and of ϵ_3 with experiment is satisfactory. The magnitude of ρ is in fair agreement with experiment. The influence of excited donor states on ρ is discussed.

I. INTRODUCTION

At sufficiently low temperatures, transport effects in doped semiconductors are not due to free carriers but occur as a result of charge transport between impurity states. The term *impurity conduction* denotes this type of transport. When the impurity concentration is high, the impurity states overlap strongly and lose their localized character. It is often said that an *impurity band* is formed and that conduction takes place in this "band." At low concentrations banding does not occur and conduction takes place by *hopping* of electrons from occupied to unoccupied localized donor states.

In recent years, many interesting experimental data on impurity transport have been published. Data are available for the resistivity and Hall effect,[1–7] effects of strain,[8] and magnetoresistance[2,9] in the temperature range of impurity transport.

We restrict our discussion throughout to those cases in which impurity "banding" does not occur and the hopping process is important. The hopping process was suggested by Conwell[10] and by Mott.[11] The same mechanism was independently proposed by Pines, Abrahams, and Anderson[12] in connection with the study of electron relaxation processes in Si.

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In this work, we shall compute the electrical resistivity for impurity conduction in the low concentration range. The model we shall use may be described as follows: Consider a semiconductor with N_D donors and N_A acceptors, $N_D > N_A$ (n type). At the low temperatures of interest the acceptors will compensate N_A of the donors and there will be N_A ionized donors, N_A ionized acceptors and $N_D - N_A$ electrons remaining in donor states. At low concentrations, the overlap between wave functions of neighboring impurity sites is small and the banding or "resonance" energy between the sites is much smaller than the energy difference between the sites due to the variation of local electric fields.[13] The local fields are produced by nearby ionized acceptors and donors. The electrons are then well localized and neighboring impurity states are nondegenerate. If one of the $N_D - N_A$ donor electrons is close to one of of the N_A vacant donor sites, it can hop into the available site and the transfer is accompanied by the emission or absorption of a phonon in order to conserve energy. The donor concentrations below which this model is appropriate are about 6×10^{15} in n-type Ge and 2×10^{17} in n-type Si. A study of the higher concentration region has been made by Kasuya.[14] Kasuya and Koide[15] have considered the low concentration region as well and their model is similar to ours.[16]

In the model we have described, charge transfer will be random in the absence of an external electric field and there will be no net current. An electric field produces an average gradient of donor state energy in the field direction which will cause an increase in the transfer rate to sites of lower field energy. Thus, a net current will flow in the field direction.

In Sec. II, we compute the transfer rate for electron transfer. In Sec. III, we consider the current. In Part A of this section, we derive the distribution function and transform to an equivalent resistance network. In Part B, we compute the Fermi energy for the distribution. In Part C, we extract the temperature dependence of the resistivity and in Part D we analyze the activation energy and the compensation dependence. We conclude Sec. II in Part E with the completion of the derivation of the resistivity expression and a discussion of the majority concentration dependence. In Sec. IV we compare our work with experiment and comment on a few related matters.

Some of the computational details are unfortunately quite complicated. They are described in detail in the Ph.D. thesis[17] of one of us (AM). Some of these details are described briefly in the Appendixes.

II. TRANSITION RATE FOR ELECTRON TRANSFER

We shall compute the transition rate for an electron hop using the deformation potential approximation for the electron-phonon interaction. The electron wave functions are taken from the effective-mass theory.[18,19] The wave functions for the lowest energy states (unperturbed by nearby impurities) of an electron on the ith donor is

$$\psi_i(\mathbf{r}) = \sum_{p=1}^{n} \alpha_p F_p(\mathbf{r}) \phi_p(\mathbf{r}), \qquad \text{(II-1)}$$

where $\phi_p(\mathbf{r})$ is the Bloch function for the pth conduction band minimum of which there are n. The $F_p(\mathbf{r})$ are hydrogenlike envelope functions which, to a good approximation, are of the form

$$F_p(x,y,z) = (\pi a^2 b)^{-\frac{1}{2}} \exp\{-[(x^2+y^2)/a^2 + z^2/b^2]^{\frac{1}{2}}\}, \qquad \text{(II-2)}$$

where the z axis is parallel to the axis containing the pth minimum. The constants a and b are the transverse and longitudinal radii of the orbit, respectively. They are given by $a = \hbar(2m_t/E_{\mathrm{obs}})^{-\frac{1}{2}}$ and $b = (m_t/m_l)^{\frac{1}{2}} a$. E_{obs} is the observed ionization energy for the donor ground state while m_t and m_l are the transverse and longitudinal effective masses.

In the present problem, we are concerned with the nature of the wave function at distances far from the impurity. We have therefore obtained Eq. (II-2) and the expressions for a and b by extending a procedure used by Kohn and Luttinger[18] for the case of isotropic mass ($m_t = m_l$). That is, we obtain the asymptotic solution of the equations which determine $F_p(x, y, z)$ [cf., Eq. (5.4) of reference 18], using E_{obs} for the eigenvalue. When the mass anisotropy is taken into account, Eq. (II-2) is obtained.

Values for E_{obs} are available from both "thermal" and "optical" methods. Since these differ slightly, we tabulate a and b in Table I, using both sets of data.

The α_p appearing in Eq. (II-1) are the coefficients of the appropriate linear combinations of the $F_p(\mathbf{r})\phi_p(\mathbf{r})$ which diagonalize the tetrahedral crystal field perturbation. In Si[18] and Ge, the ground state is the symmetrical combination $\alpha_p = n^{-\frac{1}{2}}$ ($n = 6$ and 4, respectively). In Ge, the first excited state is the degenerate triplet whose wave functions have the form of Eq. (II-1) but with the coefficients:

$$\alpha_p^{(1)} = (\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{1}{2}),$$
$$\alpha_p^{(2)} = (\tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}),$$
$$\alpha_p^{(3)} = (\tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}).$$

Suppose now that i and j are neutral and nearby ionized donor sites, respectively, separated by $\mathbf{R} = \mathbf{R}_j - \mathbf{R}_i$ with donor state energy difference

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[13] The importance of the influence of local fields was first pointed out to us in unpublished work of P. W. Anderson (see reference 12).

[14] T. Kasuya, J. Phys. Soc. Japan 13, 1096 (1958).

[15] T. Kasuya and S. Koide, J. Phys. Soc. Japan 13, 1287 (1958).

[16] The present work and that of reference 15 are independent studies.

[17] Allen Miller, Ph.D. dissertation, Rutgers University, 1960 (unpublished). Available from University Microfilms, Ann Arbor, Michigan.

[18] W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.

[19] W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955).

$\Delta=E_i-E_j$. The latter arises because the local and applied fields differ at the two sites. The wave functions of an electron at i and j are Ψ_i and Ψ_j which are solutions of an effective-mass Hamiltonian containing the potential due to donors i and j as well as the nearest ionized acceptor. The Coulomb fields of all the other ionized donors and acceptors are assumed to cancel, on the average. Thus, we write

$$\Psi_i=a_i\psi_i+a_j\psi_j. \tag{II-3}$$

We determine the linear combination, Eq. (II-3), for Ψ_i by a variational calculation on the Hamiltonian

$$H=T+V_a-e^2/\kappa_0r_i-e^2/\kappa_0r_j,$$

where T is the effective-mass kinetic energy operator, V_a is the potential due to the nearest ionized acceptor, $r_{i(j)}$ is the distance of the electron at $\mathbf{r}$ from the donor at $\mathbf{R}_{i(j)}$, and κ_0 is the static dielectric constant.

The result of the calculation is

$$a_i/a_j=(\Delta/2W)[1+(1+4WS/\Delta+4W^2/\Delta^2)^{\frac{1}{2}}],$$

where $\Delta=(\psi_i,V_a\psi_i)-(\psi_j,V_a\psi_j)$ is the zeroth order E_i-E_j and

$$W=L-SJ+(\psi_i,V_a\psi_i)-S(\psi_i,V_a\psi_i), \tag{II-4}$$

$$L=-(\psi_i,[e^2/\kappa_0r_i]\psi_j), \tag{II-5}$$

$$J=-(\psi_i,[e^2/\kappa_0r_j]\psi_i), \tag{II-6}$$

$$S=(\psi_i,\psi_j). \tag{II-7}$$

We call W the *resonance energy*. The last two terms of Eq. (II-4) are small and we therefore write

$$W=L-SJ. \tag{II-8}$$

For low concentrations, we have $W\ll\Delta$ so that

$$\begin{aligned}\Psi_i&=\psi_i+(W/\Delta)\psi_j,\\ \Psi_j&=\psi_j-(W/\Delta)\psi_i.\end{aligned} \tag{II-9}$$

The matrix element for the transition of a donor electron from site i to the ionized state j is given by

$$\langle H'\rangle=(\Psi_j,E_1\eta\Psi_i)+\Delta(\Psi_j,\delta\Psi_i), \tag{II-10}$$

where we have used the deformation potential theorem.[20] In Eq. (II-10), $E_1\eta$ and $\delta\Psi_i$ are the change in energy and wave function due to a dilation η. It is not difficult to show[17] that the second term of Eq. (II-10) is small compared to the first; we therefore drop it henceforth.

The dilation is

$$\eta=\nabla\cdot\delta\mathbf{R}(\mathbf{r})=i(\hbar/2\rho_0Vs)^{\frac{1}{2}}\sum_q q^{\frac{1}{2}}[b_\mathbf{q}\exp(i\mathbf{q}\cdot\mathbf{r})-\text{c.c.}],$$

where ρ_0, V, s are the density, volume, and velocity of longitudinal sound; $b_\mathbf{q}$, $b_\mathbf{q}^*$ are annihilation and creation operators for longitudinal phonons of wave vector $\mathbf{q}$.

We compute the matrix element of Eq. (II-10) using the wave functions of Eq. (II-9). The result, for phonon absorption, is

$$\langle H'\rangle=iE_1(\hbar qn_\mathbf{q}/2\rho_0Vs)^{\frac{1}{2}}(W/\Delta)[(\psi_j,e^{i\mathbf{q}\cdot\mathbf{r}}\psi_j)-(\psi_i,e^{i\mathbf{q}\cdot\mathbf{r}}\psi_i)], \tag{II-11}$$

where we have dropped a term involving an overlap matrix element between i and j. This term may be shown[17] to be small, and we do not include it.

TABLE I. Donor state orbit radii in S and Ge.

Host	Donor	a (A) Thermal	a (A) Optical	b (A) Thermal	b (A) Optical
S	As	20.2	19.4	8.9	8.5
	P	21.2	21.1	9.3	9.3
	Sb	22.6	21.6	9.9	9.5
Ge	As	60.5	55.7	13.6	12.9
	Sb	69.5	69.0	15.6	15.4
	Sb(3)[a]	72.0	71.3	16.2	15.8

[a] This line refers to the excited triplet state of Sb in Ge which lies about 6×10^{-4} ev above the ground state. H. Fritzsche, Phys. Rev. **115**, 336 (1959), and D. Wilson and G. Feher (private communication).

The matrix element is evaluated as follows: We write $\psi_j(\mathbf{r}-\mathbf{R})=\psi_i(\mathbf{r})$ where $\mathbf{R}$ connects i to j. The square bracket of Eq. (II-11) becomes

$$[\quad]=(e^{i\mathbf{q}\cdot\mathbf{r}}-1)(\psi_i,e^{i\mathbf{q}\cdot\mathbf{r}}\psi_i). \tag{II-12}$$

In evaluating this matrix element, we use the wave function as given by Eq. (II-1). The procedure is identical to that used by one of us previously.[21] We assume an isotropic mass and recognize that both $F_p(\mathbf{r})$ and $\exp(i\mathbf{q}\cdot\mathbf{r})$ vary slowly over a lattice spacing.[22] The result is

$$[\quad]=(e^{i\mathbf{q}\cdot\mathbf{r}}-1)[1+(a^*q/2)^2]^{-2},$$

where a^* is an average orbit radius.[23] Inserting this result into Eq. (II-11) and squaring, we get, for absorption,

$$|\langle H'\rangle|^2=(\hbar E_1{}^2/2\rho_0Vs)(W/\Delta)^2qn_\mathbf{q}(1-\cos\mathbf{q}\cdot\mathbf{R})\times[1+(qa^*/2)^2]^{-4}. \tag{II-13}$$

The transition rate is

$$U_{ij}=(2\pi/\hbar)(V/8\pi^3)\int|H'|^2\delta(\hbar sq-\Delta)d\mathbf{q}.$$

The nonoscillatory part of $|H'|^2$ contributes

$$U_{ij}=(E_1{}^2/\pi\rho_0s^5\hbar^4)W^2|\Delta|n_\mathbf{q}, \tag{II-14}$$

where we have, in accordance with reference 23, replaced the square bracket of Eq. (II-13) by unity. We have written the transition rate for absorption, $\Delta<0$. If $\Delta>0$, $n_\mathbf{q}$ is replaced by $n_\mathbf{q}+1$. The $\cos\mathbf{q}\cdot\mathbf{R}$ term of Eq. (II-13) contributes a term whose ratio to Eq.

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[20] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[21] Elihu Abrahams, Phys. Rev. **107**, 481 (1957), see Eq. (6) ff.

[22] For $n_D=10^{16}$ cm^{-3} and a compensation of 5%, $q=\Delta/\hbar s\cong10^6$ cm^{-1}.

[23] Note that this result justifies the use of an isotropic mass in this part of the calculation since the mass appears only in $1+(a^*q/2)^2\approx1$.

(II-14) is $-(\hbar s/R\Delta)\sin(R\Delta/\hbar s)$. Because of the oscillating sine factor, this term will not contribute appreciably to the conductivity. Once we know the resonance energy W, we shall have completed the discussion of the transition rate, Eq. (II-14).[24]

In order to compute W, Eq. (II-8), we first evaluate the transfer integral L from Eq. (II-5). The procedure is similar to what we have already done in the computation of the electron-phonon matrix element, Eq. (II-11) ff. We have

$$L=-(e^2/\kappa_0)\sum_{pp'}\alpha_p{}^{(i)*}\alpha_{p'}{}^{(j)}e^{-i\mathbf{p}\cdot\mathbf{R}} \times(F_p(\mathbf{r}-\mathbf{R})u_p,\,F_{p'}(\mathbf{r})u_{p'}e^{-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}}/r),\qquad\text{(II-15)}$$

where we have written $u_p(\mathbf{r})\exp(i\mathbf{p}\cdot\mathbf{r})$ for the Bloch functions $\phi_p(\mathbf{r})$ and used the fact that $u_p(\mathbf{r}-\mathbf{R})=u_p(\mathbf{r})$. The superscripts on α_p, $\alpha_{p'}$ indicate the possibility that the states on i and/or j may not be the ground donor state, in which case one must use the appropriate set of α for the state in question.

Similar arguments to those used previously[21] lead us to the conclusion that the leading term in L comes from $p=p'$ since $F(\mathbf{r}-\mathbf{R})F(\mathbf{r})/r$ is slowly varying. However, the isotropic mass approximation is not a good one in the present case, so we use Eq. (II-2) for $F_p(\mathbf{r})$. Equation (II-15) becomes

$$L=-(e^2/\kappa_0\pi a^2b)\sum_p\alpha_p{}^{(i)*}\alpha_p{}^{(j)}e^{-i\mathbf{p}\cdot\mathbf{R}}\int(d\mathbf{r}/r) \times\exp[-(r_p{}^i+r_p{}^j)/a],\qquad\text{(II-16)}$$

where

$$r_p{}^j=a[(x-x_j)^2/a^2+(y-y_j)^2/a^2+(z-z_j)^2/b^2]^{\frac{1}{2}},$$

with the z axis parallel to the axis of the pth valley. We approximate the integral in Eq. (II-16) by replacing r by $r_p{}^i$ in the denominator and evaluate it in confocal elliptic coordinates. The result is

$$L=-(e^2/\kappa_0a^2)\sum_p\alpha_p{}^{(i)*}\alpha_p{}^{(j)}e^{-i\mathbf{p}\cdot\mathbf{R}}R_p(1+a/R_p) \times e^{-R_p/a},\qquad\text{(II-17)}$$

where

$$R_p=a(x_{ij}{}^2/a^2+y_{ij}{}^2/a^2+z_{ij}{}^2/b^2)^{\frac{1}{2}},\quad x_{ij}=x_i-x_j.$$

The overlap integral S, Eq. (II-7), which is required for W is evaluated by an identical procedure. The result is

$$S=\sum_p\alpha_p{}^{(i)*}\alpha_p{}^{(j)}e^{-i\mathbf{p}\cdot R}(1+R_p/a+R_p{}^2/3a^2) \times e^{-R_p/a}.\qquad\text{(II-18)}$$

Finally, J may be evaluated from Eq. (II-6). The result if $J=-e^2/\kappa_0R$ where we have dropped a small term proportional to $\exp(-2R/a^*)$.

Introducing Eqs. (II-17, 18) and our result for J into $W=L-SJ$, we get, to lowest order in a/R_p,

$$|W|^2=(2e^2/3\kappa_0a^2)^2\sum_{pp'}\alpha_p{}^{(i)*}\alpha_{p'}{}^{(i)}\alpha_p{}^{(j)}\alpha_{p'}{}^{(j)*} \times R_pR_{p'}e^{i(\mathbf{p}'-\mathbf{p})\cdot\mathbf{R}-(R_p+R_{p'})/a}.$$

The terms for which $p\neq p'$ will oscillate and make no net contribution to the conductivity. In the beginning of this section, we have seen that for all states of interest, $|\alpha_p{}^{(i)}|^2=1/n$, where n is the number of valleys. Therefore we get

$$|W|^2=(2e^2/3n\kappa_0a^2)^2\sum_{p=1}^{n}R_p{}^2e^{-2R_p/a}.$$

In the case that the mass is sufficiently anisotropic, the angular average of W is

$$\langle|W|^2\rangle=(2e^2/3\kappa_0a^2)^2(1/n)(\pi a/4\alpha R)^{\frac{1}{2}}R^2e^{-2R/a},\qquad\text{(II-19)}$$

where $\alpha=(a/b)^2-1$. To compute the average, we have assumed $\alpha R/a\gg1$ which is valid in Si and Ge. If, however, the mass is exactly isotropic, then so is $|W|^2$ since $R_p=R$. In this case, the factor $(\pi a/4\alpha R)^{\frac{1}{2}}$ in Eq. (II-19) must be replaced by unity.

The result, Eq. (II-19), shows that the only effect of the Bloch functions in the effective mass wave functions is an interference between the minima which reduces the resonance energy W by a factor $n^{-\frac{1}{2}}$.[25]

III. THE CURRENT

A. The Steady State

In this section we consider the current in an applied field $\mathbf{F}$. Imagine a surface of area S perpendicular to $\mathbf{F}$. Let i and j denote sites above and below S, respectively. The Greek letters α, β, etc. will denote different states on the same donor, e.g., singlet, triplet. Finally, let the distribution $f_i{}^\alpha$ be the probability that the state α on donor i is occupied.

The current density is the net rate of charge flow across S. In an independent electron model, it is given by

$$j=(e/S)\sum_{\alpha\beta}\sum_{i>S,j<S}[f_i{}^\alpha(1-\sum_\gamma f_j{}^\gamma)U_{i(\alpha),j(\beta)} -f_j{}^\beta(1-\sum_\gamma f_i{}^\gamma)U_{j(\beta),i(\alpha)}],\qquad\text{(III-1)}$$

where e is the magnitude of the electron charge, $U_{i(\alpha),j(\beta)}$ is the transition rate, Eqs. (II-14, 19), from the state α on i to β on j and it must be remembered that i is above S and j is below.

If $\mathbf{F}=0$, there will be no net charge transport and the square bracket in Eq. (III-1) vanishes for each pair of sites. If $\mathbf{F}\neq0$, the U_{ij} are altered, favoring sites of low field energy and a current will flow.

The $f_i{}^\alpha$ are determined by the steady-state condition

$$\sum_\alpha\sum_{i(\neq j)}[f_i{}^\alpha(1-\sum_\gamma f_j{}^\gamma)U_{i(\alpha),j(\beta)} -f_j{}^\beta(1-\sum_\gamma f_i{}^\gamma)U_{j(\beta),i(\alpha)}]=0,\qquad\text{(III-2)}$$

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[24] Our result, Eq. (II-14) disagrees with that of reference 15. There is an error in that paper in that the third term of their Eq. (22) is neglected whereas it is actually the most important one.

[25] A similar interference effect occurs in the theory of the hyperfine interaction of a donor electron in Si with the Si^{29} nuclei. See reference 18, Sec. 7c.

since the left side is $\partial f_j^\beta/\partial t$. If $\mathbf{F}=0$, Eq. (III-2) is solved by

$$f_i^\alpha=[\sum_\gamma \exp(\beta E^{\alpha\gamma})+\exp\beta(E_i^\alpha-\zeta)]^{-1}, \quad \text{(III-3)}$$

where $\beta=1/kT$, $E^{\alpha\gamma}=E_i^\alpha-E_i^\gamma$, E_i^α is the energy of state α on donor i when $\mathbf{F}=0$, and ζ is the Fermi energy. The latter is determined by

$$\sum_{i,\alpha} f_i^\alpha=N_D-N_A, \quad \text{(III-4)}$$

since the right-hand side is just the number of electrons in donor states. To obtain Eq. (III-3), we have made use of the reciprocal relation

$$U_{i(\alpha),j(\beta)} \exp(\beta E_j^\beta)=U_{j(\beta),i(\alpha)} \exp(\beta E_i^\alpha), \quad \text{(III-5)}$$

which may be obtained from Eq. (II-14).

If $\mathbf{F}\neq 0$, Eq. (III-3) is no longer the solution. In order to solve for the f_i^α in the presence of $\mathbf{F}$, we write

$$f_i^\alpha=[\sum_\gamma \exp\beta(\epsilon_i^\alpha-\epsilon_i^\gamma)+\exp\beta(\epsilon_i^\alpha-\zeta)]^{-1}, \quad \text{(III-6)}$$

and attempt to find the ϵ_i^α. We use this form for f_i^α in the steady state condition, Eq. (III-2), and we make use of the reciprocal relations, Eq. (III-5), but with the electric field energy included in the energies of the states. These steps lead us to the following expression for the steady-state condition (where we have taken care to keep only terms which are *linear* in the electric field F chosen in the x direction):

$$\sum_{\alpha,i(\neq j)} V_{i(\alpha),j(\beta)}/Z_{i(\alpha),j(\beta)}=0, \quad \text{(III-7)}$$

where

$$V_{i(\alpha),j(\beta)}=\epsilon_i^\beta-\epsilon_i^\alpha-E_j^\beta+E_i^\alpha+eF(x_j-x_i), \quad \text{(III-8)}$$

and

$$\begin{aligned} Z_{i(\alpha),j(\beta)}=S&[1+\sum_\gamma \exp\beta(-E_j^\gamma+\zeta)] \\ &\times[1+\sum_\gamma \exp\beta(-E_i^\gamma+\zeta)] \\ &\times\exp\beta(E_i^\alpha-\zeta)[\beta e^2 U_{i(\alpha),j(\beta)}]^{-1}. \quad \text{(III-9)}\end{aligned}$$

In Eq. (II-8), x_i is the x coordinate of the ith donor.

In the same way, the current, Eq. (III-1), becomes

$$j=\sum_{\alpha,\beta}\sum_{i>S,j<S} V_{i(\alpha),j(\beta)}/Z_{i(\alpha),j(\beta)}. \quad \text{(III-10)}$$

The result of the development so far is to cast the problem into the form of a resistance network with impedance elements $Z_{i(\alpha),j(\beta)}$ connecting the states α, β of the sites i, j, with corresponding potential drops $V_{i(\alpha),j(\beta)}$. The steady-state condition, Eq. (III-7) is Kirchhoff's first law for the network; Eq. (III-8) is Kirchhoff's second law. The current is given by Eq. (III-10).

In order to compute the resistivity of the crystal, we must find the equivalent resistance of a network of N_D sites each of which consists of a neighborhood of junctions which correspond to the different states on each donor. Every pair of junctions is connected by an element of resistance $Z_{i(\alpha),j(\beta)}$. Between junctions in the same neighborhood, we have impedances $Z_{i(\alpha),i(\beta)}$.

At this point, we can note that the resistivity must vary rapidly with majority concentration since $Z_{ij} \propto \exp(2R/a)$. This is in accord with experiment. Furthermore, we see from Eq. (III-4) that the Fermi energy $\zeta=+\infty$ when $N_A=0$ and $\zeta=-\infty$ when $N_A=N_D$. Thus, from Eq. (III-9), every element $Z=\infty$ in both cases and the resistivity must have a minimum for some compensation $K=N_A/N_D$ between 0 and 1. That this must be so is clear since for $K=0$ there are no vacant sites and for $K=1$ there are no electrons. Such a minimum has recently been observed.[5,26] We also note that each Z varies exponentially as $1/T$ which is also consistent with experiment.[2]

B. The Fermi Energy

We evaluate the Fermi energy from Eq. (III-4) which may be written in the form

$$N_A=\sum_{i=1}^{N_D} [1+\exp\beta(-E_i+\zeta_g)]^{-1}, \quad \text{(III-11)}$$

where E_i is the ground-state (singlet) energy on i and ζ_g is the singlet Fermi level, that is, what ζ would be in the absence of excited states. ζ itself may be obtained from

$$e^{\beta\zeta_g}=e^{\beta\zeta}\sum_\alpha e^{-\beta\Delta_\alpha}, \quad \text{(III-12)}$$

where Δ_α is the energy of the state α above the ground state (the ground state, $\Delta_\alpha=0$, is included in the sum). Note that in the above we have used Eq. (III-3) for f_i^α which is consistent with our approximation to first order in the electric field. Terms depending on F occur only in the potential drops V_{ij}, Eq. (III-8).

To evaluate Eq. (III-11), we transform the sum to an integral by introducing a density of ground states $F(E)$. The energy distribution arises from the local field variations due to the spatial distribution of ionized acceptors. The zero of energy is taken as the energy of the donor ground state in the absence of acceptors. We have

$$N_A=N_D\int_0^\infty F(E)(1+e^{-y})dE,$$

where $y=\beta(E-\zeta_g)$. An integration by parts gives (with $K=N_A/N_D$)

$$K=1-\beta\int_0^\infty v(E)dE[(1+e^y)(1+e^{-y})]^{-1}, \quad \text{(III-13)}$$

where $v(E)=\int_0^E F(E')dE'$ is the number of singlet states with energy less than E. For low temperatures, the denominator of the integrand is sharply peaked at $y=0$ $(E=\zeta_g)$. If $v(E)$ is slowly varying we may remove it from the integral and evaluate it at ζ_g. This pro-

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[26] A. L. McWhorter, Bull. Am. Phys. Soc. 4, 186 (1959).

cedure may be justified in detail.[17] The integral may now be performed and the result is

$$1-K=v(\zeta_g)/(1+e^{-\beta\zeta_g}). \qquad \text{(III-14)}$$

In order to determine $v(\zeta_g)$, we need to know $F(E)$. In our model, $F(E)$ is determined by the Coulomb repulsion due to the nearest ionized acceptor. Thus $E=e^2/\kappa_0 r_1$, where r_1 is the distance to the nearest acceptor. If we use the Poisson formula, $P(r_1)=3(r_1^2/r_A^3)\exp(-r_1/r_A)^3$ for the distribution in r_1, we find

$$F(E)=3(E_A^3/E^4)\exp(-E_A/E)^3, \qquad \text{(III-15)}$$

where $E_A=e^2/\kappa_0 r_A$ with r_A defined as $(3/4\pi n_A)^{\frac{1}{3}}$, the average distance between acceptors. A simple integration now gives $v(E)$ and Eq. (III-14) becomes the defining equation for the singlet Fermi level ζ_g:

$$1-K=\exp(-E_A/\zeta_g)^3[1+\exp(-\beta\zeta_g)]^{-1}. \qquad \text{(III-16)}$$

An analysis of Eq. (III-16) shows that there are three interesting regions of compensation:

$$0\leqslant K\lesssim e^{-\beta E_A}, \qquad \zeta_g=-(1/\beta)\ln K; \qquad \text{(III-17a)}$$

$$e^{-\beta E_A}\lesssim K\lesssim 1-e^{-\beta E_A}, \qquad \zeta_g=-E_A/\ln^{\frac{1}{3}}(1-K); \qquad \text{(III-17b)}$$

$$1-e^{-\beta E_A}\lesssim K\leqslant 1, \qquad \zeta_g=(1/\beta)\ln(1-K). \qquad \text{(III-17c)}$$

For all available data, Eq. (III-17b) is appropriate. In this intermediate case, when K is small enough, the logarithm may be expanded and we have simply

$$\zeta_g=E_D, \qquad \text{(III-18)}$$

where $E_D=e^2/\kappa_0 r_D$, $r_D=(3/4\pi n_D)^{\frac{1}{3}}$. In the above, n_A and n_D are the acceptor and donor concentrations.

C. Resistance Network

We have to compute the resistance of a network with widely varying impedance elements given by Eq. (III-9). We proceed by decomposing the network into chains each of which threads the length of the crystal in the direction of the field. We select those chains which essentially determine the net resistance, namely those which consist of small impedances pointing primarily in the field direction. The paths of very large total impedance will not affect the total network resistance. A set of such "paths of least resistance" is found in what follows.

From a given site, the chain is continued by the following rule: Construct a solid angle centered on the field direction of magnitude $4\pi\gamma(R)$ where $\gamma(R)$ is some function, to be determined later, of the distance R from the site. Pick out that site (usually the closest one) which is connected to the starting one by the smallest impedance element in the allowed solid angle. In this scheme, one must exclude the incoming element which has just reached the starting site in order that the chain not go back on itself. In the end, we determine $\gamma(R)$ by a variational method which appropriately emphasizes the field direction and small impedances.

The total impedance of a chain is then

$$Z_c=Np_1\int ZP_1(Z)dZ+Np_2\int ZP_2(Z)dZ,$$

where N is the number of chain elements. $P_j(Z)dZ$ is probability that the jth smallest impedance in the allowed solid angle has a value in dZ. p_j is the probability that a chain element is the jth smallest in the allowed region. Either an outgoing element is the smallest ($j=1$), or the incoming one was, in which case the outgoing element is the second smallest ($j=2$).

Since the length L of the crystal is large and the impurities are distributed at random, each of the least resistance chains will have the same resistance and we shall have to take them in parallel. The number M of such chains will be estimated later. The resistivity of the crystal is then

$$\rho=p_1\rho_1+p_2\rho_2, \qquad \text{(III-19)}$$

where

$$\rho_j=(N/LM)\int ZP_j(Z)dZ. \qquad \text{(III-20)}$$

In order for our method to be valid, we must later show[27] that $\rho_{j+1}\gg\rho_j$, namely that the restriction to smallest possible impedances is a good approximation.

We now begin the computation of $P_j(Z)$. In what follows, we only consider elements lying in their allowed solid angles. Let $g(Z)$ be the probability of finding at least one element between 0 and Z. Then the probability of exactly $j-1$ elements with values less than Z is given by the Poisson distribution

$$g^{j-1}e^{-g}/(j-1)!.$$

Thus, the probability that the jth smallest lies between Z and $Z+dZ$ is given by

$$P_j(Z)dZ=g'(Z)dZg^{j-1}(Z)e^{-g(Z)}/(j-1)!. \qquad \text{(III-21)}$$

To proceed, we must calculate $g(Z)$. This is done most conveniently by treating R as the variable rather than Z. We may express $Z_{i(\alpha),j(\beta)}$ in terms of E_i^α, $E_i^\alpha-E_j^\beta$, and $U_{i(\alpha),j(\beta)}$ from Eq. (III-9). The transition rate $U_{i(\alpha),(\beta)}$ is given by Eq. (II-14) in terms of the resonance energy W which in turn, Eq. (II-19), is a function of R_{ij}. The results of Part B of this section give the Fermi energy. When these steps are carried out, we get an expression for Z which is complicated by temperature-dependent exponential factors originating from the excited donor states. However, in Appendix A we show that the result is simply expressed in terms of the impedance elements in the absence of excited states. The result for the net impedance between

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[27] The fact that the condition $\rho_{j+1}/\rho_j\gg 1$ is met can be seen from the evaluation of ρ_j which concludes this section. From Eq. (III-30), dropping the small terms in $v(R_1)$, we see that the required ratio is

$$(A_{j+1}/A_j)(2r_D/3a)^{\frac{3}{2}}=(1/j)(2r_D/3a)^{\frac{3}{2}}\gg 1.$$

sites i and j is

$$Z_{ij}=Z_{g,ij}l_e \tag{III-22}$$

$$Z_{g,ij}=BR_{ij}^{-\frac{3}{2}}e^{2R_{ij}/a}h_{ij}(T)h_g(T), \tag{III-23}$$

$$h_{ij}(T)=[1+\exp\beta(-E_i+\zeta_g)] \times[1+\exp\beta(-E_j+\zeta_g)], \tag{III-24}$$

$$h_g(T)=(\beta E_{ij})^{-1}[\exp\beta(E_i-\zeta_g) -\exp\beta(E_j-\zeta_g)], \tag{III-25}$$

$$B=S(9n/2)(\rho_0 s^5/E_1^2)(\kappa_0^2\hbar^4/e^6)(\pi\alpha a^7)^{\frac{1}{2}}. \tag{III-26}$$

In Eq. (III-22), l_e is a factor given by Eq. (A-2) of Appendix A; it depends on the energy differences between excited and ground states. $Z_{g,ij}$ is the impedance in the absence of excited states. In Eqs. (III-24, 25), E_i is the ground-state energy of the ith donor and $E_{ij}=E_i-E_j$. Eqs. (III-22–26) express Z as a function of the distance between the sites $R(=R_{ij})$, $E(=E_i)$ and $\Delta(=E_{ij})$.

With this notation, we get for the probability of finding at least one impedance between 0 and Z_0

$$g(Z_0)=4\pi n_D\int\int\gamma(R)R^2F(E)dEdR, \tag{III-27}$$

where $F(E)$ is the density of states, Eq. (III-15). In deriving Eq. (III-27), we have used the fact that the probability of finding an impedance in dR is n_D if dR lies in the allowed solid angle and zero otherwise. The distribution in Δ has disappeared from this result. The reason is that the distribution has a maximum near $\Delta=0$ and in fact can be taken to be a sharply peaked function of Δ without appreciable loss of accuracy in the computation of $g(Z_0)$. The region of integration in Eq. (III-27) is thus defined by those values of E, R for which $Z(R, E, \Delta=0)\leqslant Z_0$.

The evaluation of $g(Z_0)$ is performed in Appendix B. The result is

$$g(Z_0)=4\pi n_D\left[\int_0^{R_0}\gamma(R)R^2dR +\beta E_A a R_0^2\gamma(R_0)I/6\right], \tag{III-28}$$

where $Z(R_0,0,0)=Z_0$ defines R_0, a is as usual the transverse orbit radius, and I is a number depending only on compensation; it is defined explicitly in Appendix B. The term in I is small and will always be dropped, except when it occurs in an exponential since it contains a temperature dependence and will contribute to the activation energy.

Having found $g(Z)$, we may evaluate $P_j(Z)$ from Eq. (III-21) and compute the resistivity, Eq. (III-20). The result is that ρ_j is expressed as an integral over R which may be evaluated accurately by the saddle-point method. The result depends on the choice of $\gamma(R)$ but if we assume that this function does not vary rapidly near the extremum, we find that the latter occurs at a value, R_m, considerably larger than r_D, the average donor separation. This reflects the fact that impedance elements of greater than average length, while not occurring often, tend to retard the flow considerably. The result of the saddle-point investigation is instructive with respect to the choice we shall have to make for the allowed solid angle $\gamma(R)$. It turns out that $R_m\approx[2r_D^3/3a\gamma(R_m)]^{\frac{1}{2}}-\beta IaE_A/6$ and

$$\rho_j\propto\exp[2(2r_D/3a)^{\frac{3}{2}}\gamma^{-\frac{1}{2}}(R_m)]. \tag{III-29}$$

This shows that a variational calculation will reveal $\gamma=1$ near R_m in order to make ρ_j small. We shall therefore choose $\gamma(R)=1$ for $R>R_1$, where both R_1 and the form of $\gamma(R)$ for $R<R_1$ are still to be determined. In any case, we must have $R_1<R_m$. With these restrictions on $\gamma(R)$, the result for ρ_j is

$$\rho_j=(NS/ML)A_j a^2(a/r_D)^{\frac{3}{2}}v^{j-1}(R_1)2(1+\cosh\beta\zeta_g) \times\exp[1.09(r_D/a)^{\frac{3}{2}}+(R_1/r_D)^3-u(R_1) -\beta IE\omega/3], \tag{III-30}$$

where

$$v(R_1)=(2r_D/3_a)^{\frac{3}{2}}+u(R_1)-(R_1/r_D)^3,$$

$$u(R_1)=4\pi n_D\int_0^{R_1}\gamma(R)R^2dR,$$

$$A_j=l_e(12\alpha)^{\frac{1}{2}}\kappa_0^2 n9\pi\rho_0 s^5\hbar^4/4E_1^2e^6(j-1)!.$$

In the above l_e accounts for the excited states (Appendix A) and we have absorbed the constant B which is given by Eq. (III-26). Only the first term of $v(R_1)$ is large; the others will be neglected.

D. The Activation Energy

We have proceeded far enough to discuss the temperature and compensation dependence and activation energy of the resistivity. From Eq. (III-30) we see that the temperature and compensation dependence is given by

$$\rho\propto l_e[2+e^{\beta\zeta_g}+e^{-\beta\zeta_g}]e^{-\beta E_A I/3}.$$

For compensation K near unity, the third term in the square bracket is largest and $\rho\longrightarrow\infty$ as discussed earlier. For all data available at present, $\beta\zeta_g\gg 0$ and we may therefore write the temperature dependence as

$$\begin{aligned}\rho&\propto l_e e^{\beta\epsilon},\\ \epsilon&=\zeta_g-IE_A/3.\end{aligned} \tag{III-31}$$

It is only for Sb-doped Ge that excited states are important and l_e differs from unity. In all other cases, we shall have a simple activation energy. In general, if we define the activation energy by $\epsilon_3=d(\ln\rho)/d\beta$, we shall have

$$\begin{aligned}\epsilon_3&=\zeta_g-(IE_A/3)+\epsilon_e,\\ \epsilon_e&=l_e^{-1}dl_e/d\beta.\end{aligned} \tag{III-32}$$

The excited-state contribution ϵ_e is computed in Appendix A. In Sb-doped Ge, the activation energy is slightly increased and in all other cases ϵ_e is negligible.

We have discussed the factor I in Appendix B. For low compensations, $I=4.05$ and we have, using Eq. (III-18) for ζ_g, the result ($e^{-\beta E_A}<K<0.03$),

$$\epsilon_3 = E_D - 1.35E_A + \epsilon_e. \qquad \text{(III-33)}$$

For larger values of K we must evaluate I numerically from Eq. (B-5). In addition, we use Eq. (III-17b) for ζ_g. The results are tabulated in units of E_D in Table II.

We see from the table that ϵ_3 (and therefore ρ) attains a minimum for $0.45<K<0.55$.

E. Majority Concentration Dependence

The resistivity is given by Eq. (III-19). We have evaluated ρ_j, Eq. (III-30). All that remains is to determine R_1 and γ, the probabilities p_1 and p_2 and the geometrical factor (NS/ML) which appears in Eq. (III-30). We now discuss these quantities and extract the majority-concentration dependence.

The number of chain elements N is related to the length L of the crystal by

$$L = N\int\int [R\cos\theta/4\pi\gamma(R)][p_1P_1(R)+p_2P_2(R)]dRd\Omega,$$

where $P_j(R)dR$ is the probability that, of those impedances lying in their allowed solid angles, the jth nearest one is at a distance lying in dR. This probability is obtained from a relation just like Eq. (III-21) where g is replaced by

$$u(R) = 4\pi n_D\int_0^R \gamma(R')R'^2dR'. \qquad \text{(III-34)}$$

Also, θ is the angle between R and the field direction. The Ω integration is over the allowed solid angle. We recall that we have chosen $\gamma(R)=1$ for $R>R_1$. For $R<R_1$, it is possible to show[17] that with good accuracy $p_1=1$, $p_2=0$. Therefore, we have

$$L = 4\pi n_D N\int_0^{R_1} R^3(\gamma-\gamma^2)e^{-u(R)}dR. \qquad \text{(III-35)}$$

To proceed, we need the form of $\gamma(R)$; we choose it to minimize the resistivity. We refer to Eq. (III-30) and maximize $(1/\rho_j)$. To do this, we crudely approximate the number of chains M by assuming each site is a member of only one chain. Then $MN=n_DLS$. From Eq. (III-30) we then find that the terms in $(1/\rho_j)$ which depend upon γ and R are

$$(1/\rho_j) \propto (L/N)^2 \exp[u(R_1)-(R_1/r_D)^3]. \qquad \text{(III-36)}$$

TABLE II. Activation energy in units of E_D.

K	$\epsilon_3-\epsilon_e$	K	$\epsilon_3-\epsilon_e$
0.02	0.640	0.40	0.289
0.03	0.604	0.45	0.285
0.05	0.534	0.50	0.286
0.06	0.511	0.55	0.287
0.10	0.450	0.60	0.295
0.20	0.351	0.70	0.323
		0.80	0.356
0.33	0.298	0.90	0.391

It is not difficult to show that $\gamma\approx\frac{1}{2}$ for all $R<R_1$ leads to a maximum of $(1/\rho_j)$. If we substitute Eq. (III-35) into Eq. (III-36) and replace the exponential terms in $u(R)$ by unity, this result is exact. The justification for this procedure is that $u(R)<1$; see Eq. (III-34). On the basis of this argument, we assume for simplicity that γ is constant for $R<R_1$ and maximize Eq. (III-36) with respect to R_1 and the value of γ. The result[17] is $R_1=1.46r_D$, $\gamma=0.55$. Therefore, $L/N=0.352r_D$, and ρ_j may be determined from Eq. (III-30) by using $M=n_DLS/N$ and replacing the temperature-dependent factors (except l_e) by $\exp\beta\epsilon$, see Eq. (III-31).

Finally, we must compute the probabilities p_1, p_2. The form of γ restricts outgoing impedances to approximately a hemisphere in the field direction for $R<R_1$ and there are no restrictions for $R>R_1$. Thus, if the incoming impedance has a length less than R_1, its origin lies in the excluded region for the outgoing one and the latter is then the first smallest in the allowed region. The probability that this is so is

$$\int_0^{R_1} P_1(R)dR = 1-\exp[-\gamma(R_1/r_D)^3] = 0.817.$$

If this is not so, we estimate that the incoming element has a probability one-half of being the smallest in the allowed region of the outgoing one. If it is the smallest, the outgoing element is the second smallest. Therefore

$$p_1 = 0.817+(1/2)\exp[-\gamma(R_1/r_D)^3] = 0.909,$$
$$p_2 = 0.091.$$

Since p_1 also represents the probability that a chain element points in the field direction, we note that 90% of the elements do so.

Our task is now complete. The resistivities ρ_j are obtained from Eq. (III-30) and the conclusions of the previous paragraph. The activation energy is given in Table II and the effect of excited states, contained in the factor l_e, is discussed in Appendix A. The final result is

$$\rho = C(T)(r_D/a)[1+18.2(a/r_D)^{\frac{3}{2}}] \times\exp[1.09(r_D/a)^{\frac{3}{2}}+\beta(\epsilon_3-\epsilon_e)], \qquad \text{(III-37)}$$
$$C(T) = l_e(T)(\alpha/8)^{\frac{1}{2}}p_2\lambda\kappa_0{}^2n\rho_0s^5\hbar^4a^3/e^6E_1{}^2,$$

where p_2 we have just found to be 0.091 and λ is a numerical factor which absorbs all the factors of γ and R_1. Its value is 5.0×10^3. In Eq. (III-37) we have explicitly displayed the majority-concentration dependence and the observed activation energy ϵ_3. The calculated values of $\epsilon_3-\epsilon_e$ are obtained from Table II. When excited states are unimportant, $l_e=1$ and $\epsilon_e=0$.

IV. CONCLUSION AND COMPARISON WITH EXPERIMENT

A. Temperature Dependence

As was pointed out in Sec. IIID, a simple activation energy obtains if excited states are not important. This type of temperature dependence is generally observed.[2,6] For low compensations K, this activation energy is given by Eq. (III-33) and is

$$\epsilon=(e^2/\kappa_0)(4\pi n_D/3)^{\frac{1}{3}}(1-1.35K^{\frac{1}{3}}).$$

For higher K, the activation energy is given in Table II of Sec. IIID. We present a comparison of these results with measurements of Ray[28] on n-type Si in Table III.

There are two sets of calculated values in Table III since K is believed to be between 0.03 and 0.05. The calculated values are obtained from Table II. The agreement is satisfactory.

In Table IV we present a similar comparison for measurements of Fritzsche[4] on Sb-doped Ge near 2°K. K is again uncertain, but believed to be between 0.02 and 0.06. Since excited states are important in Sb-doped Ge, we have obtained the calculated values in Table IV from Eq. (III-33), i.e., $\epsilon_3=\epsilon+\epsilon_e$. Table II provides ϵ and ϵ_e is computed from Eq. (A-4) at $T=2$°K. The value of ϵ_e turns out to be 0.13×10^{-3} ev so that the excited state increases the activation energy slightly. Table IV shows satisfactory agreement for $K=0.06$ for the activation energy and its dependence on n_D.

In Table V we present a comparison with results of Fritzsche and Cuevas[29] on p-type Ge in which K is known to be 0.4. From Table II, the calculated activation energy is 0.289 E_A. The agreement in Table V is fair.[30]

We have remarked on the minimum in the resistivity which occurs as a function of compensation for $0.45<K<0.55$. Such a minimum has been observed[5] in p-type Ge for $0.05<K<0.6$.

TABLE III. Activation energies of n-type Si.

Sample number	n_D $\times10^{-16}$ cm^{-3}	Activation energy$\times10^3$ ev. Measured	Calculated $K=0.03$	$K=0.05$
Sb(T-15)	6.05	4.7	4.6	4.0
As(Q-6-2)	6.5	5	4.7	4.2
As(Q-6-4+2)	14	5.8	6.5	5.4

TABLE IV. Activation energies of Sb-doped Ge.

Sample number	n_D $\times10^{-15}$ cm^{-3}	Activation energy$\times10^3$ ev. Measured	Calculated $K=0.02$	$K=0.06$
-5	1.6	0.99	1.2	0.99
-7	2.3	1.1	1.35	1.1
-8	3.0	1.2	1.5	1.2
-10	5.2	1.5	1.7	1.4

B. Majority-Concentration Dependence

From Eq. (III-37) we see that the majority-concentration dependence may be tested by using the observed values for ρ and ϵ_3. If we define

$$Y=\rho(a/r_D)[1+18.2(a/r_D)^{\frac{3}{2}}]^{-1}e^{-\beta\epsilon_3}, \qquad \text{(IV-1)}$$

we have

$$\ln Y=\ln C-\beta\epsilon_e+1.09(r_D/a)^{\frac{3}{2}}, \qquad \text{(IV-2)}$$

where only the last term of Eq. (IV-2) depends on n_D. We use the experimental values at 2.5°K of reference 4, and we expect that the graph of $\ln Y$ vs $(r_D/a)^{\frac{3}{2}}$ will be a straight line with slope 1.09. In Eqs. (IV-1, 2) we need a value for the transverse orbit radius a. The samples are Sb-doped Ge and most of the conduction occurs through the excited states when $T=2.5$°K $(l_e\approx\frac{1}{3})$. The singlet state radius is 69.2A, while the triplet state radius is 71.6A. (These are obtained from the mean of the thermal and optical values of Table I.) We therefore use the weighted average $a=70.8$A. The results are shown in Table VI. The four points of $\ln Y$ vs $(r_D/a)^{\frac{3}{2}}$ lie very well on a straight line of slope 1.03.[31] The agreement is satisfactory.

C. Absolute Magnitude of Resistivity

In the last column of Table VI we have calculated the resistivity from Eq. (III-37). We have used, for n-type Ge, the values $n=4$, $s=4.92\times10^5$ cm/sec, $E_1=11.4$ ev,[32] $a=70.8$ A, $\alpha=18.8$. Thus, $C/l_e=9.6\times10^{-3}$ ohm-cm. The agreement is fair. The magnitude of ρ is the least reliable part of the calculation due to uncertainties connected with the treatment of the effective-mass anisotropy, the deformation potential constant, and the spread in orbit radius due to zero-point lattice motion. The latter will affect the computed value of ρ

TABLE V. Activation energies of p-type Ge.

Sample number	n_A $\times10^{-15}$ cm^{-3}	Activation energy$\times10^4$ ev. Measured	Calculated
1A	0.756	3.23	3.8
2 OR	1.19	5.2	4.5
3A	1.45	5.2	4.8
4A	3.20	5.9	6.2

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[28] R. K. Ray (private communication).

[29] H. Fritzsche and M. Cuevas, Phys. Rev. **119**, 1238 (1960), and private communication.

[30] Our discussion has been carried out for n type but the temperature and compensation dependences which we have derived are also valid for p type.

[31] Use of the singlet state radius rather than that of the average would make the slope 1.00. Use of the triplet radius, would make the slope 1.05 and change the calculated ρ by 30%.

[32] The value of the deformation potential constant E_1 takes into account both shearing strain and dilation.

TABLE VI. Majority concentration dependence in Sb-doped Ge.

Sample number	$n_D\times10^{-15}$ cm^{-3}	ρ (2.5°K) $\times10^{-6}$ ohm-cm	$\epsilon_3\times10^3$ ev	$(r_D/a)^{\frac{3}{2}}$	$\ln Y$	ρ (calculated) $\times10^{-6}$ ohm-cm
−5	1.6	5.8×10^3	0.99	20.4	15.3	2.2×10^4
−7	2.3	3.2×10^2	1.1	17.1	11.9	10.0×10^2
−8	3.0	50	1.2	14.9	9.56	138
−10	5.2	5.6	1.5	11.4	6.01	11.0

by about 30% and the same is true of the uncertainty arising from the choice of transverse orbit radius.[31] Because of the small transverse orbit radius in n-type Si, the magnitude of ρ is extremely sensitive to the donor concentration which is difficult to determine accurately. We therefore do not discuss the absolute magnitude of the resistivity of n-type Si. However, we have included such samples in the discussion of the activation energy since it depends only weakly on donor concentration ($\epsilon_3\propto n_D^{\frac{1}{3}}$).

D. Magnetoresistance in Weak Fields

It is possible to discuss the corrections to the electron transition rate due to the presence of a magnetic field of the order of, say, 3000 oe. The changes arise from the modification of the electron wave functions. We do not give the details[17] here but merely quote the result that the corrections are extremely small, of the order of 1% or less. This conclusion is consistent with the experimental results.[2]

E. Exchange Between Donor Sites

The exchange integral between two donor electrons, while not germane to the present problem, is of interest in other work, particularly in spin resonance studies.[33] The integral is defined by

$$J_e=\int\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)(e^2)\kappa_0 r_{12})\psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2,$$

and may be evaluated by methods similar to those we have used for the transfer integral L in Sec. II. The result is

$$|J_e|^2=n^{-4}[\sum_{pp'}I_{pp}{}^*I_{p'p'}+\sum_{p,q;\,p\neq q}|I_{pq}|^2],$$

where[34]

$$\begin{aligned}I_{pq}=(e^2/5\kappa_0 a)\{&(25/8-23R/4a\\&-3R^2/a^2-R^3/3a^3)e^{-(R_p+R_q)/a}\\&+(6a/R)[T_{pq}(\gamma+\ln R/a)\\&+V_{pq}\,\mathrm{Ei}(-2R_p/a-2R_q/a)\\&-2T_{qq}{}^{\frac{1}{2}}V_{pp}{}^{\frac{1}{2}}\,\mathrm{Ei}(-2R_p/a)]\},\end{aligned}$$

and

$$T_{pq}=(1+R/a+R^2/3a^2)^2e^{-(R_p+R_q)/a},$$

$$V_{pq}=(1-R/a+R^2/3a^2)^2e^{(R_p+R_q)/a},$$

$$\mathrm{E}_i(-x)=-\int_x^\infty(e^{-t}/t)dt,$$

$$\gamma=0.57722.$$

In the above, n is the number of conduction band minima which are labeled by p and q, and R_p is defined in connection with Eq. (II-17).

F. Time-Dependent Fields

We shall merely make a remark on the modifications necessary if the external field is time dependent.

The steady state will not be obtained so that the left-hand side of Eq. (III-2) must be set equal to $\partial f_j{}^\beta/\partial t$. If the transformation used to obtain Eqs. (III-7, 10) is again made, it is found that Eq. (III-10) still holds but that the potentials V_{ij} are determined by

$$\sum_{i(\alpha)\neq j(\beta)}V_{j(\alpha),i(\beta)}/Z_{i(\alpha),j(\beta)}=C_j{}^\beta d(E_j{}^\beta-V_{j(\beta)})/dt,$$

which replaces Eq. (III-7). In the above $V_{i(\alpha),j(\beta)}=V_{i(\alpha)}-V_{j(\beta)}$ and $C_j{}^\beta$ is defined as $(e^2/S)\beta f_j{}^\beta(1-f_j{}^\beta)$ where $f_j{}^\beta$ is given by Eq. (III-3).

This result expresses Kirchhoff's rule for a circuit similar to that described in the text. The necessary modification is that attached to each site $j(\beta)$, there is a generator with emf of value $E_j{}^\beta$. The generator, in turn, is connected to a condenser of capacity $C_j{}^\beta$ and the condenser is connected to ground.

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APPENDIX A. EFFECT OF EXCITED STATES

In general, the impedance $Z_{i(\alpha),j(\beta)}$ between states α on i and β on j is given by Eq. (III-9). Let ν be the degeneracy of the excited state and Δ_e its energy referred to the ground state. The degenerate states at

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[33] G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959), and references quoted therein; C. P. Slichter, Phys. Rev. **99**, 479 (1955); G. Feher, R. C. Fletcher, and E. A. Gere, Phys. Rev. **100**, 1784 (1955); A. Honig and E. Stupp, Phys. Rev. **117**, 69 (1960).

[34] I_{pp} has been evaluated for the hydrogen molecule by Y. Sugiura, Z. Physik **45**, 484 (1927).

a given site are at the same potential so we shall take the ν^2 impedances connecting an excited state on one site to one on another in parallel.

We do not expect the ground state to be at the same potential as the excited states at the same site. However, a calculation similar to that of Sec. II shows that the ratio of the transfer rate between neighboring sites to that between two states on the same site is of order $(W/\Delta)^2$. This is small so that it is a good approximation to take all elements between two sites in parallel.

The net impedance between sites i and j is

$$Z_{ij}^{-1}=\sum_{\alpha,\beta} Z_{i(\alpha),j(\beta)}^{-1}. \tag{A-1}$$

If we use Eq. (III-9) for $Z_{i(\alpha),j(\beta)}$ and perform the sum in Eq. (A-1), we find the results quoted in the text, $Z_{ij}=l_eZ_g$, Eqs. (III-22–26) where

$$\begin{aligned} l_e=(1+\nu e^{-\beta\Delta_e})\{1+\nu^2e^{-\beta\Delta_e}+(\nu/\Delta)(1-e^{-\beta\Delta}) \\ \times[(\Delta-\Delta_e)/(1-e^{-\beta(\Delta-\Delta_e)}) \\ +(\Delta+\Delta_e)e^{-\beta\Delta_e}/(1-e^{-\beta(\Delta+\Delta_e)})]\}^{-1}. \end{aligned} \tag{A-2}$$

We have written l_e in the case that there is a single ν-fold degenerate excited state. The generalization to other cases is straightforward. We note that Z_g is the impedance in the absence of excited states whose entire effect is contained in the factor l_e.

In the limit $\Delta_e\rightarrow 0$, $l_e^{-1}\rightarrow \nu+1$, i.e., there is a $(\nu+1)$-fold degenerate ground state. In the limit $\Delta_e\rightarrow\infty$, $l_e^{-1}\rightarrow 1$, i.e., the excited states do not contribute. In the case the phonon energy $\Delta=0$, we have

$$l_e=(1+\nu e^{-\beta\Delta_e})[1-2\beta\nu\Delta_e/(1-e^{\beta\Delta_e})+\nu^2e^{-\beta\Delta_e}]^{-1}. \tag{A-3}$$

It is possible to show[17] that the effect of zero-point lattice motion on the excited state energies does not materially affect these results or those of Sec. IIIB which give the Fermi energy.

Finally, for use in Sec. IIID, we need the excited-state contribution, ϵ_e, to the activation energy. According to Eq. (III-32), this is the logarithmic derivative with respect to β of Eq. (A-3):

$$\frac{\epsilon_e}{\Delta_e\nu}=-\frac{1}{\nu+e^{\beta\Delta e}}+\frac{2-2\beta\Delta_e/(1-e^{\beta\Delta e})-\nu(1-e^{-\beta\Delta e})}{1-e^{\beta\Delta e}-\nu^2(1-e^{-\beta\Delta e})-2\beta\Delta_e\nu}. \tag{A-4}$$

APPENDIX B. INTEGRATION FOR IMPEDANCE DISTRIBUTION

We perform the integral for the expected number of elements with impedance less than Z_0, Eq. (III-27):

$$g(Z_0)=4\pi n_D\int\int\gamma(R)R^2F(E)dEdR, \tag{B-1}$$

where the limits of integration are defined by

$$Z(R,E,\Delta=0)\leqslant Z_0. \tag{B-2}$$

From Eqs. (III-22–25), we have

$$Z(R,E,0)=Bl_eR^{-\frac{3}{2}}e^{2R/a}2[1+\cosh\beta(E-\zeta_g)]. \tag{B-3}$$

We shall perform the integral over E first, using Eq. (III-15) for $F(E)$. We define R_0 and R_g by

$$Z(R_0,0,0)=Z_0,$$
$$Z(R_g,\zeta_g,0)=Z_0.$$

Then, from Eq. (B-2), the limits on the E integral are

$$0<R<R_0,\quad 0<E<E^+(R),$$
$$R_0<R<R_g,\quad E^-(R)<E<E^+(R),$$

where

$$Z(R,E^+,0)=Z_0,$$
$$E^+-\zeta_g=\zeta_g-E^-,\quad (R_0<R<R_g).$$

The result of the integration is

$$\begin{aligned} g(Z_0)=4\pi n_D\bigg\{\int_0^{R_0}\gamma(R)R^2\exp(-E_A/E^+)^3dR \\ -\int_{R_0}^{R_g}\gamma(R)R^2[\exp(-E_A/E^-)^3 \\ -\exp(-E_A/E^+)^3]dR\bigg\}. \end{aligned} \tag{B-4}$$

The first integral of Eq. (B-4) may be evaluated by expanding the exponential about $E^+=\infty$. The first term predominates. The second integral is only over a small range in R and we therefore evaluate the slowly varying factor $\gamma(R)R^2$ at R_0. The final result is

$$g(Z_0)=4\pi n_D\left[\int_0^{R_0}\gamma(R)R^2dR+\beta E_AaR_0^2\gamma(R_0)I/6\right],$$

where the relation between Z_0 and R_0 is Eq. (B-3) with $E=0$ and I is a number depending only on compensation and is

$$I=\left(\int_{x/8}^{x}-\int_{x}^{\infty}\right)u^{-\frac{4}{3}}e^{-u}du,\quad x=(E_A/\zeta_g)^3. \tag{B-5}$$

For compensations $\leqslant 3\%$, $I=4.05$ and for larger compensations, numerical integration leads to the results quoted in Table II of Sec. IIID.