for the mean free path a quantity of order

$$l \sim b^3 q^2/(\Delta b)^2,$$

where b is the mean distance between centres, Δb the root mean square fluctuation and $q = \eta/k$ as before.

A particularly interesting application of these ideas is to the 'tight binding' case, which of course is applicable to impurity-band conduction. The overlap integral between two hydrogen-like centres, of Bohr radius a, distance b apart, is

$$j = 2W_0(1 + b/a)\exp(-b/a).$$

Elementary considerations based on a deformation potential suggest that, for a mean displacement Δb from positions in a periodic lattice, the mean free path will be of order

$$b\Big/\left(\frac{\Delta j}{j}\right)^2, \quad \Delta j = \frac{\partial j}{\partial b}\Delta b.$$

The mean free path l will be of order b when $\Delta j \sim j$ and if $b \gg a$ this will occur when $\Delta b \sim a$, and thus for $\Delta b/b \ll 1$. It is possible—and the experimental evidence reviewed in § 12 suggests that this is the case—that l may become less than b before bound states occur—that is to say, in the three-dimensional case. If so, we shall want to know what happens to formula (22) in this case. No detailed calculations have been given, but we should expect a random fluctuation of the *amplitude* of the wave function on each centre by $\exp(-\Delta b/a)$. Since the normalization of the wave function will be determined by the larger amplitudes, typical terms in the integral for $D_{nn'}$ will be reduced by just this factor. We thus expect the mean free path l to be of order $l \sim b\exp(-2\Delta b/a)$.

6.2. *Bound States in the One-dimensional Model*

The above analysis assumes that the wave functions extend through the lattice (the states are not bound). Actually in one dimension this may not be the case, but the analysis is of some interest on account of its possible extension to three dimensions.

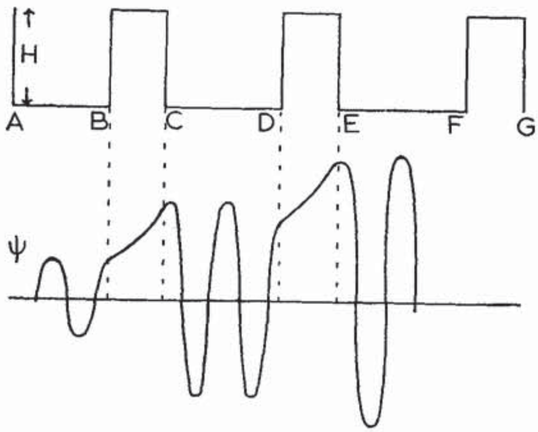
The simplest model for which this may be seen is that in which we take for V a potential of Kronig–Penney type, as shown in fig. 15, namely a series of potential barriers, a mean distance b apart, but such that the root mean square of b is Δb. We supposed that Δb is greater than or comparable with the wave length of ψ in the range AB. We suppose that the two solutions, which increase or decrease exponentially in the range BC, increase or decrease by p or $1/p$, and that p is large.

Consider an oscillating solution in the range AB of form $\psi = \cos(kx + \zeta)$. Then for all phases $\zeta\,(-\pi \leqslant \zeta \leqslant \pi)$, except those in a range of order $1/p$, ψ will increase in the range BC. If ψ has increased in the range BC, then, whatever the phase in AB, ψ will in general increase again by the factor p in DE. Thus the solution with arbitrary phase in AB increases exponentially as x increases, and by the same argument will increase exponentially as x diminishes. Such a solution is shown in fig. 15 and obviously has no physical significance.

As we have seen, for all phases ζ in AB except those in a range $\Delta\zeta \sim 1/p$, ψ increases in BC; and for these solutions ζ varies only by $1/p$ in CD, by $1/p^2$ in EF and so on. Thus our typical solution, obtained by starting with arbitrary energy and phase in an interval such as AB, will increase exponentially in both directions, the phase becoming more closely defined as the distance from AB increases. It is of course possible to choose the phase in AB so as to give an exponential solution which increases or decreases over any relevant range of x.

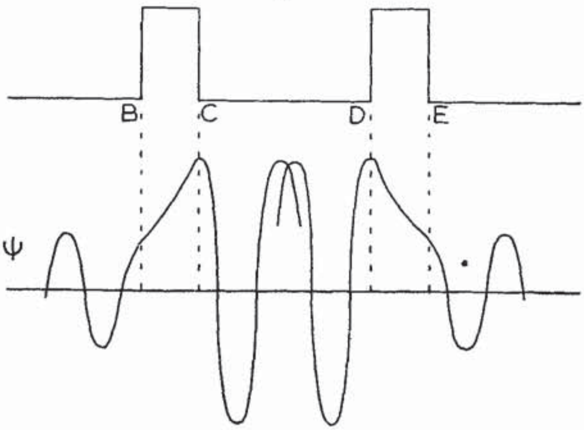
The stationary solution may be found as follows. Take any gap in the potential energy, for instance CD. For any energy W, one can set up solutions from both sides which increase as one comes towards CD. In general these solutions will not fit in the middle (fig. 16), but one can choose values of the energy such that they do. These are the quantized energy values of the problem.

Fig. 15



Wave function in a one-dimensional disordered lattice.

Fig. 16



Wave functions for a forbidden value of the energy.

Our conclusion that the stationary solutions of the problem correspond to bound states thus holds unless there is an accidental degeneracy. Although for a one-dimensional space of length L the energy levels are spaced very closely, such that

$$\Delta W \sim Wb/L,$$

two localized wave functions distant in space na apart must have the same energy to any accuracy of order $W\,(1/p)^n$ to give a resonance, and this will be unlikely.

We have assumed that $k\Delta b \sim 1$. If $k\Delta b$ is small and the energy is chosen in the allowed band-width, it is clear that the average increase of ψ in going through each barrier is not

$$p = \exp\,[b\{2m(H-E)/\hbar^2\}^{1/2}],$$

where H is the height of a barrier, but of order

$$\exp\,[\Delta b\{2m(H-E)/\hbar^2\}].$$

For a periodic field ($\Delta b = 0$) the states are of course not localized. We have not been able to extend the proof to a more general case.

§ 7. The Interaction of Localized Carriers with Lattice Vibrations

In this section we shall be dealing throughout with a three-dimensional lattice. Our problem is to discuss the movement of an electron from centre to centre under conditions in which the states are localized, so that lattice vibrations are essential in making the transitions possible. We have to distinguish between strong coupling, appropriate to ionic lattices, and weak coupling, appropriate to silicon and germanium. In the former case, we have to show how the concept of a polaron arises.

In the strong coupling case we may consider the compound $\mathrm{Li}_x\,\mathrm{Ni}_{1-x}\mathrm{O}$. Here a small fraction of Ni^{2+} ions have been replaced by Li^+ ions, with the formation of Ni^{3+} ions to preserve electrical neutrality. Each of these can be regarded as a positive hole bound to a Ni^{2+} site. We discuss the motion of this hole through the lattice of Ni^{2+} ions; the potential that hole experiences is not perfectly periodic, due to the random arrangement of Li^+ ions. This problem has been treated by Yamashita and Kurosawa (1958, 1960) and Sewell (1958). Since the carrier-lattice coupling is strong it cannot be treated as a perturbation, as is done in the usual theory of conduction by Bloch electrons. In a more exact treatment of the lattice coupling, we find that the hole bound to a given Ni^{2+} ion moves in the potential of that ion and of the polarization field produced by the displacement of the surrounding ions from their equilibrium positions. Thermal vibrations of the lattice ions are about the displaced positions. Thus the bound hole can be represented by the wave function

$$\phi_i(\mathbf{r}-\mathbf{R}_i)\prod_{\sigma} X_{n_\sigma}\{Q_\sigma(\mathbf{R}_i)\}, \qquad (23)$$

which includes explicitly the interaction between lattice and hole. Here $\mathbf{R}_i$ is the position of the ith nickel ion, $\mathbf{r}$ the coordinate of the hole, Q_σ a phonon coordinate and n_σ the number of phonons in the mode σ. The Hamiltonian of the hole can be written

$$\mathscr{H} = \mathscr{H}_{\mathrm{h}} + \mathscr{H}_{\mathrm{int}} + \mathscr{H}_{\mathrm{L}},$$

where

$$\mathscr{H}_{\mathrm{L}} = \tfrac{1}{2}\sum (P_\sigma^2 + \omega_\sigma^2 Q_\sigma^2),$$

so that $\mathscr{H}_{\mathrm{L}}$ describes the lattice vibrations and Q_σ is the displacement of the vibration σ. The term

$$\mathscr{H}_{\mathrm{h}} = p^2/2m + \sum_j U(\mathbf{r}-\mathbf{R}_j) + \Delta U(\mathbf{r}),$$

describes the hole, with momentum p, moving in the field of the potential energy $U(\mathbf{r}-\mathbf{R}_j)$ due to nickel ions at points $\mathbf{R}_j$. The sum is over all lattice sites j. ΔU describes the corrections to the periodic potential due to other positive holes and Li$^+$ ions. The lattice-hole interaction is of the form

$$\mathscr{H}_{\mathrm{int}} = \sum C_\sigma \exp(i\boldsymbol{\tau}_\sigma \mathbf{r})\, Q_\sigma, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where $\boldsymbol{\tau}_\sigma$ is the wave vector of mode σ, and C_σ includes the coupling constant. A variational technique (see, for example, Fröhlich 1954) is used to find an eigenfunction in the form $\phi_i(\mathbf{r}-\mathbf{R}_i)X_n(Q^{(i)})$ to the Hamiltonian

$$\mathscr{H}^{(i)} = \mathscr{H}_{\mathrm{h}}^{(i)} + \mathscr{H}_{\mathrm{int}} + \mathscr{H}_{\mathrm{L}},$$

where

$$\mathscr{H}_{\mathrm{h}}^{(i)} = p^2/2m + U(\mathbf{r}-\mathbf{R}_i) + \Delta U(\mathbf{r}).$$

Then ϕ_i is required to be a solution of

$$\{p^2/2m + U(\mathbf{r}-\mathbf{R}_i) + \Delta U(\mathbf{r}) + \langle X^* \,|\, \mathscr{H}_{\mathrm{int}} \,|\, X\rangle\}\phi(\mathbf{r}-\mathbf{R}_i) = \epsilon_i \phi_i(\mathbf{r}-\mathbf{R}_i). \quad (25)$$

The term $\langle X^* \,|\, \mathscr{H} \,|\, X\rangle$ describes the polarization field of the surrounding ions. We see that ϕ_i is predominantly just the wave function of a hole localised in the potential $U(\mathbf{r}-\mathbf{R}_i)$. Similarly, $X_n(Q^{(i)})$ must satisfy

$$\{\tfrac{1}{2}\sum(P_\sigma^2 + \omega_\sigma^2 Q_\sigma^2) + \langle \phi_i^*(\mathbf{r}) \,|\, \mathscr{H}_{\mathrm{int}} \,|\, \phi_i(\mathbf{r})\rangle\}X_n = \epsilon_n X_n. \quad . \quad . \quad (26)$$

From (24),

$$\langle \phi_i^* \,|\, \mathscr{H}_{\mathrm{int}} \,|\, \phi_i\rangle = \sum C_\sigma \langle \phi_i^* \,|\exp(i\boldsymbol{\tau}_\sigma \mathbf{r})\,|\, \phi_i\rangle Q_\sigma = \sum_\sigma A_\sigma^{(i)} Q_\sigma. \quad . \quad (27)$$

By a change of coordinates, namely

$$Q_\sigma = Q_\sigma^{(i)} - C_\sigma^{(i)}, \quad C_\sigma^{(i)} = A_\sigma^{(i)}/\omega_\sigma^2, \qquad . \quad . \quad . \quad . \quad (28)$$

(26) becomes

$$\tfrac{1}{2}\sum (P_\sigma^2 + \omega_\sigma^2 Q_\sigma^{(i)2})\, X_n^{(i)} = \epsilon_n{}'\, X_n^{(i)}.$$

Thus X_n is a product of single mode oscillator functions,

$$X_n^{(i)} = \prod X_{n_\sigma}[Q_\sigma^{(i)}],$$

each having the displaced coordinate $Q_\sigma^{(i)}$. The energy corresponding to the state $\phi_i X_n$ is ϵ_{in}, where

$$\epsilon_{in} = \epsilon_i + \epsilon'_n = \epsilon_i + \sum(n_\sigma + \tfrac{1}{2})\hbar\omega_\sigma - \sum |A_\sigma^{(i)}|^2/2\omega_\sigma. \quad . \quad . \quad (29)$$

We can now treat the potential $(\mathscr{H}_{\mathrm{h}} - \mathscr{H}_{\mathrm{h}}^{(i)})$ due to the other lattice sites as the perturbation which causes the hole to move. This is analogous to the usual Bloch tight-binding approach. In the Bloch case, however, one starts with a product of an atomic orbital $\psi(r-R_j)$ and phonon functions $X_n(Q)$, X_n being independent of the site R_i. A hole (or electron) with wave vector k is the described by

$$\psi_k = \{\sum_i \exp(i\mathbf{kR}_i)\,\psi(\mathbf{r}-\mathbf{R}_i)\}\,X_n(q)$$

and has energy, for example, for a simple cubic lattice with spacing a,

$$\epsilon_k = \epsilon_0 + 2M_{\mathrm{B}}(\cos\mathbf{ka}).$$

Here

$$M_{\mathrm{B}} = \{\phi_i(\mathbf{r}-\mathbf{R}_i)[\mathscr{H} - \mathscr{H}_{\mathrm{h}}^{(i)}]\,\phi_j(\mathbf{r}-\mathbf{R}_i)\,d\tau\}\langle X_n \,|\, X_n\rangle, \quad . \quad (29\,a)$$

where sites i and j are nearest neighbours. We note that the bandwidth $12M_{\mathrm{B}}$ and the effective mass m^* of the hole $(m^* = \hbar^2/(\partial^2\epsilon_k/\partial k^2)$ are independent of temperature, since $\langle X_n \,|\, X_n\rangle$ in the Bloch scheme. In a similar way, we can use the functions $\phi_i X_n^{(i)}$ to describe a polaron with wave vector k,

$$\psi_k = \sum \phi_i(\mathbf{r}-\mathbf{R}_i)\,X_n^{(i)}\exp(i\mathbf{kR}_i),$$

and energy

$$\epsilon_k = \epsilon_0 + 2M\cos(\mathbf{ka}),$$

where now

$$M = M_{\mathrm{B}}\,\langle X_n^{(i)} \,|\, X_n^{(j)}\rangle.$$

The polaron bandwidth and effective mass are temperature dependent, since the overlap $\langle X_n^{(i)} \,|\, X_n^{(j)}\rangle$ of the phonon functions is not equal to unity but is a function of the number n of phonons present. We may estimate the magnitude of this overlap at a temperature T by taking an average† value:

$$\begin{aligned}\langle X_n^{(i)} \,|\, X_n^{(j)}\rangle &= \{\prod \langle X_{n_\sigma}(Q_\sigma^{(i)}) \,|\, X_{n_\sigma}(Q_\sigma^{(j)})\rangle\}_{\mathrm{ave}} \\ &= \prod_\sigma \{2\sinh(\hbar\omega_\sigma/2kT)\} \sum_{n_\sigma} \exp\{-(n_\sigma + \tfrac{1}{2})\hbar\omega_\sigma/kT\}\langle X_{n_\sigma}(Q^{(i)}) \,|\, X_{n_\sigma}(Q^{(j)})\rangle \\ &= e^{-S}, \qquad \ldots \qquad (30)\end{aligned}$$

where

$$S = \tfrac{1}{4}\sum (C_\sigma^{(i)} - C_\sigma^{(j)})^2\,\omega_\sigma(2\bar{n}_\sigma + 1)/\hbar,$$

and $\bar{n}_\sigma$ is the mean number of phonons in mode σ at temperature T. The polaron effective mass m^* is therefore larger by a factor e^S than that calculated from the Bloch tight-binding model, and increases with temperature. This is because the moving hole must carry with it the polarisation of the surrounding lattice. Yamashita and Kurosawa (1958) have quoted values of S at $T = 0$ (appropriate to $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$ ranging from 15 for the smallest value of x to 4–5 for the larger. Thus the mobility of a hole propagating as a wave may be very small.

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† The averaging above can be performed by a method due to O'Rourke (1953).

The magnitude of S is a suitable criterion for giving meaning to the terms 'weak' or 'strong' coupling. The carrier-lattice coupling is strong if $S \gg 1$, and conversely when $S \ll 1$ the coupling is weak. This is a reasonable definition, for from (28, 30).

$$S \sim \tfrac{1}{2} \langle (\Delta l_\sigma / l_\sigma)^2 \rangle,$$

where $\Delta l_\sigma \sim C_\sigma^{(i)}/M^{1/2}$ is the shift in the centre of oscillation of mode σ, $l_\sigma = (\hbar / M\omega_\sigma)^{1/2}$ is the mean amplitude of oscillation of mode σ at $T=0$ and the averaging is over all modes σ. Thus, for example, the polaron energy spectrum ϵ_k tends to that of an electron in the usual Bloch tight-binding approximation as $S \to 0$, as would be expected for small coupling.

In the following paragraphs we shall indicate how the hole mobility is calculated when the states are localized, so that the conduction mechanism is that of a hole jumping to neighbouring sites with the emission or absorption of phonons. The probability per unit time that a hole jumps from site i to j, with a change in the phonon state from n to n', is

$$W_{in, jn'} = (2\pi/\hbar) \, | M_{in, jn'} |^2 \, \delta\, (\epsilon_{in} - \epsilon_{jn'}), \quad . \quad . \quad . \quad . \quad (31)$$

where the energies ϵ_{in} are given by (29), and

$$M_{in, jn'} = \langle \phi(\mathbf{r} - \mathbf{R}_i) X_n^{(i)} \,|\, \mathscr{H}_{\mathrm{h}} - \mathscr{H}_{\mathrm{h}}^{(i)} \,|\, \phi(\mathbf{r} - \mathbf{R}_j) X_{n'}^{(j)} \rangle.$$

To obtain the total transition rate W_{ij} of the hole from i to j, $W_{in, jn'}$ must be summed over final phonon states n' and averaged over n. Thus

$$W_{ij} = (2\pi/\hbar) | M_{\mathrm{B}} |^2 \sum_{n, n'} p_n \, | \langle X_n^{(i)} | X_{n'}^{(j)} \rangle |^2 \, \delta[\Delta\epsilon + \textstyle\sum (n_0 - n_0') \hbar\omega_0]. \qquad (32)$$

Here M_{B} is as in (29 a), p_n is the probability that the state n is occupied at temperature T, and for the energy difference $\epsilon_{in} - \epsilon_{jn'}$ the value (29) has been substituted, and

$$\Delta\epsilon = \epsilon_i - \epsilon_j = \langle \phi_i \,|\, \Delta U(\mathbf{r}) \,|\, \phi_i \rangle - \langle \phi_j \,|\, \Delta U(\mathbf{r}) \,|\, \phi_j \rangle.$$

The evaluation of the summation in W_{ij} has been performed by several authors (references are given by Yamashita and Kurosawa 1960). We have

$$W_{ij} = \frac{1}{\hbar^2} | M_{\mathrm{B}} |^2 \exp\,[-S(T)] \int_{-\infty}^{\infty} \exp\,[i\Delta\epsilon t/\hbar + G(T, t)]\, dt, \quad . \quad (33)$$

where

$$G(T, t) = \tfrac{1}{2} \sum \{ (2\bar{n}_\sigma + 1) \cos \omega_\sigma t + i \sin \omega_\sigma t \} \, \omega_\sigma \, (C_\sigma^{(i)} - C_\sigma^{(j)}) (C^{(i)} C^{(j)})^2 / \hbar \qquad (34)$$

and $S(T)$ is as derived earlier (30). We note that an expansion

$$\exp\,[G(T, t)] = 1 + G + \tfrac{1}{2} G^2 + \ldots, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

and a term by term integration over t gives essentially the contributions to W_{ij} due to zero, one, two . . . phonon transitions (since G is proportional, through $C_\sigma^{(i)}$, to the phonon-hole coupling constant squared). $G(T, t)$ can be seen to have a magnitude comparable to S for a range of t values around $t = 0$. If t is outside this range, $G(T, t)$ tends rapidly to zero. As we have seen, S can be as large as 15 for $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$. Hence if S is large enough the transitions in which phonons are emitted or absorbed will dominate the zero phonon rate, and as discussed in § 5 the electron will be 'self-trapped' at site i. Similarly, the higher terms in the expansion (35) (multiphonon transitions) will dominate the term linear in G (single phonon transitions).

The evaluation of W_{ij} from (33), which has been treated in the previous reference, is difficult and will not be discussed further here, since we are primarily interested in impurity conduction in valance semiconductors. We note that, assuming the Einstein relationship, a hole mobility μ may be calculated,

$$\mu = (ea^2/kT)W_{ij},$$

where a is the spacing of the Ni^{2+} ions (the mean jump distance of the holes).

We now discuss the case of *weak coupling*, appropriate to impurity conduction in valence semiconductors. We consider the motion of a hole bound to a donor atom (in n-type germanium with a small degree of compensation, say) surrounded by randomly placed charged donor and acceptor centres. By the same methods as in previous paragraphs we find that the strength of the interaction of the hole with the lattice depends on S, which can be estimated through the deformation potential constant E_1 (Bardeen and Shockley 1950). The 'displacement' $C_\sigma^{(i)}$ occurring in S is, from (25–28),

$$\begin{aligned} C_\sigma^{(i)} &= \frac{M^{1/2}\omega_\sigma^2}{iE_1\tau_\sigma}\langle\phi(r-R_i)|\exp\{i\boldsymbol{\tau}_\sigma(\mathbf{r}-\mathbf{R}_i)\}|\phi(\mathbf{r}-\mathbf{R}_i)\rangle \\ &= i(E_1\tau_\sigma/M^{1/2}\omega_\sigma^2)\{1+(\tfrac{1}{2}a_0\tau_\sigma)^2\}^{-2}, \qquad (36) \end{aligned}$$

assuming that $\phi(\mathbf{r}-\mathbf{R}_i)$ describes a donor electron in an s level, with effective Bohr radius a_0. If the phonons are in phase at site i, the phases at site j will be random; thus $C_\sigma^{(j)}$ can be neglected. The sum over σ can be replaced by an intergration, using a Debye spectrum (cf. Lax and Burstein 1955).

$$S = \frac{3}{\omega_m^3}\int_0^{\omega_m}\frac{\omega}{\hbar}|C_\sigma^{(i)}|^2\omega^2\,d\omega = \frac{E_i^2\hbar^2}{Ma_0^2(k\Theta_\mathrm{D})^3}, \qquad (37)$$

where

$$\omega_m = k\Theta_\mathrm{D}/\hbar$$

and Θ_D is the Debye temperature. Using constants appropriate to n-type germanium, $E_1 = 15\,\mathrm{ev}$, $a_0 = 44\,\text{Å}$, $\Theta_\mathrm{D} = 362\,^\circ\mathrm{K}$ and $M = 2{\cdot}46\times10^{-22}\,\mathrm{g}$ (twice the mass of the lattice atom since there are two atoms per unit cell), we find $S = 0{\cdot}10$. At finite temperatures,

$$S(T) = \frac{3}{\omega_m^3}\int\frac{\omega}{\hbar}|C_\sigma^{(i)}|^2\coth\frac{\hbar\omega_0}{2kT}\omega^2\,d\omega \simeq S(0)\left\{1+3\left(\frac{T}{\Delta}\right)^2\right\} \quad . \quad (38)$$

when T/Δ is small. Here, if v is the velocity of sound in the crystal, $k\Delta = \hbar v/a_0$ is the energy of a phonon with wavelength comparable to a_0; these phonons interact most effectively with the localized electrons. For germanium, using $v = 5{\cdot}3\times10^5\,\mathrm{cm\,sec}^{-1}$, we find $\Delta \simeq 9\,^\circ\mathrm{K}$. Hence $S(T)$ is small throughout the temperature region in which impurity conduction is important ($T \lesssim 5\,^\circ\mathrm{K}$) in germanium.

The transition probability W_{ij} can be calculated in a similar manner to that for the strong coupling case. We study the motion of a single electron in a random lattice of $N+1$ positive and N negative centres. This is equivalent to n-type impurity conduction, in which all except one electron are assumed to be stationary. The electron Hamiltonian is

$$\mathscr{H}_{\mathrm{e}}=p^2/2m^*+\sum_{\nu} v(\mathbf{r}-\mathbf{R}_{\nu})-\sum_{i} v(\mathbf{r}-\mathbf{R}_{i}),$$

where

$$v(\mathbf{r}-\mathbf{R})=e^2/\kappa\,|\,\mathbf{r}-\mathbf{R}\,|$$

and $\mathbf{R}_{\nu}$ is the coordinate of a negatively charged centre, $\mathbf{R}_i$ that of a positive one. The overlap between electron wave functions centred on adjacent positive centres must be treated carefully, since the conductivity will vanish in the absence of overlap. Let

$$u_i=u\,(\mathbf{r}-\mathbf{R}_i)$$

be the wave function of an electron on an isolated donor, and

$$\langle u_i\,|\,u_j\rangle=\Delta_{ij}\;(\neq 0)$$

be the overlap integral. Then (Löwdin 1956), the funtions

$$\phi_i(r)=\sum_{j}\Delta_{ij}{}^{-1/2}\,u_j(r) \qquad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

form an orthogonal set. The sum is over all positive centres. Matrix elements of $\mathscr{H}_{\mathrm{e}}$ in terms of the ϕ_i are

$$\langle\phi_i\,|\,\mathscr{H}_{\mathrm{e}}\,|\,\phi_j\rangle=\epsilon^0\,\delta_{ij}\;V_{ij},$$

where ϵ^0 is the energy of an isolated donor electron, and

$$V_{ij}=\sum_{k,\,l}\Delta_{ik}{}^{-1/2}\,V_{kl}{}^0\,\Delta_{lj}{}^{-1/2}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$V_{kl}{}^0$ is the matrix element of the electrostatic potential of all centres except the lth positive one; so that

$$V_{kl}{}^0=\langle u_k(\mathbf{r})\,|\,\sum_{\nu} v(\mathbf{r}-\mathbf{R}_{\nu})-\sum_{i\neq l} v(\mathbf{r}-\mathbf{R}_i)|\,u_l(\mathbf{r})\,\rangle. \qquad . \quad . \quad (41)$$

Thus the ϕ_i describe electrons with energy ϵ_i,

$$\epsilon_i=\epsilon^0+V_{ii},$$

the energy ϵ_{ii} arising from the potential of the surrounding randomly placed charged centres. Since the overlap Δ_{ij} is small,

$$\phi_i(r)\simeq u_i(\mathbf{r})-\tfrac{1}{2}\,\Delta_{ij}\,u_j\,(\mathbf{r}).$$

Thus ϕ_i is mainly localized about the ith positive centre, and the off-diagonal elements V_{ij} lead to transitions of the electron from i to j.

The electron-lattice interaction can now be treated in exactly the same way as for the strong coupling case. We find that associated with the state $\phi_i(\mathbf{r})$ is a set of lattice vibrations described by the oscillator functions $X_{n_\sigma}(Q_\sigma{}^{(i)})$; n_σ is the number of phonons in mode σ. The displaced coordinates $Q_\sigma{}^{(i)}$ are by (28)

$$Q_\sigma{}^{(i)}=Q_\sigma+C_\sigma{}^{(i)},$$

where $C_\sigma^{(i)}$ is given by (36) to the lowest order in the overlap. The expression for the transition probability W_{ij} is therefore of the same form as (33), with V_{ij} replacing M;

$$W_{ij} = \frac{1}{\hbar^2} |V_{ij}|^2 \exp\{-S(T)\} \int \exp\{G(T,t) + i\,(\epsilon_i - \epsilon_j)t/\hbar\}\,dt, \quad . \quad (42)$$

where $G(T,t)$ is given by (34) and

$$\epsilon_i - \epsilon_j = V_{ii} - V_{jj} \simeq \langle u_i | v(\mathbf{r} - \mathbf{R}_i) | u_i \rangle - \Delta_{ij} \langle u_j | v(\mathbf{r} - \mathbf{R}_i) u_i \rangle$$

to the lowest order in the overlap and neglecting all but the nearest-neighbour centre j. Since $S(T)$ and therefore $G(T,t)$ is small, the single phonon contributions to W_{ij} dominate, and thus in (42) $\exp G$ can be replaced by $1 + G$.

Assuming a Debye spectrum of lattice vibrations and performing the sum over modes σ as previously indicated for $S(T)$,

$$\begin{aligned} W_{ij} &\simeq \frac{1}{\hbar^2} |V_{ij}|^2 \int_{-\infty}^{\infty} dt \exp\{i(\epsilon_i - \epsilon_j)t/\hbar\} \frac{3}{2\omega_m{}^3} \int_{-\infty}^{\infty} d\omega \exp(i\omega t) \\ &\quad \times \frac{\omega^3}{2\hbar} |C_\sigma^{(i)} - C_\sigma^{(j)}|^2 \left(1 + \coth \frac{\hbar\omega_\sigma}{2kT}\right) \\ &= 3\pi\, |V_{ij}|^2 \frac{E_1{}^2}{M\hbar v^2 (k\Theta_{\mathrm{D}})^3} \frac{\epsilon_i - \epsilon_j}{[1 + \{(\epsilon_i - \epsilon_j)a_0/2v\hbar^{s2}]^4} \\ &\quad \times \left\{1 + \coth \frac{\epsilon_i - \epsilon_j}{2kT}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43) \end{aligned}$$

We have used the value of $C_\sigma^{(i)}$ calculated in (36).

The two phonon processes, which involve an integration over $\{G(T,t)\}^2$ give a contribution $\sim 10^{-2}$ times the single phonon transition rate (cf. eqn. 35).

§ 8. CALCULATIONS OF IMPURITY CONDUCTION

The theory of impurity conduction has been studied by a number of authors: Aigrain (1954), Baltensperger (1953), Conwell (1956), Erginsoy (1950, 1952), Mott (1956), and Kasuya and Koide (1958). In this section we shall outline the recent work of Miller and Abrahams (1960) and Twose (1959) on conduction in the low concentration region in germanium and silicon. The former authors use the following method.

(*a*) The probability per unit time W_{ij} that an electron jumps to a neighbouring vacant site is calculated, as a function of the separation between the two sites. A phonon is emitted or absorbed to conserve energy, as explained in the previous section.

(*b*) Equations for the rate of change of the probability that an electron occupies a given site and the net current flow, in an electric field, are written down and shown to be equivalent to Kirchoffs' Laws for charge flow in a three-dimensional random resistance network. Each link in the network corresponds to two impurity centres; the link impedance is inversely proportional to W_{ij}, the transition rate between the centres.

(*c*) The network resistivity is computed, assuming that it arises from non-intersect chains of impedances taken in parallel, each link in the chain being chosen in a suitable manner.

In evaluating W_{ij} in the previous section we assumed a simple hydrogenic form for the donor electron wave function,

$$u_i(r) = (\pi a_0{}^3)^{-1/2} \exp(-r/a_0).$$

The correct effective mass wave functions have been described in § 3. Using these wave functions, and averaging over the possible directions in the crystal of the neighbouring vacant site, these authors found

$$\langle W_{ij} \rangle_{\text{ave}} = \frac{E_1{}^2}{2\pi \rho_0 v^5 \hbar^4} U^2 \Delta \{\coth(\Delta/2kT) + 1\},$$

where

$$U^2 = (2e^2/3\kappa a^2)^2 (\pi a/4\alpha R)^{1/2} R^2/n \exp(-2R/a).$$

Here ρ_0 is the density and v the velocity of sound in the crystal, and E_1 the deformation potential constant. The coth describes the number of phonons present with energy $|\Delta|$, where Δ is the difference between the energies of the two centres. R is the distance between the two centres and $\alpha = a^2/b^2 - 1$; a, b are the Bohr radii and n the number of conduction band minima (§ 3).

If f_i is the probability that centre i is occupied by an electron,

$$\partial f_i/\partial t = \sum_j \{W_{ij} f_i (1-f_j) - W_{ji} f_j (1-f_i)\}. \quad . \quad . \quad . \quad . \quad (44)$$

This determines the equilibrium distribution. As in § 2,

$$f_i = 1/[1 + \exp\{(\epsilon_i - \zeta)/kT\}],$$

where ζ is the Fermi energy. From considerations of detailed balancing, we have

$$W_{ij} \exp(\epsilon_j/kT) = W_{ji} \exp(\epsilon_i/kT).$$

In the presence of a small electric field F in the x direction, a different equilibrium distribution f_i' of electrons is formed, determined by a steady-state condition of the form (44) but with f_i replaced by f_i', and the transition probabilities which are altered by the field now obey

$$W_{ij} \exp\{(\epsilon_j - ex_j F)/kT\} = W_{ji} \exp\{(\epsilon_i - ex_i F)/kT\}; \quad . \quad . \quad (45)$$

x_i is here the x coordinate of the ith centre. f_i' can be written formally (assuming local equilibrium), in terms of a parameter E_i, as

$$f_i' = 1/[1 + \exp\{(E_i - \zeta)/kT\}].$$

Substituting this form for f_i' in the steady state condition, using the reciprocal relation (45) and taking terms linear in F only, we find

$$(1/kT) \sum_j \{(\epsilon_i - ex_i F) - (\epsilon_j - ex_j F)\} W_{ij} f_i (1-f_i) = 0.$$

This is of the form of Kirchhoffs' first law for a network, with the term { } corresponding to a potential drop across the 'link' ij, and the link impedance,

$$Z_{ij} \propto \{W_{ij} f_i (1-f_j)\}^{-1}.$$

The problem is thus reduced to determining the impedance of an equivalent resistance network.

The solution of the network problem, in terms of chains of conducting elements, the chains being taken in parallel, is described in detail by Miller and Abrahams (1960). The final result for the resistivity can be written

$$\rho(T)=C(T)(r_{\rm D}/a)\{1+18{\cdot}2(a/r_{\rm D})^{3/2}\}\exp\{1{\cdot}09(r_{\rm D}/a)^{3/2}+(\epsilon_3-\epsilon_{\rm e})/kT\} \qquad (46)$$

where

$$C(T)=4{\cdot}55\times10^2\,l_{\rm e}(T)(\alpha/8)^{1/2}\,\kappa^2 n\rho_0\,v^5\hbar^4a^3/e^6E_1{}^2$$

and

$$r_{\rm D}=(3/4\pi N_{\rm D})^{1/3},\quad \alpha=-1+a^2/b^2.$$

Here a and b are the radii of the effective mass wave functions, n is the number of conduction band minima, ρ_0 the density and v the velocity of sound in the crystal. In the discussion above, the donor electron was assumed to occupy the ground state. $l_{\rm c}$ and $\epsilon_{\rm e}$ contain the effects of excited states, which are shown to be unimportant ($l_{\rm e}=1$, $\epsilon_{\rm e}=1$) except in the case of antimony doped germanium (cf. § 3). Thus $\rho(T)$ is of the form

$$\rho(T)=\rho_0\,(N_{\rm maj})\exp\,(\epsilon_3/kT).$$

In this calculation the whole of the compensation dependence is included in the activation energy ϵ_3, which is given by

$$\epsilon_3=\zeta-1{\cdot}35\,\epsilon_{\rm A},\quad \epsilon_{\rm A}=(e^2/\kappa)(4\pi N_{\rm A}/3)^{1/3}.$$

The determination of the Fermi energy ζ (on the assumption that the energy difference $\epsilon_i-\epsilon_j$ between sites is due to nearest neighbour charged minority sites only) has been described in § 2. If the compensation is small ($K\lesssim0{\cdot}2$)

$$\epsilon_3=\epsilon_{\rm D}-1{\cdot}35\,\epsilon_{\rm A}=(e^2/\kappa)(4\pi N_{\rm D}/3)^{1/3}\,(1-1{\cdot}35K^{1/3}).$$

For higher values of K, values of ϵ_3 are plotted in fig. 8. Although, as we have seen in § 4, the magnitude of ϵ_3 agrees well with experimental values, the temperature dependence of $\rho(T)$ is incorrect since it predicts that all curves plotting ρ against $1/T$ for the same concentration of majority impurity centres extrapolate to the same point at $T=\infty$.

Calculated values of ρ from (46) for antimony-doped germanium are compared with measured values in table 3. The agreement is satisfactory, considering that errors of at least 30% are possible from uncertainties in the effective Bohr radii and the deformation potential constant E_1.

Table 3. Resistivity ρ of germanium doped with antimony (Ω cm × 10^6)

$N_{\rm D}\times10^{-15}$ cm^{-3}	1·6	2·3	3·0	5·2
ρ (2·5 °K)	$5{\cdot}8\times10^3$	$3{\cdot}2\times10^2$	50	5·6
ρ (calculated)	$1{\cdot}1\times10^4$	$5{\cdot}2\times10^2$	89	7·8

Twose (1959) has also calculated the impurity resistivity in the low concentration region by a somewhat different method. A density matrix approach was used, similar to that of Luttinger and Kohn (1958), using as a representation the product $\phi_i(r)X_n(Q^{(i)})$ of electron and oscillator functions, described earlier (§ 7). This leads to an average electron drift velocity $\langle v \rangle$ which is a sum of 'two centre' contributions v_{ij}. Each v_{ij} depends on the charge amplitudes of the electron on sites i and j, and hence $\langle v \rangle$ should be found from a self-consistent treatment of charge diffusion onto and away from a given centre. Instead of this self-consistent approach, the electron was assumed to occupy sites with a Boltzmann probability, leading to a two centre conductivity for N_e electrons of the form

$$\sigma_{ij} = N_e F(R_{ij}) f(T, \epsilon_{ij}).$$

This must then be averaged in suitable way over the random separations R_{ij} of the impurity centres. Here

$$F(R_{ij}) = \{3\pi e^2 E_1{}^2 \hbar^2 / M a_0{}^2 (k\Theta_D)^3\} | \langle \phi_i | v | \phi_j \rangle |^2,$$

where M is the mass of the atom, Θ_D the Debye temperature, and $\langle\ \rangle$ is the matrix element of the velocity between the localized electron wave functions on centres i and j. The temperature and energy dependence of σ is contained in the equation

$$N_e f(T, \epsilon_{ij}) = \frac{(\epsilon_i - \epsilon_j)/2k\Delta}{\{1 + [(\epsilon_i - \epsilon_j)/2k\Delta]^2\}^4} \frac{1}{kT} \left\{1 + \coth \frac{\epsilon_i - \epsilon_j}{2kT}\right\} N_\epsilon \exp(-\epsilon_i/kT) / \sum \exp(-\epsilon_j/kT). \qquad (47)$$

ϵ_i is here the energy of an electron on site i, $k\Delta = \hbar v/a_0$ is the energy of a phonon of wave length comparable to the Bohr radius a_0 of the localized electron, where v is the velocity of sound. Since $\epsilon_i - \epsilon_j$ is independent of R_{ij} except for very small separations, the dependence of σ_{ij} on separation is almost entirely contained in the term $|\langle \phi_i | v | \phi_j \rangle|^2$.

In the case of small compensation, $f(T, E)$ can be approximated by use of the trapping model (§ 2). The electron jumps between the 'free' sites, where $\epsilon_i \simeq \epsilon_j$, and the Boltzmann term in (47)

$$N_e \exp(-\epsilon_i/kT) / \sum \exp(-\epsilon_j/kT),$$

leads to the number n_f of free carriers,

$$n_f = (N_{\min} N_{\mathrm{maj}})^{1/2} \exp(-\epsilon_t/2kT),$$

where ϵ_t is the energy difference between free and trap sites. Then

$$f(T, \epsilon) = n_f / k\Delta.$$

The conductivity becomes

$$\sigma = n_f e \mu_f,$$

where

$$\mu_f = \{3\pi e E_1{}^2 \hbar / M a_0 v (k\Theta_D)^3\} |\langle \phi_i | v | \phi_j \rangle|^2.$$

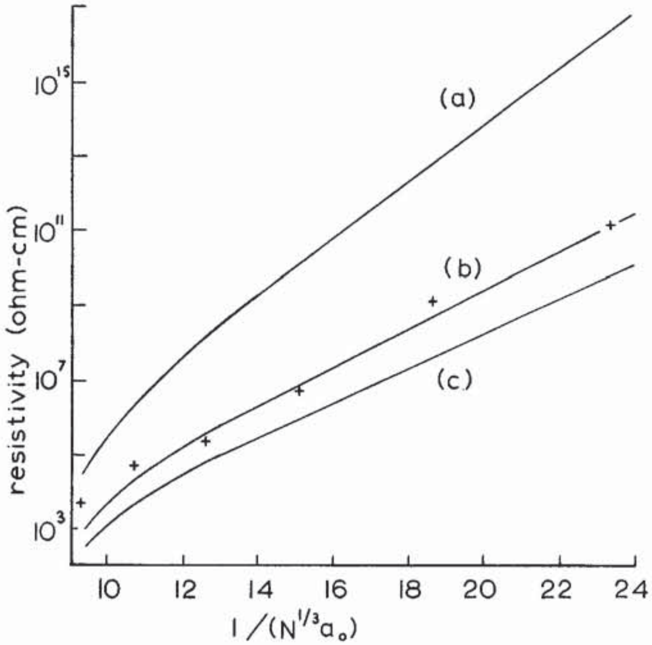
Thus the mobility is independent of temperature.

Assuming hydrogen-like wave functions for the localized electrons in evaluating the velocity matrix element, it was found that

$$\sigma_f = \frac{\pi e^6 E_1{}^2}{3\hbar\kappa^2 M v^2 (k\Theta_{\rm D})^2}\, \nu^2(\nu M)^2 \exp(-2\nu)\,(N_{\rm maj}N_{\rm min})^{1/2}\exp(-\epsilon_{\rm t}/2kT) \qquad (48)$$

where $\nu = R/a_0$. When averaging σ_f over the random centre distribution, care must be taken not to over emphasize the contribution from pairs of very close centres, since the electron will tend to be trapped on such a pair rather than move on through the lattice. One rough estimate of the average conductivity $\bar{\sigma}$ is obtained by assuming a constant impurity separation. Figure 17 shows that the observed resistivity is best fitted by $1/\bar{\sigma}$ if $\nu \sim 0{\cdot}7/N^{1/3}a_0$, implying that conductivity takes place preferentially along chains of impurities whose spacing is less than average. In evaluating $\bar{\sigma}$ in fig. 17 we have set $\frac{1}{2}\epsilon_{\rm t}$ for ϵ_3, the observed activation energy.

Fig. 17



The resistivity for n-type germanium calculated from (48) assuming a constant average centre separation ν of (*a*) $N^{-1/3}$, (*b*) $0{\cdot}7\,N^{-1/3}$ and (*c*) $0{\cdot}62\,N^{-1/3}$ The crosses are experimental points (Fritzsche 1958).

Another averaging procedure, suggested by Pippard, is the following. Suppose that a pair of centres, separated by a distance R and with ‘ two centre ’ conductivity $\sigma(R)$, can be replaced by a sphere of radius R and a uniform conductivity $\sigma(R)$. Let this sphere be imbedded in a medium with the average conductivity $\bar{\sigma}$ of the disordered lattice as a whole. When a field F is applied, the field inside the sphere becomes

$$F(R) = 3\bar{\sigma}F/\{2\bar{\sigma} + \sigma(R)\}.$$

The current density inside the sphere is $F(R)\,\sigma(R)$. If the probability of finding a sphere with radius between R and $R+dR$ is $P(R)\,dR$, then the average current density $\bar{j}$ is given by an integral equation

$$\bar{j} = \bar{\sigma}F = \int_0^\infty P(R)\,\frac{3\bar{\sigma}\sigma(R)}{2\bar{\sigma} + \sigma(R)}\,F\,dR.$$

For a random impurity distribution the probability function is

$$P(R) = 4\pi N_{\mathrm{maj}}\,R^2 \exp\left(-4\pi N_{\mathrm{maj}}\,R^3/3\right).$$

The equation was solved numerically.

Calculated values of the resistivity ρ are compared with measured values ρ_{exp} for antimony doped germanium (Fritzsche 1958), at a temperature of 2·5°K, in table 4. The observed activation energy ϵ_3 has been used to estimate ϵ_{t}, through the relation $\epsilon_3 = \frac{1}{2}\epsilon_{\mathrm{t}}$ given by the trapping model (§ 2).

Table 4

N_{D} cm^{-3}	K	ρ (Ω . cm)	ρ_{exp}(Ω . cm)
$9{\cdot}3\times10^{14}$	0·012	$6{\cdot}5\times10^{11}$	$7{\cdot}1\times10^{11}$
$1{\cdot}6\times10^{15}$	0·014	$5{\cdot}2\times10^{9}$	$6{\cdot}3\times10^{9}$
$2{\cdot}3\times10^{15}$	0·010	$7{\cdot}4\times10^{8}$	$3{\cdot}2\times10^{8}$
$3{\cdot}0\times10^{15}$	0·010	$1{\cdot}8\times10^{8}$	$7{\cdot}1\times10^{7}$
$5{\cdot}2\times10^{15}$	0·010	$2{\cdot}3\times10^{7}$	$5{\cdot}6\times10^{6}$
$8{\cdot}5\times10^{15}$	0·014	$1{\cdot}4\times10^{6}$	$1{\cdot}4\times10^{6}$
$1{\cdot}3\times10^{16}$	0·08	$6{\cdot}6\times10^{4}$	$2{\cdot}2\times10^{5}$

Both the above calculations are based essentially on choosing an average transition rate W_{ij} of the electron between two centres. The averaging procedure is critical, since W_{ij} increases exponentially with decreasing centre separation. As mentioned earlier, the large transition rate between two centres spaced closer than the average does not imply there is a correspondingly large contribution to the average conductivity, since the electron may have difficulty in proceeding from j to more distant centres. The charge on j will then build up by an amount which depends on the charge distribution on surrounding centres and on the applied electric field, until the forward transition rate $i \rightarrow j$ is balanced by the back transition rate $j \rightarrow i$.

Another point is that if f_i is the probability that centre i is occupied, the probability that the nearest neighbour j is unoccupied will be larger than $(1-f_i)$, due to Coulomb repulsion between the electrons. Miller (private communication) points out that this neglect of correlations between electrons may be the cause of the incorrect compensation dependence of his results. To conclude, a rigorous calculation of the conductivity will involve setting up a transport equation in which the charge distribution in the presence of an electric field is treated self-consistently, and with carrier–carrier correlation taken into account. A part of this programme has been completed by one of us (W.D.T.) in that the correct transport equation has been derived in the approximation that correlations are neglected; as might be expected the equation takes the form of a generalized Einstein relationship. The inclusion of the important self-consistency and correlation effects is being investigated.

PART II. THE TRANSITION TO A METALLIC FORM OF CONDUCTIVITY

§ 9. INTRODUCTION

It is a property of silicon, germanium and of many other extrinsic semiconductors that, as the concentration N of impurities increases, the activation energy ϵ_3 for conduction in the temperature range for impurity conduction decreases and, at a critical value N_c, vanishes. For values of N greater than N_c the resistivity and Hall constant are roughly independent of temperature down to the lowest temperatures for which measurements have been made.

In a number of papers one of us (Mott 1949, 1952, 1956, 1957, 1961) has given arguments to suggest that a sharp transition from a metallic to a non-metallic state must occur for a *crystalline* array of atoms as the distance between them is increased. In the paper published in 1956 it was suggested that the transition described in this paper for a random array of centres is of this type, the sharpness being lost because of the disordered arrangement. We consider that this is the correct explanation. However, another explanation is certainly possible, namely that the transition is one due essentially to the disordered lattice and occurs at the concentration at which the states for a single carrier become localized. We shall have to examine the evidence that this is not so at any rate for low K.

We shall not repeat the arguments summarized by Mott (1961) that this transition occurs for a crystalline array, remarking only that, while an exact calculation of the transition concentration has not proved possible, it should occur at a constant value of about 3 of the constant

$$\lambda = (3/4\pi N_{\text{maj}})^{1/3}/a_0 = r_s/a_0,$$

where a_0 is the Bohr radius of the centre.

We shall now summarise what we think happens in the disordered lattice in the two limiting cases, $K \ll 1$ and $1-K \ll 1$, where K is degree of compensation.

(*a*) Low compensation, $K \ll 1$. In the region of low concentration, $(N/N_c \ll 1)$, the carriers are holes, bound to minority centres by a Coulomb field $e^2/\kappa r^2$. As N increases, therefore, the holes cannot become free, because a Coulomb field always leads to bound states. The transition concentration N_c should increase slightly with compensation K, because some of the majority centres are empty and so the amount of overlap between localized centres is decreased (see below).

(*b*) High compensation, $1-K \ll 1$. Here we have at present little experimental evidence. The theoretical predictions are the following. As the concentration N of majority carriers is increased, a value will be reached for which the electrons are no longer in bound states (§ 2). Thus n electrons per unit volume (where $n=(1-K)N$) move in the random field due to fixed positive and negative charges; this random field is thus not strong enough to give bound states. There is thus the possibility of a 'crystallization' of electrons as predicted by Wigner (1938). This is discussed by Mott (1961). We are convinced that, whether or not the electrons behave like a classical liquid or a condensed electron gas, their conductivity will be high and that in this case any transition which may be observed will be due to a transition from bound to free states for a *single* electron.

The remainder of this paper will deal with the case of small or moderate value of K, for which most of the experimental work has been done.

§ 10. DEPENDENCE OF THE TRANSITION CONCENTRATION OR DEGREE OF COMPENSATION

If the transition were due essentially to the properties of the random lattice, we should expect it to depend very sensitively on K, since K determines the random field. If on the other hand the transition is due simply to overlap between occupied centres, we should expect a variation of λ according to the formula

$$\lambda = \text{const}\,(1-K)^{1/3}.$$

Some experimental support for this compensation-dependence of λ is given by measurements of the acceptor separation r_s at which the activation energy ϵ_3 disappears in p-type gallium-doped germanium (Fritzsche and Cuevas 1960 b). The results are summarized in table 5, and are shown in fig. 18.

Table 5

r_s (Å)	127	110	98
K	0·04	0·4	$0{\cdot}4 < K < 0{\cdot}7$

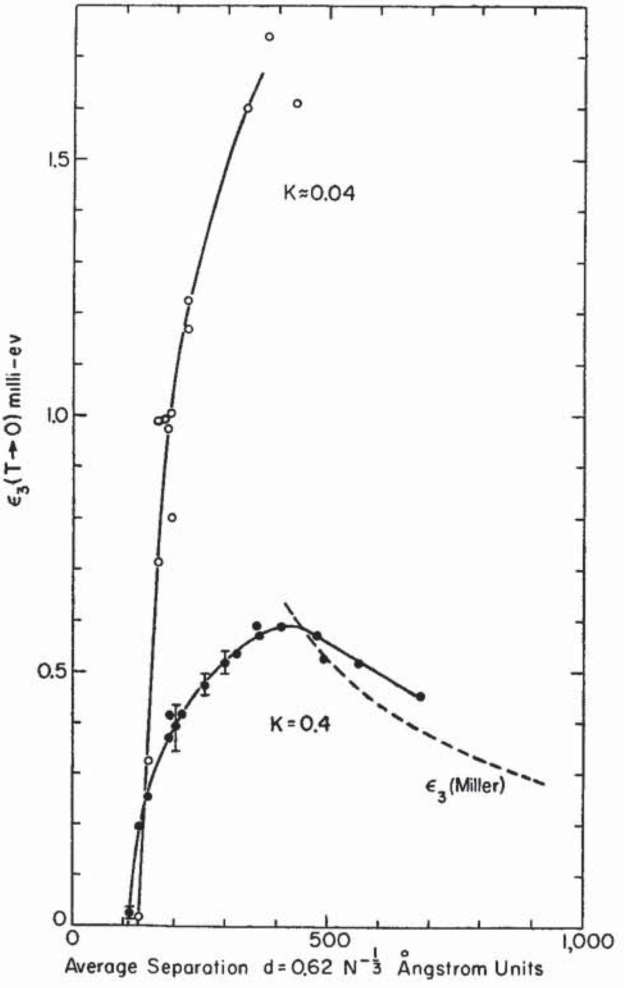
The critical separation decreases as K increases. We also note that the ratio of the separations for K equal to 0·04 and 0·4 is 1·18, while that calculated from (48) is 1·12.

The experimental value of λ is not clear, since the gallium wave functions are not accurately known. A variational calculation shows that at large distances from the impurity the wave function is a sum of two exponentials. One has a Bohr radius $a_1 = 35 \pm 7$ Å, the other $a_2 = 89 \pm 2$ Å (Miller and Abrahams 1960). Then for $K = 0{\cdot}04$,

$$\lambda_1 = r_s/a_1 = 3{\cdot}6, \quad \lambda_2 = r_s/a_2 = 1{\cdot}4.$$

Since the relative amplitudes of the two exponentials are not known, we can only deduce that $1{\cdot}4 < \lambda < 3{\cdot}6$. However, λ is probably closer to 3·6 than 1·4. One reason for this is that in the alkali metals (where the conductivity is of course 'metallic') the inter-electron separation in units of the Bohr radius range from 3·22 (lithium) to 5·57 (caesium).

Fig. 18



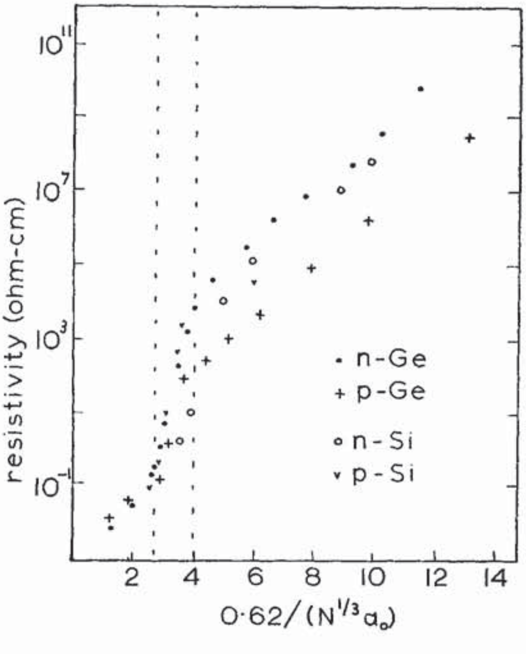
Activation energy ϵ_3 of impurity conduction of transmutation-doped p-type germanium as a function of average impurity separation for $K=0{\cdot}4$ and $K=0{\cdot}04$ (Fritzsche and Cuevas 1960 b).

§ 11. CONCENTRATION AT WHICH THE TRANSITION OCCURS

In fig. 19 we show the resistivity at 2·5°K of weakly compensated samples of n- and p-type silicon and germanium. This is plotted against λ, in other words $(3/4\pi N)^{1/3}/a_0$ or r_s/a_0, where r_s is the mean distance between impurities. The Bohr radius a_0 used here is obtained by assuming the hydrogen atom model for an impurity centre, and adjusting a_0 to fit the observed ionization energy of the impurity centre. The activation energy ϵ_3 drops rapidly in the transition region (shown in fig. 19 between the vertical dotted lines) and occurs for all substances roughly when $\lambda \simeq 3$, or $N^{1/3}a_0 \simeq 0{\cdot}2$.

Roughly the same value is deduced by Dewald (1960) from the measurements of Thomas (1959) for zinc oxide.

Fig. 19



Variation of resistivity with average impurity separation for weakly compensated specimens of germanium and silicon. The transition region is enclosed by the dotted lines. The activation energy ϵ_3 for impurity conduction vanishes at the small separation end of the transition region.

McIrvine (1960), by examining a number of semiconductors, deduces an empirical formula which relates N_c to the static dielectric constant ϵ. However, for semiconductors that are not elements, it is not clear what value of the dielectric constant one should take, the high frequency value, the static value or some mean between them; this point needs further investigation before an assessment of the meaning of McIrvine's formula can be given.

What is happening in the transition region is not clear. We have seen (fig. 2) that the ratio of the Hall constant to $1/N_{\mathrm{maj}}$ drops in this region. This suggests that the material is inhomogeneous, due to fluctuations in the density of centres, and that there are small metallic regions in series with non-metallic ones, whose relative volumes depend on temperature. If the Hall effect in the non-metallic regions is small or non-existent, one would expect, as the temperature is lowered and the volume of the non-metallic regions increases, a drop in the observed Hall constant. This is a possible explanation of the effect.

It should however be pointed out that Read and Katz (1960) have observed a Hall effect for ionic conduction in KCl; the hopping process of a point defect from one centre to another is not dissimilar to that described here.

§ 12. RESISTIVITY IN THE REGION OF METALLIC CONDUCTION

The conductivity of a metal may be written

$$\sigma = Ne^2 l/m^* v, \qquad (49)$$

where l, v are the mean free path and velocity at the surface of the Fermi distribution. Moreover, for a degenerate electron gas,

$$m^* v/\hbar = 2\pi(3N/8\pi)^{1/3}.$$

Also it is convenient to write

$$l = p/N^{1/3},$$

so that p is the number of interatomic distances on a mean free path. Then (49) becomes

$$\sigma = N^{1/3} e^2 p/\hbar(3/\pi)^{1/3},$$

or in $\text{ohm}^{-1}\,\text{cm}^{-1}$, if N is in particles per cubic angstrom,

$$\sigma = 7 \times 10^3 pN^{1/3},$$

For the specimens with highest conductivity shown in fig. 4, N is 10^{-6} and the observed conductivity is $1{\cdot}5 \times 10^2$, so p is about 2. This is shown also in the following table (Fritzsche 1960, private communication) for n-type germanium, in which v is deduced from (50) and hence the mean free path from the observed resistivity p. It is of course assumed that each centre contributes a free electron, so $N = N_D$. The last column shows the mean distance between centres. The table also shows that l tends to remain constant as N decreases, so p apparently drops below unity.

Table 6.

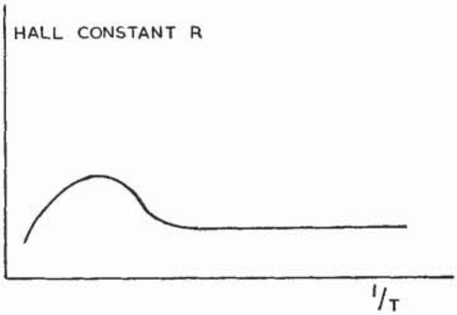
ρ (obs, Ω . cm)	N_D (cm^{-3})	v (cm/sec $\times 10^{-6}$)	l (cm $\times 10^8$)	$0{\cdot}62\ N^{-1/3}$ (cm $\times 10^8$)
0·02	2×10^{17}	6	62	106
0·0095	6×10^{17}	8·6	63	73
0·0067	10^{18}	10	64	62
0·0033	3×10^{18}	15	63	43
0·00157	10^{11}	22	59	29
0·001	2×10^{19}	28	58	23
0·00066	4×10^{19}	35	55	18

We should expect l to be given by a formula of the form

$$1/l = N\int I(\theta)\,(1-\cos\theta)\,2\pi\sin\theta\,d\theta, \quad . \quad . \quad . \quad . \quad (51)$$

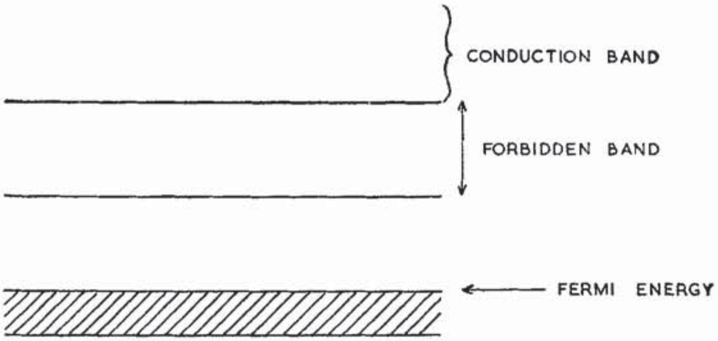
where $I(\theta)$ is the differential cross section for scattering by each centre.

Fig. 20



Hall constant near transition concentration in metallic region.

Fig. 21



An impurity band for concentration near the transition point.

That, in the metallic region, the integral is of the order of $N^{-2/3}$ is perhaps not unexpected for a totally disordered lattice. The constancy of l, however, means that the integral is proportional to $1/N$, and this is unexpected. A crude application of Born's approximation would suggest that the scattering potential energy function of each centre was of order $e^2/\kappa R\,(4\pi R^3/3 = N)$ extending over a volume R^3, so that

$$I(\theta) = \left|\frac{1}{4\pi}\frac{2m}{\hbar^2}\int \exp\{i\mathbf{k}-\mathbf{k}'\,.\,\mathbf{r}\}\frac{e^2}{\kappa R d\tau}\right|^2,$$

the integral being over a sphere of radius R and $|\mathbf{k}-\mathbf{k}'|=2k\sin\frac{1}{2}\theta$. Since kR is independent of N this must be equal to a numerical factor multiplied by $R^4/a_0{}^2$, where a_0 is the hydrogen radius $\hbar^2\kappa/m^*e^2$. Thus l should vary as R^{-1}, i.e. as $N^{1/3}$.

The observed constancy may perhaps be due to the non-Coulomb part of the field near the impurity atom, the relative importance of which will increase with N.

A point about the conductivity near the transition point may be pointed out. The Hall constant plotted against $1/T$ shows the behaviour sketched in fig. 20 (cf. also fig. 4). This suggests that there is an 'impurity band', formed from the impurity wave-functions, and not yet overlapping the conduction band. If the impurity wave functions are hydrogen-like, it is easy to estimate its width. This is, using the approximation of tight binding (Mott and Jones 1936, Chap. III, Mott 1957)

$$B=6W_0(1+\lambda')\exp(-\lambda')$$

where W_D is the ionization energy of a centre. The assumption is made that the centres are arranged in a simple cubic lattice of side b, and λ' is thus b/a_0. Values of the ratio of B to W_0 are

λ'	B/W_0
2	3·0
3	1·2
4	0·54
5	0·24

Only values less than unity have any meaning in this approximation. The experimental value of λ at the transition point is *c.* 3, and if we set

$$\lambda'=(4\pi/3)^{1/3}\lambda=1/Na_0,$$

a value of about 5 is appropriate for λ'. Near the transition concentration, then this rough estimate suggests, as do the experiments, that the impurity band does not yet overlap the conduction band.

ACKNOWLEDGMENTS

We are grateful to several of our colleagues with whom we have discussed these problems, particularly Dr. M. H. Cohen and Dr. H. Fritzsche.

APPENDIX

THE EXISTENCE OF BOUND STATES IN THREE DIMENSIONS

We give here an outline of an extension due to one of us (W.D.T.) of the work of Anderson (1958) showing that the single electron states are bound in an impurity lattice when the average impurity separation greater than a critical value; the degree of compensation is assumed close to unity.

We study the wave function of an electron in a lattice of positive and negative fixed point charges which are distributed at random in a dielectric medium. There is a density N of positive charges, and the total number of positive charges exceeds the number of negative charges by one. Let $\phi_i(r)$ be the wave function of the electron localised on the ith positive site. For simplicity, we here assume that ϕ_i is a hydrogen-like s function of the form

$$\phi_i(r) = (\pi a_0{}^3)^{-1/2} \exp(-r/a_0), \qquad \text{(A 1)}$$

and that ϕ_i, ϕ_j are orthogonal; we thus neglect the small overlap (ϕ_i, ϕ_j). (A more exact treatment can be given in terms of the orthogonalized ϕ_i of § 7, (eqn. 39). The wave function of the electron at time t can be written

$$\psi(t) = \sum a_i(t)\, \phi_i(r).$$

We assume the electron is initially localized on atom i, so that $a_i(0) = 1$ and $a_j(o) = 0$, and study the variation of $a_i(t)$ with t using the Schrodinger equation

$$i\hbar\, \partial a_i / \partial t = E_i a_i + \sum V_{ij}\, a_j. \qquad \text{(A 2)}$$

Here E_i is the energy of the electron on site i in the coulomb potential of the surrounding positive and negative charges. V_{ij} is the matrix element of the potential of all charged centres except the jth positive one:

$$V_{ij} = \left\langle \phi_i \middle| \sum_{\nu} \frac{e^2}{\kappa|\mathbf{r} - \mathbf{R}_\nu|} - \sum_{k=j} \frac{e^2}{\kappa|\mathbf{r} - \mathbf{R}_k|} \middle| \phi_i \right\rangle,$$

$\mathbf{R}_k$, $\mathbf{R}_\nu$ are the positions of the positive and negative centres respectively.

It is convenient to study the Laplace transform of (A 2), defining

$$f_i(s) = s \int_0^\infty \exp(-st)\, a_i(t)\, dt.$$

Thus s is an inverse time, and

$$\lim_{t\to\infty} a_i(t) = \lim_{s\to 0} f_i(s).$$

Then, it follows from the work of Anderson (1958) that the behaviour of $a_i(t)$ at large times depends on the convergence of an infinite perturbation series

$$V_c(s) = \sum_k V_{ik}\,(1/d_k)\{V_{ki} + \sum_m V_{km}(1/d_m)V_{mi}\}, \qquad \text{(A 3)}$$

where

$$d_k = i\hbar s - E_k. \qquad \text{(A 4)}$$

For, if t is large, Anderson shows that

$$a_i(t) \sim \exp(-t/\tau_i) \exp\{-i(E_i - \Delta_i)t/\hbar\},$$

where

$$\lim_{s\to 0+} V_c(s) = -\Delta_i + i\tau_i\hbar.$$

The imaginary part of V_c corresponds to a decay time, and the real part to an energy shift. Hence, if the Im $(V_c(s))$ vanishes as Re $(s) \to 0^+$, the amplitude of the electron on site i remains finite as $t \to \infty$, i.e. the electron is bound to that site and has energy $E_i - \Delta_i$. If the imaginary part does not vanish, then after a sufficiently long time the electron will have diffused completely away from its initial position; bound states are in general not possible at any centre i.

$V_c(s)$ should be evaluated when

$$\operatorname{Im}(s) = (E_i - \Delta_i)/\hbar.$$

Thus in (A 6)

$$d_j = i\hbar s + (E_i - \Delta_i - E_j),$$

where s is real. In the following we neglect the small energy correction Δ_i, and write

$$E_{ij} = E_i - E_j.$$

The quantities V_{ij} and E_{ij} entering V_c can be written

$$V_{ij} = \left\langle \phi_i \,\middle|\, v_{ij}(r) - \frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_i|} \,\middle|\, \phi_j \right\rangle \quad . \quad . \quad . \quad . \quad \text{(A 5)}$$

$$E_{ij} = v_{ij}(R_i) - v_{ij}(R_j),$$

where

$$v_{ij}(r) = \sum_{\nu} e^2/\kappa\,|\mathbf{r}-\mathbf{R}_\nu| - \sum_{k \neq i,j} e^2/\kappa\,|\mathbf{r}-\mathbf{R}_k|$$

is the Coulomb potential at r of all the randomly placed positive and negative centres except the ith and jth positive ones.

The dominant contributions to V_c come from small values of E_{ij} and large values of V_{ij}. From (A 1),

$$V_{ij} \sim \exp(-R_{ij}/a_0),$$

where R_{ij} is the separation of i and j; thus V_{ij} is largest when i and j are near-neighbour centres. In general, for two near neighbours, E_{ij} is small when there are no close centres to i and j. Then, it is a fair approximation to neglect $v_{ij}(r)$ in (A 5), taking

$$V_{ij} \simeq \left\langle \phi_i \,\middle|\, - \frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_i|} \,\middle|\, \phi_j \right\rangle = - \frac{e^2}{\kappa a_0}\left(\frac{R_{ij}}{a_0} + 1\right) \exp(R_{ij}/a_0).$$

Also we note that in this approximation V_{ij} and E_{ij} can be treated independently, since V_{ij} depends on centres i and j only, while E_{ij} depends on the potential of all other centres.

Let

$$V_c = -\Delta(s) + i\hbar s\, X(s), \quad . \quad . \quad . \quad . \quad . \quad \text{(A 6)}$$

where Δ, X and s are real. Then, in the limit $s \to 0^+$,

$$X = \sum_k (V_{ik}/E_{ik})\{V_{ki}/E_{ki} + \sum_m V_{km}\, V_{mi}/E_{km}\, E_{mi} + \ldots\}. \quad . \quad \text{(A 7)}$$

We treat the V_{ij} and E_{ij} as independent random variables, obtain a probability distribution for X and show that the probability that X diverges to infinity is zero if the density N of charged centres is less than a critical value N_c. Then (cf. A 6),

$$\lim_{s \to 0} \operatorname{Im} V_c(s) = 0,$$

and the electron remains localized about site i.

The steps are the following:

(i) Anderson shows that the first term in (A 7),

$$X^{(1)} = \sum_k | V_{ik} |^2 / E_{ik}{}^2,$$

is convergent in the above sense if $V_{ij}(R_{ij})$ falls off faster than $1/R_{ij}{}^{3+\epsilon}$ ($\epsilon < 0$). This condition is obviously satisfied for our case.

(ii) We must now show that the complete series V is convergent when $N < N_c$. Let

$$X = \sum_L (S_L), \quad S_L = \sum (\pm T_L)$$

where S_L is the sum of all terms of length L; the 'length' is the number of times V/E appears in the term. The sign of both S_L and T_L is random, because of the random sign of the energy denominators E_{ij}. The number of terms of length L, with value T_L in the range $T_L - T_L + dT_L$, is found to be of the form

$$n(T_L)\,dT_L = [f(N)]^L L(T_L)\,dT_L / T_L{}^2,$$

where $f(N)$ increases with N. If $L(T)$ increases, or decreases no more rapidly than $T^{-1/2}$, then the probability distribution of S_L is of the form

$$P(S_L) dS_L \sim [f(N)]^L L(S_L)\, dS_L / S_L,$$

for values of the sum S_L greater than or of order the most probable value. Since we are interested only in the convergence of X, we consider the case in which L is large. Then N_c is determined by

$$[f(N)]^L L(1) = 1. \qquad \text{(A 8)}$$

For, if $N < N_c$, $f(N) < f(N_c)$ and the probability of obtaining $S_L = 1$ is smaller by a factor of order e^{-L}. The number of S_L in X increases as L, and the probability is $1 - e^{-L}$ that each term is less than unity. Hence X must almost always converge when $N < N_c$.

The detailed derivation of $n(T)$ will not be given here. It can be obtained by the methods in Anderson's paper, with the following assumptions.

(*a*) The probability distribution of the energy differences E_{ij} is of the form

$$P(E_{ij}) = W^{-1} \quad \text{if} \quad -\tfrac{1}{2}W \leqslant E_{ij} \leqslant \tfrac{1}{2}W$$
$$= 0 \qquad \text{if} \quad | E_{ij} | > \tfrac{1}{2}W, \qquad \text{(A 9)}$$

(*b*) $$V_{ij} = V_0 \exp(-R_{ij}/a_0), \quad V_0 = e^2/\kappa a_0. \qquad \text{(A 10)}$$

The number of terms V_{ij} with values in the range $V - V + dV$ is obtained by assuming that the number of positive sites j at distance R_{ij} from i is

$$n(R_{ij}) dR_{ij} = 4\pi N R_{ij}{}^2 \, dR_{ij}.$$

Then we obtain

$$N(T)dT = \left[\frac{16^3 \pi N a_0{}^3 V_0}{3^3 W}\right]^L \{1 + \ln(T/4L) - \tfrac{1}{4}\ln(2V_0/W)\}^L dT/T^2; \qquad \textbf{(A 11)}$$

W can be determined as follows. We write

$$E_{ij} = \sum_k Z_k$$

where

$$Z_k = \pm \frac{e^3}{k}\left(\frac{1}{R_{ik}} - \frac{1}{R_{jk}}\right),$$

and k is any one of the positive or negative centres. Treating Z_k as a step in a random walk problem, the probability distribution of E_{ij} is (Chandrasekhar 1943)

$$P(\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(iE\tau)\exp\left[-4N\int \sin^2\left\{\frac{e^2\tau}{2\kappa}\left(\frac{1}{R_{jk}} - \frac{1}{R_{jk}}\right)\right\} d^3 R_{ik}\right] d\tau \quad . \quad . \quad . \quad . \quad . \quad \text{(A 12)}$$

As discussed earlier, we are interested only in small values of E, when R_{ik} or $R_{jk} > R_{ij}$. Hence we can approximate (A 16) using

$$1/R_{ij} - 1/R_{ij} = R_{ij}\cos\theta/R^2$$

where R is the mean distance from i and j to k, and θ is the angle between R_{ij} and R. Then

$$P(E) = \frac{1}{2\pi}\int \exp(iE\tau)\exp\{-4N(\pi e^2 R_{ij}/2\kappa)^{3/2}|\tau|^{3/2}\} d\tau,$$

and

$$P(0) = 2\Gamma(5/3)\kappa/\{\pi^2(4N)^{2/3} e^2/R_{ij}\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A 13)}$$

The appropriate value of W to use in the rectangular distribution (A 13) is therefore

$$W = 1/P(0) = 8{\cdot}5 e^2/\kappa a_0 n,$$

where $4\pi N a_0{}^3/3 = 1/n^3$, and n is the average separation in units of the Bohr radius. We have replaced R_{ij} in (A 17) by its average value,

$$R_{ij} = (3/4\pi N)^{1/3}.$$

Hence the critical value of n is determined from (A 12) and (A 15) by

$$(5{\cdot}46 - \ln n)/n^2 \leqslant 0{\cdot}32,$$

and thus on evaluation by $n < n_c$ where

$$n_c = 3{\cdot}6.$$

Our model corresponds to n-type germanium or silicon at the absolute zero of temperature, with degree of compensation $K \simeq 1$. The variation of n_c (the separation of the donor impurities) with K is given by

$$\{5{\cdot}46 - \ln(n/K^{1/3})\}\, n_c{}^2 K^{1/3} = 0{\cdot}32,$$

since the energy spread W is determined by the number of acceptor sites, while the jump distance of the electron depends on the separation of donor sites. Thus n_c increases as K decreases from unity.

A weakness of the above treatment is that V_{ij} and E_{ij} are treated completely independently, whereas from(A 14) and (A 16, 17) it can be seen that both are functions of R_{ij}. Thus we should carry through the treatment using the single quantity V/E as the random variable. Corrections to the above treatment are being investigated. We believe that the value $n_c = 3{\cdot}6$ is an upper limit to the critical separation. For, we have allowed a finite probability for E_{ij} to have the value zero for all separations R_{ij}. However, for two very close centres i and j there should be a term $2V_{ij}$ in the energy difference E_{ij} which prevents E_{ij} taking a zero value, and therefore the series X (A 7) should converge at smaller values of the average separations between centres.

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