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On the Statistical Mechanics of Impurity Conduction in Semiconductors

Abstract: The statistical mechanics of the impurity electron states for a semiconductor with a low density of donors, and a small amount of acceptor compensation, is analyzed. Expressions are obtained for the number of dissociated donor ion states according to the Mott model, and for the effects of multiple trapping, and of dispersion of the trapping energies, on this number. An expression for the thermoelectric power according to the Mott model is obtained. If a small proportion of "minority" donors, of a different chemical species with a smaller electron binding energy than the majority donors, were added to the impurity content they should act as additional traps for donor ion states: The statistical mechanics of this system is analyzed.

Contents

1. Introduction

It has been known for several years[1] that in electrical conduction in germanium, for small fields and at very low temperatures, the current may be carried mostly by the electrons* in the localized (donor) states, rather than by the very small fraction of the available electrons which are thermally excited to the conduction band, even though the mobility of the latter electrons is very much greater. This new mode of conduction has now been investigated in some detail. It was originally believed that the explanation of this mode of conduction was that the interaction, due to the overlap of their wave-functions, between localized electron states on neighboring donor impurity atoms causes the macroscopically degenerate donor electron level to split into a band (the so-called "impurity band") of levels, each new level corresponding to a current-carrying state. It has since been realized, however, that impurity conduction is found in circumstances where this explanation could not be correct[2], and it has been proposed that compensation then plays an essential role in the mechanism of conduction. The new view of impurity conduction at low impurity densities[2,3] is as follows:

When the donor impurities are partly compensated by acceptor impurities, the latter become negative ions by acquiring electrons from the former. Thus, if there are N_D donors and N_A acceptors, N_A electrons will be transferred from the former to the latter. This leaves N_D-N_A electrons distributed among N_D donor "orbitals."

*For the sake of brevity and clarity, throughout this paper I refer to "electrons", "donors", and "n type" although the phenomena discussed occur for both polarities of extrinsic semiconductor. Everything in the following analysis applies, *mutus mutandis*, to p type also.

For the low concentrations we are concerned with here, the interaction between these orbitals is very small; and consequently most of the $N_D!/N_A!\,(N_D-N_A)!$ states whose wavefunctions are given by assigning the N_D-N_A electrons to N_D-N_A of the N_D available single donor wavefunctions are good approximations to the true ground state, and will differ little from it in energy expectation. By mixing these state vectors, current-carrying states may be formed at little cost in excitation energy. The mode of conduction is then essentially by *permutation* of occupied and unoccupied donor states, and it will be referred to here as "permutation conduction." The broadening of the collective energy levels of this system by the lattice vibrations coupled to it will certainly be an important effect, but it is supposed not to affect the above conclusions in essence. When $N_A \ll N_D$, it is convenient to think of the current as carried by transfer of 'donor defects'—states of *absence* of an electron from a donor.

The argument above did not take into account the effect of the electrostatic repulsion between a donor electron and an ionized acceptor. Where $N_A \ll N_D$, this can be foreseen to have the effect of tending to concentrate the "donor defects" around the acceptors. Mott[4] has suggested that this effect causes the donor atoms, as sites for "defects," to divide into trapping sites—those in the neighborhood of the acceptors—and the remaining free sites: it is presumed that only the latter participate in conduction, while the former have a lower energy for a defect and so reduce the conductivity by soaking up the available defects. Since the experimental dependence of conductivity on temperature does manifest a definite activation energy, which furthermore is of the order of magnitude to be expected for the above coulomb binding energy[5,6], this picture certainly ought to be considered and tried out.

It is necessary both to consider whether Mott's hypotheses have a reasonable physical basis and to work out the properties of his model in sufficient detail for a meaningful comparison with experimental data. The following obscurities are then disclosed: (a) in spite of the facts that a random distribution of donors, with a continuous range of coulomb binding energies, is to be expected, and that there is also a coulomb *repulsion* between defects, a definite single activation energy is assumed in the model and apparently required by the data; (b) it is by no means clear how a *sharp* distinction between donor sites which participate in conduction and others which do not could be accounted for, and in fact there is no theory of the relaxation processes determining the mobility of the defects and no theory for the effect of lattice vibrations.

In the work reported in Sections 2, 3 and 4, an attempt has been made to deal with—or at least clarify—the issues (a) above, and to make some predictions of the model sufficiently specific for it to be constructively applied to experimental data. The main results are firstly to make it plausible that a single binding energy should be manifest, in spite of there being coulomb repulsion between defects and more than one nearest neighbor donor to one acceptor (the outcome of the repulsion being shown to be the same as if simultaneous occupation, by defects, of more than one of these nearest neighbors were forbidden), and secondly to obtain formulas for the distribution of defects, between free and bound states, thus predicted. An analysis is also made of the possible effect of random differences between the distributions of donors near different acceptors. It appears that this might not be too serious after all.

The available experimental evidence seems to be at least not inconsistent with the results given in Section 2. Nevertheless I do not believe that the model is yet established on a sound theoretical or experimental basis. There seems no reason to doubt that compensation is of profound importance for impurity conduction, but beyond that the physics of lightly doped compensated germanium crystals at very low temperatures is (in my opinion, at least) still quite obscure. In particular, the effect of lattice vibrations, and the nature of relaxation processes for the bound electrons, have to be elucidated.

2. The simplest version of the model

In this section we examine the statistical mechanics of the simplest version of the system according to the Mott view. Suppose a germanium crystal contains N_A acceptors and N_D donors, so that at low temperatures there are N_A acceptor ions and N_A donor defects. (For the model to be plausible, we should have $N_A \ll N_D$.) Let the coulomb fields of the acceptor ions split off $rN_A \equiv N_1$ of the N_D defect sites and make them "trap" sites, leaving $N_D - rN_A \equiv N_2$ "free" sites. The average number of defects occupying free sites is

$$n_2 = N_2/[e^{-\psi/kT}+1] \ , \tag{1}$$

where ψ is the chemical potential of a defect relative to its energy at a free site. If we assume that not more than one at a time of the r traps around an acceptor ion can be occupied, and that with a binding energy ϵ, then the average number of defects occupying traps is

$$n_1 = N_1/[e^{-(\psi+\epsilon)/kT}+r] \ . \tag{2a}$$

If on the other hand we allow any number s, $0 \leqslant s \leqslant r$, to be simultaneously occupied, with total binding energy $s\epsilon$, then

$$n_1 = N_1/[e^{-(\psi+\epsilon)/kT}+1] \ . \tag{2b}$$

To work out both cases together, we write

$$n_1 = N_1/[e^{-(\psi+\epsilon)/kT}+c] \ , \tag{2}$$

with $c=1$ (case b) or r (case a).
In addition to (1) and (2), we have

$$n_1+n_2=N_A. \tag{3}$$

From (1) and (2),

$$z(N_2n_1-n_1n_2)=N_1n_2-cn_1n_2 \ , \tag{4}$$

where

$$z \equiv \exp(-\epsilon/kT) \, .$$

Hence, by (3),

$$n_2^2(z-c)-[(N_2+N_A)z+(r-c)N_A]n_2+zN_2N_A=0 \ . \tag{5}$$

In the limit of z small, where $n_2 \ll N_A$, (5) becomes

$$z\, N_2N_A \approx c\, n_2^2+(r-c)N_An_2 \, . \tag{6}$$

If $c=r$ we then have

$$n_2 \approx (N_2 N_A z/r)^{\frac{1}{2}} . \tag{7a}$$

If, on the other hand, $c=1\neq r$, we have

$$n_2 \approx N_2 z/(r-c) = N_2 z/(r-1) . \tag{7b}$$

It is desirable to understand why the two results (7) should differ so drastically. In the conditions for which (6) and (7) apply, the average number of trapped defects per ion is very nearly one: $n_1 \simeq N_A$. If the fluctuation in this number were small in case (b), then there would be no reason to expect the result for this case, (7b), to differ much from (7a), since the condition imposed in case (a) would be very nearly satisfied in case (b) also. It is easy to show, however, that the fluctuation is in fact large. The probability that s of the r traps around an ion are occupied is, in case (b),

$$P(s) = \binom{r}{s} \zeta^s/(1+\zeta)^r , \tag{8}$$

where

$$\zeta \equiv \exp[(\psi+\epsilon)/kT]$$

The average number occupied is then

$$\frac{n_1}{N_A} = \sum_{s=0}^{r} sP(s) = \frac{r\zeta}{1+\zeta} . \tag{2b}$$

Since $n_1 \simeq N_A$, we have $\zeta \simeq 1/(r-1)$. For simplicity in what follows we will take

$$\zeta = 1/(r-1) \tag{9}$$

exactly. Then

$$P(1) = [(r-1)/r]^{r-1} . \tag{10}$$

Also

$$P(0) = [(r-1)/r]^r = [(r-1)/r]P(1) .$$

Thus, although the *average* occupation is one, the probability for the occupation number actually to be one is as follows:

$r=$	2	3	4	5	$\ldots\ \infty$
$P(1)=$	1/2	4/9	9/64	256/625	$\ldots\ 1/e$

For large r, the combined probability of occupations greater than one, $1-P(0)-P(1)$, tends to $1-2/e=0.264$. The suppression of these configurations in case (a) causes (7a) to differ from (7b). In the following section it is shown that case (b) cannot be expected to represent the actual situation in any conditions, but case (a) should apply in most circumstances. A graph of the function $n_2(z)$ according to (5) in case (a), for the full range of z, is given in the appendix of reference 5.

3. A more general theory

In the physical situation we have in mind, multiple occupation ($2 \leqslant s \leqslant r$) of the set of traps around an acceptor ion is presumably possible, but the binding energy will be less than $s\epsilon$ because of the coulomb repulsion between the donor defects. The average number, in the crystal, of acceptor ions at which $s \geqslant 2$ (for given values of ψ and T) will therefore in actuality be less than for case (b), though not zero as in case (a). In general the binding energy will not be the same for all the $\binom{r}{s}$ configurations with a given value of s, and hence what will appear in the corresponding Boltzmann factor in the theory will be the free energy for these configurations, and will be a function of T. We shall not take explicit account of this fact here. Let the binding (free) energy for s defects be ϵ_s (so that ϵ_1 is what so far we have been calling ϵ) and let

$$z_s \equiv \exp(-\epsilon_s/kT), \quad p \equiv \exp(\psi/kT) . \tag{11}$$

Then

$$\frac{n_2}{N_2} = \frac{p}{1+p} , \tag{12}$$

$$\frac{n_1}{N_A} = \frac{rp + pd\phi/dp}{z_1 + rp + \phi} , \tag{13}$$

where

$$\phi(p) \equiv \sum_{s=2}^{r} \binom{r}{s} p^s (z_1/z_s) . \tag{14}$$

On combining (12) and (13) with (3), we obtain an equation for p. Now, it follows from (12) that if $n_2 \ll N_A$ then $1 \gg (N_2/N_A)p$. We may then drop a number of terms from the equation for p, so that it simplifies to

$$r(N_2/N_A)p^2 + (pd\phi/dp - \phi) = z_1 . \tag{15}$$

Furthermore, since $n_2/N_2 \leqslant N_A/N_2 \ll 1$, eq. (12) shows that always $p \ll 1$, and hence we may substitute in (15)

$$p = n_2/N_2 . \tag{12′}$$

Then, when $\phi=0$, eq. (15) reduces to the result for case (a), namely eq. (7a). It may be made plausible that only the first term of (14) need be taken into account in (15). Since $p \ll 1$, only the terms of (14) for which $z_1 \gg z_s$—that is, the terms for which $\epsilon_s > \epsilon_1$—are appreciable. We may write

$$\epsilon_s = [s - \tfrac{1}{2}s(s-1)\lambda_s]\epsilon_1 , \tag{16}$$

where $\lambda_s \epsilon_1$ is the averaged mutual (coulomb) potential of a pair of the trapped defects. Then geometrical considerations make it reasonable to suppose that $\frac{1}{2} < \lambda_2 < 1$, $\sqrt{\frac{1}{3}} < \lambda_3 < 1$, etc. Consequently

$$\epsilon_1 < \epsilon_2 < 1.5\epsilon_1 ; \qquad 0 < \epsilon_3 < 1.27\epsilon_1 ;$$

and

$$\epsilon_4 < \epsilon_1 ; \qquad \epsilon_5 < \epsilon_1 ; \ldots . \text{ etc.}$$

Hence only the first *two* terms of (14) need be considered.

Let us first look at the consequences of taking only the *first* term in (14). Eq. (15) at once becomes

$$[r(N_2/N_A) + \tfrac{1}{2}r(r-1)z_1/z_2]p^2 = z_1 , \tag{17}$$

and hence

$$\frac{1}{n_2^2} = \frac{r}{z_1 N_2 N_A} + \frac{\frac{1}{2}r(r-1)}{z_2 N_2^2} . \tag{17′}$$

It is clear that at a high enough temperature for z_1 to be small compared with $(N_2/N_A)z_2$ the first term of (17′) will dominate and (7a) will be valid, but that at lower temperatures it is to be expected that

$$n_2 = N_2(2z_2/r(r-1))^{\frac{1}{2}} \ll (N_2N_Az_1/r)^{\frac{1}{2}} . \tag{18}$$

It is noteworthy that the superseding of (7a) by (18) does NOT imply that acceptors with two defects trapped are more probable than those with one trapped. What happens to change the value of n_2 from that given by (7a) to that given by (18) is rather that as T increases from zero most of the defects "freed" by excitation of an acceptor's trap complex from $s=1$ to $s=0$ go to occupy other complexes doubly ($s=2$) instead of going into free sites.

We now consider the effect of including the second term of (14), as well as the first, on the solution of (15). Making use of (12′) we have, instead of (17′),

$$\frac{1}{n_2^2} = \frac{r}{z_1N_2N_A} + \frac{\frac{1}{2}r(r-1)}{z_2N_2^2} + \frac{\frac{1}{3}r(r-1)(r-2)}{z_3N_2^2}\left(\frac{n_2}{N_2}\right) . \tag{19}$$

It may be shown that this equation for n_2 has only one real positive root. The ratio of the third term of (19) to the second term is $\frac{2}{3}(r-2)(z_2/z_3)(n_2/N_2)$, which is certainly small compared with z_2/z_3 for the conditions in which we are interested. It follows that if $\epsilon_3<\epsilon_2$, so that $z_2<z_3$, we may drop the third term without any further ado. However, we still have to consider the possibility, which is not excluded by the discussion above, that $\epsilon_3>\epsilon_2$. Now, it follows from (19) that

$$\frac{n_2}{N_2} < \left[\frac{2z_2}{r(r-1)}\right]^{1/2} .$$

Consequently the ratio of the third term of (19) to the second must be less than

$$\tfrac{2}{3}(r-2)[\tfrac{1}{2}r(r-1)]^{-\frac{1}{2}}(z_2^{\frac{3}{2}}/z_3) .$$

If we take for ϵ_2 the lowest value, ϵ_1, allowed by the discussion above, and for ϵ_3 the highest value, 1.27 ϵ_1, allowed, then we find for the *largest* plausible value of $z_2^{\frac{3}{2}}/z_3$ the expression $\exp(-0.23\ \epsilon_1/kT)$. For the conditions we are considering, this will be small. Consequently the third term of (19) may be neglected. It appears finally that the only appreciable effect of multiple occupation is that due to the possibility of the simultaneous trapping of *two* defects by a single acceptor ion. The influence of this on the value of n_2 is given by eq. (17′), where it is contained in the second term on the right.

4. Dispersion in the binding energies

The model considered in Section 2 may also be brought closer to the presumed reality by allowing for some dispersion in the values of the binding energy for different acceptor ions. Here the effect of this will be examined for case (a) of Section 2, with a single binding energy characterising each acceptor. Let ϵ_i be this binding energy for the i'th acceptor, and let $z_i \equiv \exp(-\epsilon_i/kT)$ and the average value of the z_i be z_0:

$$z_0 \equiv (1/N_A)\sum_{i=1}^{N_A} z_i . \tag{20}$$

Then we find, by the same procedure as led to (5),

$$\left(1-\frac{n_2}{N_A}\right)\left(1+\frac{z_0}{r}\frac{N_2}{n_2}\right) = X , \tag{21}$$

where

$$X \equiv \frac{1}{N_A}\sum_{i=1}^{N_A}\frac{z_0+r(n_2/N_2)}{z_i+r(n_2/N_2)} \tag{22}$$

and we have made use of the fact that $n_2 \ll N_2$ to replace p by n_2/N_2 in accordance with (12). Now, it follows from (2a) and (3) that $z/pr = n_2/n_1$. Consequently (in the case to which (2a) applies) where $n_2 \ll N_A$, and hence $n_2 \ll n_1$, we must have $z \ll pr$ and hence $z \ll r(n_2/N_2)$. We may suppose this result to apply for each of the z_i also, provided the dispersion of the ϵ_i is not too great. Then we may expand the summand of (22) in powers of the z_i, obtaining

$$X = 1 + \left(\frac{1}{r}\frac{N_2}{n_2}\right)^2 \frac{1}{N_A}\Sigma(z_i-z_0)^2 + \ldots\ldots \tag{23}$$

Substitution of (23), taken as far as the second term, in (21) yields

$$n_2^2 - \frac{z_0}{r}N_2N_A = -\frac{z_0}{r}N_2n_2\left[1+\frac{z_0}{r}\frac{N_2N_A}{n_2^2}\delta\right] , \tag{24}$$

where

$$\delta \equiv \frac{1}{N_A}\Sigma\frac{(z_i-z_0)^2}{z_0^2} \tag{25}$$

is the mean square dispersion of the z_i. The first term, $-z_0N_2n_2/r$, on the right of (24) may actually be dropped, since it is small compared with the second term on the left when $n_2 \ll N_A$. To get an idea of the effect of the dispersion of the binding energies we consider a definite distribution. If $G(\epsilon)d\epsilon$ is the fraction of the values of the ϵ_i lying in the infinitesimal interval $(\epsilon, \epsilon+d\epsilon)$, suppose that

$$G(\epsilon) = A\exp[-(\epsilon-\epsilon_0)^2/2\Delta^2] , \tag{26}$$

where A, ϵ_0 and Δ are constants. Then

$$\left.\begin{aligned} z_0 &= \exp\left[-\frac{\epsilon_0}{kT}-\frac{1}{2}\left(\frac{\Delta}{kT}\right)^2\right] , \\ \delta &= \exp[(\Delta/kT)^2]-1 . \end{aligned}\right\} \tag{27}$$

From (24) and (27) we may derive a rough rule for dispersion to be unimportant, so that (7a) holds (with z replaced by z_0), when $n_2 \ll N_A$. The rule is:

$$\Delta < \tfrac{1}{2}kT . \tag{28}$$

When (28) holds, the ratio of the second term to the first term in the exponential of the expression (27) for z_0 will be less than $kT/8\epsilon_0$. Therefore, since by (7a) z_0 should be small for $n_2 \ll N_A$, the ratio will be small and z_0 will be adequately approximated by $\exp(-\epsilon_0/kT)$. The second term on the right of (24) is $(n_2/N_A)\,\delta$ times the second term on the left, according to (7a), and therefore may be neglected if (28) holds. Representative numerical values might be $\epsilon_0=1$ milli ev, $kT=0.4$ milli ev, and hence, by (28), $\Delta<0.2$ milli ev: not more than 20% r.m.s. dispersion for the trap energies. At 1 degree K, this upper limit is reduced to 5%. Thus it is quite likely that at the lower temperatures the effect of dispersion is appreciable.

The possibility that the traps around a given acceptor ion have differing binding energies ought also to be considered. For this case (2a) would be replaced by

$$\frac{n_1}{N_1}=\frac{\left(\frac{1}{r}\sum_{t=1}^{r}\exp(\epsilon_t/kT)\right)}{1+r\left(\frac{1}{r}\sum_{t=1}^{r}\exp(\epsilon_t/kT)\right)}, \tag{29}$$

where the parenthesis is an average over the traps around one ion. If this average be defined as $1/z_i$, for the i'th acceptor, then (21) remains valid. Further defining ϵ_i appropriately in terms of z_i (so that it is a free energy), we may suppose it to have a dispersion of form (26) and so arrive at the same criterion (28). However, ϵ_0 will now be a function of temperature, and we need a further criterion for this to be virtually a constant. This latter criterion cannot be as simply handled, because r is not a large number and hence we cannot suppose a unique continuous spectrum for the ϵ_t. Furthermore it is not obvious that it is expedient to handle "intra-acceptor" and "inter-acceptor" dispersions separately. So far this question has not been investigated any further.

5. Thermoelectricity

The theory of the thermoelectric power, Q, for permutation conduction is quite simple. From the single assumption that the current is carried only by defects on "free" sites *all of the same energy*, it follows by the general theory of thermoelectricity that*

$$Q=-\psi/eT \tag{30}$$

and hence, from (1), that

$$Q=\left(\frac{k}{e}\right)\log\left(\frac{N_2}{n_2}-1\right). \tag{31}$$

Evidently, from measurements of Q and the conductivity absolute values of $N_2\mu$, where μ is the mobility of the free defects, may be obtained. According to the model the variation of $N_2\mu$ with temperature should give the variation of μ with temperature (the absolute values being, of course, somewhat uncertain). By (31), Q will be *positive* so long as $n_2<\frac{1}{2}N_2$.

We now examine the specific predictions of model (a) of Section 2. At the low temperature limit we have, by (7a),

$$Q\simeq(k/e)\log(N_2/n_2)$$

$$=(k/2e)\log(N_2r/N_Az).$$

That is,

$$Q\simeq\frac{1}{2}\left(\frac{k}{e}\right)\left[\log\left(\frac{N_2r}{N_A}\right)+\frac{\epsilon}{kT}\right]. \tag{32}$$

Thus, measurements of Q *versus* T should provide a means of testing this particular model, and evaluating ϵ and N_2r/N_A. On the other hand, at the high temperature limit $n_2\rightarrow N_A$ and therefore

$$Q\simeq(k/e)\log(N_2/N_A). \tag{33}$$

In principle, from absolute values of Q at both limits, both N_A/N_D and r might be determined. In practice, however, the conditions necessary for the actual thermoelectric power of the impurity mode and conduction-band mode in combination to approximate that of the impurity mode in isolation, in the high temperature limit, might not be realizable.

6. Minority donor states as traps

The general picture of impurity conduction discussed above being once accepted, one may conceive special elaborations of the impurity content which should modify the electrical properties in interesting ways. In particular, one might exploit the fact that the binding energies for chemically distinct donors may differ by as much as milli-ev,[7] and that this is the order of magnitude of the coulomb energy trapping a defect state in the neighborhood of an acceptor. Suppose we add to the impurity content a number N_D' of "minority" donors, with $N_D'\ll N_D$, for which the electron binding energy is *less than* that of the majority donors by a definite amount ϵ'.[8] Since $N_D'\ll N_D$ and $rN_A\ll N_D$, we may ignore the small proportion of the minority donors at "trap" sites in the neighborhood of an acceptor. The remainder, however, are also traps for donor defect states, since when a defect is transferred from a (non-trap) majority donor atom to a (non-trap) minority donor atom the energy of the crystal decreases by ϵ'. We may assume, in accordance with the general model, that defects at these special traps do not contribute to conduction. In this section the theory of this system is investigated for case (a) of Section 2.

Let the number of defects on minority-donor sites be n' and let

$$z'\equiv\exp(-\epsilon'/kT).$$

The number of conducting defect sites is

$$N_2\equiv N_D-rN_A.$$

Let n_2 of them be occupied by defects. Then in place of eqs. (1), (2a), (3) we have

$$\left.\begin{aligned} N_2/n_2&=1+\exp(-\psi/kT),\\ N_A/n_1&=1+(z/r)\exp(-\psi/kT),\\ N_D'/n'&=1+z'\exp(-\psi/kT),\end{aligned}\right\} \tag{34}$$

and

$$n_1+n_2+n'=N_A. \tag{35}$$

It is easily seen that the solution of these equations for ψ and the n's is unique. On eliminating n_1, n' and ψ from (34) and (35) we find, instead of (5) with $c=r$,

$$(r-z)n_2^2+[z(N_2+N_A)+fN_D']n_2-zN_AN_2=0 \tag{36}$$

where

$$f\equiv\frac{zN_2+(r-z)n_2}{z'N_2+(1-z')n_2}. \tag{37}$$

*The sign of Q here is according to the same convention as is used in reference 2, such that normally for an extrinsic semiconductor Q is positive for p type, negative for n type.

Table 1

Case			$f=$	$\frac{n_2}{N_2}=$
A	$\frac{z'}{z}\to 0$ $(\epsilon'>\epsilon)$	$N_A>N_D'$	$\frac{rN_A}{N_A-N_D'}$	$\frac{z}{r}\left(\frac{N_A-N_D'}{N_D'}\right)$
B		$N_A<N_D'$	$\frac{z}{z'}\left(\frac{N_D'-N_A}{N_D'}\right)$	$\frac{z'N_A}{N_D'-N_A}$
C	$z'=z$ $(\epsilon'=\epsilon)$	$N_A>N_D'$	$\left(\frac{N_A-N_D'}{2N_D'}\right)(q-1)$	$\left(\frac{2N_A}{N_A-N_D'}\right)\frac{z}{q-1}$
D		$N_A<N_D'$	$\left(\frac{N_D'-N_A}{2N_D'}\right)(q+1)$	$\left(\frac{2N_A}{N_D'-N_A}\right)\frac{z}{q+1}$
E	$\frac{z'}{z}\to\infty$ $(\epsilon'<\epsilon)$		$\left(\frac{rN_A}{N_D'}\frac{z}{z'}\right)^{1/2}$	$\left(\frac{N_A}{N_D'}\frac{zz'}{r}\right)^{1/2}$
F		$N_A=N_D'$	$(rz/z')^{1/2}$	$(zz'/r)^{1/2}$

We consider only the case $\epsilon'>0$; so that $z'\to 0$, as well as $z\to 0$, when $T\to 0$. To examine this low temperature limit, we assume that

$$f/z\to\infty,\ \text{as } z\to 0\,, \tag{38}$$

and

$$n_2^2/z\to 0,\ \text{as } z\to 0\,, \tag{39}$$

and shall verify (38) and (39) from the solutions then obtained. With these assumptions, in the low temperature limit (36) becomes

$$n_2 f=z\,N_2N_A/N_D'\,, \tag{40}$$

and hence

$$f=\frac{f+r(N_A/N_D')}{(z'/z)f+(N_A/N_D')}\,. \tag{41}$$

The solutions of (40) and (41) for the different possible situations are set out in Table 1. In the table (cases *C* and *D*),

$$q\equiv\left\{1+\frac{4rN_D'N_A}{(N_D'-N_A)^2}\right\}^{1/2}. \tag{42}$$

It may be verified by inspection that (38) and (39) hold in each of the six cases.

These results are quite different in character from (7a), and it is of interest to inquire under what conditions there is a range of temperature (between the low temperature limit of the foregoing results, and the high temperature "saturation" limit where $n_2\to N_A$) for which (7a) holds. The condition for (7a) to hold, according to (36), is (for $z\ll 1$)

$$z(N_2+N_A)+fN_D'\ll 2(rz\,N_AN_2)^{\frac{1}{2}}\,. \tag{43}$$

Since both terms on the left of (43) are positive, they must each be small compared with the right-hand side. Therefore (7a) will hold if

$$\left.\begin{aligned} &z\ll 4rN_AN_2/(N_A+N_2)^2\,,\\ &z\gg (fN_D')^2/4rN_AN_2\,. \end{aligned}\right\} \tag{44}$$

Then, by (7a) and the first of (44), the first term of the numerator of (37) is small compared with the second term.

Hence

$$f\simeq r/[1+z'(rN_2/zN_A)^{\frac{1}{2}}]\,.$$

The conditions (44) may therefore be written

$$z\ll 4rN_A/N_2\,, \tag{45}$$

$$\frac{N_D'}{4N_A}\ll\left(\frac{zN_2}{4rN_A}\right)^{\frac{1}{2}}+z'\left(\frac{N_2}{2N_A}\right)\,. \tag{46}$$

If $N_D'\ll N_A$, then these conditions will certainly be satisfied simultaneously for some range of T, whatever the value of ϵ'. For this range (7a) will hold (and for lower temperatures the relations given in the table, for case *A*, *C*, or *E*, will hold[9]). An alternative sufficient condition is that there exist a temperature range for which (45) is satisfied simultaneously with

$$z'\gg N_D'/2N_2\,. \tag{47}$$

This requires that $\epsilon\log(2N_2/N_D')$ exceed $\epsilon'\log(N_2/4rN_A)$ by at least a few times kT for the temperatures in question.

Case *B* is of particular interest. Here the only role of the acceptors is to provide defects, which fill the minority donor traps. As T increases from zero, the number excited to the free sites does not depend at all on the trapping property of the coulomb field of the acceptors. If this case can be realized in practice, it should be possible to study permutation conduction with an activation energy unrelated to that due to the trapping mechanism suggested by Mott. The value of the activation energy would be just the difference between the electron binding energies for the majority and minority donors.

References and footnotes

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7. See, for example, E. M. Conwell, *Phys. Rev.* **99**, 1195 (1955)
8. The minority donors might be Sb, and the majority ones As or P.
9. It should be remembered, however, that according to the analysis in Section 3 we should expect (18) to hold at the lowest temperatures, the distribution of defects then being dominated by double trapping in the acceptor neighborhoods. We have not analyzed the situation with double "Mott" trapping and minority donor trapping simultaneously taken into account.

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