Charge Transport in Disordered Solids with Applications in Electronics
Wiley Series in Materials for Electronic and Optoelectronic Applications

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Series Preface

WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at postgraduate students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such topics as electrical conduction in solids, optical properties, thermal properties, etc., all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure–property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

PETER CAPPER
SAFA KASAP
ARTHUR WILLOUGHBY
Preface

This book is written to meet the growing interest of researchers (physicists, chemists, and engineers) in charge transport properties of disordered materials. This interest is mostly caused by successful current applications of such materials in various devices and by their promise for future applications. The term ‘disordered materials’ usually describes solids without perfect crystalline atomic structure. Study of charge transport and optical properties of such systems has dominated material sciences in recent years and it is still a rapidly growing and developing research area. A brief historical overview of research in this field can be found in the introductory parts to several chapters in our book, particularly in Chapter 2.

Manufacturability and low production costs of disordered materials, along with their specific charge transport properties, make such systems extremely favorable and in some cases unique for various applications, particularly for large-area devices, where demands on the mobilities of charge carriers are not very high. Disordered materials are commercially used in electrophotography, solar cells, field transistors for flat-panel displays, optical memories, light-emitting diodes, solid batteries, etc. Current device applications of disordered solids and the potential of such materials for future applications are described in several chapters of our book, particularly in Chapters 3, 4, 7, and 11. These chapters, written by top-level researchers in the corresponding fields, should be of interest for the broad community of scientists, particularly for engineers working on the development of new devices.

Intensive study of disordered materials is, however, driven not only by their usefulness for valuable devices, but also by the exclusive interest of researchers in fundamental mechanisms determining the physical properties of such materials. The theory of how solid materials perform charge transport has been for many years mostly confined to crystalline systems with the constituent atoms in regular arrays. The discovery of how to make charge-conducting glasses, amorphous materials and alloys led to an explosion of measurements of electrical conductivity in these new materials. However, the well-known concepts for description of charge transport in crystalline solids, which are usually offered in university courses and which can be found in numerous textbooks, are not applicable to disordered materials, since these concepts are essentially based on the assumption of long-range atomic order. It has been, and still is, a challenging task to develop a consistent theory for charge transport in disordered systems without translation symmetry in the atomic structure.

In our book, we mostly focus on disordered semiconductor materials, leaving out the broad class of disordered metals. The latter systems are more traditional with respect to the description of charge transport properties. One can usually perform such a description on the basis of extended and modified concepts developed for electrical conduction in ordered crystalline systems, for example, using the Boltzmann kinetic equation.

The common feature of the disordered semiconductors considered in our book is the strong effect of the spatial localization of charge carriers on the electrical conduction. We
consider materials which differ drastically from each other by their chemical content. Some of them are organic systems, such as molecularly doped and conjugated polymers; some other materials are inorganic solids, such as glasses, amorphous and microcrystalline semiconductors. Furthermore, biological systems, such as DNA molecules, are also considered in our book with respect to their charge transport properties. In some of these disordered materials, electrical conduction is due to electrons and, in other materials, the conduction is due to ions. Nevertheless, in spite of the different chemistry and even the different nature of the charge carriers, all these materials have rather similar charge conducting properties. Electrical conduction in all these materials can often be described in the framework of rather universal theoretical concepts. This universality in description of charge transport in chemically different solids is one of the main messages of our book. Scientific communities are working sometimes separated and isolated from each other, differentiating between ‘inorganic’, ‘organic’, and ‘biological’ materials with respect to the charge transport properties. Furthermore, a theoretical description of ion transport is often opposed to that of electron transport. Our book shows, however, that charge transport properties of chemically different materials are not necessarily so different from each other.

The leading concept of our book is to present complementary chapters describing various features of analogous materials from different points of view. For instance, Chapters 1 and 2 present theoretical concepts for the description of electrical conduction in inorganic (mostly amorphous) disordered semiconductors. Chapters 3 and 5 present the techniques and results of the experimental investigation of such materials, along with some device applications, while Chapter 4 is exclusively devoted to the device applications of disordered inorganic semiconductors in modern electronics. Chapters 6 and 7 are complementary to each other with respect to the description of charge transport mechanisms in organic disordered solids and the device applications of such solids, respectively. Chapters 10 and 11 are complementary to each other, describing transport mechanisms of ion-conducting glasses and various device applications of such glasses.

The book starts with a theoretical description of weak localization effects caused by disorder potential in semiconductors. This topic is currently intensively studied both theoretically and experimentally. Therefore Chapter 1 will be of interest to the broad community of physicists, including students, who would like to learn more about the modern concepts in solid state physics and perhaps make an attempt at developing new theoretical models for charge transport. The chapters following are mostly devoted to the ‘hopping mode’ of electrical conduction. This transport regime is inherent to all disordered materials with localized charged carriers. In hopping transport, electrons move by tunneling and ions move by overcoming the potential barriers between spatially localized states. Local transition probabilities between such states have a very broad distribution of magnitudes, being exponentially dependent on the site energies, as well as on the intersite distances (for electrons) or on the intersite potential barriers (for ions). For the description of electrical conduction in such cases, one cannot use traditional averaging procedures for local scattering rates, known from theories developed for charge transport in ordered crystalline materials, where scattering rates usually have rather narrow distributions of magnitudes. In disordered materials, it is not the average rates that determine electrical conductivity, but rather the rates of the most difficult transitions that are still necessary in order to provide charge transport to a given distance. This new philosophy, in comparison to the traditional theoretical approaches developed for crystalline materials, was first used in the works of N.F. Mott and his co-workers. The corresponding concepts are introduced in the monograph by N.F. Mott and E.A. Davis, *Electronic Processes in Non-crystalline Materials*, Clarendon,

Although not only the quantitative theory, but also the analysis of possible erroneous treatments of hopping transport can be found in these monographs, some researchers, dealing with new disordered materials such as organic disordered solids, sometimes tend to use inappropriate approaches because they are probably not aware of the approved theoretical methods presented in textbooks. One possible reason for this might be the above-mentioned belief of many researchers that theoretical methods developed for the description of charge transport in some materials are not of use for the description of electrical conduction in chemically different systems. Our book demonstrates, on the contrary, that similar theoretical concepts can be applied to the description of physically similar transport processes in chemically different solids. For instance, methods in Chapters 2 and 3 for inorganic amorphous semiconductors are analogous to those for organic disordered solids described in Chapters 6 and 7. In many cases, it is not the local chemistry, but rather the long-range geometrical structure of the transport path for charge carriers that is significant, particularly for direct current, for which the long travel distances of charge carriers are decisive. The corresponding theoretical description is usually based on the percolation theory, which plays as important role for charge transport in disordered materials as the kinetic equation does for the description of charge transport in ordered crystalline solids.

In the case of direct current, the decisive spatial scale for charge transport corresponds to the correlation length of the infinite percolation cluster, which is usually very large (see the monograph by Shklovskii and Efros). In the case of alternating current, the scale of distances, through which charge carriers have to travel in order to respond to the alternating electric field, decreases with increasing frequency. For example, in the limit of the very high field frequencies, only transitions of charge carriers within pairs of localized states with very high rates can contribute to the conductivity. The intermediate regime between low frequencies (direct current) and very high frequencies (pair model) is still terra incognita for many researchers. The corresponding comprehensive theory of hopping transport in the broad frequency range is therefore presented in our book in Chapter 9. The theory in this chapter clearly shows that the general description of charge transport via localized states, based particularly on the percolation theory, is valid not only for chemically different systems, but also for systems in which electrical current is provided by different charged species—electrons or ions. The complementary information on mechanisms of ion conduction can be found in Chapter 10.

For analysis of electrical conduction as well as for device applications of any system, one of the crucial questions is how the charge carriers recombine within the material. Two chapters of our book are devoted solely to the problems of carrier recombination. In Chapter 5, a very advanced method for studying carrier recombination in disordered materials is introduced, based on the measurements of the pulsed electrically detected magnetic resonance. This investigation technique is rapidly developing and promises to become one of the most powerful tools to study carrier recombination in disordered systems. In Chapter 8, transport of charge carriers and their recombination is studied in polymer–semiconductor
nanocomposites. This chapter shows how useful a good theory can be for designing new devices based particularly on nanocomposite materials.

Currently we are witnessing a real burst in the multidisciplinary applications of physical investigation techniques. In recent years, particular attention of researchers has been devoted to studying the charge transport processes in biological systems. Such processes as transport of ions through cell membranes or transport of electrons via long biological molecules, play a vital role for living organisms. Understanding the charge transport processes in cells and biological molecules is of great importance for biology and medicine. Furthermore, many attempts are currently being made to apply biological objects, for instance DNA molecules, in electronic devices. Biological systems can be considered as noncrystalline objects, in which charge carriers are spatially localized, i.e., the wavefunctions describing the charge carriers are not spread over the whole volume of the system, as would be the case in crystalline solids, but they are rather restricted to single molecules or molecular complexes. Therefore, the physical concepts and investigation methods already developed for the description of charge transport in inorganic and organic disordered solids with spatially localized states described in this book can be of great interest for researchers dealing with charge transport in biological systems. Chapter 12 is devoted to charge transport in DNA molecules, biological systems with rather peculiar electrical conducting properties.

Our book is addressed to various groups of readers. Postgraduate students and young scientists can use this book as an introduction to the field of charge transport in a very broad class of disordered solids, while experienced scientists will find rather complete descriptions of many advanced research techniques along with experimental results and theoretical concepts, which might be of use for their scientific work. Information on current device applications of disordered materials and their potential for future applications will be of special interest for engineers.

The editor is deeply grateful to all researchers who collaborated in this project. The idea for such a book—to bring under one roof similar scientific results obtained in parallel, though sometimes isolated research fields—looks very attractive and rather simple. However, it could not have been realized without the strong effort of the international team of leading researchers who contributed to this book. Particularly, the role of Professor Safa Kasap (University of Saskatchewan) who launched and encouraged the work on this ambitious project should be emphasized. The editor is deeply grateful to his colleagues Professor Peter Thomas and Professor Florian Gebhard at the Philipps University Marburg, who provided excellent conditions for the work on this project and who were always open to discussion of various scientific issues related to this book. The concept for the book has been developed in numerous discussions with my close colleague Dr Oleg Rubel at the Philipps University Marburg, who not only co-authored two chapters, but also contributed to editing several other chapters. The editor is indebted to numerous colleagues from all over the world for valuable discussions and for providing the latest information on the subjects related to this book. Valuable help of the editors at Wiley, Ms Jenny Cossham, Ms Lynette James, Ms Alexandra Carrick and Ms Gill Whitley for realization of this project cannot be overestimated. I would also like to thank my wife Svetlana and daughter Julia for their patience and support during my work on this book.

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1 Charge Transport via Delocalized States in Disordered Materials

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1.1 INTRODUCTION

The standard theory of electron transport phenomena in ideal crystalline semiconductors is based on the band theory that determines single-electron eigenstates (Bloch waves) and energies forming energy bands (with a quasi-continuous level distribution) separated by bandgaps. Static disorder modifies the electron wavefunctions and the energy spectrum of the system. A useful characteristic of the electron states is the density of states that can be applied to the description of both ordered solids and solids with arbitrarily strong disorder. In the presence of weak disorder, the eigenstates of a disordered material differ only slightly from the eigenstates of an ideal crystal and the density of states appears to be only slightly different from that of an ideal crystal. Therefore, the description of the electronic processes in weakly disordered crystalline solids may use the concept of almost free quasi-particles (Bloch waves) modified by the interaction with the random field and by the electron–electron interaction. Interacting electrons in extended states may be often described using the Fermi-liquid approach, which assumes that a system of electrons is described by using a self-consistent field that determines the properties of almost free quasi-particles, whose energy spectrum is a function of the interaction, and the distribution function. The wavefunctions remain extended over the entire sample and have a random component that may be described as a random phase variation of the electronic wave. Accordingly, transport in a system with weak disorder may be described using the basis of the unperturbed Bloch eigenstates and assuming that a random scattering potential (related to random static deviations of the potential in the crystal from periodicity, to lattice vibrations, etc.) induces transitions between these eigenstates. The corresponding theory is based on the Boltzmann transport equation, whose condition of applicability is

\[ \hbar / \tau << \bar{\varepsilon}, \]

where \( \tau \) is the quasi-momentum relaxation time and \( \bar{\varepsilon} \) is the characteristic quasi-particle energy (equal to \( kT \) for nondegenerate electron gas or to the Fermi energy \( \varepsilon_F \) for the degenerate case). Condition (1.1.1) allows one to combine the classical description of statistical properties of the gas of quasi-particles with quantum-mechanical treatment of individual scattering events. Condition (1.1.1) may be written in the alternative form

\[ \lambda << l, \]

where \( \lambda = h / \bar{p} = \bar{k}^{-1} \) is the de Broglie wavelength of quasi-particles, \( \bar{p} \) and \( \bar{k} \) are their characteristic quasi-momentum and quasi-wave vector, \( l = \bar{v} \tau \) is their mean free path, and \( \bar{v} \) is the characteristic velocity of the quasi-particles.

In noncrystalline materials (amorphous solids and liquids), short-range order exists, even for strong structural disorder, and the electron energy spectrum is known to retain the characteristic features of the band spectrum: the regions of high electron density of states (corresponding to the allowed bands of the crystal) exist, separated by the regions where the density of states is lower (often by several orders of magnitude) corresponding to the

\(^1\)Some of the problems discussed in this chapter are also treated in books \[1–7\] and reviews \[8–11\] and references therein.
energy gaps of the band spectrum of the crystal. With increasing disorder, however, extended electron states inside the energy bands of the crystal may become localized (Anderson localization [12]); eventually, for sufficiently strong disorder, all electron states become localized. Localization implies that the envelope of the wave function decays exponentially away from some localization point \( \mathbf{R} \), \( \psi(r) \sim \exp(-r - R/\alpha) \), where \( \alpha \) is the localization length. Mott has pointed out that the role of disorder can be different for states of different energies; for intermediate disorder, localized and extended states may coexist in the same system at different energies. Typically, the states in the middle of the band may remain extended (extended states are ‘current-carrying’, i.e., the average velocity in these states is nonzero); on the other hand, near the band edges, the states are localized (Figure 1.1). Following Mott, one may introduce the energy \( \varepsilon_c \), corresponding to the localization threshold that separates extended and localized states; this localization threshold is called the mobility edge [13]. Extended states above the mobility edge contribute to the DC current even at \( T = 0 \) K and if \( \varepsilon_F > \varepsilon_c \), the conductivity \( \sigma|_{T=0K} \) (and the resistivity \( \rho|_{T=0K} \)) remains finite. A finite conductivity at \( T = 0K \) is a signature of the metallic state, whereas a vanishing conductivity (or a divergent resistivity \( \rho|_{T=0K} \)) of an infinite system as \( T \to 0K \) indicates that the system is an insulator. Therefore, a metal–insulator transition occurs as the Fermi level crosses the mobility edge \( \varepsilon_c \) passing from extended to localized states.

Mott has argued that the concept of the conduction band (the region of extended states above the mobility edge) may be used, even for materials with strong disorder (say, for amorphous semiconductors), the mobility edge \( \varepsilon_c \) playing the role of the conduction band edge. It should be noted that there is no singularity in the density of states at the mobility edge \( \varepsilon_c \). Likewise, one may introduce the concept of the mobility edge for the valence band \( \varepsilon_v \). The energy interval between \( \varepsilon_c \) and \( \varepsilon_v \) is called the mobility gap, and the states in the mobility gap are localized.

For extended states, once the electron scattering is weak, the Boltzmann equation makes it possible to calculate the transport coefficients. At finite temperatures, the usual expression

![Figure 1.1](image)

**Figure 1.1** Density of states in a disordered solid (schematic); \( \varepsilon_c \) denotes the mobility edge that separates extended and localized states.
for the conductivity in the Boltzmann transport theory (linear with respect to the electric field) may be written [1] as

$$\sigma = \int \sigma(\epsilon) \left( -\frac{\partial f(\epsilon)}{\partial \epsilon} \right) d\epsilon, \quad (1.1.3)$$

where $f(\epsilon)$ is the electron distribution function, $\sigma(\epsilon)$ is the energy-dependent conductivity, and the integration in Equation (1.1.3) is performed over the extended states in the conduction band. (To be specific, in what follows, we usually speak about electrons and the conduction band; the modification for the case of holes and the valence band is straightforward.) Equation (1.1.3) immediately follows from the Boltzmann equation for elastic electron scattering; for inelastic scattering, $\sigma(\epsilon)$ is only formally introduced by Equation (1.1.3) and must be determined from the corresponding transport theory. It follows from Equation (1.1.3) that in the region of extended states, $\sigma_{T\to0K} = \sigma(\epsilon_F)$, where $\epsilon_F$ is the Fermi level.

In the absence of long-range crystalline order, electronic states are different from Bloch states, quasi-momentum is no longer a good quantum number, the concept of the Brillouin zone cannot be used anymore, etc. Strictly speaking, for disordered (amorphous or liquid) metals and disordered degenerate semiconductors, where the Fermi level lies deeply inside the conduction band in the region of extended states, transport cannot be generally described by the Boltzmann transport theory. In disordered semiconductors, where the Fermi level lies in the region of localized states, a new transport mechanism is possible, related to inelastic tunneling between localized states (hopping). Since localized eigenstates have different energies, transitions between them must be inelastic, and the required energy is usually provided by the interaction with vibrations of the atomic matrix (phonons). Therefore, in contrast to conduction by electrons in extended states, where the interaction with phonons reduces the conductivity, the interaction with phonons stimulates hopping conductivity that vanishes as $T \to 0K$.

In this chapter we consider some of the existing concepts and approaches to the description of conduction in the region of extended states; hopping processes will be considered in subsequent chapters. The basis of our discussion is the Fermi-liquid approximation, which appeared to be successful in understanding numerous transport properties of strongly disordered solids. We also discuss some important aspects of the effect of electron–electron correlations in the presence of a random potential and their effect on transport properties of an electron gas. The electron–electron interaction effects can appear to be important, especially at low electron concentrations and in this chapter we discuss some of the features of the interplay between disorder and interactions.

1.2 TRANSPORT BY ELECTRONS IN EXTENDED STATES FAR FROM THE MOBILITY EDGES

1.2.1 Weak-scattering theories

A situation typical of metals corresponds to conduction by a degenerate gas of charge carriers whose energies are close to the Fermi level. Once the disorder is weak, the transport can be described by using the standard Fermi-liquid approach and the Boltzmann theory. In this theory, the quasi-particles (electrons) treated in the nearly free electron approxima-
tion are assumed to be weakly scattered by disorder (static random potential of structural defects, impurities, etc.). Once the interaction with the random potential is weak and Condition (1.1.1) or (1.1.2) is satisfied, it suffices to keep only the lowest-order terms and to use the Born approximation in the collision integral. The standard transport theory leads to the following expression for the conductivity:

\[ \sigma = \frac{ne^2}{m} \tau. \] (1.2.1)

Here \( n \) is the concentration of the free charge carriers (quasi-particles), \( m \) is the carrier effective mass, and \( \tau \) is the transport momentum relaxation time expressed in terms of the scattering cross-section. This expression has a form appearing in the simple Drude theory for the conductivity of a gas of free particles. The theory also makes it possible to calculate other transport coefficients (diffusion coefficient, thermopower, etc.).

For strong structural disorder, transport is not expected to be described by the conventional Boltzmann theory; nevertheless, surprisingly, sometimes the weak scattering approach works quite well for this case. An example is provided by Ziman’s theory of liquid metals [14, 15], which appeared to be quite successful in describing the properties of many liquid metals. In these systems, the electrons are scattered by the ions of the metal, and one might expect that the electron mean free path is of the order of an interatomic distance. However, in Ziman’s theory, the electrons treated in the nearly free electron approximation are assumed to weakly interact with ions of the disordered matrix of the liquid and their wave functions are taken to be plane waves. Using the expression for the conductivity in terms of the mean free path \( l \) from the Boltzmann theory and the measured conductivities, one can estimate \( l \) for different liquid metals; it appears that \( l \) can be one to two orders of magnitude greater than the interatomic spacing. This indicates that the scattering is indeed weak in spite of substantial disorder. Therefore, one is justified in using the standard transport theory for a weak scattering potential; the scattering is essentially similar to the scattering of X-rays or neutrons by liquids. In this case, the calculation of the conductivity presents no difficulties.

In Ziman’s theory, the Born approximation is used; in addition, correlations in the positions of the scattering ions described by the structure factor are taken into account. The conductivity is related to the probability of scattering between the plane wave eigenstates \( |k\rangle \) and \( |k'\rangle \), which is proportional to the square of the matrix element \( \langle k|V|k'\rangle^2 \), where \( V(x) = \sum_i v_a(x - R_i) \) is the scattering potential equal to the sum of atomic potentials \( v_a(x - R_i) \) of individual centers randomly distributed in space. As for scattering of X-rays or neutrons by liquids, we may write

\[ |\langle k|V|k'\rangle|^2 = |V(q)|^2 = N\Omega |v_a(q)|^2 S(q), \] (1.2.2)

where \( N \) is the concentration of scattering centers; \( \Omega \) is the volume of the system; \( V(q) \) and \( v_a(q) \) are the Fourier transforms of the total and atomic potentials, respectively; \( q = k' - k; |v_a(q)|^2 \) is the atomic form factor; \( S(q) \) is the structure factor

\[ S(q) = 1 + \langle \exp(iqR) \rangle = 1 + N^{-1} \int dR \exp(iqR) h(R), \] (1.2.3)
where \( \langle \ldots \rangle \) denotes the averaging over impurity configurations and \( h(R) \) is the pair correlation function related to the radial distribution function \( g(R) \) by the expression
\[
h(R) = g(R) - 1 \quad (\text{here } N g(R) dR \text{ is the probability of finding an atom in the volume element } dR \text{ at a distance } R \text{ from the origin } R = 0, \text{provided that there is an atom at the origin}).
\]
For an isotropic case, we easily obtain the standard expression
\[
S(q) = 1 + 4\pi N \int \frac{\sin q R}{q R} h(R) R^2 dR. \tag{1.2.4}
\]

The standard transport theory leads to Equation (1.2.1) for the conductivity, where \( \tau \) is the transport relaxation time, which, for elastic carrier scattering, is given by the expression
\[
\tau_p^{-1} = \frac{2\pi}{\hbar} \sum_q \langle V(q) \rangle^2 (1 - \cos \theta) \delta (\epsilon_{p+q} - \epsilon_p) \\
= 2\pi \left( \frac{m}{2\pi \hbar^2} \right)^2 N \Omega v_F \int_0^\pi d\theta \sin \theta (1 - \cos \theta) |v_e(q)|^2 S(q), \tag{1.2.5}
\]
where \( \theta = 2 \arcsin(q/2k_F) \) is the scattering angle, and \( v_F \) is the electron velocity. For a degenerate electron gas, we have
\[
\tau^{-1} = \frac{8}{\pi} \left( \frac{m}{\hbar^2} \right)^2 N v_F \int_0^1 S(2k_F x)(\Omega v_a(2k_F x))^2 x^3 dx, \tag{1.2.6}
\]
where \( v_F \) is the Fermi velocity and \( k_F \) is the Fermi momentum.

One of the spectacular applications of Ziman’s theory of liquid metals is the interpretation of the temperature dependence of the resistivity of liquid metals. It appears that the resistivity of monovalent metals (Li, Na, K, Rb, Cs) increases with temperature, whereas the resistivity of bivalent metals decreases. The reason for this is clear if one considers the form of the structure factor \( S(q) \) that was measured in numerous studies; \( S(q) \) is schematically shown in Figure 1.2. The dashed vertical lines correspond to the values \( q_{1,2} = 2k_F \) for monovalent and bivalent metals. Since the integrand in Equation (1.2.6) is a rapidly increasing function of \( x \), the main contribution to the integral comes from the region near the upper limit, i.e., near the point \( q = 2k_F \). With increasing temperature, the correlation in ion positions becomes weaker and \( S(q) \) approaches the limiting value \( S(q) = 1 \), corresponding to absolutely random positions of the ions. Thus the value \( S(q_1) \) increases with temperature and the value \( S(q_2) \) decreases.

The above simplified theory using the Born approximation works quite well for many liquid metals, indicating that the scattering may indeed be considered as weak. There are several reasons for this. First, it is well known in the electronic theory of metals that the nearly free electron model may be used if the actual ion potential is replaced by a smooth pseudopotential incorporating the effect of the core states on the states of free electrons [16, 17]. Second, the pseudopotential is screened due to electron spatial redistribution. Screening substantially suppresses the pseudopotential compared with the pseudopotential of ‘bare’ ions [15]. Third, the theory of liquid metals takes into account the correlation in spatial positions of neighboring atoms by introducing the structure factor \( S(q) \) (Equation
It appears that for many simple metals, the structure factor $S(q)$ is small at small $q$ just in the region where the screened pseudopotential has its maximum, whereas for the values of $q$, where the structure factor is large, the pseudopotential is small.

A weak-scattering theory may be also applied to degenerate heavily doped semiconductors, where the Fermi level lies in the region of extended states not very close to the mobility edge. The condition for applicability of this theory is $na_b^3 \gg 1$, where $n$ is the electron concentration, assumed to be equal to the concentration of the doping impurity, and $a_B$ is the Bohr radius; it appeared to be possible to construct an asymptotic theory for the electron energy spectrum and electron transport [18]. Once the impurity concentration is not too high (the average interimpurity distance is much greater than the lattice period), one may consider Bloch electrons scattered by screened atomic impurity potentials; moreover, the impurity atoms may be considered as randomly distributed in space. Due to screening, the scattering appears to be weak in the asymptotic limit $na_b^3 \gg 1$ and the Born approximation may be used giving Equation (1.2.1). A straightforward calculation of the higher-order terms describing both the terms corresponding to higher Born approximations for scattering by an impurity atom and to correlated many-impurity scattering were analyzed, thus establishing the applicability conditions for the transport theory in question [19, 20]. The result of the perturbation theory for transport coefficients of a degenerate semiconductor with screened ionized impurities is that the perturbation series is expected to be slowly converging and lowest-order corrections to the conductivity are of the form [19]

$$0.3\ln^{-1}(na_b^3) + 0.3(na_b^3)^{-1/6}. \quad (1.2.7)$$

These corrections obtained for $na_b^3 \gg 1$ decrease very slowly with increasing $na_b^3$. Thus using a weak scattering theory, one can expect to obtain only qualitative agreement with experiment [9, 21]. In addition, for germanium and silicon, one has to take into account the multi-valley structure of the conduction band [22].

Another example of a disordered system, for which a reliable theory exists for charge carrier transport via extended states above the mobility edge, is provided by semiconductor

![Figure 1.2: Structure factor $S(q)$ for liquid metals (schematic)](image)
solid solutions with short-range random disorder potential of the white-noise type [23–26]. Semiconductor solid solutions A\(_x\)B\(_{1-x}\) or, in other words, mixed crystals, are crystalline semiconductors in which sites of the crystalline lattice can be occupied by atoms of different types A and B; here \(x(0 \leq x \leq 1)\) is the probability that a site is occupied by an A atom. Due to the random spatial distribution of A and B atoms, local statistical fluctuations of the composition \(x\) along the sample are unavoidable. Since the position of the band edge depends on composition, the fluctuations of the band edge appear, similar to those produced by electrostatic disorder potential. To be specific, we consider the effect of the random potential on conduction band electrons. Let \(\varepsilon_c(x)\) be the conduction band minimum for a crystal with composition \(x\). In Figure 1.3, a possible dependence \(\varepsilon_c(x)\) is shown schematically. If the average composition for the whole sample is \(x_0\), the local positions of the band edge \(\varepsilon_c(x)\) fluctuate about the average value \(\varepsilon_c(x_0)\), according to the fluctuations of the composition \(x\) about \(x_0\). At small deviations \(\Delta x\) of the composition from the average value, one can use the linear relation

\[
\varepsilon_c(x_0 + \Delta x) = \varepsilon_c(x_0) + \alpha \Delta x ,
\]

(1.2.8)

where

\[
\alpha = \frac{d\varepsilon_c(x)}{dx}\Big|_{x=x_0} .
\]

(1.2.9)

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 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

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**Figure 1.3** Composition dependence of the conduction band edge \(\varepsilon_c(x)\) in a mixed crystal (schematic)
Although the disorder in such systems is called a ‘short-range’ disorder, it should be realized that this description is valid only for size fluctuations much larger than the lattice constant of the material. The term ‘short-range’ is due to the assumption on the absolutely uncorrelated statistical properties of the disorder. This means that potential amplitudes at adjacent spatial points are completely uncorrelated. Indeed, it is usually assumed that the correlation function of disorder in mixed crystals can be approximated by a white-noise correlation function of the form

\[ \langle \xi(r)\xi(r') \rangle = x(1-x)N\delta(r-r'). \]  

(1.2.11)

Then the random potential created by such composition fluctuations is described by the correlation function [26]

\[ \langle V(r)V(r') \rangle = \gamma \delta(r-r'), \]  

(1.2.12)

where

\[ \gamma = \frac{\alpha^2}{N}x(1-x). \]  

(1.2.13)

Charge carriers in mixed crystals are scattered by composition fluctuations. As usual in the kinetic description of free electrons, the fluctuations with a space scale of the order of the electron wavelength are most efficient in scattering. We have

\[ \langle |V_q|^2 \rangle = \frac{1}{\Omega} \int \exp(iqr) \langle V(r)V(0) \rangle \]  

(1.2.14)

and using the correlation function (Equation 1.2.12), we obtain the relation

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

(1.2.15)

which shows that the scattering by composition fluctuations is equivalent to that by a short-range potential [25]. Substituting Equation (1.2.15) into Equation (1.2.5), we find [26]

\[ \tau_p^{-1} = \frac{\alpha^2 x(1-x)mk}{\pi\hbar^2 N}. \]  

(1.2.16)

This formula leads to the electron mobility of the form [25, 26]

\[ \mu_c = \frac{\pi^{3/2}}{2\sqrt{2}} \frac{eh^3 N}{\alpha^2 x(1-x)m^{3/2} (kT)^{1/2}}. \]  

(1.2.17)
Very similar formulas can be found in many recent publications (see, for example [27]). It has also been modified for applications to two-dimensional systems [28] and to disordered dilute magnetic semiconductors [29].

This theoretical description can be applied to other disordered systems, provided that the correlation function of the disorder potential has the form of Equation (1.2.12) with a known amplitude $\gamma$. However, it should be noted that this short-range disorder of a white-noise type is only a simple model, which can hardly be justified for most disordered materials.

The Boltzmann theory predicts that, in the low-temperature region, charge carrier scattering is dominated by random static potential (to be specific, that of impurities). This scattering is elastic, its probability remains finite at $T = 0$, and the conductivity is almost independent of temperature. Some temperature dependence of the conductivity may exist due to the temperature dependence of the scattering processes. For most scattering mechanisms, it follows from the classical Boltzmann equation that scattering probability and, hence, the resistivity increase with temperature, i.e., the temperature coefficient of the resistivity is positive: $d\rho/dT > 0$. This is usually called a normal metallic behavior of the resistivity.

The temperature dependence of the conductivity may be due to phonon scattering whose probability increases with increasing temperature, giving rise to a positive temperature coefficient, predominantly due the increase in the number of phonons. At high temperatures, it is proportional to $kT/(\hbar\omega)$ (where $\omega$ is the phonon frequency); accordingly, we have $\sigma \sim T^{-1}$. At low temperatures, the temperature dependence of the conductivity is stronger (the Bloch–Grüneisen law, $\sigma \sim T^{-5}$).

Scattering by static disorder (impurities and defects) may also give rise to some temperature dependence of the conductivity. This is related mainly to screening effects. Screening becomes weaker with increasing temperature so that, for this scattering mechanism, one can also expect a positive temperature coefficient of the resistivity, i.e., normal metallic behavior.

Yet another scattering mechanism is electron–electron interaction. Since for a degenerate electron gas, only the electrons in the layer of width of the order of $kT$ near the Fermi level can be scattered, the scattering probability is proportional to $T^2$. The electron–electron collisions are substantially inelastic, the energy variation being of the order of $kT$. Thus classical electron–electron scattering is again expected to result in normal metallic behavior of a degenerate electron gas at low temperatures.

However, in the low-temperature range, the temperature dependence of the classical conductivity described by the Boltzmann theory becomes weaker and the effects related to quantum interference of scattered electron waves can become important. These effects that lie beyond the classical approach are discussed in Section 1.2.2.

1.2.2 Weak localization

An important feature of scattering by static disorder is that the elastic scattering is coherent and, therefore, when considering higher-order terms in the calculation of the conductivity, one must take into account the interference of the electron waves scattered by different impurities. This interference gives rise to quantum interference corrections to the Drude conductivity producing a weak localization of the electronic states [30]. Inelastic effects