

9. Charge Transport in Disordered Materials

This chapter surveys general theoretical concepts developed to qualitatively understand and to quantitatively describe the electrical conduction properties of disordered organic and inorganic materials. In particular, these concepts are applied to describe charge transport in amorphous and microcrystalline semiconductors and in conjugated and molecularly doped polymers. Electrical conduction in such systems is achieved through incoherent transitions of charge carriers between spatially localized states. Basic theoretical ideas developed to describe this type of electrical conduction are considered in detail. Particular attention is given to the way the kinetic coefficients depend on temperature, the concentration of localized states, the strength of the applied electric field, and the charge carrier localization length. Charge transport via delocalized states in disordered systems and the relationships between kinetic coefficients under the nonequilibrium conditions are also briefly reviewed.

9.1	General Remarks on Charge Transport in Disordered Materials	163
9.2	Charge Transport in Disordered Materials via Extended States	167
9.3	Hopping Charge Transport in Disordered Materials via Localized States	169
9.3.1	Nearest-Neighbor Hopping.....	170
9.3.2	Variable-Range Hopping.....	172
9.3.3	Description of Charge-Carrier Energy Relaxation and Hopping Conduction in Inorganic Noncrystalline Materials.....	173
9.3.4	Description of Charge Carrier Energy Relaxation and Hopping Conduction in Organic Noncrystalline Materials.....	180
9.4	Concluding Remarks	184
	References	185

Many characteristics of charge transport in disordered materials differ markedly from those in perfect crystalline systems. The term “disordered materials” usually refers to noncrystalline solid materials without perfect order in the spatial arrangement of atoms. One should distinguish between disordered materials with ionic conduction and those with electronic conduction. Disordered materials with ionic conduction include various glasses consisting of a “network-formers” such as SiO_2 , B_2O_3 and Al_2O_3 , and of “network-modifiers” such as Na_2O , K_2O and Li_2O . When an external voltage is applied, ions can drift by hopping over potential barriers in the glass matrix, contributing to the electrical conduction of the material. Several fascinating effects have been observed for this kind of electrical conduction. One is the extremely nonlinear dependence of the conductivity on the concentration of ions in the material. Another beautiful phenomenon is the so-called “mixed alkali effect”: mixing two different modifiers in one glass leads to an enormous drop in the conductivity in comparison to that

of a single modifier with the same total concentration of ions. A comprehensive description of these effects can be found in the review article of *Bunde et al.* [9.1]. Although these effects sometimes appear puzzling, they can be naturally and rather trivially explained using routine classical percolation theory [9.2]. The description of ionic conduction in glasses is much simplified by the inability of ions to tunnel over large distances in the glass matrix in single transitions. Every transition occurs over a rather small interatomic distance, and it is relatively easy to describe such electrical conductivity theoretically [9.2]. On the other hand, disordered systems with electronic conduction have a much more complicated theoretical description. Transition probabilities of electrons between spatially different regions in the material significantly depend not only on the energy parameters (as in the case of ions), but also on spatial factors such as the tunnelling distance, which can be rather large. The interplay between the energy and spatial factors in the transition probabilities of electrons makes the develop-

ment of a theory of electronic conduction in disordered systems challenging. Since the description of electronic conduction is less clear than that of ionic conduction, and since disordered electronic materials are widely used for various device applications, in this chapter we concentrate on disordered materials with the electronic type of electrical conduction.

Semiconductor glasses form one class of such materials. This class includes amorphous selenium, a-Se and other chalcogenide glasses, such as a-As₂Se₃. These materials are usually obtained by quenching from the melt. Another broad class of disordered materials, inorganic amorphous semiconductors, includes amorphous silicon a-Si, amorphous germanium a-Ge, and their alloys. These materials are usually prepared as thin films by the deposition of atomic or molecular species. Hydrogenated amorphous silicon, a-Si:H, has attracted much attention from researchers, since incorporation of hydrogen significantly improves conduction, making it favorable for use in amorphous semiconductor devices. Many other disordered materials, such as hydrogenated amorphous carbon (a-C:H) and its alloys, polycrystalline and microcrystalline silicon are similar to a-Si:H in terms of their charge transport properties. Some crystalline materials can also be considered to be disordered systems. This is the case for doped crystals if transport phenomena within them are determined by randomly distributed impurities, and for mixed crystals with disordered arrangements of various types of atoms in the crystalline lattice. In recent years much research has also been devoted to the study of organic disordered materials, such as conjugated and molecularly doped polymers and organic glasses, since these systems has been shown to possess electronic properties similar to those of inorganic disordered materials, while they are easier to manufacture than the latter systems.

There are two reasons for the great interest of researchers in the conducting properties of disordered materials. On the one hand, disordered systems represent a challenging field in a purely academic sense. For many years the theory of how semiconductors perform charge transport was mostly confined to crystalline systems where the constituent atoms are in regular arrays. The discovery of how to make solid amorphous materials and alloys led to an explosion in measurements of the electronic properties of these new materials. However, the concepts often used in textbooks to describe charge carrier transport in crystalline semiconductors are based on an assumption of long-range order, and so they cannot be applied to electronic transport in disor-

dered materials. It was (and still is) a highly challenging task to develop a consistent theory of charge transport in such systems. On the other hand, the explosion in research into charge transport in disordered materials is related to the various current and potential device applications of such systems. These include the application of disordered inorganic and organic materials in photovoltaics (the functioning material in solar cells), in electrophotography, in large-area displays (they are used in thin film transistors), in electrical switching threshold and memory devices, in light-emitting diodes, in linear image sensors, and in optical recording devices. Readers interested in the device applications of disordered materials should be aware that there are numerous monographs on this topic: the literature on this field is very rich. Several books are recommended (see [9.3–12]), as are numerous review articles referred to in these books.

In this chapter we focus on disordered semiconductor materials, ignoring the broad class of disordered metals. In order to describe electronic transport in disordered metals, one can more or less successfully apply extended and modified conventional theoretical concepts developed for electron transport in ordered crystalline materials, such as the Boltzmann kinetic equation. Therefore, we do not describe electronic transport in disordered metals here. We can recommend a comprehensive monograph to interested readers (see [9.13]), in which modern concepts about conduction in disordered metals are presented beautifully.

Several nice monographs on charge transport in disordered semiconductors are also available. Although many of them were published several years ago (some even decades ago), we can recommend them to the interested reader as a source of information on important experimental results. These results have permitted researchers the present level of understanding of transport phenomena in disordered inorganic and organic materials. A comprehensive collection of experimental data for noncrystalline materials from the books specified above would allow one to obtain a picture of the modern state of experimental research in the field.

We will focus in this chapter on the theoretical description of charge transport in disordered materials, introducing some basic concepts developed to describe electrical conduction. Several excellent books already exist in which a theoretical description of charge transport in disordered materials is the main topic. Among others we can recommend the books of *Shklovskii* and *Efros* [9.14], *Zvyagin* [9.15], *Böttger* and *Bryksin* [9.16], and *Overhof* and *Thomas* [9.17]. There appears to be

a time gap in which comprehensive monographs on the theoretical description of electrical conduction in disordered materials were not published. During this period

some new and rather powerful theoretical concepts were developed. We present these concepts below, along with some more traditional ones.

9.1 General Remarks on Charge Transport in Disordered Materials

Although the literature on transport phenomena in disordered materials is enormously rich, there are still many open questions in this field due to various problems specific to such materials. In contrast to ordered crystalline semiconductors with well-defined electronic energy structures consisting of energy bands and energy gaps, the electronic energy spectra of disordered materials can be treated as quasi-continuous. Instead of bands and gaps, one can distinguish between extended and localized states in disordered materials. In an extended state, the charge carrier wavefunction is spread over the whole volume of a sample, while the wavefunction of a charge carrier is localized in a spatially restricted region in a localized state, and a charge carrier present in such a state cannot spread out in a plane wave as in ordered materials. Actually, localized electron states are known in ordered systems too. Electrons and holes can be spatially localized when they occupy donors or acceptors or some other impurity states or structural defects in ordered crystalline materials. However, the localized states usually appear as δ -like discrete energy levels in the energy spectra of such materials. In disordered semiconductors, on the other hand, energy levels related to spatially localized states usually fill the energy spectrum continuously. The energy that separates the extended states from the localized ones in disordered materials is called the mobility edge. To be precise, we will mostly consider the energy states for electrons in the following. In this case, the states above the mobility edge are extended and the states below the edge are localized. The localized states lie energetically above the extended states for holes. The energy region between the mobility edges for holes and electrons is called the mobility gap. The latter is analogous to the band gap in ordered systems, although the mobility gap contains energy states, namely the spatially localized states. Since the density of states (DOS), defined as the number of states per unit energy per unit volume, usually decreases when the energy moves from the mobility edges toward the center of the mobility gap, the energy regions of localized states in the vicinity of the mobility edges are called band tails. We would like to emphasize that the charge transport properties depend significantly

on the energy spectrum in the vicinity and below the mobility edge (in the band tails). Unfortunately this energy spectrum is not known for almost all disordered materials. A whole variety of optical and electrical investigation techniques have proven unable to determine this spectrum. Since the experimental information on this spectrum is rather vague, it is difficult to develop a consistent theoretical description for charge transport *ab initio*. The absence of reliable information on the energy spectrum and on the structures of the wavefunctions in the vicinity and below the mobility edges can be considered to be the main problem for researchers attempting to quantitatively describe the charge transport properties of disordered materials.

An overview of the energy spectrum in a disordered semiconductor is shown in Fig. 9.1. The energy levels ε_v and ε_c denote the mobility edges for the valence and conduction bands, respectively. Electron states in the mobility gap between these energies are spatially localized. The states below ε_v and above ε_c can be occupied by delocalized holes and electrons. Some peaks in the DOS are shown in the mobility gap, which can be created by some defects with particularly high concentrations. Although there is a consensus between researchers on the general view of the DOS in disordered materials,

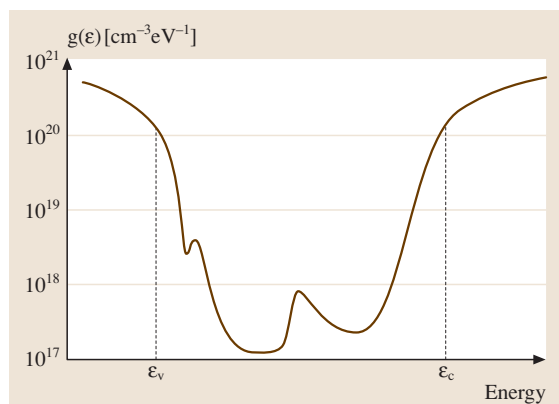


Fig. 9.1 Density of states of a noncrystalline semiconductor (schematic); ε_v and ε_c correspond to mobility edges in the conduction band and the valence band, respectively

the particular structure of the energy spectrum is not known for most disordered systems. From a theoretical point of view, it is enormously difficult to calculate this spectrum.

There are several additional problems that make the study of charge transport in disordered materials more difficult than in ordered crystalline semiconductors. The particular spatial arrangements of atoms and molecules in different samples with the same chemical composition can differ from each other depending on the preparation conditions. Hence, when discussing electrical conduction in disordered materials one often should specify the preparation conditions. Another problem is related to the long-time relaxation processes in disordered systems. Usually these systems are not in thermodynamic equilibrium and the slow relaxation of the atoms toward the equilibrium arrangement can lead to some changes in electrical conduction properties. In some disordered materials a long-time electronic relaxation can affect the charge transport properties too, particularly at low temperatures, when electronic spatial rearrangements can be very slow. At low temperatures, when tunneling electron transitions between localized states dominate electrical conduction, this long-time electron relaxation can significantly affect the charge transport properties.

It is fortunate that, despite these problems, some general transport properties of disordered semiconductors have been established. Particular attention is usually paid to the temperature dependence of the electrical conductivity, since this dependence can indicate the underlying transport mechanism. Over a broad temperature range, the direct current (DC) conductivity in disordered materials takes the form

$$\sigma = \sigma_0 \exp \left[- \left(\frac{\Delta(T)}{k_B T} \right)^\beta \right], \quad (9.1)$$

where the pre-exponential factor σ_0 depends on the underlying system and the power exponent β depends on the material and also sometimes on the temperature range over which the conductivity is studied; $\Delta(T)$ is the activation energy. In many disordered materials, like vitreous and amorphous semiconductors, σ_0 is of the order of $10^2 - 10^4 \Omega^{-1} \text{cm}^{-1}$. In such materials the power exponent β is close to unity at temperatures close to and higher than the room temperature, while at lower temperatures β can be significantly smaller than unity. In organic disordered materials, values of β that are larger than unity also have been reported. For such systems the value $\beta \approx 2$ is usually considered to be appropriate [9.18].

Another important characteristic of the electrical properties of a disordered material is its alternating current (AC) conductivity measured when an external alternating electric field with some frequency ω is applied. It has been established in numerous experimental studies that the real part of the AC conductivity in most disordered semiconductors depends on the frequency according to the power law

$$\text{Re } \sigma(\omega) = C \omega^s, \quad (9.2)$$

where C is constant and the power s is usually smaller than unity. This power law has been observed in numerous materials at different temperatures over a wide frequency range. This frequency dependence differs drastically from that predicted by the standard kinetic theory developed for quasi-free charge carriers in crystalline systems. In the latter case, the real part of the AC conductivity has the frequency dependence

$$\text{Re } \sigma(\omega) = \frac{n e^2}{m} \frac{\tau}{1 + \omega^2 \tau^2}, \quad (9.3)$$

where n is the concentration of charge carriers, e is the elementary charge, m is the effective mass and τ is the momentum relaxation time. Since the band electrons in crystalline semiconductors usually have rather short momentum relaxation times, $\tau \approx 10^{-14}$ s, the contribution of charge carriers in delocalized states to the AC conductivity usually does not depend on frequency at $\omega \ll \tau^{-1}$. Therefore, the observed frequency dependence described by (9.2) should be ascribed to the contribution of charge carriers in localized states.

One of the most powerful tools used to study the concentrations of charge carriers and their mobilities in crystalline semiconductors is the provided by measurements of the Hall constant, R_H . Such measurements also provide direct and reliable information about the sign of the charge carriers in crystalline materials. Unfortunately, this is not the case for disordered materials. Moreover, several anomalies have been established for Hall measurements in the latter systems. For example, the sign of the Hall constant in disordered materials sometimes differs from that of the thermoelectric power, α . This anomaly has not been observed in crystalline materials. The anomaly has been observed in liquid and solid noncrystalline semiconductors. Also, in some materials, like amorphous arsenic, a-As, $R_H > 0$, $\alpha < 0$, while in many other materials other combinations with different signs of R_H and α have been experimentally established.

In order to develop a theoretical picture of the transport properties of any material, the first issues to clarify

are the spectrum of the energy states for charge carriers and the spatial structure of such states. Since these two central issues are yet to be answered properly for noncrystalline materials, the theory of charge transport in disordered systems should be considered to be still in its embryonic stage.

The problem of deducing electron properties in a random field is very complicated, and the solutions obtained so far only apply to some very simple models. One of them is the famous Anderson model that illustrates the localization phenomenon caused by random disorder [9.19]. In this model, one considers a regular system of rectangular potential wells with randomly varying depths, as shown schematically in Fig. 9.2. The ground state energies of the wells are assumed to be randomly distributed over the range with a width of W . First, one considers the ordered version of the model, with W equal to zero. According to conventional band theory, a narrow band arises in the ordered system where the energy width depends on the overlap integral I between the electron wavefunctions in the adjoining

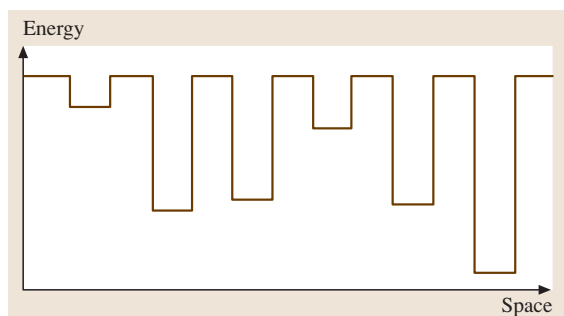


Fig. 9.2 Anderson model of disorder potential

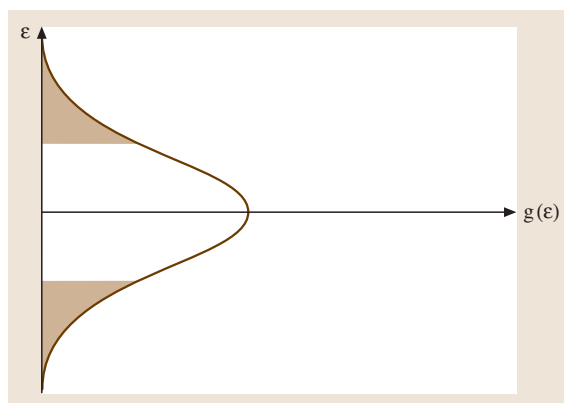


Fig. 9.3 Density of states in the Anderson model. *Hatched regions* in the tails correspond to spatially localized states

wells. The eigenstates in such a model are delocalized with wavefunctions of the Bloch type. This is trivial. The problem is to find the solution for a finite degree of disorder ($W \neq 0$). The result from the Anderson model for such a case is described as follows. At some particular value for the ratio $W/(zI)$, where z is the coordination number of the lattice, all electron states of the system are spatially localized. At smaller values of $W/(zI)$ some states in the outer regions of the DOS are localized and other states in the middle of the DOS energy distribution are spatially extended, as shown schematically in Fig. 9.3. This is one of the most famous results in the transport theory of disordered systems. When considering this result, one should note the following points. (i) It was obtained using a single-electron picture without taking into account long-range many-particle interactions. However, in disordered systems with localized electrons such interactions can lead to the localization of charge carriers and they often drastically influence the energy spectrum [9.14]. Therefore the applicability of the single-electron Anderson result to real systems is questionable. (ii) Furthermore, the energy structure of the Anderson model shown in Fig. 9.3 strongly contradicts that observed in real disordered materials. In real systems, the mobility gap is located between the mobility edges, as shown in Fig. 9.1, while in the Anderson model the energy region between the mobility edges is filled with delocalized states. Moreover, in one-dimensional and in some two-dimensional systems, the Anderson model predicts that all states are localized at any amount of disorder. These results are of little help when attempting to interpret the DOS scheme in Fig. 9.1.

A different approach to the localization problem is to try to impose a random potential $V(x)$ onto the band structure obtained in the frame of a traditional band theory. Assuming a classical smoothly varying (in space)

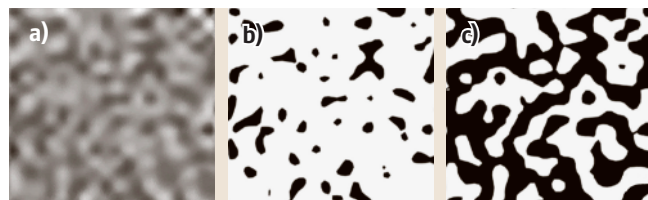


Fig. 9.4a–c Disorder potential landscape experienced by a charge carrier (a). Regions with energies below some given energy level E_c are colored black. In frame (b) this level is very low and there is no connected path through the system via black regions. In frame (c) the level E_c corresponds to the classical percolation level

potential $V(x)$ with a Gaussian distribution function

$$F(V) = \frac{1}{\varepsilon_0 \sqrt{2\pi}} \exp\left(-\frac{V^2}{2\varepsilon_0^2}\right), \quad (9.4)$$

one can solve the localization problem using the classical percolation theory illustrated in Fig. 9.4. In Fig. 9.4a, an example of a disorder potential experienced by electrons is shown schematically. In Fig. 9.4b and Fig. 9.4c the regions below a given energy level E_c are colored black. In Fig. 9.4b this level is positioned very low, so that regions with energies below E_c do not provide a connected path through the system. In Fig. 9.4c an infinite percolation cluster consisting only of black regions exists. The E_c that corresponds to the first appearance of such a connected path is called the classical percolation level [9.14]. Mathematically solving the percolation problem shows that the mobility edge identified with the classical percolation level in the potential $V(x)$ is shifted with respect to the band edge of the ordered system by an amount $\xi\varepsilon_0$, where $\xi \approx 0.96$ towards the center of the bandgap [9.15]. A similar result, though with a different constant ξ , can be obtained via a quantum-mechanical treatment of a short-range potential $V(x)$ of white-noise type [9.20]. As the amplitude ε_0 of the random potential increases the band gap narrows, while the conduction and valence bands become broader. Although this result is provided by both limiting models – by the classical one with a long-range smoothly varying potential $V(x)$ and by the quantum-mechanical one with a short-range white-noise potential $V(x)$ – none of the existing theories can reliably describe the energy spectrum of a disordered material and the properties of the charge carrier wavefunctions in the vicinity of the mobility edges, in other words in the energy range which is most important for charge transport.

The DC conductivity can generally be represented in the form

$$\sigma = e \int \mu(\varepsilon)n(\varepsilon)d\varepsilon, \quad (9.5)$$

where e is the elementary charge, $n(\varepsilon)d\varepsilon$ is the concentration of electrons in the energy range between ε and $\varepsilon + d\varepsilon$ and $\mu(\varepsilon)$ is the mobility of these electrons. The integration is carried out over all energies ε . Under equilibrium conditions, the concentration of electrons $n(\varepsilon)d\varepsilon$ is determined by the density of states $g(\varepsilon)$ and the Fermi function $f(\varepsilon)$, which depends on the position of the Fermi energy ε_F (or a quasi-Fermi energy in the case of the stationary excitation of electrons):

$$n(\varepsilon) = g(\varepsilon)f(\varepsilon), \quad (9.6)$$

where

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right)}. \quad (9.7)$$

Here T is the temperature and k_B is the Boltzmann constant.

The Fermi level in almost all known disordered semiconductors under real conditions is situated in the mobility gap – in the energy range which corresponds to spatially localized electron states. The charge carrier mobility $\mu(\varepsilon)$ in the localized states below the mobility edge is much less than that in the extended states above the mobility edge. Therefore, at high temperatures, when a considerable fraction of electrons can be found in the delocalized states above the mobility edge, these states dominate the electrical conductivity of the system. The corresponding transport mechanism under such conditions is similar to that in ordered crystalline semiconductors. Electrons in the states within the energy range of the width, of the order $k_B T$ above the mobility edge, dominate the conductivity. In such a case the conductivity can be estimated as

$$\sigma \approx e\mu_c n(\varepsilon_c)k_B T, \quad (9.8)$$

where μ_c is the electron mobility in the states above the mobility edge ε_c , and $n(\varepsilon_c)k_B T$ is their concentration. This equation is valid under the assumption that the typical energy scale of the DOS function $g(\varepsilon)$ above the mobility edge is larger than $k_B T$. The position of the Fermi level in disordered materials usually depends on temperature only slightly. Combining (9.6)–(9.8), one obtains the temperature dependence of the DC conductivity in the form

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta}{k_B T}\right), \quad (9.9)$$

described by (9.1) with $\beta = 1$ and constant activation energy, which is observed in most disordered semiconductors at high temperatures.

In order to obtain the numerical value of the conductivity in this high-temperature regime, one needs to know the density of states in the vicinity of the mobility edge $g(\varepsilon_c)$, and also the magnitude of the electron mobility μ_c in the delocalized states above ε_c . While the magnitude of $g(\varepsilon_c)$ is usually believed to be close to the DOS value in the vicinity of the band edge in crystalline semiconductors, there is no consensus among researchers on the magnitude of μ_c . In amorphous semiconductors μ_c is usually estimated to be in the range of $1 \text{ cm}^2/\text{V s}$ to $10 \text{ cm}^2/\text{V s}$. Unfortunately, there are no reliable theoretical calculations of this quantity for most disordered

materials. The only exception is provided by so-called mixed crystals, which are also sometimes called crystalline solid solutions. In the next section we describe the theoretical method which allows one to estimate μ_c in

such systems. This method can be extended to other disordered materials, provided the statistical properties of the disorder potential, essential for electron scattering, are known.

9.2 Charge Transport in Disordered Materials via Extended States

The states with energies below ε_v and above ε_c in disordered materials are believed to possess similar properties to those of extended states in crystals. Various experimental data suggest that these states in disordered materials are delocalized states. However, traditional band theory is largely dependent upon the system having translational symmetry. It is the periodic atomic structure of crystals that allows one to describe electrons and holes within such a theory as quasi-particles that exhibit behavior similar to that of free particles in vacuum, albeit with a renormalized mass (the so-called “effective mass”). The energy states of such quasi-particles can be described by their momentum values. The wavefunctions of electrons in these states (the so-called Bloch functions) are delocalized. This means that the probability of finding an electron with a given momentum is equal at corresponding points of all elementary cells of the crystal, independent on the distance between the cells.

Strictly speaking, the traditional band theory fails in the absence of translational symmetry – for disordered systems. Nevertheless, one still assumes that the charge carriers present in delocalized states in disordered materials can be approximately described by wavefunctions with a spatially homogeneous probability of finding a charge carrier with a given quasi-momentum. As for crystals, one starts from the quasi-free particle picture and considers the scattering effects in a perturbation approach following the Boltzmann kinetic description. This description is valid if the de Broglie wavelength of the charge carrier $\lambda = \hbar/p$ is much less than the mean free path $l = v\tau$, where τ is the momentum relaxation time and p and v are the characteristic values of the momentum and velocity, respectively. This validity condition for the description based on the kinetic Boltzmann equation can also be expressed as $\hbar/\tau \ll \varepsilon$, where ε is the characteristic kinetic energy of the charge carriers, which is equal to $k_B T$ for a nondegenerate electron gas and to the Fermi energy in the degenerate case. While this description seems valid for delocalized states far from the mobility edges, it fails for energy states in the vicinity of the mobility edges. So far, there has been

no consensus between the theorists on how to describe charge carrier transport in the latter states. Moreover, it is not clear whether the energy at which the carrier mobility drops coincides with the mobility edge or whether it is located above the edge in the extended states. Numerous discussions of this question, mostly based on the scaling theory of localization, can be found in special review papers. For the rest of this section, we skip this rather complicated subject and instead we focus on the description of charge carrier transport in a semiconductor with a short-range random disorder potential of white-noise type. This seems to be the only disordered system where a reliable theory exists for charge carrier mobility via extended states above the mobility edge. Semiconductor solid solutions provide an example of a system with this kind of random disorder [9.20–25].

Semiconductor solid solutions $A_x B_{1-x}$ (mixed crystals) are crystalline semiconductors in which the sites of the crystalline sublattice can be occupied by atoms of two different types, A and B. Each site can be occupied by either an A or a B atom with some given probability x between zero and unity. The value x is often called the composition of the material. Due to the random spatial distributions of the A and B atoms, local statistical fluctuations in the composition inside the sample are unavoidable, meaning that mixed crystals are disordered systems. Since the position of the band edge depends on the composition x , these fluctuations in local x values lead to the disorder potential for electrons and holes within the crystal. To be precise, we will consider the influence of the random potential on a conduction band electron. Let $E_c(x)$ be the conduction band minimum for a crystal with composition x . In Fig. 9.5 a possible schematic dependence $E_c(x)$ is shown. If the average composition for the whole sample is x_0 , the local positions of the band edge $E_c(x)$ fluctuate around the average value $E_c(x_0)$ according to the fluctuations of the composition x around x_0 . For small deviations in composition Δx from the average value, one can use the linear relation

$$E_c(x_0 + \Delta x) = E_c(x_0) + \alpha \Delta x, \quad (9.10)$$

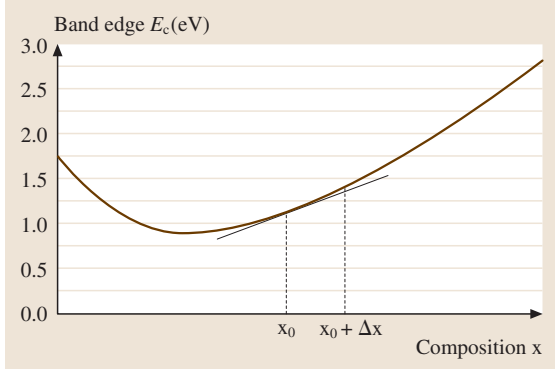


Fig. 9.5 Schematic dependence of the conduction band edge ε_c on composition x in a mixed crystal A_xB_{1-x}

where

$$\alpha = \left. \frac{dE_c(x)}{dx} \right|_{x=x_0}. \quad (9.11)$$

If the deviation of the concentration of A atoms from its mean value in some region of a sample is $\xi(r)$ and the total concentration of (sub)lattice sites is N , the deviation of the composition in this region is $\Delta x = \xi(r)/N$, and the potential energy of an electron at the bottom of the conduction band is

$$V(r) = \alpha \frac{\xi(r)}{N}. \quad (9.12)$$

Although one calls the disorder in such systems a “short-range” disorder, it should be noted that the consideration is valid only for fluctuations that are much larger than the lattice constant of the material. The term “short-range” is due to the assumption that the statistical properties of the disorder are absolutely uncorrelated. This means that potential amplitudes in the adjoining spatial points are completely uncorrelated to each other. Indeed, it is usually assumed that the correlation function of the disorder in mixed crystals can be approximated by a white-noise correlation function of the form

$$\langle \xi(r)\xi(r') \rangle = x(1-x)N\delta(r-r'). \quad (9.13)$$

The random potential caused by such compositional fluctuations is then described by the correlation function [9.20]

$$\langle V(r)V(r') \rangle = \gamma\delta(r-r') \quad (9.14)$$

with

$$\gamma = \frac{\alpha^2}{N}x(1-x). \quad (9.15)$$

Charge carriers in mixed crystals are scattered by compositional fluctuations. As is usual in kinetic descriptions of free electrons, the fluctuations on the spatial scale of the order of the electron wavelength are most efficient. Following *Shlimak et al.* [9.23], consider an isotropic quadratic energy spectrum

$$\varepsilon_p = \frac{p^2}{2m}, \quad (9.16)$$

where p and m are the quasi-momentum and the effective mass of an electron, respectively. The scattering rate for such an electron is

$$v_p = \frac{2\pi}{\hbar} \sum_q \langle |V_q|^2 \rangle (1 - \cos \vartheta_q) \delta(\varepsilon_p - \varepsilon_{p-q}), \quad (9.17)$$

where ϑ_q is the scattering angle and

$$\langle |V_q|^2 \rangle = \frac{1}{\Omega} \int d^3r \exp(iqr) \langle V(r)V(0) \rangle. \quad (9.18)$$

The quantity Ω in this formula is the normalization volume. Using the correlation function (9.14), one obtains the relation

$$\langle |V_q|^2 \rangle = \frac{\alpha^2 x(1-x)}{\Omega N}, \quad (9.19)$$

which shows that the scattering by compositional fluctuations is equivalent to that by a short-range potential [9.23]. Substituting (9.19) into (9.17) one obtains the following expression for the scattering rate [9.20]

$$v_p = \frac{\alpha^2 x(1-x)mp}{\pi \hbar^4 N}. \quad (9.20)$$

This formula leads to an electron mobility of the following form in the framework of the standard Drude approach [9.20, 23]

$$\mu_C = \frac{\pi^{3/2}}{2\sqrt{2}} \frac{e\hbar^4 N}{\alpha^2 x(1-x)m^{5/2}(k_B T)^{1/2}}. \quad (9.21)$$

Very similar formulae can be found in many recent publications (see for example *Fahy and O'Reilly* [9.26]). It has also been modified and applied to two-dimensional systems [9.27] and to disordered diluted magnetic semiconductors [9.28].

It would not be difficult to apply this theoretical description to other disordered systems, provided the correlation function of the disorder potential takes the form of (9.14) with known amplitude γ . However, it is worth emphasizing that the short-range disorder of white-noise type considered here is a rather simple

model that cannot be applied to most disordered materials. Therefore, we can conclude that the problem of theoretically describing charge carrier mobility via delocalized states in disordered materials is still waiting to be solved.

9.3 Hopping Charge Transport in Disordered Materials via Localized States

Electron transport via delocalized states above the mobility edge dominates the electrical conduction of disordered materials only at temperatures high enough to cause a significant fraction of the charge carriers fill these states. As the temperature decreases, the concentration of the electrons described by (9.9) decreases exponentially and so their contribution to electrical conductivity diminishes. Under these circumstances, tunneling transitions of electrons between localized states in the band tails dominate the charge transport in disordered semiconductors. This transport regime is called hopping conduction, since the incoherent sequence of tunneling transitions of charge carriers resembles a series of their hops between randomly distributed sites. Each site in this picture provides a spatially localized electron state with some energy ε . In the following we will assume that the localized states for electrons (concentration N_0) are randomly distributed in space and their energy distribution is described by the DOS function $g(\varepsilon)$:

$$g(\varepsilon) = \frac{N_0}{\varepsilon_0} G\left(\frac{\varepsilon}{\varepsilon_0}\right), \quad (9.22)$$

where ε_0 is the energy scale of the DOS distribution.

The tunneling transition probability of an electron from a localized state i to a localized state j that is lower in energy depends on the spatial separation r_{ij} between the sites i and j as

$$v_{ij}(r) = v_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right), \quad (9.23)$$

where α is the localization length, which we assume to be equal for sites i and j . This length determines the exponential decay of the electron wavefunction in the localized states, as shown in Fig. 9.6. The pre-exponential factor v_0 in (9.23) depends on the electron interaction mechanism that causes the transition. Usually it is assumed that electron transitions contributing to charge transport in disordered materials are caused by interactions of electrons with phonons. Often the coefficient v_0 is simply assumed to be of the order of the phonon

In the following section we present the general concepts developed to describe electrical conduction in disordered solids at temperatures where tunneling transitions of electrons between localized states significantly contribute to charge transport.

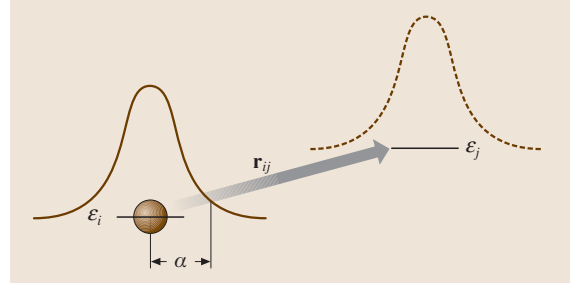


Fig. 9.6 Hopping transition between two localized states i and j with energies of ε_i and ε_j , respectively. The *solid* and *dashed* lines depict the carrier wavefunctions at sites i and j , respectively; α is the localization radius

frequency ($\approx 10^{13} \text{ s}^{-1}$), although a more rigorous approach is in fact necessary to determine v_0 . This should take into account the particular structure of the electron localized states and also the details of the interaction mechanism [9.29, 30].

When an electron transits from a localized state i to a localized state j that is higher in energy, the transition rate depends on the energy difference between the states. This difference is compensated for by absorbing a phonon with the corresponding energy [9.31]:

$$v_{ij}(r, \varepsilon_i, \varepsilon_j) = v_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right) \times \exp\left(-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{2k_B T}\right). \quad (9.24)$$

Equations (9.23) and (9.24) were written for the case in which the electron occupies site i whereas site j is empty. If the system is in thermal equilibrium, the occupation probabilities of sites with different energies are determined by Fermi statistics. This effect can be taken into account by modifying (9.24) and adding terms that account for the relative energy positions of sites i and

j with respect to the Fermi energy ε_F . Taking into account these occupation probabilities, one can write the transition rate between sites i and j in the form [9.31]

$$v_{ij} = v_0 \exp\left(-\frac{2r_{ij}}{a}\right) \times \exp\left(-\frac{|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_j - \varepsilon_i|}{2k_B T}\right). \quad (9.25)$$

Using these formulae, the theoretical description of hopping conduction is easily formulated. One has to calculate the conductivity provided by transition events (the rates of which are described by (9.25)) in the manifold of localized states (where the DOS is described by (9.22)).

9.3.1 Nearest-Neighbor Hopping

Before presenting the correct solution to the hopping problem we would like to emphasize the following. The style of the theory for electron transport in disordered materials via localized states significantly differs from that used for theories of electron transport in ordered crystalline materials. While the description is usually based on various averaging procedures in crystalline systems, in disordered systems these averaging procedures can lead to extremely erroneous results. We believe that it is instructive to analyze some of these approaches in order to illustrate the differences between the descriptions of charge transport in ordered and disordered materials. To treat the scattering rates of electrons in ordered crystalline materials, one usually proceeds by averaging the scattering rates over the ensemble of scattering events. A similar procedure is often attempted for disordered systems too, although various textbooks (see, for instance, *Shklovskii* and *Efros* [9.14]) illustrate how erroneous such an approach can be in the case of disordered materials.

Let us consider the simplest example of hopping processes, namely the hopping of an electron through a system of isoenergetic sites randomly distributed in space with some concentration N_0 . It will be always assumed in this chapter that electron states are strongly localized and the strong inequality $N_0\alpha^3 \ll 1$ is fulfilled. In such a case the electrons prefer to hop between the spatially nearest sites and therefore this transport regime is often called nearest-neighbor hopping (NNH). This type of hopping transport takes place in many real systems at temperatures where the thermal energy $k_B T$ is larger than the energy scale of the DOS. In such sit-

uations the energy-dependent terms in (9.24) and (9.25) do not play any significant role and the hopping rates are determined solely by the spatial terms. The rate of transition of an electron between two sites i and j is described in this case by (9.23). The average transition rate is usually obtained by weighting this expression with the probability of finding the nearest neighbor at some particular distance r_{ij} , and by integrating over all possible distances:

$$\langle v \rangle = \int_0^\infty dr v_0 \times \exp\left(-\frac{2r}{\alpha}\right) 4\pi r^2 N_0 \exp\left(-\frac{4\pi}{3} r^3 N_0\right) \approx \pi v_0 N_0 \alpha^3. \quad (9.26)$$

Assuming that this average hopping rate describes the mobility, diffusivity and conductivity of charge carriers, one apparently comes to the conclusion that these quantities are linearly proportional to the density of localized states N_0 . However, experiments evidence an exponential dependence of the transport coefficients on N_0 .

Let us look therefore at the correct solution to the problem. This solution is provided in the case considered here, $N_0\alpha^3 \ll 1$, by percolation theory (see, for instance, *Shklovskii* and *Efros* [9.14]). In order to find the transport path, one connects each pair of sites if the relative separation between the sites is smaller than some given distance R , and checks whether there is a continuous path through the system via such sites. If such a path is absent, the magnitude of R is increased and the procedure is repeated. At some particular value $R = R_c$, a continuous path through the infinite system via sites with relative separations $R < R_c$ arises. Various mathematical considerations give the following relation for R_c [9.14]:

$$\frac{4\pi}{3} N_0 R_c^3 = B_c, \quad (9.27)$$

where $B_c = 2.7 \pm 0.1$ is the average number of neighboring sites available within a distance of less than R_c . The corresponding value of R_c should be inserted into (9.23) in order to determine kinetic coefficients such as the mobility, diffusivity and conductivity. The idea behind this procedure is as follows. Due to the exponential dependence of the transition rates on the distances between the sites, the rates for electron transitions over distances $r < R_c$ are much larger than those over distances R_c . Such fast transitions do not play any significant role as a limiting factor in electron transport and so they can

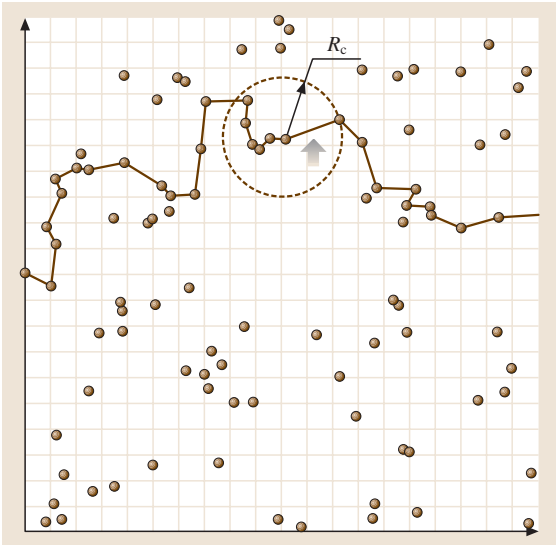


Fig. 9.7 A typical transport path with the lowest resistance. Circles depict localized states. The arrow points out the most “difficult” transition, with length R_c

be neglected in calculations of the resistivity of the system. Transitions over distances R_c are the slowest among those that are necessary for DC transport and hence such transitions determine the conductivity. The structure of the percolation cluster responsible for charge transport is shown schematically in Fig. 9.7. The transport path consists of quasi-one-dimensional segments, each containing a “difficult” transition over the distance $\approx R_c$. Using (9.23) and (9.27), one obtains the dependence of the conductivity on the concentration of localization sites in the form

$$\sigma = \sigma_0 \exp\left(-\frac{\gamma}{\alpha N_0^{1/3}}\right), \quad (9.28)$$

where σ_0 is the concentration-independent pre-exponential factor and $\gamma = 1.73 \pm 0.03$. Such arguments do not allow one to determine the exponent in the kinetic coefficients with an accuracy better than a number of the order of unity [9.14]. One should note that the quantity in the exponent in (9.28) is much larger than unity for a system with strongly localized states when the inequality $N_0 \alpha^3 \ll 1$ is valid. This inequality justifies the above derivation. The dependence described by (9.28) has been confirmed in numerous experimental studies of the hopping conductivity via randomly placed impurity atoms in doped crystalline semiconductors [9.14]. The drastic difference between this correct result and the erroneous one based on (9.26) is apparent. Unfortunately, the be-

lief of many researchers in the validity of the procedure based on the averaging of hopping rates is so strong that the agreement between (9.28) and experimental data is often called occasional. We would like to emphasize once more that the ensemble averaging of hopping rates leads to erroneous results. The magnitude of the average rate in (9.26) is dominated by rare configurations of very close pairs of sites with separations of the order of the localization length α . Of course, such pairs allow very fast electron transitions, but electrons cannot move over considerable distances using only these close pairs. Therefore the magnitude of the average transition rate is irrelevant for calculations of the hopping conductivity. The correct concentration dependence of the conductivity is given by (9.28). This result was obtained under the assumption that only spatial factors determine transition rates of electrons via localized states. This regime is valid at reasonably high temperatures.

If the temperature is not as high and the thermal energy $k_B T$ is smaller than the energy spread of the localized states involved in the charge transport process, the problem of calculating the hopping conductivity becomes much more complicated. In this case, the interplay between the energy-dependent and the distance-dependent terms in (9.24) and (9.25) determines the conductivity. The lower the temperature, the more important the energy-dependent terms in the expressions for transition probabilities of electrons in (9.24) and (9.25) become. If the spatially nearest-neighboring sites have very different energies, as shown in Fig. 9.8, the probability of an upward electron transition between these sites can be so low that it would be more favorable for this electron to hop to a more distant site at a closer energy. Hence the typical lengths of

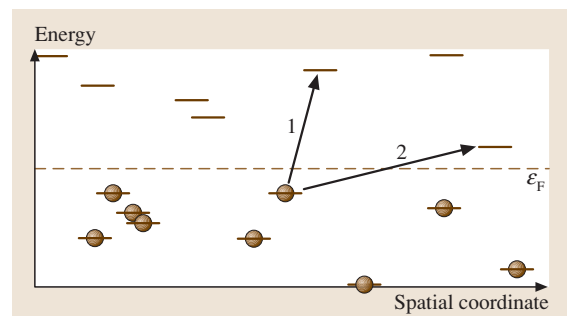


Fig. 9.8 Two alternative hopping transitions between occupied states (filled circles) and unoccupied states. The dashed line depicts the position of the Fermi level. Transitions (1) and (2) correspond to nearest-neighbor hopping and variable-range hopping regimes, respectively

electron transitions increase with decreasing temperature. This transport regime was termed “variable-range hopping”. Next we describe several useful concepts developed to describe this transport regime.

9.3.2 Variable-Range Hopping

The concept of variable-range hopping (VRH) was put forward by Mott (see *Mott and Davis* [9.32]) who considered electron transport via a system of randomly distributed localized states at low temperatures. We start by presenting Mott’s arguments. At low temperatures, electron transitions between states with energies in the vicinity of the Fermi level are most efficient for transport since filled and empty states with close energies can only be found in this energy range. Consider the hopping conductivity resulting from energy levels within a narrow energy strip with width $2\Delta\varepsilon$ symmetric to the Fermi level shown in Fig. 9.9. The energy width of the strip useful for electron transport can be determined from the relation

$$g(\varepsilon_F) \cdot \Delta\varepsilon \cdot r^3(\Delta\varepsilon) \approx 1. \quad (9.29)$$

This criterion is similar to that used in (9.27), although we do not care about numerical coefficients here. Here we have to consider the percolation problem in four-dimensional space since in addition to the spatial terms considered in Sect. 9.3.1 we now have to consider the energy too. The corresponding percolation problem for the transition rates described by (9.25) has not yet been solved precisely. In (9.29) it is assumed that the energy width $2\Delta\varepsilon$ is rather small and that the DOS function $g(\varepsilon)$ is almost constant in the range $\varepsilon_F \pm \Delta\varepsilon$. One can obtain

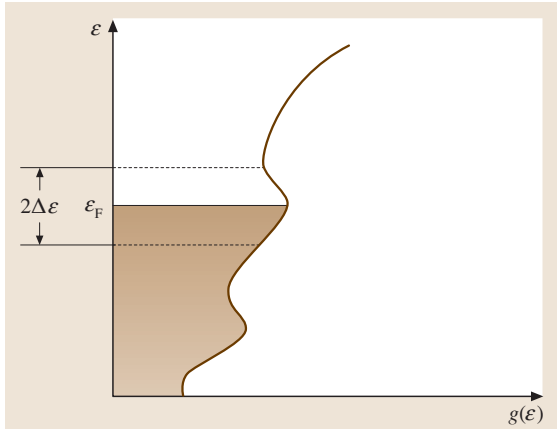


Fig. 9.9 Effective region in the vicinity of the Fermi level where charge transport takes place at low temperatures

the typical hopping distance from (9.29) as a function of the energy width $\Delta\varepsilon$ in the form

$$r(\Delta\varepsilon) \approx [g(\varepsilon_F)\Delta\varepsilon]^{-1/3}, \quad (9.30)$$

and substitute it into (9.24) in order to express the typical hopping rate

$$\nu = \nu_0 \exp\left(-\frac{2[g(\varepsilon_F)\Delta\varepsilon]^{-1/3}}{\alpha} - \frac{\Delta\varepsilon}{k_B T}\right). \quad (9.31)$$

The optimal energy width $\Delta\varepsilon$ that provides the maximum hopping rate can be determined from the condition $d\nu/d\Delta\varepsilon = 0$. The result reads

$$\Delta\varepsilon = \left(\frac{2k_B T}{3g^{1/3}(\varepsilon_F)}\right)^{3/4}. \quad (9.32)$$

After substitution of (9.32) into (9.31) one obtains Mott’s famous formula for temperature-dependent conductivity in the VRH regime

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \quad (9.33)$$

where T_0 is the characteristic temperature:

$$T_0 = \frac{\beta}{k_B g(\varepsilon_F) \alpha^3}. \quad (9.34)$$

Mott gave only a semi-quantitative derivation of (9.33), from which the exact value of the numerical constant β cannot be determined. Various theoretical studies in 3-D systems suggest values for β in the range $\beta = 10.0$ to $\beta = 37.8$. According to our computer simulations, the appropriate value is close to $\beta = 17.6$.

Mott’s law implies that the density of states in the vicinity of the Fermi level is energy-independent. However, it is known that long-range electron–electron interactions in a system of localized electrons cause a gap (the so-called Coulomb gap) in the DOS in the vicinity of the Fermi energy [9.33,34]. The gap is shown schematically in Fig. 9.10. Using simple semiquantitative arguments, *Efros and Shklovskii* [9.33] suggested a parabolic shape for the DOS function

$$g(\varepsilon) = \frac{\eta \kappa^3}{e^6} (\varepsilon - \varepsilon_F)^2, \quad (9.35)$$

where κ is the dielectric constant, e is the elementary charge and η is a numerical coefficient. This result was later confirmed by numerous computer simulations (see, for example, *Baranovskii et al.* [9.35]). At low temperatures, the density of states near the Fermi level has a parabolic shape, and it vanishes exactly at the Fermi

energy. As the temperature rises, the gap disappears (see, for example, *Shlimak et al.* [9.36]).

As we have seen above, localized states in the vicinity of the Fermi energy are the most useful for transport at low temperatures. Therefore the Coulomb gap essentially modifies the temperature dependence of the hopping conductivity in the VRH regime at low temperatures. The formal analysis of the T -dependence of the conductivity in the presence of the Coulomb gap is similar to that for the Mott's law discussed above. Using the parabolic energy dependence of the DOS function, one arrives at the result

$$\sigma = \sigma_0 \exp \left[- \left(\frac{\tilde{T}_0}{T} \right)^{1/2} \right] \quad (9.36)$$

with $\tilde{T}_0 = \tilde{\beta} e^2 / (\kappa \alpha k_B)$, where $\tilde{\beta}$ is a numerical coefficient.

Equations (9.33) and (9.36) belong to the most famous theoretical results in the field of variable-range hopping conduction. However these formulae are usually of little help to researchers working with essentially noncrystalline materials, such as amorphous, vitreous or organic semiconductors. The reason is as follows. The above formulae were derived for the cases of either constant DOS (9.33) or a parabolic DOS (9.36) in the energy range associated with hopping conduction. These conditions can usually be met in the impurity band of a lightly doped crystalline semiconductor. In the most disordered materials, however, the energy distribution of the localized states is described by a DOS function that is very strongly energy-dependent. In amorphous, vitreous and microcrystalline semiconductors, the energy dependence of the DOS function is believed to be exponential,

while in organic materials it is usually assumed to be Gaussian. In these cases, new concepts are needed in order to describe the hopping conduction. In the next section we present these new concepts and calculate the way the conductivity depends on temperature and on the concentration of localized states in various significantly noncrystalline materials.

9.3.3 Description of Charge-Carrier Energy Relaxation and Hopping Conduction in Inorganic Noncrystalline Materials

In most inorganic noncrystalline materials, such as vitreous, amorphous and polycrystalline semiconductors, the localized states for electrons are distributed over a rather broad energy range with a width of the order of an electronvolt. The DOS function that describes this energy distribution in such systems is believed to have a purely exponential shape

$$g(\varepsilon) = \frac{N_0}{\varepsilon_0} \exp \left(- \frac{\varepsilon}{\varepsilon_0} \right), \quad (9.37)$$

where the energy ε is counted positive from the mobility edge towards the center of the mobility gap, N_0 is the total concentration of localized states in the band tail, and ε_0 determines the energy scale of the tail. To be precise, we consider that electrons are the charge carriers here. The result for holes can be obtained in an analogous way. Values of ε_0 in inorganic noncrystalline materials are believed to vary between 0.025 eV and 0.05 eV, depending on the system under consideration.

It is worth noting that arguments in favor of a purely exponential shape for the DOS in the band tails of inorganic noncrystalline materials described by (9.37) cannot be considered to be well justified. They are usually based on a rather ambiguous interpretation of experimental data. One of the strongest arguments in favor of (9.37) is the experimental observation of the exponential decay of the light absorption coefficient for photons with an energy deficit ε with respect to the energy width of the mobility gap (see, for example, *Mott and Davis* [9.32]). One should mention that this argument is valid only under the assumption that the energy dependence of the absorption coefficient is determined solely by the energy dependence of the DOS. However, in many cases the matrix element for electron excitation by a photon in noncrystalline materials also strongly depends on energy [9.14, 37]. Hence any argument for the shape of the DOS based on the energy dependence of the light absorption coefficient should be taken very cautiously. Another argument in favor of (9.37) comes

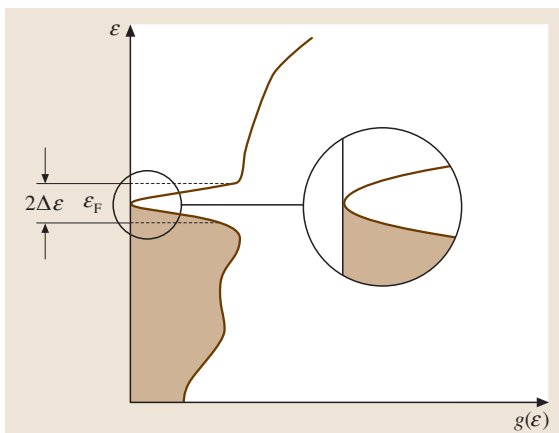


Fig. 9.10 Schematic view of the Coulomb gap. The *insert* shows the parabolic shape of the DOS near the Fermi level

from the measurements of dispersive transport in time-of-flight experiments. In order to interpret the observed time dependence of the mobility of charge carriers, one usually assumes that the DOS for the band tail takes the form of (9.37) (see, for example, *Orenstein and Kastner* [9.38]). One of the main reasons for such an assumption is probably the ability to solve the problem analytically without elaborate computer work.

In the following we start our consideration of the problem by also assuming that the DOS in a band tail of a noncrystalline material has an energy dependence that is described by (9.37). This simple function will allow us to introduce some valuable concepts that have been developed to describe dynamic effects in noncrystalline materials in the most transparent analytical form. We first present the concept of the so-called transport energy, which, in our view, provides the most transparent description of the charge transport and energy relaxation of electrons in noncrystalline materials.

The Concept of the Transport Energy

The crucial role of a particular energy level in the hopping transport of electrons via localized band-tail states with the DOS described by (9.37) was first recognized by *Grünewald and Thomas* [9.39] in their numerical analysis of equilibrium variable-range hopping conductivity. This problem was later considered by *Shapiro and Adler* [9.40], who came to the same conclusion as *Grünewald and Thomas*, namely that the vicinity of one particular energy level dominates the hopping transport of electrons in the band tails. In addition, they achieved an analytical formula for this level and showed that its position does not depend on the Fermi energy.

Independently, the rather different problem of nonequilibrium energy relaxation of electrons by hopping through the band tail with the DOS described by (9.37) was solved at the same time by *Monroe* [9.41]. He showed that, starting from the mobility edge, an electron most likely makes a series of hops downward in energy. The manner of the relaxation process changes at some particular energy ε_t , which *Monroe* called the transport energy (TE). The hopping process near and below TE resembles a multiple-trapping type of relaxation, with the TE playing a role similar to the mobility edge. In the multiple-trapping relaxation process [9.38], only electron transitions between delocalized states above the mobility edge and the localized band-tail states are allowed, while hopping transitions between the localized tail states are neglected. Hence, every second transition brings the electron to the mobility edge. The TE of *Monroe* [9.41] coincides exactly with the energy

level discovered by *Grünewald and Thomas* [9.39] and by *Shapiro and Adler* [9.40] for equilibrium hopping transport.

Shklovskii et al. [9.42] have shown that the same energy level ε_t also determines the recombination and transport of electrons in the nonequilibrium steady state under continuous photogeneration in a system with the DOS described by (9.37).

It is clear, then, that the TE determines both equilibrium and nonequilibrium and both transient and steady-state transport phenomena. The question then arises as to why this energy level is so universal that electron hopping in its vicinity dominates all transport phenomena. Below we derive the TE by considering a single hopping event for an electron localized deep in the band tail. It is the transport energy that maximizes the hopping rate as a final electron energy in the hop, independent of its initial energy [9.43]. All derivations below are carried out for the case $k_B T < \varepsilon_0$.

Consider an electron in a tail state with energy ε_i . According to (9.24), the typical rate of downward hopping of such an electron to a neighboring localized state deeper in the tail with energy $\varepsilon_j \geq \varepsilon_i$ is

$$v_{\downarrow}(\varepsilon_i) = v_0 \exp\left(-\frac{2r(\varepsilon_i)}{\alpha}\right), \quad (9.38)$$

where

$$r(\varepsilon) \approx \left[\frac{4\pi}{3} \int_{\varepsilon_i}^{\infty} g(x) dx \right]^{-1/3}. \quad (9.39)$$

The typical rate of upward hopping for such an electron to a state less deep in the tail with energy $\varepsilon_j \leq \varepsilon_i$ is

$$v_{\uparrow}(\varepsilon_i, \delta) = v_0 \exp\left[-\frac{2r(\varepsilon_i - \delta)}{\alpha} - \frac{\delta}{k_B T}\right], \quad (9.40)$$

where $\delta = \varepsilon_i - \varepsilon_j \geq 0$. This expression is not exact. The average nearest-neighbor distance, $r(\varepsilon_i - \delta)$, is based on all states deeper than $\varepsilon_i - \delta$. For the exponential tail, this is equivalent to considering a slice of energy with a width of the order ε_0 . This works for a DOS that varies slowly compared with $k_B T$, but not in general. It is also assumed for simplicity that the localization length, α , does not depend on energy. The latter assumption can be easily jettisoned at the cost of somewhat more complicated forms of the following equations.

We will analyze these hopping rates at a given temperature T , and try to find the energy difference δ that provides the fastest typical hopping rate for an electron placed initially at energy ε_i . The corresponding energy

difference, δ , is determined by the condition

$$\frac{d\nu_{\uparrow}(\varepsilon_i, \delta)}{d\delta} = 0. \quad (9.41)$$

Using (9.37), (9.39) and (9.40), we find that the hopping rate in (9.40) has its maximum at

$$\delta = \varepsilon_i - 3\varepsilon_0 \ln \frac{3\varepsilon_0(4\pi/3)^{1/3} N_0^{1/3} \alpha}{2k_B T}. \quad (9.42)$$

The second term in the right-hand side of (9.42) is called the transport energy ε_t after *Monroe* [9.41]:

$$\varepsilon_t = 3\varepsilon_0 \ln \frac{3\varepsilon_0(4\pi/3)^{1/3} N_0^{1/3} \alpha}{2k_B T}. \quad (9.43)$$

We see from (9.42) that the fastest hop occurs to the state in the vicinity of the TE, independent of the initial energy ε_i , provided that ε_i is deeper in the tail than ε_t ; in other words, if $\delta \geq 0$. This result coincides with that of *Monroe* [9.41]. At low temperatures, the TE ε_t is situated deep in the band tail, and as the temperature rises it moves upward towards the mobility edge. At some temperature T_c , the TE merges with the mobility edge. At higher temperatures, $T > T_c$, the hopping exchange of electrons between localized band tail states becomes inefficient and the dynamic behavior of electrons is described by the well-known multiple-trapping model (see, for instance, *Orenstein and Kastner* [9.38]). At low temperatures, $T < T_c$, the TE replaces the mobility edge in the multiple-trapping process [9.41], as shown in Fig. 9.11. The width, W , of the maximum of the hopping rate is determined by the requirement that near ε_t the hopping rate, $\nu_{\uparrow}(\varepsilon_i, \delta)$, differs by less than a factor of e from the value $\nu_{\uparrow}(\varepsilon_i, \varepsilon_i - \varepsilon_t)$. One finds [9.42]

$$W = \sqrt{6\varepsilon_0 k_B T}. \quad (9.44)$$

For shallow states with $\varepsilon_i \leq \varepsilon_t$, the fastest hop (on average) is a downward hop to the nearest spatially localized state in the band tail, with the rate determined by (9.38) and (9.39). We recall that the energies of electron states are counted positive downward from the mobility edge towards the center of the mobility gap. This means that electrons in the shallow states with $\varepsilon_i \leq \varepsilon_t$ normally hop into deeper states with $\varepsilon > \varepsilon_i$, whereas electrons in the deep states with $\varepsilon_i > \varepsilon_t$ usually hop upward in energy into states near ε_t in the energy interval W , determined by (9.44).

This shows that ε_t must play a crucial role in those phenomena, which are determined by electron hopping in the band tails. This is indeed the case, as shown in numerous review articles where comprehensive theories based on the concept of the TE can be found (see,

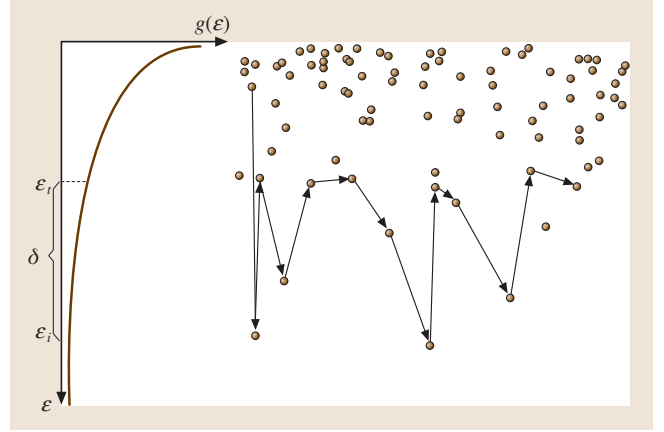


Fig. 9.11 Hopping path via the transport energy. In the left frame, the exponential DOS is shown schematically. The right frame depicts the transport path constructed from upward and downward hops. The upward transitions bring the charge carrier to sites with energies close to the transport energy ε_t

for instance, *Shklovskii et al.* [9.42]). We will consider only one phenomenon here for illustration, namely the hopping energy relaxation of electrons in a system with the DOS described by (9.37). This problem was studied initially by *Monroe* [9.41].

Consider an electron in some localized shallow energy state close to the mobility edge. Let the temperature be low, $T < T_c$, so that the TE, ε_t , lies well below the mobility edge, which has been chosen here as a reference energy, $\varepsilon = 0$. The aim is to find the typical energy, $\varepsilon_d(t)$, of our electron as a function of time, t . At early times, as long as $\varepsilon_d(t) < \varepsilon_t$, the relaxation is governed by (9.38) and (9.39). The depth $\varepsilon_d(t)$ of an electron in the band tail is determined by the condition

$$\nu_{\downarrow}[\varepsilon_d(t)] t \approx 1. \quad (9.45)$$

This leads to the double logarithmical dependence $\varepsilon_d(t) \propto \varepsilon_0 \ln[\ln(\nu_0 t)] + C$, where constant C depends on $\varepsilon_0, N_0, \alpha$ in line with (9.38) and (9.39). Indeed, (9.38) and (9.45) prescribe the logarithmic form of the time dependence of the hopping distance, $r(t)$, and (9.37) and (9.39) then lead to another logarithmic dependence $\varepsilon_d[r(t)]$ [9.41]. At the time

$$t_c \approx \nu_0^{-1} \exp\left(\frac{3\varepsilon_0}{k_B T}\right) \quad (9.46)$$

the typical electron energy, $\varepsilon_d(t)$, approaches the TE ε_t , and the style of the relaxation process changes. At $t > t_c$, every second hop brings the electron into states in the vicinity of the TE ε_t from where it falls downward in

energy to the nearest (in space) localization site. In the latter relaxation process, the typical electron energy is determined by the condition [9.41]

$$v_{\uparrow} [\varepsilon_d(t), \varepsilon_t] t \approx 1, \quad (9.47)$$

where $v_{\uparrow} [\varepsilon_d(t), \varepsilon_t]$ is the typical rate of electron hopping upward in energy toward the TE [9.41]. This condition leads to a typical energy position of the relaxing electron at time t of

$$\varepsilon_d(t) \approx 3\varepsilon_0 \ln [\ln (v_0 t)] - \varepsilon_0 \left[8 / (N_0 \alpha^3) \right]. \quad (9.48)$$

This is a very important result, which shows that in a system where the DOS has a pure exponential energy dependence, described by (9.37), the typical energy of a set of independently relaxing electrons would drop deeper and deeper into the mobility gap with time. This result is valid as long as the electrons do not interact with each other, meaning that the occupation probabilities of the electron energy levels are not taken into account. This condition is usually met in experimental studies of transient processes, in which electrons are excited by short (in time) pulses, which are typical of time-of-flight studies of the electron mobility in various disordered materials. In this case, only a small number of electrons are present in the band tail states. Taking into account the huge number of localized band tail states in most disordered materials, one can assume that most of the states are empty and so the above formulae for the hopping rates and electron energies can be used. In this case the electron mobility is a time-dependent quantity [9.41]. A transport regime in which mobility of charge carriers is time-dependent is usually called dispersive transport (see, for example, *Mott and Davis* [9.32], *Orenstein and Kastner* [9.38], *Monroe* [9.41]). Hence we have to conclude that the transient electron mobility in inorganic noncrystalline materials with the DOS in the band tails as described by (9.37) is a time-dependent quantity and the transient electrical conductivity has dispersive character. This is due to the nonequilibrium behavior of the charge carriers. They continuously drop in energy during the course of the relaxation process.

In some theoretical studies based on the Fokker–Planck equation it has been claimed that the maximum of the energy distribution of electrons coincides with the TE ε_t and hence it is independent of time. This statement contradicts the above result where the maximum of the distribution is at energy $\varepsilon_d(t)$, given by (9.48). The Fokker–Planck approach presumes the diffusion of

charge carriers over energy. Hence it is invalid for describing the energy relaxation in the exponential tails, in which electron can move over the full energy width of the DOS (from a very deep energy state toward the TE) in a single hopping event.

In the equilibrium conditions, when electrons in the band tail states are provided by thermal excitation from the Fermi energy, a description of the electrical conductivity can easily be derived using (9.5)–(9.7) [9.39]. The maximal contribution to the integral in (9.5) comes from the electrons with energies in the vicinity of the TE ε_t , in an energy range with a width, W , described by (9.44). Neglecting the temperature dependence of the pre-exponential factor, σ_0 , one arrives at the temperature dependence of the conductivity:

$$\sigma \approx \sigma_0 \exp \left(-\frac{2r(\varepsilon_t)}{B_c^{-1/3} \alpha} - \frac{\varepsilon_F - \varepsilon_t}{k_B T} \right), \quad (9.49)$$

where coefficient $B_c \approx 2.7$ is inserted in order to take into account the need for a charge carrier to move over macroscopic percolation distances in order to provide low-frequency charge transport.

A very similar theory is valid for charge transport in noncrystalline materials under stationary excitation of electrons (for example by light) [9.42]. In such a case, one first needs to develop a theory for the steady state of the system under stationary excitation. This theory takes into account various recombination processes for charge carriers and provides their stationary concentration along with the position of the quasi-Fermi energy. After solving this recombination problem, one can follow the track of the theory of charge transport in quasi-thermal equilibrium [9.39] and obtain the conductivity in a form similar to (9.49), where ε_F is the position of the quasi-Fermi level. We skip the corresponding (rather sophisticated) formulae here. Interested readers can find a comprehensive description of this sort of theory for electrical conductivity in the literature (see, for instance, *Shklovskii et al.* [9.42]).

Instead, in the next section we will consider a very interesting problem related to the nonequilibrium energy relaxation of charge carriers in the band tail states. It is well known that at low temperatures, $T \leq 50$ K, the photoconductivities of various inorganic noncrystalline materials, such as amorphous and microcrystalline semiconductors, do not depend on temperature [9.44–46]. At low temperatures, the TE ε_t lies very deep in the band tail and most electrons hop downward in energy, as described by (9.38) and (9.39). In such a regime, the

photoconductivity is a temperature-independent quantity determined by the loss of energy during the hopping of electrons via the band-tail states [9.47]. During this hopping relaxation, neither the diffusion coefficient D nor the mobility of the carriers μ depend on temperature, and the conventional form of Einstein's relationship $\mu = eD/k_B T$ cannot be valid. The question then arises as to what the relation between μ and D is for hopping relaxation. We answer this question in the following section.

Einstein's Relationship for Hopping Electrons

Let us start by considering a system of nonequilibrium electrons in the band tail states at $T = 0$. The only process that can happen with an electron is its hop downward in energy (upward hops are not possible at $T = 0$) to the nearest localized state in the tail. Such a process is described by (9.37)–(9.39). If the spatial distribution of localized tail states is isotropic, the probability of finding the nearest neighbor is also isotropic in the absence of the external electric field. In this case, the process of the hopping relaxation of electrons resembles diffusion in space. However, the median length of a hop (the distance r to the nearest available neighbor), as well as the median time, $\tau = v_{\downarrow}^{-1}(r)$, of a hop [see (9.38)] increases during the course of relaxation, since the hopping process brings electrons deeper into the tail. Nevertheless, one can ascribe a diffusion coefficient to such a process [9.42]:

$$D(r) = \frac{1}{6} v_{\downarrow}(r) r^2. \quad (9.50)$$

Here $v_{\downarrow}(r)r^2$ replaces the product of the “mean free path” r and the “velocity” $r \cdot v_{\downarrow}(r)$, and the coefficient $1/6$ accounts for the spatial symmetry of the problem. According to (9.37)–(9.39) and (9.50), this diffusion coefficient decreases exponentially with increasing r and hence with the number of successive electron hops in the relaxation process.

In order to calculate the mobility of electrons during hopping relaxation under the influence of the electric field, one should take into account the spatial asymmetry of the hopping process due to the field [9.47, 48]. Let us consider an electron in a localized state at energy ε . If an external electric field with a strength F is applied along direction x , the concentration of tail states available to this hopping electron at $T = 0$ (in other words those that have energies deeper in the tail than ε) is [9.47]

$$N(\varepsilon, x) = N(\varepsilon) \left(1 + \frac{eFx}{\varepsilon_0} \right), \quad (9.51)$$

where

$$N(\varepsilon) = \int_{\varepsilon}^{\infty} g(\varepsilon) d\varepsilon = N_0 \exp\left(-\frac{\varepsilon}{\varepsilon_0}\right). \quad (9.52)$$

It was assumed in the derivation of (9.51) that $eFx \ll \varepsilon_0$.

Due to the exponential dependence of the hopping rate on the hopping length r , the electron predominantly hops to the nearest tail state among the available states if $r \gg \alpha$, which we assume to be valid. Let us calculate the average projection $\langle x \rangle$ on the field direction of the vector \mathbf{r} from the initial states at energy ε to the nearest available neighbor among sites with a concentration $N(\varepsilon, x)$ determined by (9.51). Introducing spherical coordinates with the angle θ between r and the x -axis, we obtain [9.48]

$$\begin{aligned} \langle x \rangle &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \\ &\times \int_0^{\infty} [dr \cdot r^3 \cos(\theta) \cdot N(\varepsilon, r \cos\theta)] \\ &\times \exp \left[- \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \right. \\ &\left. \times \int_0^r dr' r'^2 N(\varepsilon, r' \cos\theta) \right]. \end{aligned} \quad (9.53)$$

Substituting (9.51) for $N(\varepsilon, r \cos\theta)$, calculating the integrals in (9.53) and omitting the second-order terms

$$\left(\frac{eN^{-1/3}(\varepsilon)F}{\varepsilon_0} \right)^2 \ll 1, \quad (9.54)$$

we obtain

$$\langle x \rangle = \frac{eFN^{-2/3}(\varepsilon)}{3\varepsilon_0} \frac{\Gamma(5/3)}{(4\pi/3)^{2/3}}, \quad (9.55)$$

where Γ is the gamma-function and $N(\varepsilon)$ is determined by (9.52). Equation (9.55) gives the average displacement in the field direction of an electron that hops downward from a state at energy ε to the nearest available neighbor in the band tail. The average length $\langle r \rangle$ of

such a hop is

$$\begin{aligned} \langle r \rangle &= \int_0^{\infty} dr 4\pi r^3 N(\varepsilon) \exp\left[-\frac{4\pi}{3} N(\varepsilon) r^3\right] \\ &= \left(\frac{4\pi N(\varepsilon)}{3}\right)^{-1/3} \Gamma\left(\frac{4}{3}\right). \end{aligned} \quad (9.56)$$

One can ascribe to the hopping process a mobility

$$\begin{aligned} \mu &= \frac{v}{F} = \frac{\langle x \rangle v(\langle r \rangle)}{F} \\ &= \frac{e N^{-2/3}(\varepsilon) v(\langle r \rangle)}{3\varepsilon_0} \frac{\Gamma(5/3)}{(4\pi/3)^{2/3}} \end{aligned} \quad (9.57)$$

and a diffusion coefficient

$$\begin{aligned} D &= \frac{1}{6} \langle r \rangle^2 v(\langle r \rangle) \\ &= \frac{1}{6} N^{-2/3}(\varepsilon) v(\langle r \rangle) \frac{\Gamma^2(4/3)}{(4\pi/3)^{2/3}}. \end{aligned} \quad (9.58)$$

Expressions (9.57) and (9.58) lead to a relationship between μ and D of the form

$$\mu = \frac{2\Gamma(5/3)}{\Gamma^2(4/3)} \frac{e}{\varepsilon_0} D \approx 2.3 \frac{e}{\varepsilon_0} D. \quad (9.59)$$

This formula replaces the Einstein's relationship $\mu = eD/k_B T$ for electron hopping relaxation in the exponential band tail. Several points should be noted about this result. First of all, one should clearly realize that (9.59) is valid for nonequilibrium energy-loss relaxation in which only downward (in energy) transitions between localized states can occur. This regime is valid only at low temperatures when the TE ε_t is very deep in the band tail. As the temperature increases, the upward hops become more and more efficient for electron relaxation. Under these circumstances, the relation between μ and D evolves gradually with rising temperature from its temperature-independent form at $T = 0$ to the conventional Einstein's relationship, $\mu = eD/k_B T$ [9.50, 51]. Secondly, one should realize that (9.59) was derived in the linear regime with respect to the applied field under the assumption that $eFx \ll \varepsilon_0$. According to (9.55), the quantity $\langle x \rangle$ is proportional to $N^{-2/3}(\varepsilon) = N_0^{-2/3} \exp[2\varepsilon/(3\varepsilon_0)]$, in other words it increases exponentially during the course of the relaxation toward larger localization energies ε . This means that for deep localized states in the band tail, the condition $eFx \ll \varepsilon_0$ breaks down. The boundary energy for application of the linear theory depends on the strength of the electric field, F . As F decreases, this boundary energy

drops deeper into the tail. However, for any F , there is always a boundary energy in the tail below which the condition $eFx \ll \varepsilon_0$ cannot be fulfilled and where nonlinear effects play the decisive role in the hopping conduction of charge carriers. In the next section we show how one can describe these nonlinear effects with respect to the applied electric field.

Nonlinear Effects in Hopping Conduction

Transport phenomena in inorganic noncrystalline materials, such as amorphous semiconductors, under the influence of high electric fields are the foci for intensive experimental and theoretical study. This is due to observations of strong nonlinearities in the dependencies of the dark conductivity [9.11, 52, 53], the photoconductivity [9.49] and the charge carrier drift mobility [9.54–56] on the field for high electric fields. These effects are most pronounced at low temperatures, when charge transport is determined by electron hopping via localized band tail states (Fig. 9.12).

Whereas the field-dependent hopping conductivity at low temperatures has always been a challenge to describe theoretically, theories for the temperature dependence of the hopping conductivity in low electric fields have been successfully developed for all of the transport regimes discussed: for the dark conductivity [9.39], for the drift mobility [9.41], and for the photoconductivity [9.42]. In all of these theories, hopping transitions of electrons between localized states in the exponential band tails play a decisive role, as described above in (9.37)–(9.59).

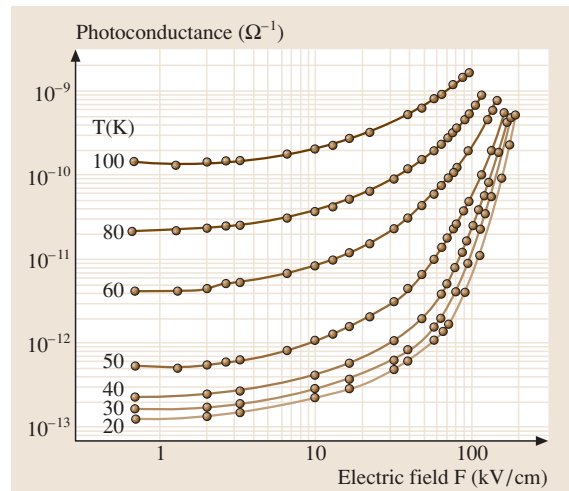


Fig. 9.12 Dependence of the photoconductivity in a-Si:H on the electric field at different temperatures [9.49]

Shklovskii [9.57] was the first to recognize that a strong electric field plays a similar role to that of temperature in hopping conduction. In order to obtain the field dependence of the conductivity $\sigma(F)$ at high fields, *Shklovskii* [9.57] replaced the temperature T in the well-known dependence $\sigma(T)$ for low fields by a function $T_{\text{eff}}(F)$ of the form

$$T_{\text{eff}} = \frac{eF\alpha}{2k_B}, \quad (9.60)$$

where e is the elementary charge, k_B is the Boltzmann constant, and α is the localization length of electrons in the band tail states. A very similar result was obtained later by *Grünwald* and *Movaghar* [9.58] in their study of the hopping energy relaxation of electrons through band tails at very low temperatures and high electric fields. The same idea was also used by *Shklovskii* et al. [9.42], who suggested that, at $T = 0$, one can calculate the field dependence of the stationary photoconductivity in amorphous semiconductors by replacing the laboratory temperature T in the formulae of the low-field finite-temperature theory by an effective temperature $T_{\text{eff}}(F)$ given by (9.60).

It is easy to understand why the electric field plays a role similar to that of temperature in the energy relaxation of electrons. Indeed, in the presence of the field, the number of sites available at $T = 0$ is significantly enhanced in the field direction, as shown in Fig. 9.13. Hence electrons can relax faster at higher fields. From the figure it is apparent that an electron can increase its energy with respect to the mobility edge by an amount $\varepsilon = eFx$ in a hopping event over a distance x in the direction prescribed by the electric field. The process is reminiscent of thermal activation. The analogy becomes tighter when we express the transition rate for this hop as

$$\begin{aligned} \nu &= \nu_0 \exp\left(-\frac{2x}{\alpha}\right) = \nu_0 \exp\left(-\frac{2\varepsilon}{eF\alpha}\right) \\ &= \nu_0 \exp\left(-\frac{\varepsilon}{k_B T_{\text{eff}}(F)}\right), \end{aligned} \quad (9.61)$$

where $T_{\text{eff}}(F)$ is provided by (9.60).

This electric field-induced activation at $T = 0$ produces a Boltzmann tail to the energy distribution function of electrons in localized states as shown by numerical calculations [9.59, 60]. In Fig. 9.12, the field-dependent photoconductivity in a-Si:H is shown for several temperatures [9.49]. If we compare the photoconductivity at the lowest measured temperature,

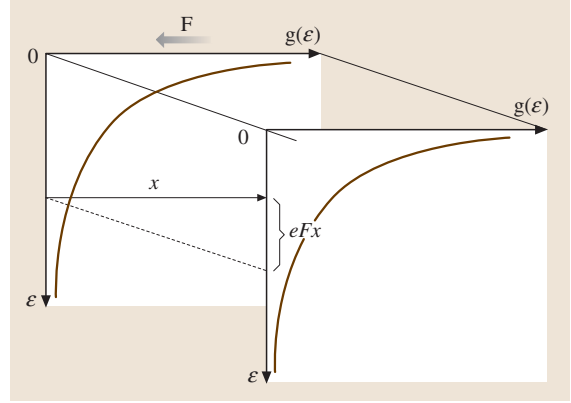


Fig. 9.13 Tunneling transition of a charge carrier in the band tail that is affected by a strong electric field. Upon traveling the distance x , the carrier acquires the energy eFx , where F is the strength of the electric field, and e is the elementary charge

$T = 20$ K in Fig. 9.12, with the low-field photoconductivity at $T = T_{\text{eff}} = \frac{eF\alpha}{2k_B}$ as measured by *Hoheisel* et al. [9.44] and by *Siradins* and *Fritzsche* [9.45], we come to the conclusion that the data agree quantitatively if one assumes that the localization length $\alpha = 1.05$ nm [9.42], which is very close to the value $\alpha \approx 1.0$ nm found for a-Si:H from independent estimates [9.11]. This comparison shows that the concept of the effective temperature based on (9.60) provides a powerful tool for estimating transport coefficient non-linearity with respect to the electric field using the low-field results for the temperature dependencies of such coefficients.

However, experiments are usually carried out not at $T = 0$ but at finite temperatures, and so the question of how to describe transport phenomena in the presence of both factors, finite T and high F , arises. By studying the steady state energy distribution of electrons in numerical calculations and computer simulations [9.59, 60], as well as straightforward computer simulations of the steady-state hopping conductivity and the transient energy relaxation of electrons [9.61], the following result was found. The whole set of transport coefficients can be represented by a function with a single parameter $T_{\text{eff}}(F, T)$

$$T_{\text{eff}}(F, T) = \left[T^\beta + \left(\gamma \frac{eF\alpha}{k_B} \right)^\beta \right]^{1/\beta}, \quad (9.62)$$

where $\beta \approx 2$ and γ is between 0.5 and 0.9 depending on which transport coefficient is considered [9.61]. We

are aware of no analytical theory that can support this numerical result.

To wrap up this section we would like to make the following remark. It is commonly claimed in the scientific literature that transport coefficients in the hopping regime should have a purely exponential dependence on the applied electric field. The idea behind such statements seems rather transparent. Electric field diminishes potential barriers between localized states by an amount $\Delta\varepsilon = eFx$, where x is the projection of the hopping radius on the field direction. The field should therefore diminish the activation energies in (9.24) and (9.25) by this amount, leading to the term $\exp(eFx/k_B T)$ in the expressions for the charge carrier mobility, diffusivity and conductivity. One should, however, take into account that hopping transport in all real materials is essentially described by the variable-range hopping process. In such a process, as discussed above, the interplay between spatial and energy-dependent terms in the exponents of the transition probabilities determine the conduction path. Therefore it is not enough to solely take into account the influence of the strong electric field on the activation energies of single hopping transitions. One should consider the modification of the whole transport path due to the effect of the strong field. It is this VRH nature of the hopping process that leads to a more complicated field dependence for the transport coefficients expressed by (9.60)–(9.62).

We have now completed our description of electron transport in inorganic disordered materials with exponential DOS in the band tails. In the next section we tackle the problem of charge transport in organic disordered materials.

9.3.4 Description of Charge Carrier Energy Relaxation and Hopping Conduction in Organic Noncrystalline Materials

Electron transport and energy relaxation in disordered organic solids, such as molecularly doped polymers, conjugated polymers and organic glasses, has been the subject of intensive experimental and theoretical study for more than 20 years. Although there is a wide array of different disordered organic solids, the charge transport process is similar in most of these materials. Even at the beginning of the 1980s it was well understood that the main transport mechanism in disordered organic media is the hopping of charge carriers via spatially randomly distributed localized states. Binary systems like doped polymeric matrices provide canonical examples of disordered organic materials that exhibit

the hopping transport mechanism. Examples include polyvinylcarbazole (PVK) or bis-polycarbonate (Lexan) doped with either strong electron acceptors such as trinitrofluorenone acting as an electron transporting agent, or strong electron donors such as derivatives of tryphenylamine or triphenylmethane for hole transport [9.62, 63]. To avoid the need to specify whether transport is carried by electrons or holes each time, we will use a general notation of “charge carrier” below. The results are valid for both types of carrier – electrons or holes. Charge carriers in disordered organic materials are believed to be strongly localized [9.18, 62–64]. The localization centers are molecules or molecular subunits, henceforth called sites. These sites are located in statistically different environments. As a consequence, the site energies, which are to great extent determined by electronic polarization, fluctuate from site to site. The fluctuations are typically on the order of 0.1 eV [9.65]. This is about one order of magnitude larger than the corresponding transfer integrals [9.65]. Therefore carrier wavefunctions can be considered to be strongly localized [9.65].

As discussed above, the crucial problem when developing a theoretical picture for hopping transport is the structure of the energy spectrum of localized states, DOS. It is believed that, unlike inorganic noncrystalline materials where the DOS is believed exponential, the energy dependence of the DOS in organic disordered solids is Gaussian (see Bässler [9.18] and references therein),

$$g(\varepsilon) = \frac{N_0}{\varepsilon_0 \sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2\varepsilon_0^2}\right), \quad (9.63)$$

where N_0 is the total concentration of states and ε_0 is the energy scale of the DOS. The strongest evidence in favor of such an energy spectrum in disordered organic materials is the ability to reproduce the observed experimentally temperature dependence of the carrier mobility and that of hopping conductivity assuming the Gaussian DOS in computer simulations [9.18, 66]. It has been observed in numerous experimental studies [9.67–73] that the temperature dependence of the drift mobility of charge carriers in disordered organic solids takes the form

$$\mu \propto \exp\left[-\left(\frac{T_0}{T}\right)^2\right] \quad (9.64)$$

with a characteristic temperature T_0 , as shown in Fig. 9.14a. Computer simulations and theoretical calculations [9.65, 66, 74, 75] with the Gaussian DOS

described by (9.63) give a dependence of the form

$$\mu \propto \exp \left[- \left(C \frac{\varepsilon_0}{k_B T} \right)^2 \right], \quad (9.65)$$

where C is a numerical coefficient. Computer simulations [9.65, 66] give a value $C \approx 0.69$ for this coefficient, and analytical calculations [9.74, 75] predict a similar value of $C \approx 0.64$. Equation (9.65) is often used to determine the parameter ε_0 of the DOS from experimental measurements of the $\ln(\mu)$ versus $(1/T)^2$ dependences (see, for example, Ochse et al. [9.71]).

One may wonder whether the theoretical description of hopping conduction and carrier energy relaxation in a system with a Gaussian DOS (9.63) should differ significantly from the theory described above for disordered

systems with a purely exponential DOS (9.37). The answer to this question is yes. The reason becomes clear if one considers the behavior of a single charge carrier in an empty system. In an empty system with an exponential DOS, a charge carrier always (on average) falls downward in energy if $k_B T < \varepsilon_0$ [see (9.45)–(9.48)], and its mobility continuously decreases with time; however, in a system with a Gaussian DOS, a particular energy level ε_∞ determines the equilibrium energy position of a charge carrier. When it is located at some site with high energy in the Gaussian DOS, the charge carrier first hops via localized states so that its average energy $\varepsilon_d(t)$ decreases until it achieves the energy level ε_∞ after some typical time period τ_{rel} . At times $t < \tau_{\text{rel}}$ the behavior of the carrier qualitatively resembles that seen for the purely exponential DOS. The downward hops are then replaced by relaxation hops that send the carrier upward to the transport energy, and the carrier mobility at $t < \tau_{\text{rel}}$ decreases with time. However, in contrast to the case for the exponential DOS, in a Gaussian DOS the carrier mobility becomes time-independent after a time τ_{rel} , when the average carrier energy reaches the level ε_∞ . At $t > \tau_{\text{rel}}$, the dispersive transport regime with time-dependent carrier mobility is replaced by a quasi-equilibrium so-called “Gaussian transport” regime, in which the spatial spreading of the carrier packet with time can be described by the traditional diffusion picture with a time-independent diffusion coefficient.

The peculiarity of the hopping energy relaxation of charge carriers in a system with a Gaussian DOS described above makes it easier to describe charge transport at times $t > \tau_{\text{rel}}$ than in the case of the exponential DOS. In the latter case, only the presence of a significant number of carriers in a quasi Fermi level can make kinetic coefficients such as mobility, diffusivity and conductivity time-independent and hence conventionally measurable and discussible quantities. In the case of the Gaussian DOS, these kinetic coefficients are not time-dependent at times $t > \tau_{\text{rel}}$. Moreover, in diluted systems one can calculate these coefficients by considering the behavior of a single charge carrier. This makes theoretical considerations of electrical conductivity in organic disordered solids with a Gaussian DOS much easier than when considering inorganic noncrystalline materials with an exponential DOS. Let us now calculate ε_∞ , τ_{rel} and μ in disordered organic solids with a Gaussian DOS.

Computer simulations [9.66] and analytical calculations [9.74, 75] show that the mean energy of the independently hopping carriers, initially distributed randomly over all states in the Gaussian DOS, decreases

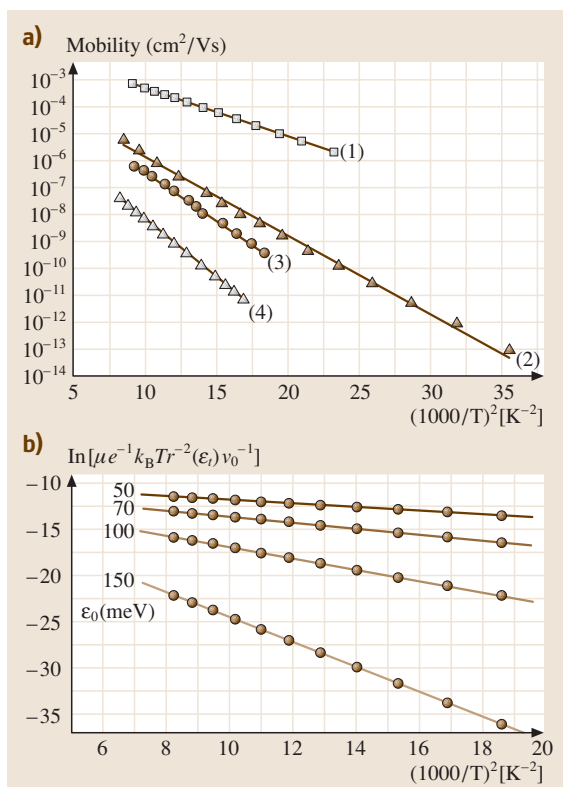


Fig. 9.14a,b Temperature dependence of the zero-field mobility in organic semiconductors. Experimental data (a): (1) di-*p*-tolylphenylamine containing (DEASP)-traps [9.69]; (2) (BD)-doped polycarbonate [9.70]; (3) (NTDI)-doped poly(styrene) [9.68]; (4) (BD)-doped TTA/polycarbonate [9.72]. Theoretical results (b) were obtained via (9.73)

with time until it approaches the thermal equilibrium value

$$\varepsilon_\infty = \frac{\int_{-\infty}^{\infty} \varepsilon \exp\left(-\frac{\varepsilon}{k_B T}\right) g(\varepsilon) d\varepsilon}{\int_{-\infty}^{\infty} \exp\left(-\frac{\varepsilon}{k_B T}\right) g(\varepsilon) d\varepsilon} = -\frac{\varepsilon_0^2}{k_B T}. \quad (9.66)$$

The time τ_{rel} required to reach this equilibrium is of key importance in the analysis of experimental data [9.65], since at $t < \tau_{\text{rel}}$ the carrier mobility decreases with time (dispersive transport) until it reaches its equilibrium, time-independent value at $t \approx \tau_{\text{rel}}$. It has been established by computer simulations that τ_{rel} strongly depends on temperature [9.18]:

$$\tau_{\text{rel}} \propto \exp\left[\left(B \frac{\varepsilon_0}{k_B T}\right)^2\right] \quad (9.67)$$

with $B \approx 1.07$. Given that the same hopping processes determine both μ and τ_{rel} , researchers were puzzled for many years by the fact that they had different coefficients B and C (in other words they have different temperature dependencies) [9.65]. Below we show how to calculate both quantities – μ and τ_{rel} – easily, and we explain their temperature dependencies (obtained experimentally and by computer simulations as expressed by (9.64), (9.65) and (9.67)).

Our theoretical approach is based on the concept of transport energy (TE), introduced in Sect. 9.3.3, where it was calculated for the exponential DOS given by (9.37). Literally repeating these calculations with the Gaussian DOS, given by (9.63), we obtain the equation [9.76, 77]

$$\exp\left(\frac{x^2}{2}\right) \left[\int_{-\infty}^{\frac{x}{\sqrt{2}}} \exp(-t^2) dt \right]^{4/3} = \left[9(2\pi)^{1/2} N_0 \alpha^3 \right]^{-1/3} \frac{k_B T}{\varepsilon_0}. \quad (9.68)$$

If we denote the solution of (9.68) as $X_t(N_0 \alpha^3, k_B T/\varepsilon_0)$, then the transport energy in the Gaussian DOS is equal to

$$\varepsilon_t = \varepsilon_0 \cdot X_t\left(N_0 \alpha^3, k_B T/\varepsilon_0\right). \quad (9.69)$$

Charge carriers perform thermally activated transitions from states with energies below the TE, ε_t , to the states with energies close to that of the TE [9.76]. Charge carriers hop downward in energy from states with energies

above the TE to the spatially nearest sites with rates determined by (9.38) and (9.39).

Now that we have clarified the relaxation kinetics of charge carriers in the Gaussian DOS, it is easy to calculate the relaxation time τ_{rel} and the drift mobility μ . We consider the case $\varepsilon_\infty < \varepsilon_t < 0$, which corresponds to all reasonable values of material parameters $N_0 \alpha^3$ and $k_B T/\varepsilon_0$ [9.76]. The energy relaxation of most carriers with energies ε in the interval $\varepsilon_\infty < \varepsilon < \varepsilon_t$ occurs via a multiple trapping-like process, well described in the literature (see, for example, *Orenstein and Kastner* [9.38] or *Marschall* [9.78]). Below ε_t the average energy of the carriers $\varepsilon(t)$ moves logarithmically downward with time t . States above $\varepsilon(t)$ achieve thermal equilibrium with states at ε_t at time t , while states below $\varepsilon(t)$ have no chance at time t to exchange carriers with states in the vicinity of ε_t . Hence the occupation of those deep states does not correspond to the equilibrium one, being determined solely by the DOS of the deep states. The system reaches thermal equilibrium when the time-dependent average energy $\varepsilon(t)$ achieves the equilibrium level ε_∞ , determined by (9.66). This happens at $t = \tau_{\text{rel}}$. Since the relaxation of carriers occurs via thermal activation to the level ε_t , the relaxation time τ_{rel} is determined by the time required for activated transitions from the equilibrium level ε_∞ to the transport energy ε_t . Hence, according to (9.40) and (9.47), τ_{rel} is determined by the expression

$$\tau_{\text{rel}} = \nu_0^{-1} \exp\left[\frac{2r(\varepsilon_t)}{\alpha} + \frac{\varepsilon_t - \varepsilon_\infty}{k_B T}\right]. \quad (9.70)$$

From (9.68)–(9.70) it is obvious that the activation energy of the relaxation time depends on the parameters $N_0 \alpha^3$ and $k_B T/\varepsilon_0$. Hence, generally speaking, this dependence cannot be represented by (9.67) and, if at all, the coefficient B should depend on the magnitude of the parameter $N_0 \alpha^3$. However, numerically solving (9.68)–(9.70) using the value $N_0 \alpha^3 = 0.001$, which was also used in computer simulations by *Bässler* [9.18, 65], confirms the validity of (9.67) with $B \approx 1.0$. This result is in agreement with the value $B \approx 1.07$ obtained from computer simulations [9.18, 65]. A way to describe the temperature dependence of the relaxation time τ_{rel} by (9.67) is provided by the strong temperature dependence of ε_∞ in the exponent in (9.70), while the temperature dependencies of the quantities ε_t and $r(\varepsilon_t)$ in (9.70) are weaker and they almost cancel each other out. However, if $N_0 \alpha^3 = 0.02$, the relaxation time is described by (9.67) with $B \approx 0.9$. This

shows that (9.67) can only be considered to be a good approximation.

Now we turn to the calculation of the carrier drift mobility μ . We assume that the transition time t_{tr} necessary for a carrier to travel through a sample is longer than τ_{rel} , and hence the charge transport takes place under equilibrium conditions. As described above, every second jump brings the carrier upward in energy to the vicinity of ε_t , and is then followed by a jump to the spatially nearest site with deeper energy, determined solely by the DOS. Therefore, in order to calculate the drift mobility μ , we must average the hopping transition times over energy states below ε_t , since only these states are essential to charge transport in thermal equilibrium [9.77, 80]. Hops downward in energy from the level ε_t occur exponentially faster than upward hops towards ε_t . This means that one can neglect the former in the calculation of the average time $\langle t \rangle$. The carrier drift mobility can be evaluated as

$$\mu \approx \frac{e}{k_B T} \frac{r^2(\varepsilon_t)}{\langle t \rangle}, \quad (9.71)$$

where $r(\varepsilon_t)$ is determined via (9.39), (9.63), (9.68) and (9.69). The average hopping time takes the form [9.80]

$$\langle t \rangle = \left[\int_{-\infty}^{\varepsilon_t} g(\varepsilon) d\varepsilon \right]^{-1} \times \int_{-\infty}^{\varepsilon_t} v_0^{-1} g(\varepsilon) \times \exp\left(\frac{2r(\varepsilon)B_c^{1/3}}{a} + \frac{\varepsilon_t - \varepsilon}{k_B T}\right) d\varepsilon, \quad (9.72)$$

where $B_c \approx 2.7$ is the percolation parameter. This numerical coefficient is introduced into (9.72) in order to warrant the existence of an infinite percolation path over the states with energies below ε_t . Using (9.63), (9.68), (9.69), (9.71) and (9.72), one obtains the following relation for the exponential terms in the expression for the carrier drift mobility:

$$\begin{aligned} & \ln \left[\mu / \left(\frac{er^2(\varepsilon_t)v_0}{k_B T} \right) \right] \\ &= -2 \left[\frac{4\sqrt{\pi}}{3B_c} N_0 \alpha^3 \int_{-\infty}^{X_t/\sqrt{\pi}} \exp(-t^2) dt \right]^{-1/3} \\ & \quad - \frac{X_t \varepsilon_0}{k_B T} - \frac{1}{2} \left(\frac{\varepsilon_0}{k_B T} \right)^2. \end{aligned} \quad (9.73)$$

It is (9.73) that determines the dependence of the carrier drift mobility on the parameters $N_0 \alpha^3$ and $k_B T/\varepsilon_0$.

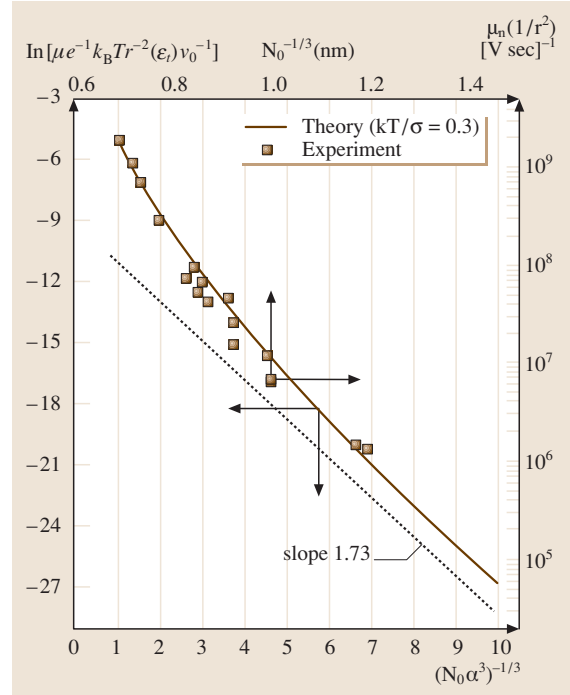


Fig. 9.15 Concentration dependence of the drift mobility evaluated from (9.73) (solid line), and the dependence observed experimentally (circles) for TNF/PE and TNF/PVK [9.79]

In Fig. 9.14b, the dependence of the drift mobility on the temperature at $N_0 \alpha^3 = 0.01$ is depicted for several values of ε_0 . The sensitivity of the mobility to temperature is clear from this picture. Comparison of these dependencies with experimental measurements of $\ln(\mu)$ versus $(1/T)^2$ [some are shown in Fig. 9.14a] provides information on the energy scale, ε_0 , of the DOS (see, for example, Bässler [9.18] and Ochse et al. [9.71]).

In Fig. 9.15, the dependence of the drift mobility on $N_0 \alpha^3$ is shown for $k_B T/\varepsilon_0 = 0.3$. Experimental data from Gill [9.81] are also shown in the figure. It is clear that the slope of the mobility exponent as a function of $(N_0 \alpha^3)^{-1/3}$ given by the theory described above agrees with the experimental data. At a very low concentration of localized states, N_0 , when the probability of carrier tunneling in space dominates the transition rate in (9.24), charge carriers hop preferentially to the nearest spatial sites. In this regime of nearest-neighbor hopping, the concentration dependence of the drift mobility is described by (9.28), as illustrated by the dashed line in Fig. 9.15.

So far we have discussed the drift mobility of charge carriers under the assumption that the concentration of charge carriers is much less than that of the localized states in the energy range relevant to hopping transport. In such a case one can assume that the carriers perform independent hopping motion and so the conductivity can be calculated as the product

$$\sigma = en\mu, \quad (9.74)$$

9.4 Concluding Remarks

Beautiful effects have been observed experimentally by studying the charge transport in disordered organic and inorganic materials. Among these, the transport coefficients in the hopping regime show enormously strong dependencies on material parameters. The dependence of the charge carrier mobility on the concentration of localized states N_0 (Fig. 9.15) spreads over many orders of magnitude, as does its dependence on the temperature T (Fig. 9.14) and on the (high) electric field strength F (Fig. 9.12). Such strong variations in physical quantities are typical, say, in astrophysics, but they are not usual in solid state physics. This makes the study of the charge transport in disordered materials absolutely fascinating. The strong dependencies of kinetic coefficients (like drift mobility, diffusivity and conductivity) in disordered materials on various material parameters makes these systems very attractive for various device applications. Since they are relatively inexpensive to manufacture too, it is then easy to understand why disordered organic and inorganic materials are of enormous interest for various technical applications.

These materials also provide a purely academic challenge with respect to their transport phenomena. While traditional kinetic theories developed for crystalline materials are largely dependent on the systems having translational symmetry, there is no such symmetry in disordered materials. However, we have shown in this chapter that it is still possible to develop a reliable theoretical approach to transport phenomena in disordered materials. Particularly interesting is the hopping transport regime. In this regime, charge carriers perform incoherent tunneling jumps between localized states distributed in space and energy. The enormously strong (exponential) dependence of the transition rates on the distances between the sites and their energies call for a completely new set of ideas compared to those for crystalline solids. Conventional transport theories based on the averaging of transition rates lead to ab-

where n is the concentration of charge carriers in the material and μ is their drift mobility. If, however, the concentration n is so large that the Fermi energy at thermal equilibrium or the quasi-Fermi energy at stationary excitation is located significantly higher (energetically) than the equilibrium energy ε_α , a more sophisticated theory based on the percolation approach is required [9.82]. The result obtained is similar to that given by (9.49).

surd results if applied to hopping transport in disordered materials. One can use ideas from percolation theory instead to adequately describe charge transport. One of the most important ideas in this field is so-called variable-range hopping (VRH) conduction. Although the rate of transitions between two localized states is a product of exponential terms that are separately dependent on the concentration of localized states N_0 , the temperature of the system T , and also on the field strength F (for high field strengths), it is generally wrong to assume that the carrier drift mobility, diffusivity or conductivity can also be represented as the product of three functions that are separately dependent on N_0 , T and F . Instead one should search for a percolation path that takes into account the exponential dependences of the hopping rates on all of these parameters simultaneously. Such a procedure, based on strong interplay between the important parameters in the exponents of the transition rates, leads to very interesting and (in some cases) unexpected results, some of which were described in this chapter. For example, it was shown that the effect of a strong electric field on transport coefficients can be accounted for by renormalizing the temperature. Most of the ideas discussed in this chapter were discussed in the early works of Mott and his coauthors (see, for example, *Mott and Davis* [9.32]). Unfortunately, these ideas are not yet known to the majority of researchers working in the field of disordered materials. Moreover, it is often believed that transport phenomena in different disordered materials need to be described using different ideas. Mott based his ideas, in particular the VRH, mostly on inorganic glassy semiconductors. Most of the researchers that are studying amorphous inorganic semiconductors (like a-Si:H) are aware of these ideas. However, new researchers that are working on more modern disordered materials, such as organic disordered solids and dye-sensitized materials, are often not aware of these very useful and powerful ideas developed by Mott and his

followers that can be used to describe charge transport in inorganic disordered systems. In this chapter we have shown that the most pronounced charge transport effects in inorganic and organic disordered materials can be successfully described in a general manner using these ideas.

Although we have presented some useful ideas for describing charge transport in disordered systems above, it is clear that the theoretical side of this field is still embryonic. There are still no reliable theories for charge transport via extended states in disordered materials. Nor are there any reliable theoretical descriptions for the spatial structure of the localized states (DOS) in organic and inorganic noncrystalline materials. All of the theoretical concepts presented in this chapter were developed using very simple models of localization centers with a given energy spectrum that are randomly distributed in

space. No correlations between the spatial positions of the sites and the energies of the electronic states at these sites were considered here. Some theoretical attempts to account for such correlations can be found in the literature, although the correlations have not been calculated ab initio: instead they are inserted into a framework of model assumptions. This shows how far the field of charge transport in disordered materials is from a desirable state. Since these materials are already widely used in various technical applications, such as field transistor manufacture, light-emitting diodes and solar cells, and since the sphere of such applications is increasing, the authors are optimistic about the future of research in this field. The study of fundamental charge transport properties in disordered materials should develop, leading us to a better understanding of the fundamental charge transport mechanisms in such systems.

References

- 9.1 A. Bunde, K. Funke, M. D. Ingram: *Solid State Ionics* **105**, 1 (1998)
- 9.2 S. D. Baranovskii, H. Cordes: *J. Chem. Phys.* **111**, 7546 (1999)
- 9.3 C. Brabec, V. Dyakonov, J. Parisi, N.S. Sariciftci: *Organic Photovoltaics: Concepts and Realization* (Springer, Berlin, Heidelberg 2003)
- 9.4 M. H. Brodsky: *Amorphous Semiconductors* (Springer, Berlin, Heidelberg 1979)
- 9.5 G. Hadziioannou, P. F. van Hutten: *Semiconducting Polymers* (Wiley, New York 2000)
- 9.6 J. D. Joannopoulos, G. Locowsky: *The Physics of Hydrogenated Amorphous Silicon I* (Springer, Berlin, Heidelberg 1984)
- 9.7 J. D. Joannopoulos, G. Locowsky: *The Physics of Hydrogenated Amorphous Silicon II* (Springer, Berlin, Heidelberg 1984)
- 9.8 A. Madan, M. P. Shaw: *The Physics and Applications of Amorphous Semiconductors* (Academic, New York 1988)
- 9.9 M. Pope, C. E. Swenberg: *Electronic Processes in Organic Crystals and Polymers* (Oxford Univ. Press, Oxford 1999)
- 9.10 J. Singh, K. Shimakawa: *Advances in Amorphous Semiconductors* (Gordon and Breach/Taylor & Francis, London 2003)
- 9.11 R. A. Street: *Hydrogenated Amorphous Silicon*, Cambridge Solid State Science Series (Cambridge Univ. Press, Cambridge 1991)
- 9.12 K. Tanaka, E. Maruyama, T. Shimada, H. Okamoto: *Amorphous Silicon* (Wiley, New York 1999)
- 9.13 J. S. Dugdale: *The Electrical Properties of Disordered Metals*, Cambridge Solid State Science Series (Cambridge Univ. Press, Cambridge 1995)
- 9.14 B. I. Shklovskii, A. L. Efros: *Electronic Properties of Doped Semiconductors* (Springer, Berlin, Heidelberg 1984)
- 9.15 I. P. Zvyagin: *Kinetic Phenomena in Disordered Semiconductors* (Moscow University Press, Moscow 1984) (in Russian)
- 9.16 H. Böttger, V. V. Bryksin: *Hopping Conduction in Solids* (Wiley, New York 1985)
- 9.17 H. Overhof, P. Thomas: *Electronic Transport in Hydrogenated Amorphous Semiconductors* (Springer, Berlin, Heidelberg 1989)
- 9.18 H. Bässler: *Phys. Status Solidi B* **175**, 15 (1993)
- 9.19 P. W. Anderson: *Phys. Rev.* **109**, 1492 (1958)
- 9.20 A. L. Efros, M. E. Raikh: Effects of Composition Disorder on the Electronic Properties of Semiconducting Mixed Crystals. In: *Optical Properties of Mixed Crystals*, ed. by R. J. Elliott, I. P. Ipatova (Elsevier, New York 1988)
- 9.21 D. Chattopadhyay, B. R. Nag: *Phys. Rev. B* **12**, 5676 (1975)
- 9.22 J. W. Harrison, J. R. Hauser: *Phys. Rev. B* **13**, 5347 (1976)
- 9.23 I. S. Shlimak, A. L. Efros, I. V. Yanchev: *Sov. Phys. Semicond.* **11**, 149 (1977)
- 9.24 S. D. Baranovskii, A. L. Efros: *Sov. Phys. Semicond.* **12**, 1328 (1978)
- 9.25 P. K. Basu, K. Bhattacharyya: *J. Appl. Phys.* **59**, 992 (1986)
- 9.26 S. Fahy, E. P. O'Reily: *Appl. Phys. Lett.* **83**, 3731 (2003)
- 9.27 V. Venkataraman, C. W. Liu, J. C. Sturm: *Appl. Phys. Lett.* **63**, 2795 (1993)
- 9.28 C. Michel, P. J. Klar, S. D. Baranovskii, P. Thomas: *Phys. Rev. B* **69**, 165211-1 (2004)
- 9.29 T. Holstein: *Philos. Mag. B* **37**, 49 (1978)

- 9.30 H. Scher, T. Holstein: *Philos. Mag.* **44**, 343 (1981)
- 9.31 A. Miller, E. Abrahams: *Phys. Rev.* **120**, 745 (1960)
- 9.32 N. F. Mott, E. A. Davis: *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford 1971)
- 9.33 A. L. Efros, B. I. Shklovskii: *J. Phys. C* **8**, L49 (1975)
- 9.34 M. Pollak: *Disc. Faraday Soc.* **50**, 13 (1970)
- 9.35 S. D. Baranovskii, A. L. Efros, B. L. Gelmont, B. I. Shklovskii: *J. Phys. C* **12**, 1023 (1979)
- 9.36 I. Shlimak, M. Kaveh, R. Ussyshkin, V. Ginodman, S. D. Baranovskii, H. Vaupel, P. Thomas, R. W. van der Heijden: *Phys. Rev. Lett.* **75**, 4764 (1995)
- 9.37 S. D. Baranovskii, P. Thomas, G. J. Adriaenssens: *J. Non-Cryst. Solids* **190**, 283 (1995)
- 9.38 J. Orenstein, M. A. Kastner: *Solid State Commun.* **40**, 85 (1981)
- 9.39 M. Grünewald, P. Thomas: *Phys. Status Solidi B* **94**, 125 (1979)
- 9.40 F. R. Shapiro, D. Adler: *J. Non-Cryst. Solids* **74**, 189 (1985)
- 9.41 D. Monroe: *Phys. Rev. Lett.* **54**, 146 (1985)
- 9.42 B. I. Shklovskii, E. I. Levin, H. Fritzsche, S. D. Baranovskii: Hopping photoconductivity in amorphous semiconductors: dependence on temperature, electric field and frequency. In: *Advances in Disordered Semiconductors*, Vol. 3, ed. by H. Fritzsche (World Scientific, Singapore 1990) p. 3161
- 9.43 S. D. Baranovskii, F. Hensel, K. Ruckes, P. Thomas, G. J. Adriaenssens: *J. Non-Cryst. Solids* **190**, 117 (1995)
- 9.44 M. Hoheisel, R. Carius, W. Fuhs: *J. Non-Cryst. Solids* **63**, 313 (1984)
- 9.45 P. Stradins, H. Fritzsche: *Philos. Mag.* **69**, 121 (1994)
- 9.46 J.-H. Zhou, S. D. Baranovskii, S. Yamasaki, K. Ikuta, K. Tanaka, M. Kondo, A. Matsuda, P. Thomas: *Phys. Status Solidi B* **205**, 147 (1998)
- 9.47 B. I. Shklovskii, H. Fritzsche, S. D. Baranovskii: *Phys. Rev. Lett.* **62**, 2989 (1989)
- 9.48 S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas, G. J. Adriaenssens: *J. Non-Cryst. Solids* **198-200**, 214 (1996)
- 9.49 R. Stachowitz, W. Fuhs, K. Jahn: *Philos. Mag. B* **62**, 5 (1990)
- 9.50 S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas: *Phys. Status Solidi B* **205**, 87 (1998)
- 9.51 S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas: *J. Non-Cryst. Solids* **227-230**, 158 (1998)
- 9.52 A. Nagy, M. Hundhausen, L. Ley, G. Brunst, E. Holzenkämpfer: *J. Non-Cryst. Solids* **164-166**, 529 (1993)
- 9.53 C. E. Nebel, R. A. Street, N. M. Johanson, C. C. Tsai: *Phys. Rev. B* **46**, 6803 (1992)
- 9.54 H. Antoniadis, E. A. Schiff: *Phys. Rev. B* **43**, 13957 (1991)
- 9.55 K. Murayama, H. Oheda, S. Yamasaki, A. Matsuda: *Solid State Commun.* **81**, 887 (1992)
- 9.56 C. E. Nebel, R. A. Street, N. M. Johanson, J. Kocka: *Phys. Rev. B* **46**, 6789 (1992)
- 9.57 B. I. Shklovskii: *Sov. Phys. Semicond.* **6**, 1964 (1973)
- 9.58 M. Grünewald, B. Movaghar: *J. Phys. Condens. Mat.* **1**, 2521 (1989)
- 9.59 S. D. Baranovskii, B. Cleve, R. Hess, P. Thomas: *J. Non-Cryst. Solids* **164-166**, 437 (1993)
- 9.60 S. Marianer, B. I. Shklovskii: *Phys. Rev. B* **46**, 13100 (1992)
- 9.61 B. Cleve, B. Hartenstein, S. D. Baranovskii, M. Scheidler, P. Thomas, H. Baessler: *Phys. Rev. B* **51**, 16705 (1995)
- 9.62 M. Abkowitz, M. Stolka, M. Morgan: *J. Appl. Phys.* **52**, 3453 (1981)
- 9.63 W. D. Gill: *J. Appl. Phys.* **43**, 5033 (1972)
- 9.64 S. J. Santos Lemus, J. Hirsch: *Philos. Mag. B* **53**, 25 (1986)
- 9.65 H. Bässler: *Advances in Disordered Semiconductors*. In: *Hopping and Related Phenomena*, Vol. 2, ed. by M. Pollak, H. Fritzsche (World Scientific, Singapore 1990) p. 491
- 9.66 G. Schönherr, H. Bässler, M. Silver: *Philos. Mag. B* **44**, 369 (1981)
- 9.67 P. M. Borsenberger, H. Bässler: *J. Chem. Phys.* **95**, 5327 (1991)
- 9.68 P. M. Borsenberger, W. T. Gruenbaum, E. H. Magin, S. A. Visser: *Phys. Status Solidi A* **166**, 835 (1998)
- 9.69 P. M. Borsenberger, W. T. Gruenbaum, E. H. Magin, S. A. Visser, D. E. Schildkraut: *J. Polym. Sci. Polym. Phys.* **37**, 349 (1999)
- 9.70 A. Nemeth-Buhin, C. Juhasz: Hole transport in 1,1-bis(4-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene. In: *Hopping and Related Phenomena*, ed. by O. Millo, Z. Ovadyahu (Racah Institute of Physics, The Hebrew University Jerusalem, Jerusalem 1995) pp. 410-415
- 9.71 A. Ochse, A. Kettner, J. Kopitzke, J.-H. Wendorff, H. Bässler: *Chem. Phys.* **1**, 1757 (1999)
- 9.72 J. Veres, C. Juhasz: *Philos. Mag. B* **75**, 377 (1997)
- 9.73 U. Wolf, H. Bässler, P. M. Borsenberger, W. T. Gruenbaum: *Chem. Phys.* **222**, 259 (1997)
- 9.74 M. Grünewald, B. Pohlmann, B. Movaghar, D. Würtz: *Philos. Mag. B* **49**, 341 (1984)
- 9.75 B. Movaghar, M. Grünewald, B. Ries, H. Bässler, D. Würtz: *Phys. Rev. B* **33**, 5545 (1986)
- 9.76 S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas: *J. Phys. C* **9**, 2699 (1997)
- 9.77 S. D. Baranovskii, H. Cordes, F. Hensel, G. Leising: *Phys. Rev. B* **62**, 7934 (2000)
- 9.78 J. M. Marshall: *Rep. Prog. Phys.* **46**, 1235 (1983)
- 9.79 W. D. Gill: *J. Appl. Phys.* **43**, 5033 (1972)
- 9.80 O. Rubel, S. D. Baranovskii, P. Thomas, S. Yamasaki: *Phys. Rev. B* **69**, 014206-1 (2004)
- 9.81 W. D. Gill: Electron mobilities in disordered and crystalline tritrofluorenone. In: *Proc. Fifth Int. Conf. of Amorphous and Liquid Semiconductors*, ed. by J. Stuke, W. Brenig (Taylor and Francis, London 1974) p. 901
- 9.82 S. D. Baranovskii, I. P. Zvyagin, H. Cordes, S. Yamasaki, P. Thomas: *Phys. Status Solidi B* **230**, 281 (2002)