4. Conductivity, Localization, and the Mobility Edge

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With 8 Figures

The many forms of amorphous silicon, hydrogenated to a greater or lesser extent, appear to have widely differing structures and electrical properties. A major aim of theory in the field of amorphous materials must be to relate electrical, magnetic and optical properties to structure. The purpose of this chapter is to describe the extent to which this can be done. We shall ask, whether the concept of a mobility edge is theoretically justified and experimentally observed, what are the roles of short-range variations of potential, such as might exist in a continuous random network, relative to those of long-range fluctuations, caused either by charged defects or fluctuations in composition. We describe the meaning of a "defect" in an amorphous material and give possible explanations of the double sign anomaly in the Hall effect, found in all amorphous silicons investigated up till now, and discuss the applications of the concept of a polaron to this material.

4.1 Background

Much of our understanding of the conduction bands of amorphous materials comes from the classical paper of *Anderson* [4.1] on "The Absence of Diffusion in Certain Random Lattices". In this and subsequent sections we shall see what can be deduced about conductivity from the model of Anderson's paper, and later in this chapter apply these results to amorphous silicon. In Anderson's paper a crystalline array of potential wells is considered, as shown in Fig. 4.1, with depths spread in a random way over a range of energies V_0. If B is the tight-binding bandwidth in the absence of disorder, then Anderson showed that, if V_0/B exceeds a certain critical value $(V_0/B)_{\mathrm{crit}}$, all states in the band are localized; that is to say, following later analysis [4.2], their wave functions may be written

$$\Psi = [\Sigma\, C_n\, e^{i\phi_n}\, \psi_n]\, e^{-\alpha r} , \tag{4.1}$$

where ψ_n is an atomic wave function on the well n, ϕ_n a random phase and c_n a coefficient which, in its turn, will vary in some random way from site to site. Each eigenstate Ψ is localized at some point in space, falling off exponentially with distance from it. The quantity varies with energy in the band and
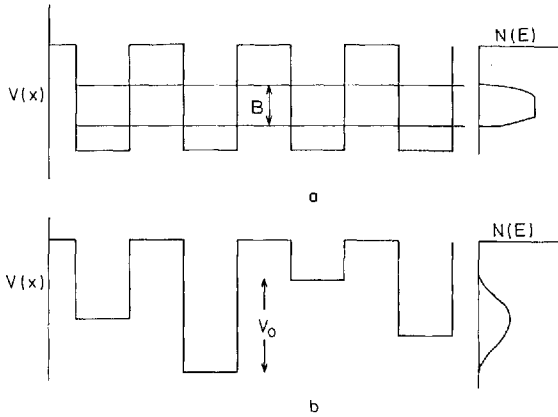
Fig. 4.1. Potential energy $V(x)$ of an electron in a lattice with diagonal disorder. (a) With $V_0 = 0$; (b) With a finite value of V_0. The density of states $N(E)$ is also shown. B is the bandwidth without disorder

tends to zero as V_0/B tends to the critical value. This depends on the coordination number z; for $z = 6$ it is probably [4.3] about 2, differing considerably from that in Anderson's original paper.

If states are localized, then an electron can move from one state to another only through thermal activation, for instance, by phonons. The present author [4.4] first pointed out that if V_0/B were less than the critical value, a tail to the band would none the less exist and states in the band tail would still be localized, and for a rigid lattice, localized states would be separated from nonlocalized ones by a sharp[1] energy E_c; electrons with energies below E_c can move only through thermal activation, while those with energies above will have an unactivated mobility. For this reason, the energy E_c has been named the "mobility edge" [4.5].

A great deal of our understanding of the electrical properties of amorphous and liquid semiconductors has been obtained through the application, to the conduction bands of these materials, of results obtained from the Anderson model of Fig. 4.1, although of course, the potential in real materials is very different; the experimental situation nearest to the Anderson model is that of an impurity band in a doped and fairly heavily compensated ($\sim 50\%$) semiconductor, though here there is the additional complication that the wells of Fig. 4.1 (the donors) are random in space. We shall then first outline the predictions of the Anderson model, with references when appropriate to impurity conduction.

The position of the mobility edge in this model has been calculated by *Abou-Chacra* and *Thouless* [4.6]. If V_0/B lies some way below the critical value, we expect a tail of localized states, as shown in Fig. 4.2, which illustrates only the lower part of the band. The tail extends over a range of energies V_0, and these authors show that if $V_0/B \ll 1$, practically the whole tail is localized. This is because no fluctuation of depth V_0 will itself produce a

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1 If interaction with phonons is taken into account, a lifetime τ will lead to a broadening h/τ.
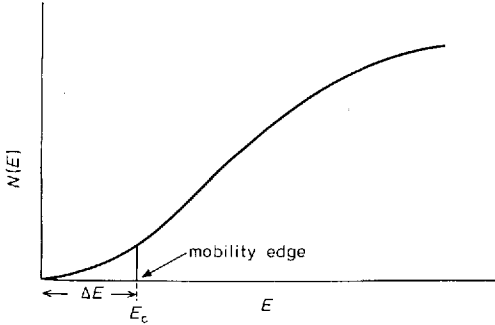
Fig. 4.2. Density of states in the conduction band of a noncrystalline material showing the mobility edge (E_c)

trap, but only groups of deep wells near together. Such groupings are rare and so extended states cannot be formed from them. Only when $V_0/B \sim 1$ does E_c move down into the tail.

As regards the conductivity, we may consider two cases:

a) The Fermi energy lies in the band of localized and extended states; this case is appropriate to impurity bands. Then if E_c lies below E_F, the conductivity will depend little on phonon scattering and be roughly constant except at high temperatures. On the other hand, if E_F lies below E_c, we expect two forms of conduction. These are: at high temperatures (by excitation to a mobility edge) when the conductivity will be of the form

$$\sigma = \sigma_{min} \exp[-(E_c - E_F)/kT] , \tag{4.2}$$

(the significance of σ_{min} being discussed below), and at low T (variable-range hopping by electrons with energies near the Fermi energy) where an *approximate* formula for the conductivity is

$$\sigma = A\, e^{-B/T^{1/4}} . \tag{4.3}$$

This is discussed in Sects. 4.5, 12.

b) The Fermi energy lies below the band. Here again, two forms of conduction are expected, one given by (4.2) and the other, at low tempera-
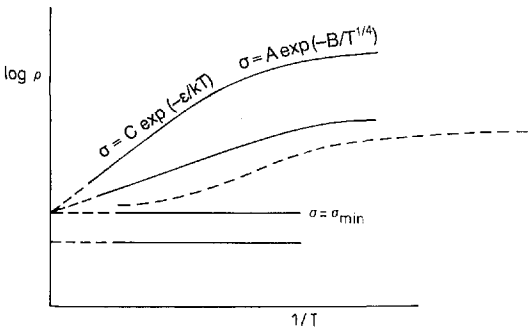

Fig. 4.3. Typical behaviour of the resistivity ϱ of a degenerate electron gas showing a metal-insulator transition of the Anderson type. ε denotes E_c-E_F. The dotted line shows the behaviour if there is no minimum metallic conductivity

tures, resulting from hopping between band-edge localized states. This is a form of variable-range hopping, treated theoretically by *Grant* and *Davis* [4.7], but does *not* lead to a conductivity of the form (4.3).

It may be noted that in case b, any lifetime broadening of the mobility edge will be a consequence of interaction with phonons, while in case a, the stronger Auger interaction with the degenerate electron gas in states below E_F will be important, except when E_F lies at E_c.

Figure 4.3 shows the resistivity to be expected in case a if the relative positions of E_F and E_c are moved, either through change of composition, magnetic field or in other ways. For comparison with experiment for impurity bands and inversion layers, see [4.2, 8–10]. A metal-insulator transition is observed.

4.2 The Minimum Metallic Conductivity

This quantity was introduced by the present author [4.11] and estimated to be

$$\sigma_{min} \sim C\,e^2/\hbar a_E \ . \tag{4.4}$$

Here C is a numerical constant, which depends both on the coordination number and on the square of V_0/B for the Anderson localization criterion, and is probably in the range of 0.025–0.05. If the mobility edge lies near mid-gap, $a_E \simeq a$, where a is the distance between wells; otherwise [4.12],

$$(a/a_E)^3 = \int_{-\infty}^{E} N(E)dE/\int_{-\infty}^{\infty} N(E)dE \ . \tag{4.5}$$

The quantity σ_{min} may be used in two ways. a) As the pre-exponential factor in (4.2). b) A smallest value of the unactivated conductivity.

Early considerations by *Cohen* and *Jortner* [4.13] based on classical percolation theory, and a more recent approach due to *Götze* [4.14] suggest that there is no discontinuous change in the mobility at E_c; the present author believes these to be incorrect in the limit of high T, and that (4.2) is then valid. At the time of writing, however, there is considerable doubt [4.14–17] about whether σ_{min} exists in the limit of low T. In other words, do values of $(E_F - E_c)$ exist for which ϱ behaves like the dotted line in Fig. 4.3, tending as $T \to 0$ to a finite value much above $1/\sigma_{min}$, and to infinity when $E_F = E_c$? The present author believes that the answer to this question, though of great theoretical interest and likely to be relevant to impurity bands at low temperatures, will not affect the properties of amorphous silicon in any practical case. In [4.17] he related it to the properties of the coefficients c_n in (4.1); σ will tend to zero as $E \to E_c$ only if these show long-range fluctuations with changing position (i.e., with n), with a correlation length tending to infinity as $E \to E_c$. This, in its turn, depends on the way $a \to 0$ in (4.1) as $E \to E_c$; if

this is as $(|E - E_c|)^s$, these fluctuations will occur only if $s < 2/3$. Theoretical estimates of s are 0.6 or 2/3, so the question remains open at the time of writing.

The conclusion that (4.2) is valid for conduction at a mobility edge is queried by some authors (e.g., *Götze* [4.14], and *Belize* and *Götze* [4.18] pointed out how difficult it is to use experimental data to test this. According to their analysis, $\sigma \sim \sqrt{(E - E_c)}$ near a mobility edge, and they show this to be consistent with some of the earlier experimental work on the temperature-dependence of the conductivity.

In what follows we shall, however, assume (4.1) to be valid for charge transport at a mobility edge.

4.3 Hall Mobility and Thermopower for Charge Transport at a Mobility Edge

The Hall mobility μ_H has been calculated for electrons or holes with energies at a mobility edge by *Friedman* [4.19], using a method derived from the theory of polarons (Sect. 4.4). According to this analysis,

$$\mu_H \simeq 0.1\, ea_E^2/\hbar \tag{4.6}$$

and the sign should be negative (n-type), whether for electrons or holes. This is smaller than the "conductivity mobility" μ_c; if we write

$$\sigma = e\mu_c N(E_c)kT\, e^{-W/kT} \tag{4.7}$$

and equate the pre-exponential term to σ_{min} ($\simeq 0.05\, e^2/\hbar a_E$), we see that

$$\mu_c \sim 0.05\, ea_E^2\, \Delta E/kT\ , \tag{4.8}$$

or if $N(E_c) \sim 1/\Delta E\, a_E^3$,

$$\mu_c \sim 0.05\, ea_E^2\, \Delta E/kT\ . \tag{4.9}$$

Here ΔE is the range of localized states; if $\Delta E/kT \gg 1$, μ_c should be the larger.

The thermopower when charge transport is by electrons at a mobility edge is given by [4.2, 20]

$$S = \frac{k}{e}\left(\frac{E_c - E_F}{kT} + 1\right)\ . \tag{4.10}$$

If the Fermi energy shifts linearly with temperature, we may write

$$E_c - E_F = \varepsilon - \gamma T \;. \tag{4.11}$$

Then (4.2) becomes

$$\sigma = \sigma_0 e^{-\varepsilon/kT} \;, \qquad \sigma_0 = \sigma_{min} e^{\gamma/k} \;. \tag{4.12}$$

There has been some dispute in the literature as to whether the same substitution can be made in (4.12), but this appears to be the case [4.2]. The problem of the shift in the Fermi energy is discussed further in Sect. 4.10.

4.4 Polarons

The extent to which polarons play a role in charge transport in noncrystalline semiconductors has been a matter of controversy, and a few lines on their nature are added here [4.2, 21]. In crystalline materials, they are of two kinds.

a) Dielectric polarons, limited to ionic crystals. An electron or hole will always polarize its surroundings outside a sphere having a "polaron radius" r_p, creating a potential well for itself. In principle, this is found by minimizing the sum of the potential energy $(- e^2/r_p)(1/\kappa_\infty - 1/\kappa)$ and the kinetic energy $h^2/2m_e r_p^2$. Here κ_∞ and κ are the high-frequency and static dielectric constants. If r_p is much greater than the lattice parameter a, a "large polaron" is formed which can increase the effective mass but is of little importance here. For large m_{eff} (e.g., in d-bands), r_p can be comparable with a, and the polaron is then called "small".

b) Acoustic or molecular (small) polarons are formed when the carrier allows a bond to form between two adjacent atoms, or in molecular crystals when the presence of the carrier deforms a molecule. As shown in different ways by *Toyozawa* [4.22], *Emin* [4.23], and *Mott* and *Stoneham* [4.24], no polaron of this type is formed at all unless the coupling between the carrier and the localized phonon is strong enough, and the effective mass large enough.[2]

Small polarons of both types move at high temperatures $(T > \Theta_D/2)$ by "hopping" with mobility of the form

$$\mu = \mu_0 \exp(- W_H/kT) \;. \tag{4.13}$$

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2 *Towozawa* [4.22], and also *Mott* and *Stoneham* [4.24], have shown that there must be a delay in the formation of this kind of polaron involving an activation energy, which has been estimated numerically by *Mott* [4.25]. *Mott* and *Stoneham* [4.24] described evidence for such a delay from the migration of excitons (an electron in the field of a hole which can be self-trapped). The first observation for holes was due to *Laredo* et al. [4.26] in AgCl.

At low temperatures, band motion is possible, with effective mass greatly enhanced, of order

$$m_p \sim 5\,m \exp\left[W_H\middle/\left(\frac{1}{2}\,\hbar\omega\right)\right]^{-1}.$$
(4.14)

It is doubtful if this has been observed; such high values of the effective mass would lead to Anderson localization [4.27] if there were a very small random field, caused, for instance, by charged impurities. What has been observed, however, is a drop in W_H to very low values (for instance, in vanadium phosphate glasses [4.2, 25]) where disorder does give some localization but the main activation energy for conduction is of polaron type.

Some peculiarities of the acoustic polaron are worth mentioning. In one-dimensional systems a polaron will *always* form (because in one dimension any well, however shallow, will trap an electron). In three dimensions one expects an equilibrium between free and trapped carriers so that as the temperature rises, charge transport would be due to free carriers [4.29].

For polarons in the range of temperatures for hopping, the Hall effect is explained by a mechanism quite different from that for free carriers. *Friedman* and *Holstein* [4.30] were the first to show, using a three-site model and assuming s-like wave functions, that
a) the Hall effect would be n-type both for electrons and holes, and
b) the activation energy in μ_H is $W_H/3$.

We see therefore that, in contract to the behaviour of free carriers in a conduction band, there are different activation energies for conduction, thermopower and Hall mobility. The only material in which to our knowledge all three have been observed is slightly reduced $LiNbO_3$ ([4.31] and [Ref. 4.2, p. 84]).

A feature of a-Si-H is the double sign reversal of the Hall effect, electrons showing p-type behaviour and holes of n-type; this occurs also in amorphous III–V compounds (references are in Sect. 4.8). With a view to understanding this, *Emin* [4.32] considered polarons formed on bonds (rather than atoms) and showed that the anomaly could be explained by supposing that hopping was predominantly round the rings and that odd-membered rings predominated. Some criticisms and refinements of the theory were given by *Grünewald* et al. [4.33]. Whether these ideas can be related to amorphous silicon will be discussed in Sect. 4.8.

The application of the polaron concept to noncrystalline materials in general is as follows. For band-edge localized states, as also for any bound states such as donors in crystals, there must be some deformation of the network or lattice by the carrier. If, however, the criterion for (acoustic) polaron formation in the corresponding crystal is not met by some margin, it seems to us unlikely that there will be polaron effects for carriers above the mobility edge. If, however, polarons are formed in the crystal (or would be if some softening of the phonons due to amorphicity were taken into account),

it will be appropriate to take the polaron in the noncrystalline material as a heavy quasiparticle and consider its behaviour in whatever random field exists in the material. If W_H is large enough ($> \sim 0.1$ eV) for hopping motion to be observed when $T > \Theta_D/2$, the effective mass (4.9) for low temperatures will probably be large enough to ensure Anderson localization throughout the band, with no mobility edge; the mobility will behave like

$$\exp\left[-\left(W_H + \frac{1}{2}w\right)/kT\right] \qquad T > \frac{1}{2}\,\Theta_D$$

$$\exp\left(-w/kT\right), \qquad T \ll \frac{1}{2}\,\Theta_D$$

where w is a small hopping energy due to disorder. However, systems probably exist where polaron formation gives some mass enhancement, but there is still a mobility edge; according to the present author, $La_{1-x}Sr_xVO_3$ is one [Ref. 4.2, p. 144].

4.5 Variable-Range Hopping

Two forms must be distinguished.

a) Hopping by electrons excited into localized states at a band edge; here an analysis was given by *Grant* and *Davis* [4.7].

b) Hopping by electrons with energies near the Fermi level; this is a phenomenon observed in impurity bands as well as in some amorphous semiconductors. For this phenomenon, a theory which neglects electron-electron interaction can be shown by various methods [4.34–36] (see also [Ref. 4.2, p. 33]) to yield the law

$$\sigma = A \exp\left[-(T_0/T)^{1/4}\right]. \tag{4.15}$$

However, if electron-electron interaction is taken into account, major changes in this behaviour are predicted, especially at low temperatures, which have not with certainty been observed and for which several theories exist [4.37, 38].

The thermopower S has been discussed by several authors [Ref. 4.2, p. 55]. It behaves like

$$S = (k/e)(W^2/kT)(d\ln N/dE)_{E\,=\,E_F}. \tag{4.16}$$

Here W is the hopping energy given by $W^2/kT = k(T_0T)^{1/2}$ for variable-range hopping, so that S is proportional to $T^{1/2}$. According to *Whall* [4.39], (4.13) is also valid for nearest-neighbour hopping, so S should *decrease* at high T.

The contribution of the spins to the thermopower is believed [4.10] to add a term

$(k/e)\ln 2$

if these are random.

The Hall effect is expected to be small; recent theoretical approaches are not in complete agreement [4.41–43], but give the same order of magnitude.

Since variable-range hopping is between localized states, there must always be some distortion of the surroundings when the occupation of a site changes, so effects of polaron type are present. According to *Mott* and *Davis* [Ref. 4.2, p. 87], in the limit of low T this will simply decrease the pre-exponential factor by $\exp(-4W_H/\hbar\omega)$ but will not greatly affect the term within the exponential. As the temperature is raised, however, an activation energy of the type of W_H will gradually be introduced.

In view of all there complications, it is hardly to be expected that a $T^{1/4}$ law will always be observed, and it is perhaps surprising how accurately it represents experimental data in some cases [4.2] and the corresponding $T^{1/3}$ law for two dimensions [4.8].

4.6 Application of Theory to Amorphous Silicon

In seeking to apply theoretical models to amorphous silicon, the following are some of the relevant considerations:

a) There is a wide variety in the properties of silicon films prepared by various methods, both as regards hydrogen content, concentration of defects and probably structure, and some at least cannot be regarded as homogeneous.

b) All films show the double-sign anomaly in the Hall effect; that is, when they are *n*-type (according to thermopower measurements), the Hall effect is positive, and when *p*-type (for instance, through doping), the Hall effect is *n*-type. For Si, results are due to *Le Comber* et al. [4.44], *Beyer* et al. [4.45] and *Dresner* [4.46]; for Ge, *Seager* et al. [4.47]; and *Beyer* and *Mell* [4.48] for some amorphous III–V compounds.

c) There is a wide variety in the pre-exponential factors σ_0 of (4.8) in the conductivity; σ_0, in general, increases with activation energy.

d) In general, the activation energies for conduction (E_σ) and thermopower (E_S) are not equal, but $E_\sigma > E_S$, though they approach each other for "good" specimens. Whether this is so or not is conveniently tested by a plot of $\ln \sigma + (e/k)S$ versus $1/T$. The temperature dependence of the activation energy, namely $-\beta T$, cancels out in this expression, as was first pointed out by *Beyer* et al. [4.49]. Figure 4.4, reproducing results from *Jones* et al. [4.50] and later work by Jones shows that specimens can be obtained in
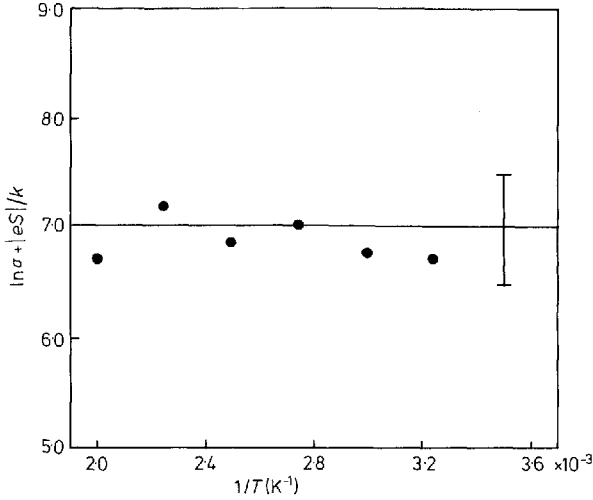
Fig. 4.4. Plot of $\ln \sigma + eS/k$ versus $1/T$ for a specimen of a-Si [4.59]. No difference between E_σ and E_S is apparent, but if the high temperature point were in error, a difference of up to 0.1 eV would be consistent with the data

which, according to these workers, $E_s \simeq E_\sigma$. On the other hand, if, as Beyer maintains, the high temperature results are not reliable, even the flattest curves may have a slope of $(E_\sigma - E_S)$ in the range from 0.05 to 0.1 eV. In any case, a larger slope is observed when hydrogen is driven off, and indeed is seen frequently in other work. Thus, *Beyer* et al. [4.49] investigated glow-discharge-deposited silicon doped with lithium and found $E_\sigma - E_S$ in the range 0.1 to 0.2 eV, with no evidence for two-channel conduction above 200 K.

This last fact could, in principle, be explained in two ways. One is to assume that the carriers are small polarons, and this has been proposed. However, if this were so it is difficult to see why $(E_\sigma - E_S)$ should vary from specimen to specimen and increase, for instance, on bombardment. The alternative explanation, developed particularly by *Overhof* and *Beyer* [4.51, 52], is that silicon films normally contain *long-range* fluctuations of potential, caused either by charged defects, lack of homogeneity or fluctuations in the concentration of deep states, and that these should be treated as opaque to tunnelling, so that electrons travel along potential valleys and E_σ is determined by the height of the passes separating them, while E_S is determined by the height of the bottoms of the valleys above E_F. We know of no other model which will explain the facts and shall adopt it in this chapter.

If this is so, it might be tempting to abandon altogether the concept of a mobility edge treated as a consequence of Anderson localization; long-range fluctuations will, of course, lead to an activated mobility and as shown, for instance, by *Pistolet* [4.53] and by *Dusseau* [4.54], most of the electrical properties can be accounted for on this model; earlier models of this kind are by *Fritzsche* [4.55] and *Shklovskii* and *Efros* [4.56]. In our view, the strongest argument for not doing this is the double sign anomaly in the Hall effect. As
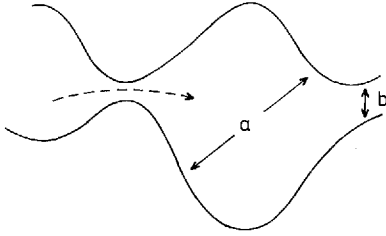
Fig. 4.5. Showing schematically a percolation path (---) in a material with long-range fluctuations of potential

shown below, although in terms of charge transport at a mobility edge we have no fully accepted the explanation of this phenomenon, it is predicted for polarons and is perhaps not unexpected; certainly classical behaviour in long-range fluctuations will not yield it. We shall, therefore, in this chapter, try to combine the idea of a mobility edge with that of long-range fluctuations in potential.

We suppose also that the position of the Fermi energy E_F is determined by a low density of gap states and is highly T-dependent, thus accounting for the abnormal values[3] of σ_0. These and other features of the gap states will be discussed in Sect. 4.10.

4.7 Long-Range Fluctuations of Potential

If a material contains long-range fluctuations of potential *and no other scattering mechanism*, then in our view the concept of a minimum metallic conductivity should be applicable with σ_{min} given by (4.4) and with a equal to the linear dimensions of the fluctuations. There is evidence that this is so from the experiments of *Abeles* et al. [4.51] on the conductivity of metallic particles of Ni, Pt and Au of size less than 100 Å prepared by co-sputtering with SiO_2 or Al_2O_3 [Ref. 4.2, p. 157].

If, on the other hand, there is, in addition, a scattering mechanism giving a mean-free path small compared with a, or polaron hopping, then classical percolation theory should apply; in the former case, the mobility should increase as $(E-E_c)^{1.6}$ as the energy rises above the height of the passes. If this scattering leads to a mobility edge at an energy ΔE above E_A, then E_σ should be the sum of ΔE and $(E-E_F)$ where E lies at the top of the passes. Although the model should lead to some decrease in the pre-exponential factor below σ_{min}, we do not think this should be important. If, in Fig. 4.5, a is the radius of the long-range fluctuations and b the width of the passes, then if ϱ is the resistivity in the neighbourhood of the pass, the resistance of each pass is ϱb and the bulk resistivity is $\varrho b/a$. We might suppose that b is given by

$$\Delta W(b/a)^2 = \Delta E , \tag{4.17}$$

3 See, however, Sect. 4.10 for an alternative explanation due to *Spear*.

where ΔW is the magnitude of the long-range fluctuations, so b/a is unlikely to be small.

We suggest then that the activation energy appearing in the drift mobility and conductivity is the sum of two terms: ΔE, as illustrated in Fig. 4.2; and ΔW, the difference in energies between valleys and passes.

ΔW may have its origin in charged-point defects and fluctuations in defect density near E_F (Sect. 4.9). It should be highly sensitive to the method of preparation. On the other hand, we believe that ΔE is characteristic of the disorder in a continuous random network, that is the result of random dihedral angles and perhaps stretched bonds. Obviously it will depend on composition, but as we shall see below, it is rather insensitive to moderate hydrogen content.

We next ask, what evidence is there for a mobility edge in other noncrystalline materials. In vitreous silica the mobility of electrons has been measured and increases with temperature ([4.58]; cf. [Ref. 4.2, p. 572]), so if a mobility edge exists, ΔE is small compared with kT down to liquid air temperatures. The same is true of the liquid rare gases [4.59]. The present author believes that this is to be expected if the wave function is s-like at the bottom of the band [4.2]. For holes in chalcogenides, the thermopower and Hall effect have been analysed first by *Nagels* et al. [4.60] and in detail by *Mytilineou* and *Davis* [4.61] in terms of a mobility edge with $\Delta E \sim 0.1$ eV. An equally satisfactory analysis was given by *Emin* and coworkers [4.62] in terms of the hypothesis that holes form small polarons. For the present author's arguments against this hypothesis, see [Ref. 4.2, Chap. 10].

In silicon various calculations exist; we first describe one by *Davies* [4.63]. The essence of this method is to calculate the scattering, and hence the mean free path in midband, to be expected from a random orientation of the silicon tetrahedra; that is to say, random values of the dihedral angle. It is then assumed that the relationship between the mean free path L and ΔE is the same as in the Anderson model, with [4.2]

$$L \sim 4\pi b (B/V)^2 ,$$ (4.18)

and ΔE, according to *Abou-Chacra* and *Thouless* [4.6], given by

$$\Delta E/V = (12\, b/L)^{1/2} + 4\pi b/3\, L .$$ (4.19)

The first term is the important one, giving the displacement of the band edge due to disorder. In calculating L, a value of the effective mass m_{eff} in midband must be assumed; reasons are given for taking $m_e = m_{eff}$. The calculated value of ΔE is 0.28 eV.

The observed effect of hydrogen is to widen the gap from 1.8 to 2.2 eV for 15% hydrogen [4.64] but this, as shown in [4.71], is due to a shift of the valence band, the conduction band being little affected. By considering the maximum change in the level of the conduction band due to hydrogen and

estimating the scattering by a potential hill (or well) that would produce this displacement, Davies found that a 10% concentration of hydrogen would increase ΔE by 0.02 eV or less. It is known that the hydrogen is not uniformly distributed. We believe, however, that our conclusion (that the effect on the conduction band is small) is correct.

The treatment given here neglects any effect on the mobility edge due to stretched bonds; the localized states are at regions in the CRN where variations in the dihedral angle are abnormally small. The assumption that stretched bonds do not play a major role in determining the mobility edge is not proved [4.65]. What is clear, as we shall see, is that states (E_Y in Fig. 4.7) exist above the valence band with no states of corresponding density below the conduction band, so that one assumption could be that there are about 10^{19} cm^{-3} very stretched bonds which trap holes, but not electrons. Other models are possible, which on the whole we prefer (cf. [4.71] and Sect. 4.9).

As regards other treatments of the band edge, *Yonezawa* and *Cohen* [4.66] using a tight-binding Hamiltonian found 0.1 eV for the tail; thus, if we accept from the work of Abou-Chacra and Thouless that the range of localized states fills most of the tail, the results agree as regards the order of magnitude with those of Davies. *Bonch-Bruevich* [4.67] found, however, a much smaller value.

There is much evidence that in silicon the mobility is activated; Spear's work estimates the range of tail states to be ~ 0.2 eV [4.00]. In future work, an attempt to separate ΔE from ΔW, for instance, by determining $(E_\sigma - E_S)$, would be valuable, as would also work on CVD material. *Tiedje* et al. [4.68] in recent work found that the mobility in hydrogenated silicon ranges between 0.05 and 0.8 cm^2/V s, that its temperature-dependence shows only minor variations, while the dispersion parameter ranged from 0.1 to 0.7 with increasing hydrogen.

By no means are all interpretations of the mobility based on the concept of a mobility edge. An exponential tail of localized states is assumed, for instance, by *Döhler* [4.60] and by *Tiedje* et al. [4.70].

4.8 The Hall Effect in Amorphous Silicon

We turn next to the Hall effect and the double-sign anomaly described in Sect. 4.6. We have first of all the polaron hypothesis of *Emin* [4.32], namely, that the effect can be explained if small polarons of acoustic type are formed on Si–Si bonds and odd membered rings predominate. Against this it can be argued [4.71]:

a) the phenomenon is also observed in III–V compounds [4.45] for which odd membered rings should be few;
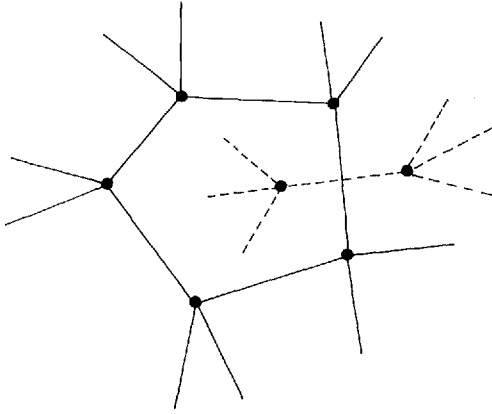b) no argument is given to show why polarons should form in the amorphous material and not in crystals;

Fig. 4.6. Suggested form of bonds giving rise to the Hall effect in a-Si. The dotted line represents another bond in a ring above the plane of the paper

c) the activation energy for hopping can be only a small fraction of the whole, since this is structure-dependent. If so, the arguments of *Sumi* [4.26] show that at high temperatures, transport should be by free carriers which would give a normal sign to the Hall constant. This has not been observed.

Another possibility is to assume a random change of phase from bond to bond, as assumed by *Friedman* [4.72], which would allow the application of Emin's argument. However, this in our view would imply a zero bandwidth and would also necessitate the assumption of odd-membered rings. The present author [4.73] has suggested that Emin's argument could be combined with Friedman's discussion of conduction at a mobility edge by linking three sites at a distance a_E with wave functions $f(x,y,z)\exp(-\alpha r)$. The Hall anomaly would follow if f had odd parity and it was argued that for the conduction band this should be so. This suggestion is, however, highly speculative and we attempt another one here.

In the sense of the tight-binding approximation, we may suppose that the phase ϕ_n of the wave function changes slowly in moving from one bond to another along the rings, but that the Hall effect arises from three-site coincidence where there is sufficient overlap between antibonding orbitals on *different* rings. For the latter, we may well assume a random phase. We suppose, then, that such configurations are as illustrated in Fig. 4.6. We think that, in the spirit of Friedman's work of 1971 and that of Emin, the anomaly in the Hall constant might thus be explained[4].

If long-range fluctuations exist, then according to *Fritzsche* [4.74], the Hall coefficient should be determined by electrons in the valleys rather than at the passes. Thus, the activation energy in the Hall mobility should be the same as $(E_\sigma - E_S)$. *Le Comber* et al. [4.75] found that, for lightly doped n-type samples, μ_H seems virtually independent of T, as in earlier work in chal-

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4 For an alternative discussion, see [4.78]

cogenides [4.76]; in silicon on doping an activation energy appeared. Further investigation to see if any relation exists between the $(E_\sigma - E_S)$ and the Hall mobility would be useful.

That the sign anomaly depends on short-range disorder seems to be substantiated by the work of *Spear* et al. [4.77] who have investigated the Hall effect in microcrystalline silicon films as a function of crystallite size. It will be seen that the effect regains its normal sign at about 20 Å. Although we are far from having a satisfactory theory of this effect, we conjecture that it shows that $a_E \sim 20$ Å for amorphous silicon and that the sign anomaly depends on having disorder within a smaller distance [4.78].

4.9 Defects and States in the Gap

It has been argued in the literature that the concept of a point defect in an amorphous substance is not acceptable [4.79]. While we agree for a material such as a "metallic glass", for glasses and for deposited films for which the structure can be represented by a continuous random network, which we believe to be the case for amorphous silicon and oxide and chalcogenide glasses, defects seem to have a real existence. A true defect, in our view, will have *either* a spin (e.g., a dangling bond) *or* a charge (e.g., an unoccupied or doubly charged dangling bond). Examples are the singly (C_1^-) and triply coordinated (C_3^+) chalcogens in the chalcogenide glasses, the threefold coordinated silicons in SiO_2 which are positively charged or neutral (E^1 centres), and the nonbridging oxygens. In silicon, a continuous random network will contain as part of the disorder of the "perfect" network odd and even-numbered rings, a random distribution of dihedral angles and doubtless stretched bonds.

Defects analogous to vacancies and divacancies may exist, without spin in the neutral state. These are not to be *sharply* distinguished from fluctuations in density.

Whether the concept of valence alternation pairs, with positive and negative charges (negative Hubbard U), is applicable to a-Si is uncertain, though it has been suggested [4.80]. It should however, be noted that in crystalline silicon, *Watkins* and *Troxell* [4.81] have given evidence that the positively charged vacancy has this property; if it is denoted by V^+, the reaction

$$2V^+ \rightarrow V^{++} + V$$
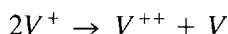
is found to be exothermic. A similar possibility exists for the amorphous material.

The inhomogeneity of amorphous silicon films has been discussed by many authors [4.82] and will not be described in detail here. An important point made particularly by *Revesz* et al. [4.83] is that hydrogen renders the

network more flexible with a reduction in number of the stretched bonds and voids. We believe, however, that a strained network, containing dangling bonds, is a useful model with which to start.

In amorphous silicon hydrogenated and otherwise, the esr signal shows a line with the g-value 2.0055. This is clearly to be identified with the dangling bond and has been observed by *Stuke* and coworkers [4.84] at the interface between crystalline silicon and SiO_2. Its strength is enhanced when hydrogen is driven off [4.85]. Other lines observed under illumination are assigned by *Street* and *Biegelson* [4.86] as follows:

g = 2.0043   localized electrons in a conduction band tail state

g = 2.010–2.013   hole in the valence band tail states.

Voget-Grote et al. [4.87] identified spin signals from positively and negatively charged vacancies in crystals with g = 2.011 and 2.0045, respectively.

No density-of-states curve which neglects correlation (the Hubbard U) can be meaningful in a-Si (or in doped crystalline silicon for that matter). The fact that centres are singly occupied and thus show an esr signal and Curie behaviour is essentially dependent on correlation, as emphasized by *Schweitzer* et al. [4.88]. Thus, in a curve such as that of Fig. 4.7, A is the band of levels for dangling bonds, broadened by disorder; B is the band of levels for doubly occupied bonds of which only a few in specially low states will normally be occupied. If the zero-temperature Fermi energy is determined by the overlapping of these bands, we see that if conductivity is observable, $\beta = (E_c - E_F)/kT$ must be such that $e^{-\beta}$ is not negligible, but that if new dangling bond states are introduced, for instance, by irradiation, E_F may change.

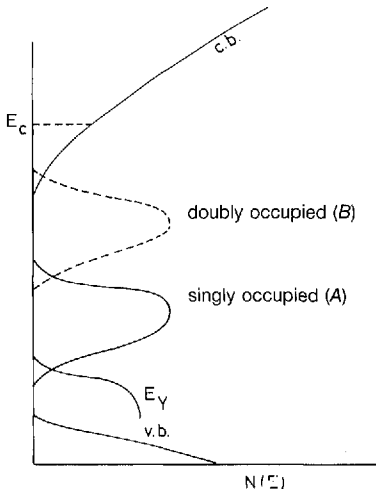The E_Y state is though to be a hole trap associated with hydrogen [4.89].

Fig. 4.7. Density of states in hydrogenated amorphous silicon (schematic)

It has already been emphasized that for any trap, particularly a deep trap, some Stokes shift is to be expected. For the E_Y state, *Tsang* and *Street* [4.90] gave some evidence for a Stokes shift in the photoluminescence line at 1.6 eV, ascribed to transitions between band edge localized states in the conduction band and holes at E_Y; the magnitude of the shift was found to be 0.2 eV.

Stokes shift, namely, a distortion of the surroundings, is, of course, relevant to the magnitude of the Hubbard U; for instance, that required to shift an electron from one occupied dangling bond to another, creating two charged states. This will always reduce U, and in chalcogenides it is normally negative. In crystalline silicon, as we have seen, *Watkins* and *Troxell* [4.81] show that a charged vacancy has this property though there is no firm evidence that this is so for any defect in amorphous silicon. However, if the Hubbard U is to be small enough for doubly charged dangling bond states to lie in the gap, then some deformation must be present to lower its value. *Chakraverty* [4.91] estimates this, without deformation, to be ~ 1.7 eV. This is too large to allow the doubly occupied dangling bond state to lie in the gap. *Dersch* et al. [4.84], however, concluded from the doping dependence of the spin density that the effective correlation energy of the dangling bond amounts to 0.4 to 0.5 eV. The model set out in great detail by *Street* [4.92] to describe luminescence also puts the doubly occupied dangling bond below the conduction band.

The model of dangling bond or other states with energies overlapping so that positive and negatively charged states exist, is reinforced by much evidence, such as that of *Anderson* and *Spear* [4.93] on recombination in doped material. Further evidence comes from the effects of removing hydrogen from a-Si:H annealing. *Fritzsche* [4.85] and *Tsai* et al. [4.94] showed that annealing increases the density of gap states and the paramagnetic susceptibility. The same process leads to a reduction in the photo-current [4.87] and in the luminescence [4.95]. It appears then that spin states act as recombination centres, producing states at the Fermi energy to which electrons can fall. *Hasegawa* and *Imai* [4.96] traced the relationship between photoconductivity and ESR linewidth.

We might add that pinning of the Fermi level is not necessarily due to overlap between the positively and negatively charged dangling bond states. Thus, *Voget-Grote* et al. [4.87] took into account both these and vacancy-like states. *Chakraverty* [4.91], as we have seen, considered that U is too large for the negative state to exist, so the pinning is due to a balance between neutral and positively charged dangling bond states and charged vacancy states. Such a model implies neutral and positively charged dangling bonds and neutral and negatively charged vacancies (V states). *Stuke* [4.84 a], on the other hand, found evidence that overlap between neutral and negatively charged states is responsible for pinning, and that this fits his evidence on the Staebler-Wronski effect which he ascribes to an enhancement of the dangling bond density [4.11].

Street ([4.92] and private communication) considers that the best evidence for pinning by dangling bond states is that the ESR line at $g = 2.0025$ occurs in undoped material, but that in doped material in the dark it disappears but can be induced by illuminating at low temperatures. He also emphasizes the strong evidence that the line at $g = 2.0055$ is indeed from a dangling bond because the same g-value is observed at the interface between crystalline silicon and SiO_2.

4.10 The Pre-Exponential Factor in the Conductivity

We have seen that the pre-exponential factor for a material without long-range fluctuations in potential should be

$$\sigma_0 = \sigma_{min} e^{\beta/k} , \tag{4.20}$$

with $\sigma_{min} \sim 200 \ \Omega^{-1} \ cm^{-1}$. In fact, very large ranges of σ_0 are observed, from 1 to $10^6 \ \Omega^{-1} \ cm^{-1}$, and this will now be discussed.

Solomon et al. [4.97, 98] have claimed that this variation is the result of the production of an accumulation layer by surface changes, giving some band bending downwards. They found that when corrections are made for this, σ_0 is sensibly independent of preparation conditions and of order 10^4 $\Omega^{-1} \ cm^{-1}$. Other workers [4.99] claim to avoid these effects and still find a large variation of σ_0, and in certain cases that σ_0 obeys the Meyer-Nelden rule [4.100,102] in the form

$$\sigma_0 = const \ e^{E_\sigma/kT} \tag{4.21}$$

when E_σ is varied by doping.

As regards the variation of $(E_c - E_F)$ with temperature and the term $\exp(\beta/k)$, it has long been recognised [4.2] that the optical band gap changes with temperature, that this is probably due to a shift of the valence band and that if the Fermi energy is pinned to the valence band, a similar shift of $E_c - E_F$ should occur, linear above the Debye temperature. Such a shift could give at most $\exp(\beta/k) \sim 100$, but would account nicely for a value of order 10^4 $\Omega^{-1} \ cm^{-1}$, since $100 \ \Omega^{-1} \ cm^{-1}$ is a reasonable estimate for σ_{min} with a_E ~ 10–20 Å. To account for larger variations, and particularly for large values of the order $10^6 \ \Omega^{-1} \ cm^{-1}$, there are two possibilities.

a) *Spear* and co-workers [4.99, 103] have given evidence to show that the quantity $\Delta E = E_c - E_A$, that is, the height of the mobility edge above the bottom of the band, decreases with temperature and disappears (or nearly so) at ~ 400 K. This *only* occurs for undoped specimens for which ε_σ is in the range 0.65–0.8 eV and for which σ_0 has these high values (10^5–$10^6 \ \Omega^{-1} \ cm^{-1}$). It does not occur for doped specimens for which the conduction channel
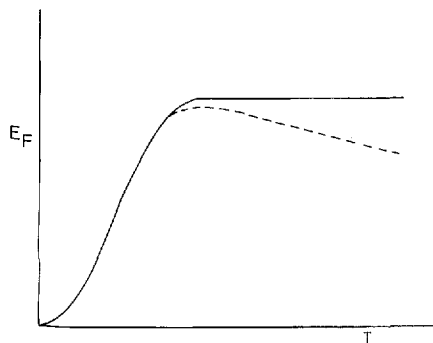
Fig. 4.8. Suggested temperature-dependence of the Fermi energy in amorphous silicon

E_F

T

seems to be in an impurity band. From the theoretical viewpoint, however, we have no satisfactory model to show why either ΔE or ΔW would be so sensitive to the temperature; if this behaviour is established, perhaps quite a new description of the mobility edge may be needed.

b) *Overhof* and *Beyer* [4.104], on the other hand, pointed out the possibility of a strong temperature-dependence of the Fermi energy under certain conditions. Perhaps this is most easily seen by considering a semiconductor in which the Fermi energy is "pinned" by deep donors (E_D below E_c) with low compensation. Then at zero temperature, $E_c - E_F = E_D$. As the temperature is raised, E_F will increase as $(kT)^2 N'(E_F)$. At higher temperatures, however, it will move towards $\frac{1}{2} E_D$, as in Fig. 4.8; it should then drop on account of thermal expansion as shown by the dotted line[5].

Determinations of the position of the Fermi energy by ultraviolet photo-emission spectroscopy (UPS) which compare its energy with that of inner levels [4.105] will reveal shifts due to thermal expansion but *not* the temperature dependent effect shown here.

Such a model does reproduce one feature of the Meyer-Nelden rule, that σ_0 is large for a large value of the gap. However, the temperature at which a linear regime should set it must depend on the degree of compensation. We think this could depend on the homogeneity of the specimen. Neither the hydrogen content nor the concentration of dangling bonds are thought to be homogeneous, so the Fermi energy would vary from one region to another if each region remained neutral. Charge will be transferred from one region to another, setting up fields and giving another kind of long-range potential fluctuation in the conduction band. This could well increase any overlap between the dangling-bond band E_x and the doubly charged band of Fig. 4.8, thus raising the temperature at which the linear regime occurs.

In any case, then, we expect σ_0 to be very sensitive to homogeneity.

Possibly the Meyer-Nelden rule is normally to be accounted for by shifts in the Fermi energy of this type. There are, however, other models. Thus,

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5 An analysis of this behaviour was given by *Roberts* [4.101]

Roberts [4.101] postulated a conduction band with an exponential tail but constant mobility and shows that a Meyer-Nelden form can be reproduced. We think this explanation is open to the criticism that in an exponential tail, Anderson localization should occur and the mobility should be a strong function of energy.

Deep level transient spectroscopy in the hands of *Cohen* et al. [4.106] and *Lang* et al. [4.107] has given evidence for a very low density of states $(10^{14}-10^{15} \text{ eV}^{-1} \text{ cm}^{-3})$ and a rapid variation with energy, of the kind which would produce a large change of Fermi energy with temperature. The results are not, however, confirmed by determination of $N(E_F)$ from the space-charge limited current ([4.108] and Chap. 3), found values some 3–10 times smaller than that deduced from the field effect and thus of order $\sim 10^{16} \text{ eV}^{-1}$ cm^{-3} and little dependent on energy. If these are correct, the large values of σ_0 cannot be due to a shift in the Fermi energy and the only explanation available is a dependence of E_c on temperature [4.109].

4.11 The Staebler-Wronski Effect

A photoinduced ESR signal which is stable at low temperatures is found in many amorphous semiconductors; it was observed by *Bishop* et al. [4.110] in chalcogenides and interpreted in terms of the trapping of electrons in defects already existing, namely, the charged valence alternation pairs C_1^- and C_3^+. In principle, any electron or hole trap could give rise to photoinduced ESR.

Staebler and *Wronski* [4.111] report that when glow-discharge deposited a-Si is exposed at room temperature to broad band illumination (1.4 to 2.1 eV), a decrease in the conductivity by four orders of magnitude is observed which can be annealed out by heating to 150 °C with an activation energy of 1.52 eV. The metastable state contains about double the density of unpaired spins. The effect was observed only in lightly doped samples. Completely undoped films have been observed to show an inverse effect, while heavily doped films do not show it.

What has to be emphasized is that the trapped charges which produce the effect do not communicate with the conduction band, as do electrons at states near the Fermi energy at any temperature where the conduction is observed. It is also to be noted that the activation energy for annealing is greater than the band gap. We have to ask, then, whether electrons are trapped in a deep state stabilized by a large Stokes shift, or whether defects are formed.

One interpretation is that light induces two T_3^0 states (dangling bonds). This, as stated in Sect. 4.9, is the view of the Marburg group. A model of this type is that of *Elliott* [4.112]. These models were criticised by *Adler* [4.78]. The energy of the exciting light seems much less than that required to break two bonds and the lack of any exchange narrowing in the photoinduced ESR line indicates that any photoinduced T_3^0 centres must be more than 10 Å

apart. It seems to us likely that spinless traps exist, for instance, vacancies which do give very stable trapping. Adler postulates states with negative U, but this does not seem essential though we note that in crystalline silicon, two V^+ (where V is a vacancy) should dissociate into V^{++} and V.

As regards the mechanism of the effect, Adler suggests that more point charges of one sign than the other will be produced so that to preserve charge neutrality, the Fermi energy will be pushed one way or the other. The effect will thus only be significant if $N(E_F)$ is small.

Hirabayashi et al. [4.113] and *Morigaki* et al. [4.114, 115] reported that prolonged irradiation produces $\sim 10^{17}$ cm^{-3} ESR centres; they claim that this is evidence for defects because the g-value indicates that these are dangling bonds. If illumination creates such bonds, e.g., by driving off hydrogen, it is not clear that they would produce the charge needed to give a considerable shift in the Fermi energy. They might, if $N(E_F)$ is very low, produce a shift for other reasons, namely, by changing the density of states. Strong evidence for this model was given by *Dersch* [4.84 b, 116].

4.12 Variable-Range Hopping in Silicon

Our discussion in Sect. 4.5 has shown that a $T^{1/4}$ law is deduced on the assumption that $N(E)$ is constant in the neighbourhood of E_F and that the "Coulomb gap" caused by the interaction between carriers is neglected.

If, as is generally supposed, variable-range hopping, when observed in insufficiently hydrogenated material, is a phenomenon in which electrons jump from a singly occupied dangling-bond state to a charged one (empty or doubly occupied), then Fig. 4.8 shows
a) no relationship between $N(E_F)$ and the number of spins is to be expected, and
b) $N(E_F)$ may well be far from constant.

In the latter case, though calculations with particular models are missing, we think that a hopping formula of the form

$$\sigma = A \exp(- T_0/T)^S \tag{4.22}$$

with $\frac{1}{4} < S < \frac{1}{2}$ is to be expected; the lower limit $\frac{1}{2}$ comes from the calculations of *Hamilton* [4.117] for the form for the density of states

$$N(E) \propto (E - E_F)^2 \ . \tag{4.23}$$

Observations seem to give, particularly in a-Ge, a fair approximation to the $T^{1/4}$ law, but with a much higher pre-exponential factor than can be expected from interaction with phonons. It may well be that this is sometimes

a consequence of forcing the observations to a $T^{1/4}$ law and that with a higher index, the prefactor would be reasonable.

Kalbitzer and co-workers [4.118, 119], have made detailed investigations of hopping transport in ion-bombarded amorphous silicon, determining the index in the expression $\exp[(T_0/T)^n]$ by a method due to *Hill* [4.120]. A value of $n \sim \frac{1}{2}$ is frequently found. A mechanism similar to that of *Abeles* et al. [4.57] for metallic particles dispersed in an insulator is proposed.

The thermopower for materials in which variable-range hopping is observed appears independent of T and can be explained *qualitatively* by (4.12), though the value is normally smaller. A rise in S at low temperatures observed by *Lewis* et al. [4.121] has been discussed by the present author [4.35] in terms of the Coulomb gap.

The Hall effect for hopping conduction has not been observed; for discussions of its magnitude see [4.41–43].

A relationship between the width of the ESR line with $g \sim 0.0055$ (due to dangling bonds) and hopping conduction has been found by the Marburg School, and *Movaghar* et al. [4.122] ascribe this to a locally fluctuating magnetic field due to the hopping, giving a relation of the form

$$\delta H(T) = C[\sigma(T)]^n ; \tag{4.24}$$

for further developments see *Dersch* et al. [4.84 b] and *Grünewald* et al. [4.123] and *Overhof* [4.124] who related the temperature-dependence of the ESR line with $g = 2.01$ to the density of states that he assumes in order to interpret the shift in the Fermi level.

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