STATISTICAL- KINETIC THEORY OF CHARGE CARRIERS TRANSPORT IN SEMICONDUCTORS

856A-0-0-0 | QC 311 .D7 2001

BY

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Submitted in partial fulfillment of the requirements
Of M .Sc .degree of Physics
AL- Quds University
Jerusalem, Palestine

August, 2001

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856A-0-0-0-1

Declaration

I certify that this thesis submitted for the degree of physics is the result of my own research, except master of where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution .

Signed……………………..

(Amani M.K. Drabe'a)

Date………………………

Acknowledgments

Special thanks to Dr . M.M Abu-Samreh It for Suggesting the topic the thesis to me and who supported my work not only by numerous discussions but who also helped me on many other points that made this work successful . Furthermore, it was he who developed the computer program used in my calculations.

I would like also to thank Dr . Abdelkarim M. Saleh for helping me in making some plots on the computer and his valuable scientific suggestions .

My thanks also go to Dr . M.I Abu-Taha for supervising the master program for the last seven years .

I am also in debt to Dr. Saker Darwish and Dr. Ismael Badran for their participation as committee members and their valuable suggestions .

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ABSTRACT

This thesis presents a semiclassical microscopic approach based on the Boltzmann transport equation for studying electrical and thermal properties of semiconductors. The relaxation-times are investigated through a microscopic model that incorporates the Boltzmann collision term with the relaxation-time approximation.

Thermal conductivity and thermal mobility are calculated as well as their temperature and density dependencies. The electronic contribution to the thermal conductivity of semiconductor materials is due to heat being transported by charge carriers, which are electrons in the n-type semiconductors or holes in the p-type material. The charge carriers also act as scattering centers for phonons and cause a reduction in lattice thermal conductivity. At temperatures sufficiently high to excite carriers across the semiconductor energy gap, the electron-hole pairs transport heat and give rise to the bipolar contribution to the thermal conductivity.

At low concentrations electrons and holes in a semiconductor do not significantly influence the thermal conductivity. Their contribution to the energy flux is typically less than the phonon contribution by a factor of 10^{-4} or less. In addition, the electron-phonon scattering does not contribute significantly to phonon relaxation and the thermal conductivity

Is much like that of an insulator . On the other hand, if the esmiconductor is heavily doped and the temperature is high the material then behaves more like a metal .

The electric thermal conductivity and the electric mobility are calculated and their temperature and density dependencies are also examined. The electronic contribution to thermal conductivity k is significant at very low doping levels but becomes increasingly important as the doping levels are increased . A good agreement with experimental and previous results is achieved. The AC conductivity exhibits also a temperature dependence.

The numerical calculation of the collision term are the most important part of the investigation. They involve three-and five-dimensional integrations evaluated by using Gaussian and Simpson's numerical methods.

To my mother and my husband

(STATISTICAL-KINETIC THEORY OF CHARGE CARRIERS TRANSPORT IN SEMICONDUCTORS)

Student Name: Amani Mohammed Khaleel Al Darabe'a

Thesis submitted for examination on Sunday 26, August 2001 and accepted by the examining committee formed of the following.

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Al Quds University

2001

Chapter One

Introduction and Purpose

1.1 Introduction

A semiconductor is a crystalline solid, such as silicon (Si) or germanium (Ge), with an electrical conductivity, σ_{elc}, (typically 10^{5}-10^{-7} simens per meter) at room temperature intermediate between that of a conductor (up to 10^{9} s/m) and an insulator (as low as 10^{-15} s/m) (Broply, 1977). Besides, the electrical resistivity, ρ, values of semiconductors are also found to be intermediate between those of metals and those of insulators, generally in the ranges 10^{-4}-$10^{7}\Omega$.m at room temperature. Semiconductor elements form the fourth column in the periodic table.

As the atoms in the crystalline solid become close together, orbits of their electrons overlap and their individual energy levels are spread out into energy bands (Hagelberg, 1973). A general model for the energy levels of semiconductor consists of a series of allowed energy bands (conduction) alternating with forbidden energy bands (valence). The conduction and the valence bands are separated by an energy gap with the localized states corresponding to donor and acceptor impurities existing near the band edges. The band structure for an ideal semiconductor is shown in Figure 1.1.

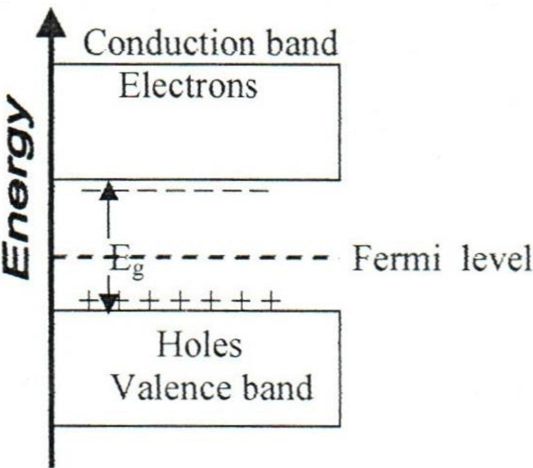


Figure 1.1. Energy level diagram for an intrinsic semiconductor. At room temperature some electrons are excited to the conduction band, leaving a hole behind. Energy levels in between the valence and conduction bands are not allowed to the electrons. The Fermi level lies at the middle of the forbidden band.

Such an arrangement of energy levels is a characteristic of semiconductors, which are insulators at 0 K and become poor conductors at some higher temperatures.

Conduction occurs in semiconductors as the result of a net movement of electrons in the conduction band and holes in the valence band, under the influence of thermal excitation or an applied electric and magnetic fields. Thermal agitation gives some electrons enough energy to jump to conduction band. The excited electrons serve as conduction electrons. Each electron raised to the conduction band leaves a vacancy, or a hole, in the valence band. The resulting holes are available for conduction in the valence band. A hole behaves as if it was an electron with a positive

charge. Electrons and holes are known as charge carriers in semiconductors. The type of the charge carrier that predominates in a particular region or material is called the majority carrier, and that with the lower concentration is the minority carrier.

As the temperature is increased semiconductors become steadily better conductors because more electrons are transferred to the conduction band. The minimum energy required for moving an electron from one of the valence bands into one of the conduction bands is called the energy gap, E_g, (Kittle, 1993). In other words, the energy gap is energy between the valence and conduction band. In this case the conduction band lies a small amount of energy above the full valence band typically 1eV (Broply, 1977). Generally, the band energy for a pure semiconductor is between 0.1 and 2.5 eV. For silicon, E_g is 1.09 eV and for germanium it is 0.72 eV. These energy values are small enough for a significant number of electrons to be excited to the conduction band at room temperature.

Semiconductors are classified into intrinsic and extrinsic ones. In intrinsic semiconductors the charge carriers are electron-hole pairs resulting from thermal excitation or optical excitation and are equally divided between electrons and holes. On the other hand, in extrinsic semiconductors the type of conduction that predominates depends on the number of the impurity atom present in the valence band. Germanium and silicon atoms have a valence of four electrons, which form four covalent

bonds with neighboring atoms. The structure of pure Ge crystals has the semiconductor arrangement of energy states which consists of a completely filled energy band separated from an empty higher-lying conduction level by a small energy gap, E_g, as shown in Figure 1.2.

When impurity atoms with a valence of five electrons, such as arsenic, antimony, or phosphorous is added to the lattice, an extra electron per atom available for the conduction, i.e., a single electron which is not supposed to pair with the four valence electrons of the germanium or the silicon. The n-type semiconductor is an extrinsic semiconductor doped

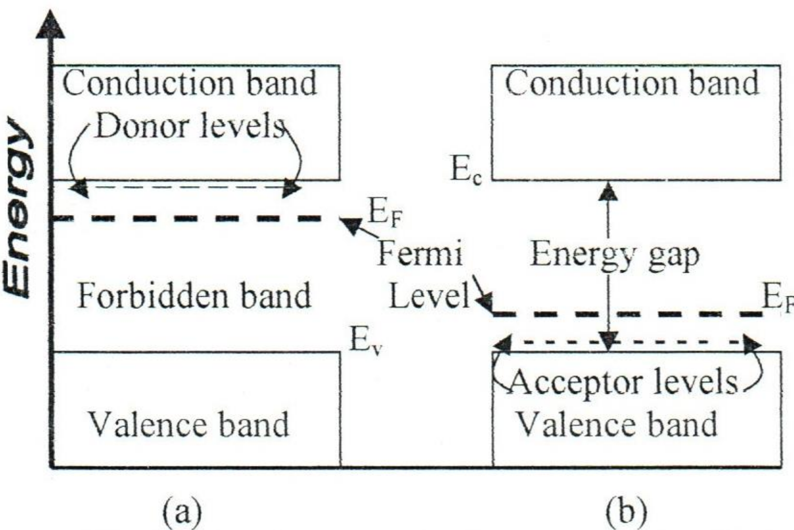


Figure 1.2. Isolated energy level are introduced in the forbidden energy band of semiconductor by doping it with impurity atoms. (a) Donor atoms give levels just below the conduction band and raise the Fermi level above the middle of the forbidden band. (b) Acceptor atoms introduce levels just above the valence band and lower the Fermi energy below the middle of the forbidden band.

with atoms having a valence of five electrons and having electrons as

majority carriers. Similarly, the p-type semiconductors is that one in which the impurity atoms have a valence band of three electrons, such as boron, aluminum, indium, or gallium, and one hole per atom is created by the unsatisfied bond. Consequently, the majority carriers are holes.

Solid state devises in electronic semiconductors are extrinsic semiconductors. These are accomplished by adding a small amount of impurity in the form of atoms that replace the original atom in the lattice but having a different number of valence electrons. A p-type semiconductor might be formed, for example, by introducing gallium as an impurity into silicon lattice. For an n-type semiconductor, arsenic might be used into germanium lattice. Illustrations of these processes are shown in Figure 1.3.

When a donor impurity is added to an intrinsic semiconductor the position of Fermi level (top most energy level at 0 K) is raised as a result of increasing the number of electrons in the conduction band and decreases the number of holes in the valence band. On the other hand, when an acceptor impurity is added to an intrinsic semiconductor the position of Fermi level is lowered, because electrons are captured from both conduction and valence bands to fill the acceptor level (Smith, 1979).

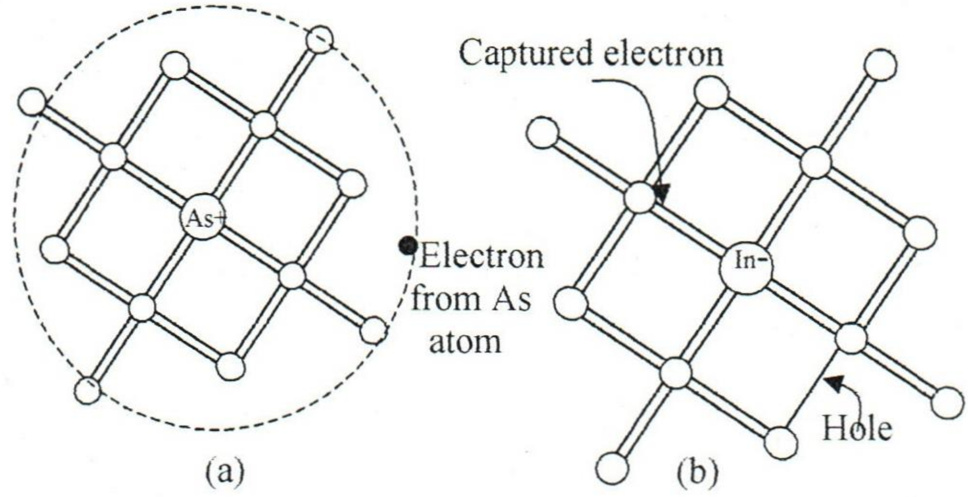


Figure 1.3. (a) In a doped germanium crystal an arsenic impurity atom brings five electrons where only four are required to complete the covalent bonds with neighboring germanium atoms; the fifth electron is very loosely bound and readily excited to the conduction band. (b) An indium acceptor atom in a germanium crystal provides only three of the four valence electrons needed to complete the covalent bond. Much of the time an electron from some other part of the crystal is captured by the indium atom, leaving a hole in the crystal.

When n-type material is brought in contact to a p-type material, they form what is called a pn-junction. At the contact point of a pn-junction electrons from the donor atoms near the junction fill the nearby acceptor states just across the junction. This makes the p-region negative and raises the Fermi level there; while the loss of electrons in the n-region leaves it positively charged. In the intermediate vicinity of the junction there is a limited number of free carriers of either sign. Thus, at the junction a relatively poor conductor depletion layer (see Figure 1.4) with

a double layer of bound charges, negative on the p-side and positive on the n-side might be formed.

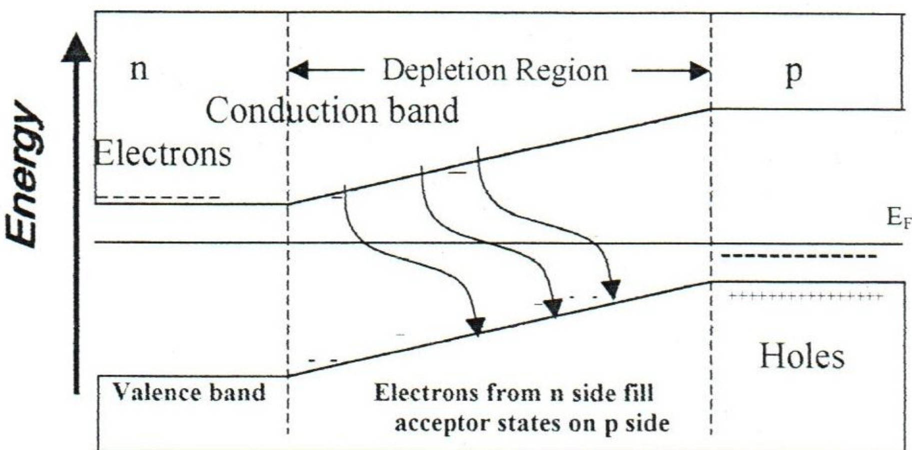


Figure 1.4. Energy level diagram for an unbiased np junction. Electrons from donor atoms on the n side fill acceptor levels on the p side, making the p material negatively charged. A scarcity of charge carriers in the transition region increases the resistivity there. At equilibrium electrons diffuse from the n side at the same rate as electrons from the p side move "downhill" to n side.

Generally speaking, a dynamic equilibrium is achieved between the thermal production of holes and conduction of electrons and the destruction of these carrier pairs by electrons doping to the lower energy states.

1.2 Models and theories

There are several theoretical models that have been developed for explaining the transport of charge carriers ~~transport~~ in semiconductors among these:

The Green's function method was the earliest model introduced (Mahan, 1981) and was used by many theorists to derive equations which, when solved, provide an accurate numerical description of many processes in semiconductors and solid state. This method is complicated and subtle.

The electron-phonon model (Christman, 1988), assumes a longitudinal optical (LO) mode with constant frequency. It also assumes energy conservation but with the imaginary part of the self-energy is set to equal to zero and the mean-free-path is infinite. This assumption implies that the Brillouin-Wigner perturbation theory (Manham, 1988) is exact at 0 K. In practice, this does not happen, consequently the Brillouin-Wigner theory is usually a poor approximation for studying conduction in semiconductors.

The Tamm-Dancoff (TD) approximation constitutes of solving Brillouin-Wigner perturbation theory with only one-phonon self-energy (Hiramdo, 1988). The TD approximation gives poor results in intermediate coupling region. Better results are obtained when more terms are included in the self-energy expression.

The Rayleigh-Schrodinger (RS) perturbation theory or the on-mass shell perturbation theory (Jones and Manch, 1985) is a standard quantum model type (Schiff, 1955). Its basic assumption is that energy and momentum are no longer treated as separate variables. The RS is a good

approximation when the imaginary part of the self-energy is set to be equal to zero.

The strong coupling theory for polarons (the word polaron describes a coupled system of electrons and ions) was introduced by Landau and Pekar (1946). The calculation method for this model is radically quite different from that of perturbation theory. Basically, it is a variational method uses a Gaussian wave function. Besides, it assumes that the particle is not quite localized and the total wave function is simply written as the product of the electron and the phonon wave functions. One needs also to know the charge carrier effective mass to calculate the energy parameters. There are several properties that worth mentioning here for polarons in strong coupling theory. The first is that localization may occur anywhere. The second, is that polaron have excited states which are also localized.

The polaron model may not be solved exactly but it can be approximated using the adiabatic approximation (Fistul, 1969). In such approximation, the electron has sufficient binding energy that makes its oscillatory motion in the potential well much faster than the vibrational frequency of phonons. Phonons are treated as a rigid potential well, in which the electron adiabatically oscillates.

Transport models (statistical mechanics models) deal with unstable systems or systems in a non-equilibrium state. The non-equilibrium state

of a semiconductor system is attributed to many effects among these: electric fields magnetic fields and temperature gradients.

Theoreticians had developed several theoretical transport models for studying charge carrier transport in semiconductors. Theory of electron transport in semiconductors can be worked out by treating the conduction electrons as Fermi particles and investigating their kinetics. The particle and energy fluxes are expressed in terms of the electron velocity and distribution function. The distribution function is then related to the external fields and temperature gradient.

The "linear response" theory was developed by Kubo (Kubo, 1957) for studying thermal conduction in semiconductors and developing a general expression for the thermal conductivity. In this model, one assumes that currents are proportional to the electric and magnetic fields and the proportionality constants can be evaluated at equilibrium. This method works well, because one assumes that the applied fields are small, and the system is only infinitesimally disturbed from equilibrium.

The Boltzmann transport model (Kac, 1956) basically assumes the existance of a distribution function to describe the non-equilibrium state of the particle. The ditribution function depends on three variables: the velocity, the position and time (Gupta, 1995). Then, one writes a differential equation for the motion of particles in a non-equilibrium system (Wannier, 1966) in phase-space. For small fields, the system is

close to equilibrium and one is expected to reproduce the linear response solutions. This method can be extended to include systems far from equilibrium by solving Boltzmann numerically.

The quantum Boltzmann equation (QBE) was pioneered by Kadanoff and Bayman (1962) and was derived for a particle in a weak electric field. The intent of this model is, therefore, to describe interacting systems that have a small current flowing in response to small electric fields. Instead of introducing a many-body theory to describe the problem, the charge carriers are supposed to experience some random quantum jumps, called collisions. In solid state physics, by analogy, electrons and holes are absorbing or emitting other excitations present in solid, especially phonons. An exact treatment of the QBE is not possible because of the complexity of collision term that can not be solved exactly.

The relaxation-time approximation (RTA) model was introduced as an approximate model for the QBE (Wannier, 1966). The basic assumption of this model is that conduction in solids is attributed to be individual particles (electrons or holes), with no interactions between them, neither with any type of particles, except for the quenched potential created by the fixed nuclei (Schulz, 1998). Besides, the RTA consists in summarizing all dissipative effects into a unique parameter called the relaxation-time. The relaxation-time describes the effective average time

separating two constructive collisions and plays a major role in the electronic contribution to the thermal conductivity.

In the present work we advocate the QBE and the relaxation-time approximation (RTA) models. The choice of these two models is motivated by several considerations. First, the QBE describes the physics of collision process and includes energy conservation, momentum conservation, and the Pauli exclusion principle. Second, the QBE can be used to study the transition from non-equilibrium to equilibrium states. Third, the relaxation-time method provides a simpler context for the collision term, which gives many practical results with less work. Fourth, by equating the relaxation-time collision term with the QBE collision term, we can calculate the relaxation-times and the rates.

1.3 Statement of the problem

In a solid, the transport process includes the flow of charge or energy or both. Some of electrons from the top of the valence band excited across the energy gap to the next higher band (the conduction band) due to external fields such as electric field, magnetic field and due to temperature gradients (thermal effects), which are referred to as "forces". As electrons obey Fermi-Dirac statistics, all states in all the lowest bands are fully occupied while all states in the highest bands are empty. Consequently, conduction in a completely filled band is not possible because of the Pauli exclusion principle. Furthermore, when a system of

electrons in equilibrium, the number of electrons in any volume element is constant in time and there is no net flow. Of course, the electrons are constantly moving, but on the average, the number of electrons entering the volume element is equal to the number of electrons leaving it. When electric or magnetic fields act on the system, electrons will accelerate in a direction determined by the field and a drift motion will thereby be superimposed on the random movements of the electrons, giving rise to a directional net flow.

Consider an electron with velocity $\vec{\upsilon}$ in a state labeled by the wave number vector $\vec{k}$, then it's kinetic energy is given by

$$E_k = \frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m} \tag{1.1}$$

and its momentum $\vec{p}$ is

$$\vec{p} = m\vec{v} = \hbar\vec{k} \tag{1.2}$$

where $\hbar$ is Planck's constant divided by 2π. The net flow of electrons in a semiconductor is achieved by imposing the semiconductor to one of the following mechanisms:

Firstly, applying an electric field $\vec{\varepsilon}$. In the presence of an external electric field, there will be a flow of charge in the valence band with sites vacated by electrons moving in a direction which is opposite to that of electrons

in the conduction band. In order to move an electron under the influence of an electric field an electron must be capable of being accelerated by the field. Acceleration implies a continuous change in the electron momentum $\vec{p}$ and hence the wave vector $\vec{k}$, but there were no empty states of different $\vec{k}$ in a completely filled band into which an electron can go. Hence, electrons in a full band can not contribute to conduction in semiconductors. Consequently, the electrical conduction arises from the existance of partially filled electron bands. Assuming that the electric field $\vec{\varepsilon}$ is switched on at a particular time t_0. By Newton's second law, the field exerts a force $-e\vec{\varepsilon}$ on the electron, where e is the magnitude of the electron charge. Since the force is the time rate of change of the momentum, the electric force acting on the electron can be written as follows

$$F_e = \frac{d\vec{p}}{dt} = \hbar \frac{d\vec{k}}{dt} \tag{1.3}$$

Equation (1.3) can be integrated to yield $\vec{k}$ as a function of time. If the initial switching time t_0 is taken to be zero, then after integration equation (1.3) gives

$$\vec{k} = \vec{k}_0 - \frac{e\vec{\varepsilon}}{\hbar} t \tag{1.4}$$

where t is the time of switching, and $\vec{k}_0$ is the wave number vector before

the field was turned on. Equation (1.4) is valid for all electrons and shows that the effect of the electric field is to shift the entire Fermi sphere along the field direction by an amount that is the same for all electrons and proportional to time. This effect is displaced in Figure 1.5.

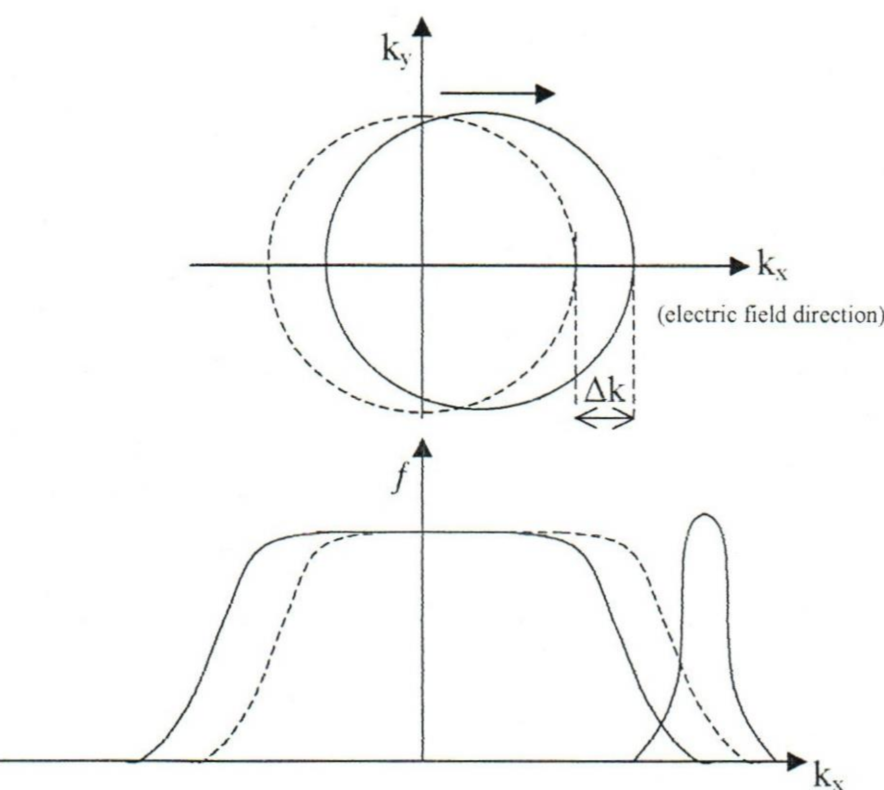


Figure 1.5 Particle distribution function in a semiconductor in k-space, showing the effect of applying a small electric field.
(a) Displacement of Fermi sphere due to electric field.
(b) Displacement of Fermi distribution in presence of electric field. Solid line is f^0, dotted line is f and the peak on the right shows the distribution function derivative (gradient of f^0).

Secondly, applying a magnetic field. An analogous situation exists if the electron is acted on by a magnetic field $\vec{B}$. In this case, the magnetic force $\mathbf{F}_m$ acting on an electron of velocity υ is

$$\vec{F}_m = -e\vec{\upsilon} \times \vec{B} \tag{1.5}$$

If the average velocity after turning on the magnetic field is υ_{av}, then equation (1.5) can be integrated to give

$$\vec{v} = \vec{v}_0 - \frac{e}{m}\vec{v}_{av} \times \vec{B}t \tag{1.6}$$

Equation (1.6) tells us that the magnetic field has the effect of superimposing a velocity on the electron that is perpendicular to both the magnetic field vector and the electron velocity vector. In terms of a wave vector, equation (1.6) becomes

$$\vec{k} = \vec{k}_0 - \frac{e}{m}\vec{k}_{av} \times \vec{B}t \tag{1.7}$$

Unlike the electric field, the magnetic field does not affect all electrons equally, irrespective of wave number because the magnetic forces are velocity dependent.

Thirdly, applying a temperature gradient. When a temperature gradient is applied, there will be a net flow of electrons from hot regions to cold regions. This is because temperature is a measure of kinetic energy, the average velocity of electrons in hot regions will be greater than the average velocity in cold regions. These electrons carry kinetic energy with them; therefore, there is a corresponding net heat flow. The temperature gradient also gives rise to a shift in the Fermi distribution. This shift has two origins. First, the distribution function depends on the

temperature, and if the gradient exists, the distribution will vary with position. Second, the distribution depends on the Fermi level, and to the extent that this level varies with temperature, it will vary with position.

There is one more comment to make at this point. Electrons carry both kinetic energy and charge. Therefore, the flow of heat caused by temperature gradients should be accompanied by electrical effects. Conversely, the current caused by electric and magnetic fields should be accompanied by heat and thermal effects. The theory developed in this work describes these effects as well as the ordinary electrical and thermal conductivity.

Consider a full band in a semiconductor (i.e. the valence band) having a large number of carriers (electrons) where statistical transport methods are usually employed. A probability distribution function, $f_i(\vec{k},\vec{r};t)$, is introduced as a single particle distribution function that describes the occupancy of allowed energy states. The most probable number of electrons in the volume element $d^3\vec{k}$ of $\vec{k}$-space at time t is given by (Ziman, 1960):

$$N = \frac{2}{8\pi^3} f_i(\vec{k},\vec{r};t) \tag{1.8}$$

where i is the band index and will normally be used in future equations.

The distribution in the neighborhood of $\vec{r}$ may change due to a number of mechanisms, among these; an external force $\vec{F}$, diffusion process, and

collision process. Electrons are scattered by atomic vibrations (phonons), impurity atoms, vacant lattice sites, dislocations, and grain boundaries. Therefore, external fields cannot accelerate electrons indefinitely. They eventually interact with imperfections, transfer energy and momentum to it, and move out again in some other direction. Each of its interaction may be thought as a collision that erases the electron's memory of its interaction with the field. After each collision, the field has to start fresh to exert its influence on the electron. The final result is a balance between the field, which tries to bring the electrons away from equilibrium, and the collisions that try to restore equilibrium. The total time rate of change of the distribution function, f, is represented by the following transport equation

$$\frac{df}{dt} = \left(\frac{df}{dt}\right)_{field} + \left(\frac{df}{dt}\right)_{diffusion} + \left(\frac{df}{dt}\right)_{collision} \tag{1.9}$$

Equation (1.9) is the Boltzmann equation in its general form. In the steady state this must equal to zero. Then, by substituting for the various rates, one obtains (Bardeen and Shockley, 1950)

$$-\left(\frac{df}{dt}\right)_{collision} = -\vec{v}_{\vec{k}}.\vec{\nabla}_{r}.f - \frac{1}{\hbar}\vec{F}.\vec{\nabla}_{k}f = I_{collision} \tag{1.10}$$

where I_{coll} is the collision term to be discussed in Chapter Two.

The basic problem is to solve this equation for f_k. Obtaining a solution of the Boltzmann equation is difficult owing to the complexity of the collision term. Two methods of approach; namely, the variational method and the relaxation-time method. For the present case, our approach is limited to the relaxation-time approach. If $f(\vec{k})$ is the probability that an electron in a state $\vec{k}$, we can, therefore, write

$$f(\vec{k}) = f^{0}(\vec{k}) + \Delta f(\vec{k}) \tag{1.11}$$

where $f^{0}(\vec{k})$ is the equilibrium Fermi distribution function and $\Delta f(\vec{k}) \langle\langle f^{0}$ In the RTA model, the collision term is approximated by $(f_k - f^{0})/\tau$ where τ is the relaxation-time, (Wannier, 1966).

The current density of the flow of electrons and that of energy can then be obtained from (Bube, 1974),

$$-\mathrm{J} = \frac{1}{4\pi^3}\int \vec{\mathrm{v}}_k \mathrm{f}(\vec{\mathrm{k}})\, \mathrm{d}^3\vec{\mathrm{k}} \tag{1.12}$$

$$W = \frac{1}{4\pi^3}\int \mathrm{E}_k\, \vec{\mathrm{v}}_k \mathrm{f}(\vec{\mathrm{k}})\, \mathrm{d}^3\vec{\mathrm{k}} \tag{1.13}$$

Transport and physical parameters are then calculated as soon as the distribution function and the relaxation-times are determined. Therefore, the entire theory of thermal and electrical conduction is contained in these two flux equations. Note that all of the external influences contribute to the electric and thermal fluxes. Thus, there is an electric current arising not only from the electric field $\vec{\varepsilon}$, but also from the temperature gradient

$\vec{\nabla}T$ and the magnetic field $\vec{B}$. Similarly, the electric and magnetic fields, as well as the temperature gradient, contribute to heat flow.

All that is needed to extract the transport parameters from the flux equations is a computation of the various integrals. In computing these integrals, it will be assumed that the derivatives of the distribution function can be replaced by the values they would have at equilibrium. Since we are dealing with small deformations (disturbances) of the distribution function from the equilibrium, this is a sufficiently a good approximation. Furthermore, expressions for the relaxation-times for the different scattering processes will be calculated from the collision terms involved in the calculations.

Chapter Two

The Quantum Boltzmann Transport Equation (QBE)

2.1 Introduction

The transport of electrons and holes in semiconductors are named as the transport phenomena of kinetic effects. There are several methods for doing transport studies. The true microscopic theory for studying transport properties in semiconductors is based on the Boltzmann equation. Boltzmann equation assumes that large portion of the system is described by a distribution function $f(\vec{r},\vec{k};t)$, which gives the behavior of particles. Besides, the Boltzmann equation gives the probability of the distribution function of a single particle in phase-space as a function of time.

Generally, the Boltzmann transport equation describes changes produced in the distribution function by applied fields, temperature gradients, and scattering processes. The advantage of the Boltzmann equation method is that one can also try to solve the equation when the system is far from equilibrium (Richi, 1980) as in Kubo's method (Kubo, 1957).

In this chapter we present the Boltzmann equation as a starting point and discussed its origin for various kinds of collisions (scattering). The

relaxation-time approximation (RTA) model is introduced as an approximate method to the general form of the Boltzmann equation.

2.2 The quantum Boltzmann transport equation for electrons

In this section we shall discuss the origin of the Boltzmann equation and consider its solution for a solid or a metal sample in constant uniform fields.

We shall consider a single band where the occupation probability of an electron state at point $(\vec{r},\vec{k})$ in the phase-space at time t is represented by the distribution function $f(\vec{r},\vec{k},t)$. The number of electrons per unit volume at time t in the volume element $d^3\vec{r}d^3\vec{k}$ about the phase-space point $\vec{r},\vec{k}$ is given by

$$dn = g\, f_i(\vec{r},\vec{k},t)\frac{d^3\vec{r}d^3\vec{k}}{(2\pi\hbar)^3} \tag{2.1}$$

where g=2, represents a probability of spin-flip occurring during a scattering process and $\frac{d^3\vec{r}d^3\vec{k}}{(2\pi\hbar)^3}$ is the density of states in phase-space. This implies that each state accommodate two electrons of opposite spins. The non-equilibrated distribution function, $f(\vec{r},\vec{k},t)$, will eventually approaches the Fermi-Dirac distribution $f^0(\vec{k})$ (Rief, 1965) for electrons in equilibrium, that is, $f(\vec{r},\vec{k},t)$ is reduced to

$$f^0(\vec{r},\vec{k}) = \frac{1}{e^{(E-E_F)k_BT(\vec{r})}+1} \tag{2.2}$$

where E_F (or μ) is the Fermi energy or the chemical potential and T is the local temperature of the electron.

If the solid is in a non-equilibrium state, f may change with time and transitions of particles from one state to another may occur. The change of the non-equilibrium distribution function of a system in time may be resulted from particle scattering, temperature gradient and external fields. The total rate of change of the ditribution function with time, therefore, can be written as

$$\left(\frac{df(\vec{r},\vec{k};t)}{dt}\right) = \left(\frac{\partial f(\vec{r},\vec{k};t)}{\partial t}\right)_{field} + \left(\frac{\partial f(\vec{r},\vec{k};t)}{\partial t}\right)_{diff} + \left(\frac{\partial f(\vec{r},\vec{k};t)}{\partial t}\right)_{coll} + \frac{\partial f(\vec{r},\vec{k};t)}{\partial t} \tag{2.3}$$

The first term on the right-hand side of equation (2.3) is the drift derivative that originates in the fields and temperature gradients and represents the change of the distribution function due to applied field external fields (electric or magnetic fields) and temperature gradients; while the second term represents the diffusion process (particles pass in and out of the volume element around $\vec{r}$ because of their motion). The third term is the scattering term or collision derivative (particles are

scattered into and out of the volume element $d^3\vec{r}d^3\vec{k}$). The fourth term represents the space change of the distribution function in time. We shall treat each term separately.

The drift derivative may be related to the external influences by following the motion of a given group of particles. A particle at $\vec{r}$ and $\vec{k}$ at time t must have been at $\vec{r} - \upsilon(\vec{k})dt, \vec{k} - \vec{F}dt/\hbar$, at time t-dt, where $\upsilon(\vec{k})$ and $\vec{F}$ represent the velocity and the force on the electron, respectively. However the number of particles in the group has not changed, so that

$$f(\vec{r}, \vec{k}, t) = f(\vec{r} - \upsilon(\vec{k})dt, \vec{k} - \frac{\vec{F}dt}{\hbar}, t - dt) \tag{2.4}$$

If there were no collisions, then every particle at the point $\vec{r} - \upsilon(\vec{k})dt, \vec{k} - \vec{F}dt/\hbar$ will reach the point $\vec{r}, \vec{k}$ in phase-space with the following new distribution function $f(\vec{r} - \upsilon(\vec{k})dt, \vec{k} - \vec{F}dt/\hbar, t - dt)$. Since Δt can be arbitrary small, then expanding the right-hand side of equation (2.4) in a Taylor series about the initial phase-space point and keeping only terms of the first order in Δt, one finds that

$$\Delta t\left[\vec{v}.\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}} + \frac{\partial f}{\partial t}\right] = 0 \tag{2.5}$$

The time derivative of the distribution function in equation (2.5) is known as the drift derivative and this derivative is given by

$$\left(\frac{\partial f}{\partial t}\right)_{drift} = -\left[\vec{v}.\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}\frac{\partial f}{\partial \vec{k}}\right] \tag{2.6}$$

The first term on the right-hand side of equation (2.6) is known as the diffusion term which represents the diffusion process. In any diffusion process electrons from neighboring regions may enter into regions near the point $\vec{r}$, while others may leave this point as a result of their drift velocities $\upsilon_{\vec{k}'}$. Consequently, contribution of diffusion rate to the rate of change of $f(\vec{r},\vec{k})$ may be rewritten as (Ziman, 1972)

$$\left(\frac{\partial f}{\partial t}\right)_{diff} = -\frac{d\vec{r}}{dt}\cdot\vec{\nabla}_r f = -\vec{\upsilon}_{\vec{k}'}\cdot\vec{\nabla}_{\vec{r}'} f \tag{2.7}$$

Next, let us consider the effect of external fields on changing the distribution function. An external force $\vec{F}$ causes electrons to move from their places and come closer together which leads to stronger interaction between them. Besides, there is a possibility for particle's to collide with each other and with the impurity atoms in the lattice sites. The effect of such collisions would result in moving particles occupying a volume $d^3\vec{r}d^3\vec{k}$ around the point $\vec{r},\vec{k}$ in phase-space to a new volume $d^3\vec{r}'d^3\vec{k}'$ around $\vec{r}',\vec{k}'$. Then, the rate of change of the wave vector $\vec{k}$ will be (Kittle, 1993)

$$\frac{d\vec{k}}{dt}=\frac{\vec{F}}{\hbar} \tag{2.8}$$

The second term in equation (2.6) connects the transport properties to the external fields through the acceleration $\frac{\vec{F}}{\hbar}$, and to the temperature gradients through the derivative $\frac{\partial f}{\partial \vec{r}}$. Therefore, the time rate of change of f that corresponds to the externally applied electric and magnetic fields induced motion may be written as

$$\left(\frac{\partial f}{dt}\right)_{\text{field}}=-\frac{d\vec{k}}{dt}\cdot\vec{\nabla}_{\vec{k}}f=-\frac{\vec{F}}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f \tag{2.9}$$

Finally, let us calculate the third term in equation (2.3), the collision term or the change of f due to scattering. If there were collisions between carriers or collision of particles with lattice imperfections (phonon) or interaction of particles with impurities and dislocations and lattice defects,--etc, particles go either in or out of the state and produce a change in the distribution function that should be added to equation (2.4) The result is

$$f(\vec{r},\vec{k},t)=f(\vec{r}-\upsilon(\vec{k})dt,\vec{k}-\frac{\vec{F}dt}{\hbar},t-dt)+\left(\frac{\partial f}{\partial t}\right)_{out}dt+\left(\frac{\partial f}{\partial t}\right)_{in}dt \tag{2.10}$$

Expanding the left-hand side of equation (2.10) in power series about the initial phase-space point, keeping linear terms to the first order in dt and taking the limit as dt, one obtains

$$\frac{\partial f}{\partial t}+\vec{\upsilon}.\frac{\partial f}{\partial \vec{r}}+\frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}}=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2.11}$$

Equation (2.11) is the well-known quantum Boltzmann equation (QBE) for electrons and includes the quantum effects of systems. For a system under constant electric and magnetic fields with intensities given by $\vec{\varepsilon}$ and $\vec{B}$, respectively, the force on an electron is given by the Lorentz equation

$$\vec{F}_L = m\vec{a} = -e\vec{\varepsilon} - e\vec{v}\times\vec{B} \tag{2.12}$$

Since $\vec{\varepsilon}$ and $\vec{B}$ do not vary with position, the spatial derivative of f must be related to the temperature gradient by

$$\frac{\partial f}{\partial \vec{r}}=\frac{\partial f}{\partial T}\frac{\partial T}{\partial \vec{r}}=\frac{\partial f}{\partial T}\vec{\nabla}T \tag{2.13}$$

The use of equation (2.12) and equation (2.13) in the left-hand side of equation (2.11) gives

$$\frac{\partial f}{\partial t}+\vec{\upsilon}.\frac{\partial f}{\partial \vec{r}}+\frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}}=\frac{\partial f}{\partial t}+\frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T-\frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}}-\frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}}=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2.14}$$

This is the QBE in its general form. The time rate of change of the distribution function f within a volume element $d^3\vec{r}d^3\vec{k}$ is, therefore, governed by Boltzmann equation in its most general form equation (2.14). The statistical content of the QBE lies in the calculation of the distribution function f.

2.3 The transition probability

In order to describe the way in which the collisions restore equilibrium, we need to define the collision term as well as the transition probability function $\omega_{kk'}$. The collision term will be discussed after introducing the transition rate.

The transition probability $\omega_{kk'}$ from one microstate to another is needed to calculate the time rate of change of the distribution function. Let us take a transition probability that describes the way in which collisions restore equilibrium. We define the transition probability function $\omega_{kk'}$ for a particle whose initial momentum $\vec{k}$, in such a way that the probability that its momentum changes in the time dt is $\omega_{kk'}d\vec{k}dt$. The central point in this case is to relate the transition probability to the particle-particle cross

$|\vec{k}\rangle$ into state $|\vec{k}'\rangle$ is often calculated by using the Fermi-Golden rule (Schiff, 1955),

$$\omega_{kk'} = \frac{2\pi}{\hbar}\delta\left(E(\vec{k}) - E(\vec{k}')\right)\left|\langle\vec{k}|V|\vec{k}'\rangle\right|^2 \tag{2.15}$$

where V is the perturbed potential and the δ is the Dirac delta function introduced to ensure the conservation of energy during the scattering process, as shown in Figure 2.1, where the scattered states also lie on the same spherical surface in momentum-space of radius $\vec{k}$.

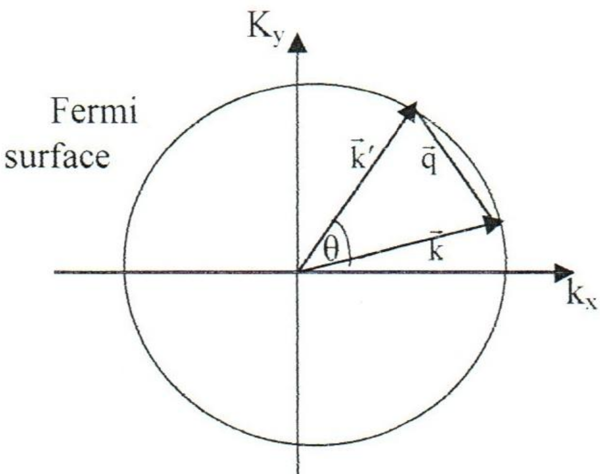


Figure 2.1. Elastic scattering due to stationary atom.

The first order Born approximation (Schiff, 1955) can be used to relate $\omega_{kk'}$ to the scattering differential cross section as:

$$\frac{d\sigma}{d\Omega} = \int \psi^* V \psi d^3\vec{r} \tag{2.16}$$

where $d\Omega$ is the solid angle. Therefore, when equation (2.16) is substituted into equation (2.15), the transition probability becomes

$$\omega_{kk'} = \frac{2\pi}{\hbar}\delta\left(E(\vec{k}) - E(\vec{k}')\right)\left(\frac{d\sigma}{d\Omega}\right)^2 \tag{2.17}$$

The total probability per unit time for the collision (or the collision rate) is then calculated by summing over all final states wave vectors $\vec{k}'$. The reversibility principle implies that $\omega_{kk'} = \omega_{k'k}$.

The inverse of the relaxation-time or the relaxation rate, $1/\tau$,can be expressed in terms of $\omega_{kk'}$ as

$$\frac{1}{\tau(\vec{r},\vec{k})} = \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\omega_{kk'}\left(1 - f(\vec{r}',\vec{k}')\right) \tag{2.18}$$

If the angle between $\vec{k}$ and $\vec{k}'$ is θ, then equation (2.18) can be simplified to

$$\frac{1}{\tau(\vec{r},\vec{k})} = \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\frac{2\pi}{\hbar}\delta\left(E(\vec{k}) - E(\vec{k}')\right)\left(\frac{d\sigma}{d\Omega}\right)^2\left(1 - f(\vec{r}',\vec{k}')\right)(1 - \cos\theta) \tag{2.19}$$

From Figure 2.1, it is obvious that the scattering angle θ and the wave vector, $\vec{k}$, are related geometrically by $q = 2k\sin\left(\frac{\theta}{2}\right)$. Substituting this expression into equation (2.19), we get

$$\frac{1}{\tau(\vec{r},\vec{k})} = \frac{4\,m\,k}{2\,\pi\hbar^3}\int \delta\left(E(\vec{k}) - E(\vec{k}')\right)\left(\frac{d\sigma}{d\Omega}\right)^2\left(1 - f(\vec{k}')\right)\sin\theta\,(1 - \cos\theta)\left(\frac{q}{2k}\right)^3 d\left(\frac{q}{2k}\right) \tag{2.20}$$

This is the general form of the relaxation-time.

2.3 The collision term

For the completion of our derivation of the QBE, an expression for the collision term should be derived. The basic problem is to obtain $\left(\frac{\partial f}{\partial t}\right)_{coll}$ in equation (2.14) which depends upon the characteristic properties of material.

The description for the collision term is based on the use of the probability per unit time that an electron (particle) with wave vector $\vec{k}'$ will be scattered with the wave vector $\vec{k}$ as a result of collision. The scattering probability is defined in terms of the transition probability $\omega_{kk'}$ in the following manner: The probability per unit time that an electron known to be occupying the state $\vec{k}$ be scattered into an infinitesimal volume $d^3\vec{k}'$ about $\vec{k}'$ known to be unoccupied is given by $\frac{\omega_{kk'}d^3\vec{k}'}{(2\pi\hbar)^3}$. The rate of transition must be reduced by the fraction $\left(1-f(\vec{r}',\vec{k}')\right)$. This fraction tells us that the state the particle is supposed to scatter in is unoccupied and is known as Pauli blocking (Kohler, 1985). Since electrons are not only scattered out of state $\left|\vec{k}\right\rangle$ but are also scattered into it from other states $\left|\vec{k}'\right\rangle$, we may present equation (2.20) in a different way.

First, we define $\left(\frac{df}{dt}\right)_{out}$ on the basis that in time interval dt a fraction $\frac{dt}{\tau}$ of the electrons with a wave vector $\vec{k}$ near position $\vec{r}$ will suffer a collision that alters the wave vector of the electrons but not the distribution function. The decrease in the number of particles in a volume element $d^3\vec{r}$ with momenta in the range $d^3\vec{k}$ in a time dt is

$$d^3\vec{r}\, d^3\vec{k}\, dt \int f(\vec{r},\vec{k};t)\, \omega_{kk'}\, d^3\vec{k}' \tag{2.21}$$

Equation (2.21) is resulted from counting all particles with momentum $\vec{k}$, multiplying by the probability that a particle's momentum will change to $\vec{k}'$ and then integrating over all $\vec{k}'$. If equation (2.21) is divided by $d^3\vec{r} d^3\vec{k}' dt$, we get the rate at which f changes with time due to the scattering out of the present state, which can be written symbolically as

$$\left(\frac{df}{dt}\right)_{out} = -f(\vec{r},\vec{k}) \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3} \omega_{kk'} \left(1 - f(\vec{r}',\vec{k}')\right) \tag{2.22}$$

Similarly, the increase in the number of particles in a volume element $d^3\vec{r}$ with momenta in the range $d^3\vec{k}$ in a time dt can be written as

$$d^3\vec{r}\, d^3\vec{k}\, dt \int f(\vec{r},\vec{k}';t)\, \omega_{k'k}\, d^3\vec{k}' \tag{2.23}$$

Equation (2.23) is also obtained by counting the particles with momenta

changes from $\vec{k}'$ to $\vec{k}$, and integrating over all $\vec{k}'$. If equation (2.23) is divided also by $d^3\vec{r}d^3\vec{k}'dt$, we get the scattering in part of the collision term. Thus

$$\left(\frac{df}{dt}\right)_{in} = \left(1 - f(\vec{r},\vec{k})\right)\int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\omega_{k'k} f(\vec{r}',\vec{k}') \tag{2.24}$$

The total rate of change of f due to collision processes is obtained by combining equations (2.22) and (2.24) together. The result is

$$\left(\frac{df}{dt}\right)_{coll} = \left(\frac{df}{dt}\right)_{in} + \left(\frac{df}{dt}\right)_{out} \tag{2.25}$$

In terms of the transition probabilities $\omega_{kk'}$ equation (2.25) can be written as

$$\left(\frac{df}{dt}\right)_{coll} = -\int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\left\{\omega_{kk'} f(\vec{r},\vec{k})\left[1 - f(\vec{r}',\vec{k}')\right] - w_{k'k} f(\vec{r}',\vec{k}')\left[1 - f(\vec{r},\vec{k})\right]\right\} \tag{2.26}$$

This is the general expression for the quantum collision term for electrons. This term is usually abbreviated by I_{coll}. According to the reversibility principle $\omega_{kk'} = \omega_{k'k}$ and equation (2.26) becomes

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int \frac{d^3\vec{k}'}{(2\pi)\hbar^3}\omega_{kk'}\left[f(\vec{r}',\vec{k}')(1 - f(\vec{r},\vec{k})) - f(\vec{r},\vec{k})(1 - f(\vec{r}',\vec{k}'))\right] = I_{coll} \tag{2.27}$$

Let us now equate the right-hand of equation (2.26) with the left-hand side of equation (2.11) side to get

$$\frac{\partial f}{\partial t} + \vec{\upsilon}.\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$
$$= \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\left\{\omega_{kk'} f(\vec{r},\vec{k})\left[1 - f(\vec{r}',\vec{k}')\right] - w_{k'k} f(\vec{r}',\vec{k}')\left[1 - f(\vec{r},\vec{k})\right]\right\} \quad (2.28)$$

Equation (2.28) can be written in a more detailed form by equating the right-hand side of equation (2.26) and the left-hand side of equation (2.14). The result is

$$\frac{\partial f}{\partial t} + \vec{\upsilon}.\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T - \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} - \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$
$$= \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\left\{\omega_{kk'} f(\vec{r},\vec{k})\left[1 - f(\vec{r}',\vec{k}')\right] - \omega_{k'k} f(\vec{r}',\vec{k}')\left[1 - f(\vec{r},\vec{k})\right]\right\} \quad (2.29)$$

This is the general quantum Boltzmann equation. It is the equation that must be solved in order to obtain the distribution function $f(\vec{r},\vec{k};t)$ which can be used to get the transport properties. The general form of the quantum Boltzmann equation can be modified to include the conservation of energy and momentum. The final form may be written as

$$\frac{\partial f}{\partial t} + \vec{\upsilon}.\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{\hbar}.\frac{\partial f}{\partial \vec{k}} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T - \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} - \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$
$$= \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3}\delta(E(\vec{k}) - E(\vec{k}'))\left\{\omega_{kk'} f(\vec{r},\vec{k})\left[1 - f(\vec{r}',\vec{k}')\right] - \omega_{k'k} f(\vec{r}',\vec{k}')\left[1 - f(\vec{r},\vec{k})\right]\right\} \quad (2.30)$$

The appearance of the delta functions in the collision term is to ensure the conversation laws of energy and momentum and takes full account of the Pauli exclusion principle. When the collision term is zero, the system attains an equilibrium state (or a thermalized state) because the scattering of particles out of the state is exactly balanced by the scattering of other particles into the state.

Solving the general form of the QBE is not an easy task to do. People thought of simplifying the equation by introducing approximate method, such as the linearized QBE and the RTA methods.

The linearized Boltzmann equation is obtained by assuming f to be close to the equilibrium distribution function f^0 and the difference, $\delta f = f - f^0$, is small. The second two terms in equation (2.28) can be treated by approximate expansions of the equilibrated distribution function f^0 function, as discussed by several textbooks.

2.5 The relaxation-time approximation (RTA)

The collision term in the Boltzmann equation (2.28) is the most interesting one. This term can be evaluated exactly by integrating the right-hand side of equation (2.30) or it can be evaluated by using the so-called the relaxation-time approximation (RTA).

In the RTA the collision term is replaced by an approximate expression

proportional to the difference between the non-equilibrated distribution function at a certain time t and the Fermi-Dirac distribution, this simplifies to

$$I_{coll} = -\frac{1}{\tau(\vec{r},\vec{k})}\left(f(\vec{r},\vec{k};t) - f^0(\vec{r},\vec{k})\right) = -\frac{\delta f(\vec{r},\vec{k})}{\tau(\vec{r},\vec{k})} \tag{2.31}$$

where τ is the relaxation-time that characterizes the average rate at which collision between particles in the system tend to reset a state of equilibrium, and f^0 represents the equilibrium distribution function (for $\frac{\partial f}{\partial t} = 0$ when $f = f^0$) which is the Fermi distribution at finite temperature as in equation (2.2). The collision rate $\frac{1}{\tau(\vec{r},\vec{k})}$ might depend on position $\vec{r}$ and wave vector $\vec{k}$.

With this discussion in mind, let us now equate the right-hand side of equation (2.31) with the left-hand side of equation (2.14), the Boltzmann transport equation in the relaxation-time approximation reads,

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T - \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} - \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}} = -\frac{f(\vec{k},t) - f(\vec{k})}{\tau(\vec{r},\vec{k})} \tag{2.32}$$

According to Boltzmann theory, the electrons are described by a non-equilibrium distribution function $f(\vec{r},\vec{k};t)$. This statement violates the uncertainty principle according to which both the position and

momentum of the electron can not be specified at the same time. For this reason, we may assume that r to be fixed within the interval $\Delta\vec{r}$ and the electron might be represented by a wave packet with a spread of $\Delta\vec{k}$ in $\vec{k}$-space such that $\Delta\vec{k}\Delta\vec{r} \geq 1$. Assuming a homogenous system, the distribution function is no longer $\vec{r}$ dependent. The $\vec{r}$ independent distribution function $f(\vec{k};t)$ will represent the number of particles at time t in momentum-space volume $d^3\vec{k}$ about the point $\vec{k}$. Accordingly, the relaxation-time is expected to depend on momentum only.

The relaxation-time is obtained by using the collision rate equation (2.28) and equation (2.32), the relaxation-time expression can be simplified into,

$$\frac{1}{\tau(\vec{k})} = \frac{2\pi}{h}\int \delta\left(E(\vec{k}) - E(\vec{k}')\right)\frac{d\sigma}{d\Omega}\left(1 - f(\vec{k}')\right)\frac{d^3\vec{k}'}{(2\pi\hbar)^3} \tag{2.33}$$

Some of the complex wave number dependence of $\omega_{kk'}$ may be condensed into a wave number dependent relaxation-time, $\tau(\vec{k})$, which is sometimes is simplified to $\tau' = \tau(E)$ or a single relaxation-time with the proper choice of τ. However, it leads to an accurate description of the electron distribution in many situations. According to the above discussion, the Boltzmann transport equation reads,

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T - \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} - \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}} = -\frac{f(\vec{k},t) - f(\vec{k})}{\tau(\vec{k})} \tag{2.34}$$

The general solution to equation (2.34) can be written as,

$$f(\vec{k};t) = f^0(\vec{k}) + \tau(\vec{k})\left[\frac{\partial f}{\partial t} - \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T + \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} + \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}}\right] \tag{2.35}$$

Equation (2.35) is the basis for studying transport phenomenon in Fermi systems which includes electrons, protons, holes,----etc. In the following chapters, equation (2.35) will be used for studying thermal and electrical conduction in semiconductors. A certain approximation may be introduced as needed.

2.6 Multiple scattering mechanisms

Usually more than one scattering mechanism operates on the same system and, as a simplest case in this model, we presume that the different mechanisms do not affect each other. To find the collision term, $\left(\frac{\partial f}{\partial t}\right)_{coll}$, we sum similar terms, each due to a different mechanism and each is calculated in the absence of the other types of scattering mechanisms. In the RTA each collision term is inversely proportional to a relaxation-time which characterizes that scattering mechanism, so each mechanism contributes to the collision term and the collision term should be written as

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f-f^0}{\tau_1} - \frac{f-f^0}{\tau_2} - \frac{f-f^0}{\tau_3} - - - - - - - \tag{2.36}$$

where τ_i is the relaxation-time associated with ith mechanism , and there are as many terms on the right-hand side of equation (2.36) as there are mechanisms. Equation (2.36) can be put in the same form as equation (2.34) just by defining a combined relaxation-time by

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \tag{2.37}$$

where τ is the overall relaxation-time of the system and the sum is over all mechanisms. The relaxation-time τ_i governs the approach to equilibrium of a non-equilibrium distribution function describing the ith mechanism. Its value obviously depends on the collision mehanism, and τ_i should be different for different mechanisms. If the relaxation-time for one mechanism is much shorter than all others, scattering takes place predominately via other mechanisms.

2.7 Formal flux equations

The entire theory of thermal and electrical conduction is contained in the thermal and electric fluxes. Therefore, it is of great importance to study them separately.

Now let us derive the fundamental flux equations by a kinetic argument. Choose a plane in the system across which the flux is to be calculated, and consider all particles (electrons) in a surface area Δa with a velocity $\vec{\upsilon}$. In a small time interval dt, a particle of velocity $\vec{\upsilon}$ will reach

the flux plane if it is anywhere within a distance $\Delta z = \vec{\upsilon}.\hat{k}\,dt$, where $\hat{k}$ is a unit vector along the z-axis normal to the flux plane and Δz is measured along the z direction. Therefore, all of the electrons with velocity $\vec{\upsilon}$ that are contained in the volume element $\vec{\upsilon}.\hat{k}\,\Delta z\,dt$ will cross the area element Δa in time dt. If $f(\vec{r},\vec{\upsilon};t)d^3\vec{r}d^3\vec{\upsilon}$ is the number of electrons at time t in a volume element $d^3\vec{r}$ with velocities in the range $\vec{\upsilon}$ and $\vec{\upsilon}+d\vec{\upsilon}$, then the number that cross Δa in time dt with velocity $\vec{\upsilon}$ is

$$N = f(\vec{r},\vec{\upsilon};t)\,\vec{\upsilon}.\hat{k}\,dt\,\Delta a\,d^3\vec{\upsilon} \tag{2.38}$$

Equation (2.38) can be expressed in terms of momentum as

$$N = f(\vec{r},\vec{k};t)\left(\frac{\hbar}{m}\right)^2 \vec{k}.\hat{k}\,dt\,\Delta a\,d^3\vec{k} \tag{2.39}$$

Equation (2.39) is used to derive the electric and heat fluxes.

2.7.1 The electric flux equation

The total electric charge crossing Δa is obtained by multiplying equation (2.39) by –e and integrating over $\vec{k}$:

$$Q = -e\,\Delta a\,dt\left(\frac{\hbar}{m}\right)^2 \int \vec{k}.\hat{k}\,f(\vec{r},\vec{k};t)\,d^3\vec{k} \tag{2.40}$$

The electric flux of electrons in the $\hat{k}$ direction is the flow per unit area per unit time, which is just equation (2.40) divided by $\Delta a\,dt$

$$J_z = -e\left(\frac{\hbar}{m}\right)^2 \int \vec{k}.\hat{k}\, f(\vec{r},\vec{k};t)\, d^3\vec{k} \tag{2.41}$$

The component of the flux normal to the flux plane is related to the flux vector $\vec{J}$ by $J_z = \vec{J}.\hat{k}$ and, therefore, the electric flux vector can be written as

$$\vec{J} = -e\left(\frac{\hbar}{m}\right)^2 \int \vec{k}\, f(\vec{r},\vec{k};t)\, d^3\vec{k} \tag{2.42}$$

To get the electric current flux equation, substitute equation (2.35) into equation (2.42) to get

$$\vec{J} = -e\left(\frac{\hbar}{m}\right)^2 \int \vec{k}\left[f^0(\vec{k}) + \tau(\vec{k})\left[\frac{\partial f}{\partial t} - \frac{\partial f}{\partial T}\vec{\upsilon}.\vec{\nabla}T + \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} + \frac{e}{\hbar}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}}\right]\right] d^3\vec{k} \tag{2.43}$$

Integration of the first term in equation (2.43) gives zero because of the antisymmetry of $\vec{\upsilon} f^0$. Therefore, the current flux equation becomes

$$\vec{J} = e\left(\frac{\hbar}{m}\right)^2 \int \vec{k}\left[\tau(\vec{k})\left[\frac{\partial f}{\partial T}\frac{\hbar}{m}\vec{k}.\vec{\nabla}T - \frac{e}{\hbar}\vec{\varepsilon}.\frac{\partial f}{\partial \vec{k}} - \frac{e}{m}(\vec{\upsilon}\times\vec{B}).\frac{\partial f}{\partial \vec{k}}\right]\right] d^3\vec{k} \tag{2.44}$$

2.7.2 The energy flux equation

The flux of energy is obtained by multiplying equation (2.39) by the kinetic energy $\frac{\hbar^2 k^2}{2m}$ and integrating over $\vec{k}$. The result is

$$\vec{J} = \frac{me}{2}\left(\frac{\hbar}{m}\right)^4 \int k^2\, \vec{k}\, f(\vec{r},\vec{k};t)\, d^3\vec{k} \qquad (2.45)$$

where $\vec{J}$ is the heat flux vector. The heat current vector is obtained by combining equation (2.35) with equation (2.45). The result can be written as

$$\vec{J} = -\frac{me}{2}\left(\frac{\hbar}{m}\right)^4 \int k^2\, \vec{k}\, \tau \left[\frac{\hbar}{m}\frac{\partial f}{\partial T}(\vec{k}.\vec{\nabla}T) - \frac{m}{\hbar}\frac{\partial f}{\partial \vec{k}}.\vec{\varepsilon} - (\vec{k}\times\vec{B})\frac{\partial f}{\partial \vec{k}}\right] d^3\vec{k} \qquad (2.46)$$

Clearly, the external effects contribute to the electric and thermal fluxes as seen in equations (2.44) and (2.46).

Chapter Three

Thermal Conductivity

3.1 Introduction

The theory of thermal conductivity has received much attention during the last three decades and it is now possible to provide a theoretical explanation of thermal conductivity behavior of semiconductors over a wide range of temperatures.

When a temperature gradient is applied to a solid, charge and energy flow through it. Thermal conduction in most semiconductors and all insulators is due to phonon flow. Besides, in heavily doped semiconductors the concentration of electrons and holes is extremely high, the charge carriers give rise to an electronic contribution to thermal conductivity.

Electrons are important in the study of heat transport in semiconductors as they (along with holes) act as heat carriers and contribute to electronic thermal conductivity. They also act as scattering agents for phonons and thus influence the lattice thermal conductivity. Scattering of electrons and phonons from impurities and from vibrating atoms plays an important role in thermal conduction. Several books, for example Drabble and Goldsmid (1961) and Kittle (1976) have discussed the electronic behavior in crystalline solids. In this work, we shall consider only the electronic

conduction that has a direct effect on heat transport in semiconductors. Moreover, we shall study the fundamental process of thermal conduction that resulted from the diffusion of both electrons and phonons in a temperature gradient. Results are used to develop expressions for thermal conductivity of semiconductors.

We shall consider systems in which the deviation from equilibrium is small. When the temperature gradient is switched off, the system returns to its equilibrium state in the time scale set by the relaxation-time. The study of the variation of thermal conductivity with temperature and impurity concentration will provide a deeper understanding to the nature of vibrational modes and various scattering processes that serve to limit the mean-free-path of heat carriers (phonons) and electrons or holes. The availability of reliable thermal conductivity data has proved to be considerable use in selection of semiconductors for a wide range of applications such as thermoelectric generators, refrigerators, and heat storage systems.

Transport parameters such as thermal conductivity and thermal mobility are then calculated as soon as the distribution function and the relaxation-times are determined. Therefore, the entire theory of thermal conduction is contained in the flux equations (2.44) and (2.46) derived in CHAPTER TWO.

The electric and magnetic fields, as well as the temperature gradient, contribute to heat flow or thermal fluxes. Thus, there is an electric current arising not only from the electric field $\vec{\varepsilon}$, but also from the temperature gradient $\vec{\nabla}T$ and the magnetic field $\vec{B}$.

Numerical calculations are based on calculating the various integrals in the flux equations. Since we are interested with small deformations (disturbances) of the distribution function from the equilibrium the derivatives of the distribution function is replaced by the values they would have at equilibrium. In this chapter, the RTA approach will be followed for investigating the general behavior of thermal conductivity K.

3.2 Thermal fluxes

Early investigations of thermal conductivity of solids are based on the principle of energy conservation; the amount of heat flowing across a certain cross-section can be written as a sum of the heat absorbed by that section of the material and the heat lost by radiation. In any theoretical analysis of thermal conductivity, the electronic contribution must be separated from the lattice component; the latter can then be analyzed in terms of phonon transport. When two regions with different particle concentrations are brought into contact, particles cross the boundary in both directions. In case of different concentrations, particles leave the region of higher concentration per unit time than enter it. Particles are

said to diffuse from regions of high concentrations to regions of low concentrations.

In this chapter we are interested in the energy carried by electrons and phonons as they diffuse in a temperature gradient. The role of the gradient is simply to maintain the diffuse of particle concentrations in different regions of a semiconductor. According to heat conduction principles, the rate of heat transfer by conduction in a solid across an element of surface area A is proportional to the surface area of that element, to the temperature gradient at that part and the cosine of the angle between the normal to the surface element and the temperature gradient. Assuming a solid to be aligned with the z-axis, the coefficient of the thermal conductivity κ is then defined by the following equation:

$$\dot{Q}' = \frac{dQ}{dt} = -\kappa\, A \left(\frac{dT}{dz} \right) \cos\varphi \tag{3.1}$$

Here $\dot{Q}' = \frac{dQ}{dt}$ is the rate of heat transfer across the area element whose normal makes an angle φ with the temperature gradient. The energy flux for a collection of particles each carrying energy E and moving with velocity υ, is given by (Christman, 1988)

$$\vec{Q} = n\, E\, \vec{\upsilon} \tag{3.2}$$

where n is the particle concentration. We sum contributions from all

modes and states, each with its own energy, particle concentrations, and particle velocity. The lattice and electronic thermal conductivities are treated separately.

3.3 The lattice thermal conductivity

3.3.1 The phonons Boltzmann transport equation in the RTA.

To understand the mechanism of heat conduction in semiconductors, one should consider collective vibrations of the system as a whole. The thermal conduction can be described as the propagation of energy through the sample by these lattice waves (phonons). Many thermal properties of semiconductors can be described in terms of phonons behavior.

In thermal equilibrium, the average number of phonons is

$$n^0 = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \tag{3.3}$$

and the average energy for the normal mode is $k_B T$. Equation (3.3) is reduced to $k_B T/\hbar\omega$ for $\hbar\omega/k_B T \ll 1$.

Let us now derive the Boltzmann equation for phonons. We shall start by considering a phonon in state with a propagation wave vector $\vec{q}$ and this phonon is allowed to scatter to state with a propagation wave vector $\vec{q}'$. The sample under consideration is divided into small regions, large enough that the vibration spectrum for each region is the same as for the bulk material. Let $n(\vec{r},\vec{q};t)$ be the phonon concentration near $\vec{r}$ in a mode

with a propagation wave vector $\vec{q}$. The phonon concentration changes with time because phonons diffuse into and out of the region. Besides, scattering processes may also change the number of phonons in any mode. There must, therefore, exist processes which tend to oppose the (concentration) density change due to the drift of phonons and help in bringing the distribution to a steady state.

Phonons may encounter resistance due to various processes, such as scattering by other phonons, impurities, charge carriers, grain boundaries,....etc. The time rate of change in the phonon distribution due to all processes can be written as

$$\left(\frac{\partial n}{\partial t}\right)=\left(\frac{\partial n}{\partial t}\right)_{diff}+\left(\frac{\partial n}{\partial t}\right)_{scatt} \tag{3.4}$$

This is the Boltzmann equation for phonons which is similar to the QBT for electrons with f is replaced by n. In the steady state cases equation (3.4) can be written as

$$\left(\frac{\partial n}{\partial t}\right)_{diff}+\left(\frac{\partial n}{\partial t}\right)_{scatt}=0 \tag{3.5}$$

Let us calculate the diffusion and the collision terms in equation (3.5).

In calculating the diffusion term, the phonon concentration to the first approximation in Δt may be approximated by

$$n(\vec{r},\vec{q};t+\Delta t)=n(\vec{r}-\vec{\upsilon}\Delta t,\vec{q};t)=n(\vec{r},\vec{q};t)-\vec{\upsilon}\vec{\nabla}n\Delta\Delta t \tag{3.6}$$

The time rate of change of the diffusion term of the phonon distribution, n, is

$$\left(\frac{\partial n}{\partial t}\right)_{diff} = -\vec{\upsilon}\vec{\nabla}n \tag{3.7}$$

where υ is the phonon velocity. Since the vibrational energy is transported with the group velocity of the wave, the phonon velocity is taken to be as the wave group velocity. Thus

$$\vec{\upsilon} = \vec{\nabla}_q \omega = \frac{\partial \omega}{\partial q} \tag{3.8}$$

For long wavelengths in an acoustical branch, υ is the speed of sound.

In the RTA, the rate of change of the phonon distribution function due to the scattering processes is approximated by

$$\left(\frac{\partial n}{\partial t}\right)_{scatt} = -\frac{\left(n - n^0\right)}{\tau_{ph}(\vec{q})} \tag{3.9}$$

where τ_{ph} is the phonon relaxation-time. Substituting equations (3.7) and (3.9) in equation (3.4) we get,

$$\left(\frac{\partial n}{\partial t}\right) = -\vec{\upsilon}\cdot\vec{\nabla}_n - \frac{n - n^0}{\tau} \tag{3.10}$$

If $\vec{q}'$ lies in the range $d\vec{q}'$, the transition probability can be written as

$$Q_{\vec{q}\vec{q}'} = n_{\vec{q}}(1 + n_{\vec{q}'})\,\omega_{\vec{q}\vec{q}'}\,d^3\vec{q}' \tag{3.11}$$

where $\omega_{\vec{q}\vec{q}'}$ is the intrinsic transition probability and $n_{\vec{q}}(1+n_{\vec{q}'})$ is the population factor. The rate of change of the distribution function is then given by (Ziman, 1960)

$$\left(\frac{\partial n}{\partial t}\right)_{Scatt} = -\frac{\left(n-n^{0}\right)}{\tau_{ph}(\vec{q})} = \int\left[n_{\vec{q}'}(1+n_{\vec{q}})\,\omega_{\vec{q}'\vec{q}} - n_{\vec{q}}(1+n_{\vec{q}'})\,\omega_{\vec{q}\vec{q}'}\right]d^{3}\vec{q}' \tag{3.12}$$

We sum over all states $\vec{q}'$ from which a phonon may come to the state $\vec{q}$ and into which it may go. The relaxation-time can be extracted from equation (3.12), the result is

$$\frac{1}{\tau_{ph}(\vec{q})} = \int\left[-(1+n_{\vec{q}'})\,\omega_{\vec{q}\vec{q}'}\right]d^{3}\vec{q}' \tag{3.13}$$

The phonon collision term can be simplified by assuming that the phonon distribution function is close to its equilibrium value. Introducing a function $\Phi_{\vec{q}}$ that measures the deviation of the distribution function from equilibrium as

$$n_{\vec{q}} = n_{\vec{q}}^{0} - \Phi_{\vec{q}}\frac{\partial n_{\vec{q}}^{0}}{\partial E_{\vec{q}}} \tag{3.14}$$

Using the principle of microscopic reversibility, $\omega_{\vec{q}\vec{q}'} = \omega_{\vec{q}'\vec{q}}$, we can write equation (3.12), after some simplification

$$\left(\frac{\partial n}{\partial t}\right)_{Scatt} = \frac{1}{k_{B}T}\int(\Phi_{\vec{q}'} - \Phi_{\vec{q}})\,\omega_{\vec{q}\vec{q}'}\,d^{3}\vec{q}' \tag{3.15}$$

For the momentum conserving processes, the trial function may be written as

$$\Phi_{\vec{q}} = \frac{\vec{q}.\vec{u}}{q^{n}} \tag{3.16}$$

where $\hat{u}$ is a unit vector along $\vec{\nabla}T$ and n is an integer.

The general solution to equation (3.10) may be simplified by considering a small temperature gradient and seeking to the steady state solution to equation (3.9); that is, $\frac{\partial n}{\partial t} = 0$ and taking n to be close enough to Planck's distribution n^{0} for phonons. Consequently, the density gradient ∇n can be approximated by

$$\nabla n^{0} = \frac{\partial n^{0}}{\partial T} \nabla T \tag{3.17}$$

Finally, evaluating the derivative at the average temperature sample, the general steady state solution maybe written as

$$n(\vec{r},\vec{q}) = n^{0}(\vec{r},\vec{q}) - \tau \frac{\partial n}{\partial T} \vec{\upsilon}.\vec{\nabla}T \tag{3.18}$$

where n is time independent in the steady state solution.

3.3.2 The lattice thermal conductivity

Having assumed the existance of a relaxation-time, obtaining a generalized expression for the lattice thermal conductivity becomes straightforward operation. Substitute equation (3.18) into equation (3.5)

to find the single mode's contribution to the energy flux, then summing over all modes contributions to find the total heat flux. Since each phonon carriers energy $E = \hbar\omega$ and the containing n^0 sums to zero, the heat flux tensor becomes

$$\vec{Q} = \sum_{\text{modes}} \hbar\omega\, \vec{\upsilon}(\vec{q})\, n(\vec{r},\vec{q}) = -\sum_{\text{modes}} \hbar\omega\, \tau \frac{\partial n^0}{\partial T} \vec{\upsilon}\, \vec{\upsilon} \cdot \vec{\nabla} T \tag{3.19}$$

Besides, the energy flux is usually written in different forms as

$$Q_i = -\sum_j \kappa_{ij} \frac{\partial T}{\partial x_j} \tag{3.20}$$

where,

$$\kappa_{ij} = \sum_{\text{modes}} \hbar\omega\tau \frac{\partial n^0}{\partial T} \vec{\upsilon}_i \vec{\upsilon}_j \tag{3.21}$$

are the elements of thermal conductivity tensor. For cubic and amorphous materials this tensor is diagonal and equation (3.20) becomes

$$\vec{Q} = -\kappa\, \vec{\nabla} T \tag{3.22}$$

where κ is the scalar thermal conductivity, which equals to one third of the diagonal elements of the tensor. Furthermore, equation (3.22) sometimes written as, $\vec{\nabla} T = -\rho \vec{Q}$ where, $\rho = \frac{1}{\kappa}$ is the thermal resistivity of the sample. Introducing the diagonal elements of the thermal conductivity κ as κ_{xx}, κ_{yy}, and κ_{zz}, the thermal conductivity tensor can be expressed in terms of these elements as

$$\kappa = \frac{1}{3}\left(\kappa_{XX} + \kappa_{YY} + \kappa_{ZZ}\right) \tag{3.23}$$

Making use of equation (3.20), we get

$$\kappa = \frac{1}{3}\sum_{\text{modes}} \hbar\omega\tau \frac{\partial n^0}{\partial T} \upsilon^2 \qquad (3.24)$$

It is convenient to replace the summation over $\vec{q}$ by an integral over ω. If $g(\omega)d\omega$ is the number of phonon modes in the frequency interval ω and $\omega + d\omega$, then equation (3.24) becomes

$$\kappa = \frac{1}{3}\sum_{\text{modes}} \int g(\omega)\, \hbar\omega\, \tau \frac{\partial n^0}{\partial T} \upsilon^2 d\omega \qquad (3.25)$$

Evaluation of the thermal conductivity in equation (3.25) can be simplified by means of the Debye model. Assuming the Debye temperature to be T_D, the average speed of the sound is υ, and the angular frequency ω will be the same for all modes. This implies that the phonon spectrum is isotropic and the thermal conductivity is a scalar.

The Debye model provided a simplification to the integrals in equation (3.25) by assuming a linear dispersion relation and taking the phonons density of states in the simple form

$$g(\omega) = \frac{\omega^2}{2\pi^2\upsilon^3} = \frac{9N\hbar^3}{k_B{}^3 T_D{}^3}\omega^2 \qquad (3.26)$$

where N is the Number of primitive unit cells in the sample. Equation (3.26) is valid for frequencies $\omega \langle \omega_D$ (Debye characteristic frequency) and zero for higher frequencies. Furthermore,

$$\frac{\partial n^0(\omega)}{\partial T} = \frac{\hbar\omega}{k_B T^2} \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left\{ e^{\frac{\hbar\omega}{k_B T}} - 1 \right\}^2} \tag{3.27}$$

Substitution for $g(\omega)$ and $\frac{\partial n^0}{\partial T}$ in equation (3.25) gives

$$\kappa = \frac{1}{6\pi^2} \sum_{\text{modes}} \int \frac{1}{\upsilon} \hbar\omega^3 \tau(\omega) \frac{\hbar\omega}{k_B T^2} \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left\{ e^{\frac{\hbar\omega}{k_B T}} - 1 \right\}^2} d\omega \tag{3.28}$$

The density of modes automatically includes a sum over the three acoustically branches. Optical branches do not usually contribute significantly to the thermal conductivity at low- temperatures so they are neglected. This is the usual starting point for a large number of thermal conductivity calculations.

The low-temperature calculations is obtained by replacing $\frac{\hbar\omega}{k_B T}$ by x, and the upper limit of the integral over x by ∞, equation (3.28) becomes

$$\kappa = \frac{4\pi^4 \tau \upsilon^2}{5V} k_B \left(\frac{T}{T_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx \tag{3.29}$$

The value of the integral is $\int_0^\infty \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx = \frac{4\pi^4}{15}$, so

$$\kappa = \frac{4\pi^4 \tau \upsilon^2}{5V} k_B \left(\frac{T}{T_D} \right)^3 \tag{3.30}$$

According to the variational model, the thermal conductivity is also obtained by equating any two phonon rates of entropy production (Ziman, 1960). The result is as follows:

$$\frac{1}{\kappa}=\frac{\frac{1}{2k_BT^2}\iint\{\Phi_{\vec{q}}-\Phi_{\vec{q}'}\}\omega_{\vec{q}\vec{q}'}\,d^3\vec{q}d^3\vec{q}}{\left[\frac{1}{T}\int E_{\vec{q}}\upsilon_{\vec{q}}\Phi_{\vec{q}}\frac{\partial n^0_{\vec{q}}}{\partial E_{\vec{q}}}d^3\vec{q}\right]^2} \tag{3.31}$$

There are several forms of $\Phi_{\vec{q}}$ which give similar results for the general behavior of κ. For the two phonons type of scattering a suitable trial function is (Holland, 1971)

$$\Phi_{\vec{q}}=\frac{\vec{q}.\hat{u}}{q^4} \tag{3.32}$$

3.4 Transport equations for electrons and holes in semiconductors

The inclusion of impurities into the lattice brings about changes in the phonon spectrum and the impurities may also act as scattering centers for phonons. The doping of a semiconductor introduces electrons and holes in the conduction and valence bands which can act as carriers of heat. On the other hand, they may also act as scattering centers for phonons, hence, the phonon-electron interaction plays an important part in limiting the mean-free-paths of both types of heat carriers.

3.4.1 Intrinsic conduction

Consider a full band in a semiconductor (i.e the valence band) with some of the electrons from the top of the band excited thermally across the energy gap to the next higher band (the conduction band). In the presence of an external electric field, there will be a flow of charge in the valence band with sites vacated by the electrons moving in the direction which is opposite to that of electrons in the conduction band. Such a vacant site in a band otherwise filled with electrons is called a hole and conduction in a nearly full band can be considered in terms of the motion of positively charged carriers. Electrons of the bottom of the conduction band have a positive effective mass and a negative charge while holes at the top of the valence band have a positive effective mass and a positive charge Figure 3.1.

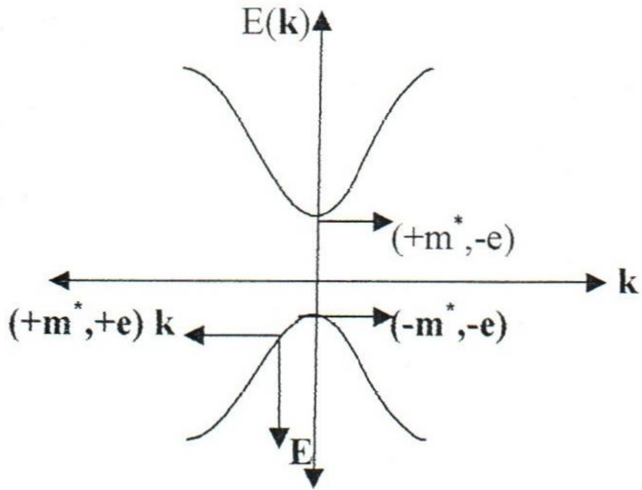


Figure 3.1. Electrons at the conduction and valence band edges and holes at the valence band edge.

If a sufficient number of electrons are thermally excited across the energy gap into the conduction band the subsequent movement of electrons in the conduction band and holes in the valence band give rise to electrical conduction. This type of conduction is called the intrinsic conduction and is significant only at high temperatures.

3.4.2 Extrinsic (Impurity) conduction

The addition of certain a type of impurities to semiconductors alter drastically the electrical properties of semiconductors. For instance the addition of boron to silicon in the proportion of $1 \text{ to } 10^5$ increases the electrical conductivity by a factor 10^3 at room temperature (Ziman, 1966). In terms of energy band model, the introduction of donor or acceptor impurities into the lattice introduces donor or acceptor energy levels close to the bottom of the conduction band and the top of the valence band, respectively. In Si and Ge with energy gaps of 1.2 and 0.78 eV phosphorous levels are around 0.05 and 0.01 eV below the band edge. The ionization of donor impurities give rise to negative charge carriers (electrons) in the conduction band; while acceptor impurities give rise to a positive carriers (holes) in the valence band. At low temperatures the carriers are 'frozen' into the donor or acceptor levels. In heavily doped semiconductors it is possible to attain electron (hole) concentration in excess of $10^{26} m^{-3}$. The charge carriers in these materials make a significant contribution to the thermal conductivity and this contribution

maybe as high as $(25-30)\%$ in a number of materials at room temperature.

3.4.3 Thermal flux equations

If the only external influence acting on our system of electrons is a temperature gradient, electrons will move from hot to cold regions. As a result of spatial rearrangement of electrons caused by the temperature gradient, an internal electric field will be established in the system. This internal field induces an electron flow in the opposite direction to that resulting from the temperature gradient. An analysis of thermal conduction, therefore, requires the use of both the charge and heat-flow equations.

Let us consider a sample divided into regions that are small on a macroscopic scale but are large enough on the a microscopic scale that energy bands in each of them are essentially the same as for the sample (crystal) as a whole. First, consider a single band of volume V_s and take $f(\vec{k};t)/V_s$ to be the concentration of electrons near $\vec{r}$ in a state with crystal momentum $\hbar k$. In terms of f, the energy flux is given by:

$$\vec{Q}=\frac{1}{V_s}\sum_{states}E(\vec{k})\,\vec{\upsilon}(\vec{k})f(\vec{r};t) \tag{3.33}$$

where $E(\vec{k})$ is the electron energy and $\upsilon(\vec{k})$ is the electron velocity.

The change in f is attributed to the electric fields, the scattering of

electrons and the diffusion of electrons from regions of high concentration to ones of low concentrations. Taking the rate at which f changes due to diffusion meachanisms to be $-\vec{\upsilon}.\vec{\nabla}_r f$, then the Boltzmann equation for electrons becomes

$$\frac{\partial f}{\partial t} = \frac{e}{\hbar}\vec{\varepsilon}\cdot\vec{\nabla}_k f - \vec{\upsilon}\cdot\vec{\nabla}_r f - \frac{f - f^0}{\tau} \tag{3.34}$$

where f^0 is the Fermi-Dirac distribution function. In the steady state equation (3.34) must equal to zero. Therefore, the Boltzmann equation for electrons becomes

$$-\frac{e}{\hbar}\vec{\varepsilon}\cdot\vec{\nabla}_k f - \vec{\upsilon}\cdot\vec{\nabla}_r f = -\left(\frac{\partial f}{\partial t}\right)_{Coll} = -\frac{f - f^0}{\tau} \tag{3.35}$$

The electron relaxation-time may be written as

$$\frac{1}{\tau} = \int (1 - f(\vec{k}')\,\omega_{kk'}\,\frac{d^3\vec{k}'}{(2\pi\hbar)^3} \tag{3.36}$$

The basic problem is to solve this equation for f; the flow of electrons and that of energy followed. To solve equation (3.35), let $f = f^0 + f_1$, and suppose f_1 is sufficiently small that it may be neglected in the field and the diffusion terms. In the steady state, $\frac{\partial f}{\partial t} = 0$, and hence;

$$f_1 = \frac{e\tau}{\hbar}\vec{\varepsilon}\cdot\vec{\nabla}_k f^0 - \tau\vec{\upsilon}\cdot\vec{\nabla} f^0 \tag{3.37}$$

In this part of study, our interest is focused on the flow of energy when the current is zero. To produce this situation, an electric field must be present. The field may be applied externally or it may be due to charges in material. In either case, we retain the field dependent terms of equation (3.37). In such a case, the gradients of f in equation (3.37) may have the following forms

$$\vec{\nabla}_k f^0 = \frac{\partial f^0}{\partial \mathrm{E}} \vec{\nabla}_k \mathrm{E} = \hbar \left(\frac{\partial f^0}{\partial \mathrm{E}} \right) \vec{\upsilon} \tag{3.38}$$

and

$$\vec{\nabla} f^0 = \frac{\mathrm{d} f^0}{\mathrm{dT}} \vec{\nabla} \mathrm{T}. \tag{3.39}$$

After substituting equations (3.38) and (3.39) into equation (3.37), we get

$$f_1 = \tau \frac{\partial f^0}{\partial E} \vec{\mathrm{v}} \cdot \vec{\varepsilon} - \tau \frac{\partial f^0}{\partial \mathrm{T}} \vec{\upsilon} \cdot \vec{\nabla} \mathrm{T} \tag{3.40}$$

Some common quantities between the field and the diffusion terms can be factorized by writing,

$$\frac{\partial f^0}{\partial \mathrm{T}} = \frac{\partial f^0}{\partial \mathrm{E}} \mathrm{T} \frac{\mathrm{d}}{\mathrm{dT}} \left(\frac{\varepsilon - \mu}{\mathrm{T}} \right) \tag{3.41}$$

A relationship becomes obvious once the two derivatives, $\partial f^0 / \partial \varepsilon$ and $\partial f^0 / \partial t$, are obtained. Including the temperature dependence of the Fermi energy, one may write equation (3.39) as (Drabble and Goldsmild, 1961)

$$f_1 = \tau \frac{\partial f^0}{\partial E} \vec{\upsilon} \cdot \left[e\vec{\varepsilon} + \vec{\nabla} T \left(\frac{E}{T} + T \frac{d}{dT} \left(\frac{\mu}{T} \right) \right) \right] \qquad (3.42)$$

Inserting equation (3.42) into equation (3.33), the energy flux tensor becomes,

$$\ddot{Q} = \frac{1}{V_s} \sum_{states} \tau \frac{\partial f^0}{\partial E} E \, \vec{\upsilon}\vec{\upsilon} \cdot \left[e\vec{\varepsilon} + \vec{\nabla} T \left(\frac{E}{T} + T \frac{d}{dT} \left(\frac{\mu}{T} \right) \right) \right] \qquad (3.43)$$

The current density $\vec{J}$ can be introduced in terms of the distribution function as:

$$\vec{J} = \frac{-e}{V_s} \sum_{states} f(\vec{k}) \, \vec{\upsilon}(\vec{k}) \qquad (3.44)$$

Substituting equation (3.42) into equation (3.44) we get,

$$\vec{J} = \frac{-e}{V_s} \sum_{states} \tau \frac{\partial f^0}{\partial E} \vec{\upsilon}\vec{\upsilon} \cdot \left[e\vec{\varepsilon} + \vec{\nabla} T \left(\frac{E}{T} + T \frac{d}{dT} \left(\frac{\mu}{T} \right) \right) \right] \qquad (3.45)$$

The appearance of $\partial f^0 / \partial E$ in the $\vec{J}$ and $\ddot{Q}$ expressions indicates that states with energy near the Fermi energy dominant the sums. For a semiconductor only electrons near the bottom of the conduction band and holes near the top of the valence band are responsible for charge transport. If the current density $\vec{J}$ is set equal to zero in equation (3.45), then equations (3.44) and (3.33) can be solved simultaneously for both $\ddot{Q}$

and $\vec{\varepsilon}$.

Although the idea is simple, the procedure is complicated by the appearance of $\vec{\varepsilon}$ and $\vec{\nabla}T$ in the scalar product with $\vec{\upsilon}$. Rather than treating the general situation, we consider the situation for which the energy flux is due to electrons in a single isotropic band restricted to scatter in one dimension and take the temperature gradient to be in the z-direction, so that $\vec{\nabla}T = \left(\frac{dT}{dz}\right)\hat{z}$, then, the sums are converted to integrals over the band boundaries.

If the temperature gradient is along the z-axis, the heat flow equation (2.45) becomes

$$J_z = -\frac{me}{2}\left(\frac{\hbar}{m}\right)^4 \int k^2\, k_z\, \tau \left[\frac{\hbar}{m}\frac{\partial f}{\partial T}\frac{\partial T}{\partial z} - \frac{m}{\hbar}\frac{\partial f}{\partial k_z}\varepsilon_z^T\right] d\vec{k} \qquad (3.46)$$

where ε_z^T is the electric field induced by the temperature gradient.

Thermal conduction measurements are carried out under open electrical circuits conditions. The electric current vector in equation (2.44), therefore, vanishes. Since, in the present case, $\nabla T \rightarrow \frac{dT}{dz}, \varepsilon \rightarrow \varepsilon_z^T$, and B=0, we can set $\vec{J}_{elc} = 0$ in equation (2.44) and solve for ε_z^T. The result is

$$\varepsilon_z^T = \frac{\hbar}{e}\frac{\int \tau k_z^2 \frac{\partial f}{\partial k_z}\, d^3\vec{k}}{\int \tau \upsilon_z \frac{\partial f}{\partial k_z}\, d^3\vec{k}}\frac{dT}{dz} \qquad (3.47)$$

Now ε_z^T can be eliminated from equation (3.46) to give the heat flow in terms of the temperature gradient above. This gives

$$Q_{zz} = -\frac{m}{2}\left[\frac{\Gamma_2\Gamma_3 - \Gamma_1\Gamma_4}{\Gamma_2}\right]\frac{dT}{dz} \tag{3.48}$$

where the Γ's are defined by

$$\Gamma_1 = \left(\frac{\hbar}{m}\right)^3 \int \tau\, k_z^2 \frac{\partial f}{\partial T} d^3\vec{k} \tag{3.49}$$

$$\Gamma_2 = \left(\frac{\hbar}{m}\right) \int \tau\, k_z \frac{\partial f}{\partial k_z} d^3\vec{k} \tag{3.50}$$

$$\Gamma_3 = \left(\frac{\hbar}{m}\right)^5 \int \tau\, k_z^2 k^2 \frac{\partial f}{\partial T} d^3\vec{k} \tag{3.51}$$

$$\Gamma_4 = \left(\frac{\hbar}{m}\right)^3 \int \tau\, k_z k^2 \frac{\partial f}{\partial k_z} d^3\vec{k} \tag{3.52}$$

To evaluate the above integrals, it is convenient to express the above integrals in terms of energy rather than momenta. To do this replace $\frac{\partial f}{\partial k_z} = \frac{\partial f}{\partial E}\frac{\partial E}{\partial k_z} = \hbar k_z \frac{\partial f}{\partial E}$, $d^3\vec{k} = 4\pi\, k^2 dk$, $\upsilon_z^2 = \frac{1}{3}\upsilon^2$. The results are as follows

$$\Gamma_1 = \frac{-e}{3V_s}\int \tau\, \upsilon^2 \frac{\partial f_0}{\partial E}\rho(E)\, dE, \tag{3.53}$$

$$\Gamma_2 = \frac{-e}{3V_s}\int \tau\, \upsilon^2 \left[\frac{E}{T} + T\frac{d}{dt}\left(\frac{\mu}{T}\right)\right]\frac{\partial f_0}{\partial E}\rho(E)\, dE \tag{3.54}$$

$$\Gamma_3 = \frac{-e}{3V_s}\int \tau\, \upsilon^2 E \frac{\partial f_0}{\partial E}\rho(E)\, dE \tag{3.55}$$

and

$$\Gamma_4 = \frac{-1}{3V_s}\int \tau\, \upsilon^2 E \left[\frac{E}{T} + T\frac{d}{dt}\left(\frac{\mu}{T}\right)\right]\frac{\partial f_0}{\partial E}\rho(E)\, dE \tag{3.56}$$

By definition, the coefficient of $-\frac{dT}{dz}$ on the right-hand side equation of (3.48) is the thermal conductivity κ. Therefore, by comparing equation (3.48) and equation (3.16), one obtains the following expression for the thermal conductivity

$$\kappa = \frac{m}{2}\left[\frac{\Gamma_2\Gamma_3 - \Gamma_1\Gamma_4}{\Gamma_2}\right] \tag{3.57}$$

For completion the derivation of thermal conductivity, let us evaluate the gamma functions appeared in equations (3.53)-(3.57) assuming uniform of relaxation-time. This can be done by replacing υ^2 by $2E/m^*$ (m^* is the effective mass) and the density of states $\rho(E)$, shown in Figure 3.2, by $\left(\sqrt{2}V_S(m^*)^{\frac{3}{2}}/\pi^2h^2\right)\sqrt{E}$ (Kittle 1976). The results are then summarized in the following expressions (Chirstman 1988):

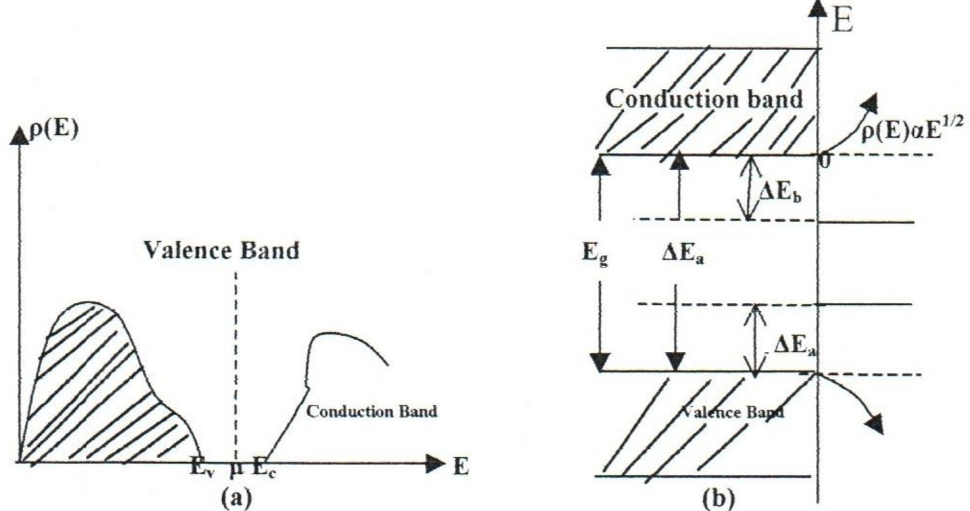


Figure 3.2.(a) Electronic density of states for a semiconductor (b)Semiconductor model showing conduction and valence bands.

$$\Gamma_1 = \frac{2\sqrt{2m^*}\tau}{3\pi^2\hbar^3} e^2 \mu^{\frac{3}{2}} \tag{3.58}$$

$$\Gamma_2 = \frac{2e\sqrt{2m^*}\tau}{9\hbar^3} k_B^2 T \mu^{\frac{1}{2}} \tag{3.59}$$

$$\Gamma_3 = e\frac{2\sqrt{2m^*}\tau}{3\pi^2\hbar^3} \mu^{\frac{5}{2}} \tag{3.60}$$

and

$$\Gamma_4 = \frac{4\sqrt{2m^*}\tau}{9\hbar^3} k_B{}^2 T\mu^{\frac{3}{2}} \tag{3.61}$$

When expressions (4.58)-(4.61) are substituted into equation (3.57) and μ is replaced by the expression $\left(\frac{\hbar^2}{2m^*}(3\pi^2 n)^{\frac{2}{3}}\right)$, where n is the electron concentration, we get

$$\kappa = \frac{\pi^2 n\,\tau}{3m^*} k_B^2 T \tag{3.62}$$

Note that the relaxation-time enters into the final result only through its value for $E = \mu$. If the relaxation-time or the effective mass depends on energy, their values corresponding to the Fermi energy should be used in equation (3.62).

3.5 The scattering processes

In the simplest transport model, atomic equilibrium positions are arranged throughout all space with perfect periodicity and each atom is assumed to move under the influence of harmonic forces (phonons) only. Electrons are assumed to occupy single particle states and to influence each other through their average electrostatic interaction. The number of electrons in each state and the number phonons in each vibrational mode remain constant in time. Relaxation-times are infinite and charge or energy flux continues unabated once it is created.

3.5.1 Scattering by phonons

The potential energy function that describes the interaction between atoms contains anharmonic terms. Energy is transferred between harmonic modes or, in the language of quantum mechanics, phonon-phonon scattering occurs. In the most likely phonon-phonon event, two phonons disappear and another appears. Assuming normal scattering events, energies and crystal momenta obey

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \qquad (3.63)$$

and

$$\hbar\vec{q}_1 + \hbar\vec{q}_2 = \hbar\vec{q}_3 \qquad (3.64)$$

respectively, where subscript 1 and 2 refer to the original phonon and 3

$$E(\vec{k}') = E(\vec{k}) \pm \hbar\omega(\vec{q}) \qquad (3.67)$$

or

$$\frac{\hbar^2 k'^2}{2m} = \frac{\hbar^2 k^2}{2m} \pm \hbar\omega(\vec{q}) \qquad (2.68)$$

And rhe conservation of momentum equation satisfies

$$\hbar\,\vec{k} \pm \hbar\,\vec{q} = \hbar\,\vec{k}' + \hbar\vec{G} \qquad (3.69)$$

The positive and negative signs correspond to the absorption and the emission of a phonon of wave vector $\vec{q}$. The vector $\vec{G}$ is known as the reciprocal lattice vector; $\vec{G} = 0$ corresponds to electron-phonon normal processes and $\vec{G} \neq 0$ corresponds to the Umklapp or U-processes. The number of scattering events per unit time is proportional to the number of phonons available with appropriate propagation constants and is therefore temperature dependent. The relaxation-time is inversely proportional to the number of scattering events (Christman, 1988). The Boltzmann equation may be written as

$$-\upsilon_e.\vec{\nabla}T\frac{\partial f}{\partial T} - \upsilon_{\vec{q}}.\vec{\nabla}T\frac{\partial n_q}{\partial T} = \iint \{ f(\vec{k})\, n_{\vec{q}'}(1 - f(\vec{k}')) - (1 + n_{\vec{q}})(1 - f(\vec{k}))(f(\vec{k}') \} \times \omega_{\vec{q}\vec{q}'} d^3\vec{k} d^3\vec{k}' \qquad (3.70)$$

The difficulty in solving the electron Boltzmann equation when phonons act as scattering agents that requires a knowledge of the phonon distribution as well as the electron distribution is simplified by replacing

the phonon distribution by its equilibrium value. This assumption implies that the electron and phonon systems produce entropy independently of each other since they are associated with the departures of the corresponding distribution functions from equilibrium. This in turn neglects the phonon drag effects that emerge as a direct consequence of coupling the entropy production of the two systems via the electron-phonon interaction.

3.5.3 Scattering by defects

All structural defects affect the atomic vibrations and the electron distribution function. A point defect may have a different distribution of atoms around it, may couple with different force constants to neighboring atoms, may have different mass, and may be responsible for a different electron potential energy function. Similar effects occur for boundaries and dislocations. As a result, defects provide mechanisms by which the number of phonons in a normal mode and the occupation probability of an electron state may change.

The influence of the structural effects can be discussed in terms of the mean-free-path ℓ of electrons or phonons. It is related to the relaxation-time by $\ell = \upsilon\tau$, where υ is the electron or phonon speed, and it gives the average distance traveled by a phonon or electron between scattering events. When point defect scattering dominates, we expect the man-free-path for both phonons and electrons to be of the order of defect

separations or sample dimensions. In either case, it is relatively insensitive to the temperature and, as a result, so is the relaxation-time. When three-phonon normal processes are considered along with the defect scattering, the thermal conductivity expression is written as (Bhandari *et al*, 1988)

$$\frac{1}{\kappa}=\frac{\frac{1}{2k_BT^2}\iint\left\{\Phi_{\vec{q}}-\Phi_{\vec{q}'}\right\}\omega_{\vec{q}\vec{q}'}\,d^3\vec{q}d^3\vec{q}'+\iiint\left\{\Phi_{\vec{q}}+\Phi_{\vec{q}'}-\Phi_{\vec{q}''}\right\}\omega_{\vec{q}\vec{q}'}\,d^3\vec{q}d^3\vec{q}'d^3\vec{q}''}{\left[\frac{1}{T}\int E_{\vec{q}}\upsilon_{\vec{q}}\Phi_{\vec{q}}\frac{\partial n_{\vec{q}}^0}{\partial E_{\vec{q}}}d^3\vec{q}\right]^2} \tag{3.71}$$

3.5.4 Multiple scattering mechanisms

Thermal conduction in semiconductors requires more than one scattering mechanism may operate on the same system. The simplest case in this model assumes different mechanisms are not affected by each other, so that each mechanism has its own collision term and its contributes to the total collision term is added to other mechanisms contributions. Thus

$$\left(\frac{\partial f}{\partial t}\right)_{scatt}=-\frac{n-n^0}{\tau_{ph}}-\frac{f-f^0}{\tau_e}-\frac{f-f^0}{\tau_{imp}}------- \tag{3.72}$$

where τ_{ph} is phonon relaxation-time, τ_e is the electron relaxation-time, τ_{imp} is the impurity relaxation-time----. There are as many terms on the right-hand side of equation (3.72) as there are mechanisms.

If the relaxation-time for one mechanism is much shorter than all others, scattering takes place predominately via other mechanisms.

The thermal and electrical resistivities, not conductivities, are proportional to the reciprocal of the relaxation-time so, in each case, the total resistivity may be written as a sum of contributions of the various scattering mechanisms. In this study, the electron and the phonon contributions to the thermal conductivity play a major part in calculating the total thermal conductivity.

state $\vec{k}+\left(\frac{e\vec{\varepsilon}}{h}\right)\Delta t$ moves to the state $\vec{k}$, so,

$$f(\vec{k},t+\Delta t)=f\left(\vec{k}+\frac{e\,\vec{\varepsilon}\,\Delta t}{\hbar},t\right)+\frac{e\vec{\varepsilon}\cdot\vec{\nabla}_k f}{\hbar}\Delta t \tag{4.3}$$

In the limit as Δt becomes small, then,

$$\left(\frac{\partial f}{\partial t}\right)_{\text{field}}=\lim_{\Delta t\to 0}\frac{f(\vec{k},t+\Delta t)-f(\vec{k};t)}{\Delta t}\Bigg|_{\text{field}}=\frac{e}{\hbar}\vec{\varepsilon}.\vec{\nabla}_k f \tag{4.4}$$

The scattering term according to the RTA is taken to be

$$\left(\frac{\partial f}{\partial t}\right)_{\text{scatt}}=-\frac{f(\vec{k};t)-f^{0}(\vec{k})}{\tau} \tag{4.5}$$

Where τ is the relaxation-time, and f^0 is the Fermi-Dirac distribution function. If the solid is not in the thermal equilibrium, f may change with time because both the electric field and the scattering cause transitions, so we write,

$$\frac{\partial f}{\partial t}=\left(\frac{\partial f}{\partial t}\right)_{\text{field}}+\left(\frac{\partial f}{\partial t}\right)_{\text{scatt}} \tag{4.6}$$

or

$$\frac{\partial f}{\partial t}=\frac{e}{\hbar}\vec{\varepsilon}\cdot\vec{\nabla}_k f-\frac{f(\vec{k};t)-f^{0}(\vec{k})}{\tau} \tag{4.7}$$

This is the Boltzmann transport equation that specialized to a situation for which only an electric field is applied.

When electrons have a non-equilibrium distribution $f(\vec{k};0)$ at time $t=0$ and no electric field exists, the distribution function according to the RTA then satisfies.

$$\frac{\partial f}{\partial t} = -\frac{f - f^{0}}{\tau} \tag{4.8}$$

This differential equation (4.8) has a solution of the form

$$f(\vec{k};t) = f^{0}(\vec{k}) + \left[f(\vec{k};0) - f^{0}(\vec{k})\right]e^{\frac{-t}{\tau}} \tag{4.9}$$

The distribution relaxes exponentially to the equilibrium distribution and, after a time interval equal to a small multiple of τ; the electron system is essentially in thermal equilibrium.

Let us now try to solve equation (4.7) in the presence of a small electric applied and the electron distribution is nearly close to thermal equilibrium distribution. In this case the distribution function f can be written as $f(k,t) = f^{0} + f_{1}(k,t)$, where f_{1} is small disturbance of f and assume $\left(\vec{\varepsilon}.\vec{\nabla}_{k} f_{1}\right)$ is negligible. Then equation (4.8) becomes,

$$\frac{\partial f_{1}}{\partial t} = \frac{e}{\hbar}\vec{\varepsilon}\cdot\vec{\nabla}_{k} f^{0} - \frac{f_{1}}{\tau} = e\vec{\varepsilon}\cdot\vec{\upsilon}\,\frac{\partial f^{0}}{\partial E} - \frac{f_{1}}{\tau} \tag{4.10}$$

To obtain the second equality, the chain rule for differentiation was used to $\vec{\nabla}_{k} f^{0} = \frac{\partial f^{0}}{\partial E}\vec{\nabla}_{k}E$ and $\hbar\vec{\upsilon}$ was substituted for $\vec{\nabla}_{k}E$. If the field is turned on at time t=0, and the electron distribution is in thermal equilibrium,

then,

$$f_1(\vec{k};t) = e\vec{\varepsilon}\cdot\vec{\upsilon}\tau\frac{\partial f^0}{\partial E}\left(1-e^{\frac{-t}{\tau}}\right) \qquad (4.11)$$

For t >>τ, the electron system will reach a steady state with,

$$f(\vec{k}) = f^0(\vec{k}) + f_1(\vec{k}) = f^0(\vec{k}) + e\vec{\varepsilon}\cdot\vec{\upsilon}\,\tau\frac{\partial f^0}{\partial E} \qquad (4.12)$$

Where the argument has been omitted since the distribution is no longer time dependent.

Since $\frac{\partial f^0}{\partial E}$ is negative, equation (4.12) predicts that states for which the electron velocity is directed opposite to the field have a slightly higher probability of being occupied than they do in thermal equilibrium. Similarly, states for which the electron velocity is in the same direction as the field have a slightly lower probability. But $\frac{\partial f^0}{\partial E}$ is only large near the Fermi surface and only these states which lie near this surface are at first altered by the field. A steady state will finally be obtained at finite temperature when the affected of the applied field is balanced by the effect of the applied field is balanced by the effect of the collision. When such a state is reached, the distribution function is the one that satisfies equation (4.12), then steady state conduction is used to derive the relaxation-time expression in this case:

iii) The elastic scattering takes the particle from the f_1 distribution to the f_s distribution. This step has a relaxation time constant τ_1.

iv) The isotropic distribution f_s relaxes back to the equilibrium distribution f^0. This step has a different relaxation time τ_0, usually slower than τ_1.

The relaxation-time τ_1 from elastic scattering determines the rate at which particle scatter out of state f_1 distribution into the distributions such as f_s and f_2. The current is determined by τ_1 since it gives the steady state amplitude f_1.

4.4 The relaxation-time of the distribution function

There remains an important task, deriving a formula for the relaxation-time $\tau(\vec{k})$. It is not the time between scattering events, but the time needed by a system to thermalize.

The collision term can approximated using the relaxation time approximation as:

$$-\left(\frac{df}{dt}\right)_{coll} = \frac{f(\vec{k}) - f_0(\vec{k})}{\tau_1(\vec{k})}$$

$$= 2\pi\, n_i \int \frac{d^3\vec{k}'}{(2\pi)^3} \delta(E_k - E_{k'}) \omega_{kk'} f(\vec{k})[1 - f(\vec{k}')] - \omega_{k'k} f(\vec{k}')[1 - f(\vec{k})] \quad (4.16)$$

where $\omega_{kk'}$ is the transition rate and n_1 is the concentration of impurities.

The transition rate $\omega_{kk'}$ is related to the T-matrix by

$$\omega_{kk'} \sim T^2_{kk'} \tag{4.17}$$

the quantity $T_{kk'}$ is the scattering matrix element for scattering from $\vec{k}$ to $\vec{k}'$ states. The T matrix is symmetric in its indices $T_{\vec{k}\vec{k}'} = T_{\vec{k}'\vec{k}}$, so that we can simplify equation (4.16) to

$$\frac{f(\vec{k}) - f^0(\vec{k})}{\tau_1} = 2\pi\, n_i \int \frac{d^3\vec{k}'}{(2\pi\hbar)^3} \delta(E_k - E_{k'}) |T_{kk'}|^2 \left[f(\vec{k})(1 - f(\vec{k}') - f(\vec{k}')(1 - f(\vec{k}) \right] \tag{4.18}$$

the integrand in equation (4.18) contains the factor $f(\vec{k}) - f(\vec{k}')$. The integrand may be evaluated by assuming the form in equation (4.12), which is written as:

$$\left.\begin{aligned} f(\vec{k}) &= f^0(\vec{k}) + \vec{k}.\vec{\varepsilon}c(\vec{k}) \\ f(\vec{k}') &= f^0(\vec{k}) + \vec{k}'.\vec{\varepsilon}c(\vec{k}) \end{aligned}\right\} \tag{4.19}$$

since $|\vec{k}| = |\vec{k}'|$ and $f^0(\vec{k}) = f(\vec{k})$, the quantities $f(\vec{k})$ and $f(\vec{k}')$ differ only in the angular part of the second term. The angular part is treated as follows: define the coordinate system in which the z-direction is $\hat{k}$, so that.

$$\begin{aligned} &\hat{k}.\hat{\varepsilon} = \cos\theta \\ &\hat{k}'.\hat{k} = \cos\theta' \\ &\hat{k}'.\hat{\varepsilon} = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\varphi. \end{aligned} \tag{4.20}$$

where we have used the law of cosines in the last identity. The difference

of the two distribution functions may now be written out in terms of these angular variables:

$$\begin{aligned} f(\vec{k}) - f(\vec{k}') &= f(\vec{k}) - f^0(\vec{k}) - \left[f(\vec{k}') - f^0(\vec{k})\right] \\ &= \mathrm{k}\,\varepsilon\,\mathrm{c}(\mathrm{k})\left[\cos\theta(1-\cos\theta') - \sin\theta\sin\theta'\cos\varphi\right] \end{aligned} \tag{4.21}$$

the last term on the right, which contains the factor $\cos\varphi$ will vanish when we do the integral $\int_0^{2\pi} d\varphi$. There is no other φ dependence in the integrand of equation (4.18), and the average of $\cos\varphi$ is zero. The remaining term may be written as:

$$\begin{aligned} \int d\Omega_{k'}\left[f(\vec{k}) - f(\vec{k})\right] &= \mathrm{k}\varepsilon\,\mathrm{c}(\mathrm{k})\cos\theta'\int d\Omega_{\mathrm{k}'}(1-\cos\theta') \\ &= \left[f(\vec{k}) - f^0(\vec{k})\right]\int d\Omega_{\mathrm{k}'}(1-\cos\theta') \end{aligned} \tag{4.22}$$

the term $f(\vec{k}) - f^0(\vec{k})$ is the factored from both sides of the equation (4.18), which leaves the definition for the reciprocal of the relaxation-time:

$$\frac{1}{\tau_1(\mathrm{k})} = 2\pi\ \mathrm{n_i}\int\frac{d^3\vec{\mathrm{k}}'}{(2\pi\hbar)^3}\delta(\mathrm{E_k} - \mathrm{E_{k'}})|\mathrm{T_{kk'}}|^2(1-\cos\theta')(1 - f(\vec{\mathrm{k}}')) \tag{4.23}$$

where θ' is the angle between $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$. The factor $(1-\cos\theta')$ weights the amount of scattering of the electron by the impurity. Small angle scattering, where $\cos\theta' \cong 1$, is relatively unimportant in contribution to τ^{-1}. These events do little to impede the flow of electrons and so contribute

little to resistivity. The factor $(1-\cos\theta')$ obviously favors large angle scattering events, which are more important for electrical resistivity

4.5 The electron current density, J

The current density J for a collection of a moving charged particles, each moving with velocity υ and carrying a charge q, is given by $\vec{J} = nq\vec{\upsilon}$, where n is the particle concentration, J is a vector in the direction of particle velocity for positive charges and in the opposite direction for negative charges.

The current density $\vec{J}$ in a solid, is the product of the electron charge –e, the electrons density n_0, and the average velocity $\langle\vec{\upsilon}\rangle$, which is obtained by averaging over the electron distribution. Taking $f(\vec{k})/V_s$ where V_s is the sample volume, to be the electron concentration associated with a state and summing the contribution of all electrons to get:

$$\vec{J} = -en_0\langle\upsilon\rangle = \frac{-en_0}{V_s}\sum_{states} f(\vec{k})\,\vec{\upsilon}(\vec{k}) \qquad (4.24)$$

By changing the summation into integration, we have for the current density

$$\vec{J} = 2\int d^3\vec{k}\, n_0 e\, \vec{\upsilon}\frac{f(\vec{k})}{(2\pi\hbar)^3} \qquad (4.25)$$

where the factor 2 is for spin degeneracy. The distribution function is

In a homogenous, isotropic system, the current $\vec{J}$ flows in the direction of $\vec{\varepsilon}$. The quantity $f^0(\vec{k})$ is independent of $\vec{k}$ directions. The only angular factors are $\vec{\upsilon}_k(\vec{\upsilon}_k, \vec{\varepsilon})$. Since $\partial f^0 / \partial \vec{k}$ is only non-zero over a small range of $\vec{k}$ at the Fermi surface, and treating $\partial f^0 / \partial \vec{k}$ as a delta function to obtain

$$-\int_0^\infty \frac{\partial f_0}{\partial k} d^3\vec{k} = -1 \qquad (4.30)$$

The angular integrals will average this to $\frac{1}{3}\upsilon_k^2\vec{\varepsilon}$. The conductivity σ is the ratio between the magnitudes of $\vec{J}$ to $\vec{\varepsilon}$, which gives the following formula for the electrical conductivity

$$\sigma = \frac{J}{\varepsilon} = \frac{-e^2 n_0}{3} \int \frac{d^3\vec{k}}{(2\pi\hbar)^3} \tau \upsilon_k^2 \frac{\partial f^0}{\partial E_k} = \frac{n_0 e^2}{3m^2} \int \frac{d^3\vec{p}}{(2\pi\hbar)^3} \delta(E_p)\tau(p)P^2 \qquad (4.31)$$

Where τ is the relaxation-time.

At zero temperature, the derivative $\frac{\partial f^0}{\partial E_k}$ becomes a delta function $-\delta(E_k)$ which fixed $k = k_f$ (k_f = Fermi momentum), that is

$$f^0(k) = \frac{2}{n_0} \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \qquad (4.32)$$

and

$$\lim_{T \to 0} \frac{\partial f^0}{\partial E_k} = \frac{-2}{n_0} \delta(E\varepsilon_k) \qquad (4.33)$$

wave vector space. The scattering tends to relax the Fermi distribution back to its undisturbed configuration.

As shown in Figure 4.1 electrons in the leading edge of the displaced

where the factor 2 is for spin degeneracy. The angular integrals have already been done, so that we obtain

$$\sigma = \frac{2}{3}e^2\frac{4\pi}{(2\pi\hbar)^3}\upsilon_F^2 m k_F \tau(k_F) = \frac{e^2 n_0 \tau(k_F)}{m} \tag{4.34}$$

where we have used $n_0 = \frac{k_F^3}{3\pi^2}$. The relevant relaxation-time is for electrons at the Fermi surface. Yet the conductivity is proportional to the density n_0 of all conduction electrons and not just to those at the Fermi surface. When the electric field is first imposed, the equation $\dot{\vec{k}} = -\frac{e\vec{\varepsilon}}{\hbar}$ shows that all electrons in the Fermi sea is translationally shifted in the wave vector space. The scattering tends to relax the Fermi distribution back to its undisturbed configuration.

As shown in Figure 4.1, electrons in the leading edge of the displaced Fermi distribution are scattered back to the rear regions. Only those electrons at the Fermi surface can scatter. The electrons well below Fermi

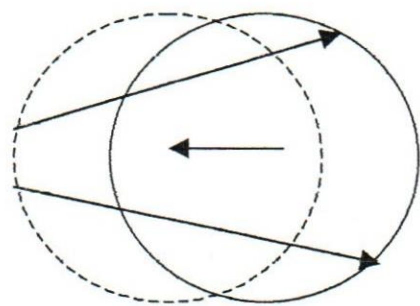


Figure 4.1 The circle represents the Fermi sea, which begins to move in response to applied electric field. Steady state is maintained by relaxation back to other points on the Fermi surface

surface can not elastically scatter, since all states with the same energy are already occupied with other electrons. Above the Fermi surface there are no thermally excited electrons. Thus, only electrons at the Fermi surface are available to elastically scatter to other points on the Fermi surface and equation (4.29) holds in the steady state if the field is weak, so

$$J_i = e\sum_{bands}\left[n\sum_j \mu_{ij}\,\varepsilon_j\right] \tag{4.35}$$

According to equation (4.35), the current density is proportional to the applied field and the relationship is usually written as:

$$J_i = \sum_j \sigma_{ij}\varepsilon_j \tag{4.36}$$

where

$$\sigma_{ij} = e\sum_{bands} n\,\mu_{ij} \tag{4.37}$$

is an element of the conductivity tensor. A tensor must be used, since the current density may not in the same direction as the field. For cubic crystals and amorphous metal materials, the conductivity tensor is diagonal with the three diagonal elements equal, so that

$$\vec{J} = \sigma\vec{\varepsilon} \tag{4.38}$$

Where σ is one of the diagonal elements. The current density and field

are in the same direction for such materials equation (4.38) is often written as $\varepsilon=\rho J$, where $\rho=1/\sigma$ is the electrical resistivity of the material.

4.7 The electron mobility of semiconductors

The average value of the current operator is the particle density n_0 times the charge e times the average velocity $\langle \upsilon \rangle$. In the steady state the average electron velocity is proportional to the applied electric field ε and the constant of proportionality is called the mobility. That is, $\langle \vec{\upsilon} \rangle = \mu \vec{\varepsilon}$ and

$$\vec{J} = -n_0 e \mu \vec{\varepsilon} \tag{4.39}$$

The mobility μ is defined as the average velocity of each electron per unit applied electric field. Of course, it is strictly defined in the limit of vanishing electric field. Since the electrical conductivity $\sigma = n_0 e^2 \frac{\tau}{m} = -n_0 e\mu$ is the ratio of the current density J to the electric field ε, the electron mobility is $\mu = \frac{-e\tau}{m^*}$.

For many metals the average electron velocity is not parallel to the electric field and the mobility is represented by a tensor. If υ_{avi} is the average electron velocity in a certain direction i and ε_j is the applied electric field in j direction, then elements μ_{ij} of the mobility tensor are defined by

$$\upsilon_{avei} = -\sum_j \mu_{ij} \varepsilon_j \tag{4.40}$$

The average velocity is often called the electron drift velocity. To obtain an expression for μ_{ij}, start with,

$$\upsilon_{avei} = \frac{1}{N}\sum_{states} \vec{\upsilon}_i(\vec{k})\, f(\vec{k}) \tag{4.41}$$

Where N is the number of electrons in the band, and substitute for $f(\vec{k})$ from equation (4.13). Terms containing $f^0(\vec{k})$ sum to zero and terms containing $\frac{\partial f^0}{\partial E}$ yields:

$$\upsilon_{avei} = \frac{e}{N}\sum_{ststes} \upsilon_i \vec{\varepsilon}\cdot\vec{\upsilon}\,\tau \frac{\partial f^0}{\partial E} \tag{4.42}$$

Comparison with equation (4.40) reveals that,

$$\mu_{ij} = \frac{-e}{N}\sum_{states} \tau\, \vec{\upsilon}_i\, \vec{\upsilon}_j \frac{\partial f^0}{\partial E} \tag{4.43}$$

Since, $\frac{\partial f^0}{\partial E}$ decreases rapidly as the distance between the energy and the Fermi energy increases. States that are close in energy to the Fermi energy dominate the sum in equation (4.43). For semiconductors only mobility associated with conduction bands is significant.

Consider a band for which the mobility is a scalar and start by converting equation (4.43) to an integral over energy as

$$\mu = \frac{-e}{3N}\int \tau\, \upsilon^2 \frac{\partial f^0}{\partial E}\rho(E)\,dE \tag{4.44}$$

where $\rho(E)$ is the density of the states per unit volume. When $i \neq j$ $\upsilon_i\upsilon_j$ and $-\upsilon_i\upsilon_j$ occur with equal weighting factor, so terms containing these factors cancel. Furthermore weighting factors for υx^2, υy^2, and υz^2 are all the same, so $\mu_{xx}=\mu_{yy}=\mu_{zz}$ and the scalar mobility μ is taken to be the any one of the diagonal elements.

Next, consider the conduction band of a semiconductor, well above the Fermi energy. The Fermi-Dirac distribution can then be approximated by,

$$f^0 \cong e^{-\left(\frac{E-\mu}{k_B T}\right)}, \tag{4.45}$$

and

$$\frac{\partial f^0}{\partial E} = -\frac{1}{k_B T} e^{-\left(\frac{E-\mu}{k_B T}\right)}. \tag{4.46}$$

If the electron energy is given by $E(k) = \frac{\hbar^2 k^2}{2m^*}$ where m* is the effective mass of the electron. The density of states is $\rho(E) = A\sqrt{E}\ \sqrt{E}$, where A is a constant, and equation (4.44) becomes,

$$\mu = \frac{2\,eAB}{3Nm^* k_B T}\int_0^\infty \tau E^{\frac{3}{2}} e^{-\frac{(E-\mu)}{k_B T}}\, dE \tag{4.47}$$

As we shall see, the relaxation-time is different for different states and must be considered a function of energy. Since the number of electrons in the band is given by,

$$N = \int f^0(E)\rho(E)\,dE \tag{4.48}$$

integration of equation (4.48) by parts yields,

$$N = \left(\frac{2A}{3k_B T}\right)\int E^{\frac{3}{2}} e^{-\frac{(E-\mu)}{K_B T}} dE \tag{4.49}$$

When this expression is solved for A/N and substituted in equation (4.47), factors containing the Fermi energy cancel and the result becomes,

$$\mu_e = \frac{e\langle\tau\rangle}{m^*} \tag{4.50}$$

where,

$$\langle\tau\rangle = \frac{\int \tau E^{\frac{3}{2}} e^{-\left(\frac{E-\mu}{k_B T}\right)} dE}{\int E^{\frac{3}{2}} e^{-\left(\frac{E-\mu}{k_B T}\right)} dE} \tag{4.51}$$

Both integrals in equation (4.51) are evaluated overall the conduction band energy. Equation (4.50) has the same form as the electron mobility for metals but an average relaxation-time is used rather than the value corresponding to the Fermi level.

4.8. The hole electrical transport properties

4.8.1 The Boltzmann transport equation for holes

Properties of a nearly full band are usually ascribed to holes rather than electrons. Although the number of holes in a band equals the number of empty states, a hole is not simply an empty state. In particular, a single hole in a full band must account for the collective properties of all electrons in the band.

Consider a single band and let $f_h(\vec{k};t)$ represents the probability that a state with a wave vector k_h is occupied at time t with a hole. In the relaxation-time approximation, the hole distribution function , f_h,obeys

$$\frac{\partial f_h}{\partial t} = \frac{-e}{\hbar}\vec{\varepsilon}.\vec{\nabla}_{kh} f_h - \frac{f_h - f_{h_0}}{\tau_h} \qquad (4.52)$$

Where f_{h0} is the hole equilibrium distribution that can be written as

$$f_{h0} = \frac{1}{e^{\frac{-(E-\mu)}{k_B T}} - 1} \qquad (4.53)$$

Equation (4.52) looks like equation (4.7) except that the hole momentum replaces the electron momentum and the sign of the charge is changed. When steady state is reached in a weak electric field,

$$f_h(\vec{k}_h) = f_{h0}(\vec{k}_h) + e\vec{\varepsilon}.\vec{\upsilon}\,\tau\frac{\partial f_h}{\partial E} \qquad (4.54)$$

where

$$\vec{\nabla}_{kh} f_{h_0} = \left(\frac{\partial f_{h0}}{\partial E}\right)\vec{\nabla}_{kh}E = -\left(\frac{\partial f_{h_0}}{\partial E}\right)\hbar\,\vec{\upsilon} \qquad (4.55)$$

If there are N holes in the band, their average velocity is

$$\vec{\upsilon}_{h\ ave} = \frac{1}{N}\sum_{states}\vec{\upsilon}(\vec{k})f_h(\vec{k}) \qquad (4.56)$$

Which has a linear dependence on electric field.

4.8.2. The hole mobility

The hole mobility tensor, with elements μ_{ij}, is defined by

$$(\upsilon_h)_{ave\ i} = \sum_j \mu_{ij}\varepsilon_j \qquad (4.57)$$

This definition differs from that for electrons only in the sign. Once equation (4.54) is substituted in equation (4.56) and a comparison is made with equation (4.62), the hole mobility tensor may be expressed as

$$\mu_{ij} = \frac{e}{N}\sum_{states} \upsilon_i \upsilon_j \frac{\partial f_{h_0}}{\partial E} \qquad (4.58)$$

For cubic crystals the off-diagonal elements of mobility tensor vanish and diagonal all elements are all equal and $(\upsilon_h)_{ave} = \mu\varepsilon_{ij}$. Accordingly,

$$\mu_h = \frac{e}{3N}\sum_{states} \upsilon^2 \tau \frac{\partial f_{h_0}}{\partial E} \qquad (4.59)$$

Since $\frac{\partial f_{h0}}{\partial E}$ is positive, μ_h is positive and the average hole velocity is in the same direction as the applied field.

As an illustration of the hole mobility, we consider a valence band with energy given by $E = -\frac{\hbar^2 k^2}{2m_h^*}$, where m_h^* is the hole effective mass. The zero of the energy is taken to be zero at the top of the band. The density of states can be written $\rho(E)=A(\sqrt{-E})$. If the valence band is well below the Fermi energy, then the equilibrium distribution function of holes can

be approximated by: $f_{h0}=\exp((E-\mu)/k_BT)$. The calculation is similar for that of electrons and the result in this case can be written as

$$\mu_h = \frac{e\langle\tau\rangle}{m_h^*} \tag{4.60}$$

where,

$$\langle\tau\rangle = \frac{\int \tau\,(-E)^{\frac{3}{2}}\, e^{\frac{E-\mu}{k_BT}}\, dE}{\int (-E)^{\frac{3}{2}}\, e^{\frac{E-\mu}{k_BT}}\, dE} \tag{4.61}$$

Both integrals are over the valence band energies. The average relaxation-time for holes in a valence band is not usually the same as that for electrons in a conduction band.

4.8.3. The hole current density

The hole current density is obtained by replacing the electron distribution function by $f(\vec{k}) = 1 - f_h(\vec{k})$ in equation (4.24), then the contribution of valence bands to the current density is

$$\vec{J} = \frac{e}{V_s}\sum\left[1 - f_h(\vec{k})\right]\vec{\upsilon} = \frac{e}{V_s}\sum f_h(\vec{k})\,\vec{\upsilon} \tag{4.62}$$

where the sums are over all states of the band. The last equality is valid since the sum of velocities associated with all states in a band vanishes. It is worth to note that holes contribute to the current density as particles with positive charges.

4.9 The current density and the electrical conductivity of semiconductors

The electrical properties of semiconductors are due to the motion of electrons and holes under the effect of applied electric field. For a semiconductor, the contribution of conduction band states are written in terms of electrons; while contributions of valence band states are written in terms of holes; thus,

$$\vec{J}_h = -\frac{e}{V_s}\sum_{cD} f(\vec{k})\vec{\upsilon} + \frac{e}{V_s}\sum_{vD} f_h(\vec{k})\vec{\upsilon} \qquad (4.63)$$

The first sum is over conduction band states and the second is over valence band states. In the steady state the average of both electron and hole velocities is proportional to the applied electric field and, for semiconductors with a single valence band, both velocities are isotropic, then the current density

$$\vec{J} = e(n_e\,\mu_e + n_h\,\mu_h)\vec{\varepsilon} \qquad (4.64)$$

Here n_e is the concentration (density) of electrons in the conduction band, n_h is the concentration of holes in the valence band, μ_e and μ_h are the electron and hole mobilities, respectively. Since the direction of the current is always conventionally taken to be the direction of flow of positive charges, the current in the semiconductor will be in the same

direction of flow of holes in both n-type and p-type semiconductors. The electric conductivity of a semiconductor is given by,

$$\sigma = e\left(n\mu_e + p\mu_h\right) \tag{4.65}$$

For intrinsic semiconductors, where the electron and hole concentrations are equals (n_e=n_h=n), the concentration of particles are given by (Kittle, 1975),

$$n = \frac{e}{4\pi^3}\left(\frac{2\pi\left(m_e^* m_h^*\right)^{\frac{1}{2}} k_B T}{\hbar^2}\right)^{\frac{3}{2}} e^{\frac{-E_g}{2k_B T}}\left(\mu_e + \mu_h\right) \tag{4.66}$$

Substituting equation (4.66) into equation (4.65), the electrical conductivity of semiconductors becomes:

$$\sigma_i = \frac{e}{4\pi^3}\left[\frac{2\pi\left(m_e^* m_h^*\right)^{\frac{1}{2}} k_B T}{\hbar^2}\right]^{\frac{3}{2}} e^{\frac{-E_g}{2k_B T}}\left(\mu_e + \mu_h\right) = en\ \left(\mu_e + \mu_h\right) \tag{4.67}$$

4.9.2. The AC electrical conductivity of semiconductors

An expression for the frequency dependent conductivity can be obtained from the Boltzmann transport equation, the general procedures are as follows: Consider electrons in a single band and use the relaxation time approximation to write,

$$\frac{\partial f}{\partial t} = \frac{e}{\hbar}\vec{\upsilon}\cdot\vec{\nabla}_k f - \vec{\upsilon}\cdot\vec{\nabla} f - \frac{f - f_0}{\tau} \tag{4.68}$$

Although, we have assumed that the temperature gradient vanishes, we must include the second term on the right-hand side of equation (4.68) because the electric field depends on r.

Consider a plane electromagnetic wave traveling in the positive z-direction with its electric field given by,

$$\vec{\varepsilon} = \varepsilon_0 \, e^{i(k_z z - \omega t)} \hat{z} \tag{4.69}$$

For a weak field assuming that,

$$f = f_0 + f_{10} e^{i(k_z z - \omega t)} \tag{4.70}$$

Where the second term is small compared to the first. The expression for f_{10} is obtained after substituting equation (4.70) into equation (4.68), neglecting the product $f_{10}\varepsilon$ and making use of the following expression

$$\nabla_k f = \frac{\partial f^0}{\partial E} \nabla_k E = \frac{\partial f^0}{\partial E} \hbar \vec{\upsilon} \tag{4.71}$$

The result is

$$f_{10} = \frac{e \, \varepsilon_0 \, \upsilon_x \, \tau}{1 - i\omega \tau + ik_z \upsilon_z \tau} \frac{\partial f^0}{\partial E} \tag{4.72}$$

The ratio $\frac{k_z \upsilon_z \tau}{\omega \tau}$ is small compared to 1, so the last term in the dominator can be neglected. Then, the z component of the current density, J_z, is

$$J_z = \frac{-e}{V_s}\sum_{states} \upsilon_z f_{10} e^{i(k_z z-\omega t)} = \frac{-e^2 \varepsilon}{V_s}\sum_{states}\frac{\tau \upsilon_z^2}{1-i\omega\omega}\frac{\partial f^0}{\partial E} = \sigma\,\varepsilon \qquad (4.73)$$

where the sum is over all energy states of the band. The factor that multiplies the electric field, ε, is the conductivity. Hence,

$$\sigma(\omega) = \frac{-e}{V_s}\sum \frac{\tau \upsilon_z^2}{1-i\omega\,\tau}\frac{\partial f^0}{\partial E} \qquad (4.74)$$

If the relaxation-time is independent of k, $\frac{1}{1-i\omega\,\tau}$ can be factorized from the sum and equation (4.74) can be written as:

$$\sigma(\omega) = \frac{\sigma_0}{1-i\omega\,z} = \frac{\sigma_0(1+i\omega\,\tau)}{1+\omega^2\tau^2} \qquad (4.75)$$

Where σ_0 is the dc conductivity or for ω=0. The real and the imaginary parts of σ displayed explicitly in the second expression of equation (4.75) remains a reasonable approximation even if the relaxation-time depends on k, provided τ is replaced by appropriate average.

Chapter Five

Charge Transport in Magnetic Fields

5.1. Introduction

Since nearly free electrons contribute to the magnetic properties of metals and semiconductors, so the application of a static magnetic field to a nearly free electrons system has two important consequences. Firstly, the propagation vector of each electron changes with time and secondly, the electron states and energy spectrum change.

In this chapter we consider several important phenomena that result from the motion of electrons in a magnetic field alone or in crossed electric and magnetic fields. We assume that the fields are weak and the electron distribution satisfies the Boltzmann transport equation.

5.2 The Boltzmann transport equation

As in previous chapters, let $f(\vec{k};t)$ represents the number of electrons in a state with propagation vector $\vec{k}$. When a solid in thermal equilibrium, then the distribution is the Fermi-Dirac distribution function f^0. At t+dt the number of electrons in a state with propagation vector $\vec{k}$ is the same as the number in a state with propagation constant $\vec{k}-\left(\frac{d\vec{k}}{dt}\right)dt$ at time t; that is,

$$f(\vec{k},t+dt)=f\left[\vec{k}-\frac{d\vec{k}}{dt}dt,t\right] \tag{5.1}$$

or

$$\frac{\partial f}{\partial t} = -\vec{\nabla}_k f . \frac{d\vec{k}}{dt} \tag{5.2}$$

In order to reproduce the Boltzmann transport equation for electrons in an electric field $\vec{\varepsilon}$ and a magnetic induction field $\vec{B}$, the Lorentz force, $\left(\frac{-e}{\hbar}\right)(\vec{\varepsilon} + \vec{v} \times \vec{B})$ is substituted for $\frac{d\vec{k}}{dt}$ and a relaxation term has to be added to equation (5.4). The result is

$$\frac{\partial f}{\partial t} = \frac{e}{\hbar} \vec{\nabla}_k f . (\vec{\varepsilon} + \vec{\upsilon} \times \vec{B}) - \frac{f - f^0}{\tau} \tag{5.3}$$

Where τ is the relaxation-time. The temperature is assumed to be uniform through out the sample. Since the fields are weak we may write $f = f^0 + f_1$ where f_1 is small, and take the product of $\vec{\nabla}_k f_1 \cdot \vec{\varepsilon}$ to be negligible. The same approximation can not be made for the magnetic field term without loosing the influence of the field. The following expression

$$\vec{\nabla}_k f^0 = \left(\frac{\partial f^0}{\partial E}\right) \vec{\nabla}_k E = \hbar \left(\frac{\partial f^0}{\partial E}\right) \vec{\upsilon}, \tag{5.4}$$

is a quantity perpendicular to $\vec{\upsilon} \times \vec{B}$. In the weak-field approximation, the Boltzmann equation becomes

$$\frac{\partial f}{\partial t} = e \frac{\partial f}{\partial E} \vec{\upsilon} . \vec{\varepsilon} + \frac{e}{\hbar} \vec{\nabla}_k f_1 \cdot (\vec{\upsilon} \times \vec{B}) - \frac{f_1}{\tau} \tag{5.5}$$

5.3. The current density and the conductivity

In the most general situation we consider an electric field, $\varepsilon = \varepsilon_0 \exp(i\omega t)$, perpendicular to a constant magnetic field $\vec{B}$. A static electric field is obtained by setting $\omega = 0$. If the electric component of an electromagnetic wave, $\vec{\varepsilon}$, has a sufficiently long wavelength, the spatial variation of ε and f may be neglected. In this case, the solution of equation (5.5) may be written as

$$f_1 = e\,\tau\left(\frac{\partial f_0}{\partial E}\right)\vec{\upsilon}\cdot\vec{A} \qquad (5.6)$$

where the vector A is independent of $\vec{k}$ and is proportional to $e^{i\omega t}$. Substituting equation (6.6) into equation (5.5), we get

$$i\omega\,\tau\,\vec{\upsilon}\cdot\vec{A} - \vec{\upsilon}\cdot\vec{\varepsilon} - \frac{e\,\tau}{\hbar}\vec{\nabla}_k\left(\vec{\upsilon}.\vec{A}\right)\cdot\left(\vec{\upsilon}\times\vec{B}\right) + \vec{\upsilon}\cdot\vec{A} = 0 \qquad (5.7)$$

Let us look at the simplest case when electrons are supposed to be in a band whose energy and velocity are given by,

$$E = \frac{\hbar^2 k^2}{2m^*}, \qquad (5.8)$$

$$\vec{\upsilon} = \frac{\hbar k}{m^*} = \frac{1}{\hbar}\frac{\partial E}{\partial \vec{k}} = \frac{1}{\hbar}\vec{\nabla}_k E(\vec{k}) \qquad (5.9)$$

where effective mass tensor is obtained by differentiating equation (5.9) with respect to time. The third term in equation (5.7) reads

$$\vec{\nabla}_k(\vec{\upsilon}\cdot\vec{A})-(\vec{\upsilon}\times\vec{B})=\frac{\hbar}{m^*}\vec{A}\cdot(\vec{\upsilon}\times\vec{B})=\frac{\hbar}{m^*}(\vec{B}\times\vec{A})\cdot\vec{\upsilon} \tag{5.10}$$

Substituting equation (5.8) and equation (5.10) into equation (5.7), we get

$$\vec{\upsilon}\cdot\left[i\,\omega\,\tau\,\vec{A}-\vec{\varepsilon}-\frac{e\,\tau}{m^*}\vec{B}\times\vec{A}+\vec{A}\right]=0 \tag{5.11}$$

The vector in brackets is not necessarily perpendicular to $\vec{\upsilon}$, so it vanishes. Assuming that ε, B, and $\vec{\varepsilon}\times\vec{B}$ are mutually orthogonal, the vector A may have the following term

$$\vec{A}=\alpha\vec{\upsilon}+\beta\vec{B}+\gamma\vec{\upsilon}\times\vec{B} \tag{5.12}$$

Substituting this form into equation (5.11), and using the vector identity,

$$\vec{B}\times\left(\vec{\varepsilon}\times\vec{B}\right)=B^2\vec{\varepsilon}-\vec{B}\cdot\vec{\varepsilon}\vec{\varepsilon}=B^2\vec{\varepsilon} \tag{5.13}$$

and solve for the three coefficients α,β and γ. The result for A can be written as

$$\vec{A}=\frac{1+i\omega\,\tau}{(1+i\omega\,\tau)^2+\omega_c^2\tau^2}\vec{\varepsilon}-\frac{e\tau}{m^*}\frac{\vec{\varepsilon}\times\vec{B}}{(1+i\omega\,\tau)^2+\omega_c^2\tau^2} \tag{5.14}$$

where $\omega_c=\dfrac{eB}{m^*}$.

The current density becomes

$$\vec{J}=\frac{-e}{V_s}\sum_{\text{states}}\vec{\upsilon}f_1(\vec{k})=\frac{-e^2}{V_s}\sum_{\text{states}}\tau\frac{\partial f^0}{\partial E}\vec{\upsilon}\vec{\upsilon}\cdot\vec{A}=\sigma_0\vec{A} \tag{5.15}$$

Where the sums over all states in the band and σ_0 is the dc conductivity in the absence of a magnetic field. In evaluating the sum over states we assumed the band is isotropic. For semiconductors τ and ω_c represent appropriate averages over the band, while for a metal they have values corresponding to the Fermi energy. When equation (5.14) is used, equation (5.15) becomes.

$$\vec{J} = \frac{\sigma_0 (1 + i\omega\,\tau)}{(1 + i\omega\,\tau)^2 + \omega_c^2 \tau^2} \vec{\varepsilon} - \frac{e\,\tau}{m^*} \frac{\sigma_0}{(1 + i\omega\,\tau)^2 + \omega_c^2 \tau^2} \vec{\varepsilon} \times \vec{B} \qquad (5.16)$$

Note the first term is along $\vec{\varepsilon}$ and the second is perpendicular to it, so the conductivity of a sample in a magnetic field is a tensor quantity.

5.4. Holes current density.

A similar analysis can be carried out for holes. In the relaxation-time approximation, the distribution function for holes f_h obeys a Boltzmann type:

$$\frac{\partial f_h}{\partial t} = \frac{-e}{\hbar} \vec{\nabla}_k f_h \cdot \left(\vec{\varepsilon} + \vec{\upsilon}_h \times \vec{B}\right) - \frac{f_h - f_{h_0}}{\tau} \qquad (5.17)$$

Following the same procedures as in section (5.3), we get,

$$\vec{J}_h = \frac{\sigma_{0h} (1 + i\omega\,\tau)}{(1 + i\omega\,\tau)^2 + \omega_c^2 \tau^2} \vec{\varepsilon} - \frac{e\,\tau}{m_h^*} \frac{\sigma_{0h}}{(1 + i\omega\,\tau)^2 + \omega_c^2 \tau^2} \vec{\varepsilon} \times \vec{B} \qquad (5.18)$$

5.5. The Hall coefficient

Measured values of Hall voltage, the magnetic field, and the current can be used to obtain information about the concentration of charge carriers and their mobilities. In some cases the sign of the Hall voltage can be used to determine the sign of the charge carriers and to distinguish n- from p- type semiconductors.

Consider a magnetic field $\vec{B}$ in the positive z direction, the applied electric field $\vec{\varepsilon}_a$ to be in the positive x-direction, and the Hall field ε_H to be only in the positive y-axis. We suppose the effective mass for electrons is m* and with ω=0, the current density is:

$$\vec{J} = \sigma_0 \vec{A} = \sigma_0 \frac{\varepsilon_a - \omega_c \tau \varepsilon_H}{1+\omega_c^2 \tau^2} \hat{x} + \sigma_0 \varepsilon_H + \frac{\omega_c \tau \varepsilon_a}{1+\omega_c^2 \tau^2} \hat{y} \qquad (5.19)$$

In the steady state J_y=0, so,

$$\varepsilon_H = -\omega_c \tau \varepsilon_a \qquad (5.20)$$

The x component of the current density is then $J_x = \sigma_0 \varepsilon_a$, just as if the magnetic field has vanished. Substitute $\varepsilon_a = \frac{J_x}{\sigma_0}$ into equation (5.20) and rearrange to find,

$$\frac{\varepsilon_H}{J_x B} = -\frac{\omega_c \tau}{\sigma_0 B} \qquad (5.21)$$

The ratio defined by $R_H = \frac{\varepsilon_H}{J_x B}$ is called the Hall coefficient. For electrons

where $\sigma_0 = \frac{e^2 n\tau}{m^*}$ and $\omega_c = \frac{eB}{m^*}$, the Hall coefficient becomes

$$R_H = -\frac{1}{ne} \tag{5.22}$$

and

$$n = -\frac{1}{eR_H} \tag{5.23}$$

Since $\sigma_0 = \mu en$, the electron mobility μ can also be found once R_H and σ_0 are known. It is usually given by $\mu = -R_H\sigma_0$.

If the charge is carried predominantly by holes, the sign of the Hall voltage is positive for the configuration described above. The Hall coeffecient, still given by equation (5.22), is now related to the hole concentration p by:

$$p = \frac{1}{eR_H} \tag{5.24}$$

The hole mobility is given by $\mu = R_H\sigma_0$ and R_H is positive.

Both electrons and holes contribute to the Hall effect in a lightly doped or in an intrinsic semiconductors. Although both types of carriers are swept to the same side of the sample by a magnetic field, the Hall voltage does not necessarily vanish.

Suppose a current consists of two groups of carriers, perhaps with different effective masses, relaxation-time, and concentrations. If the particles labeled 2 are holes and labeled 1 are electrons, we replace σ_1 by $en\mu_n$, $\omega_{c1}\tau_1$ by $\mu_n B, \sigma_2$ by $ep\mu_h$, and ω_{c2} by $-\mu_h B$. The total current density is given by

$$\vec{J} = \sigma_1 \vec{A}_1 + \sigma_2 \vec{A}_2 \tag{5.25}$$

To derive an expression for the Hall coefficient, first set J_y=0 and solve for ε_H in terms of ε_a, then evaluate $R_H = -\frac{\varepsilon_H}{J_y B}$. For simplicity we suppose $\omega\tau \langle\langle 1$ for each particle. Then,

$$\vec{J} = (\sigma_1 + \sigma_2)\varepsilon_a \hat{x} + [(\sigma_1 + \sigma_2)\varepsilon_H + (\sigma_1\omega_{c1}\tau_1 + \sigma_2\omega_{c2}\tau_2)\varepsilon_a]\hat{y} \tag{5.26}$$

By setting J_y equals to zero in equation (5.26), we get

$$\varepsilon_H = -\frac{\sigma_1\omega_{c1}\tau_1 + \sigma_2\omega_{c2}\tau_2}{\sigma_1 + \sigma_2}\varepsilon_a \tag{5.27}$$

The Hall coefficient is then follows

$$R_H = \frac{\varepsilon_H}{J_x B} = -\frac{\sigma_1\omega_{c1}\tau_1 + \sigma_1\omega_{c2}\tau_2}{(\sigma_1 + \sigma_2)^2} \tag{5.28}$$

Then making use of equations (5.23) and (5.24), equation (5.28) becomes

$$R_H = \frac{p\mu_h^2 - n\mu_n^2}{e(p\mu_h + n\mu_n)^2} \tag{5.29}$$

For intrinsic semiconductor, n=p, the Hall coefficient is simplified to

$$R_H = \frac{\mu_h - \mu_n}{en(\mu_n + \mu_h)} \tag{5.30}$$

If more than one type carrier contributes to the Hall effect, values of the Hall coefficient and conductivity are not sufficient to obtain carrier concentrations and mobilities.

Chapter Six

Results and Discussion

6.1. Introduction

In this chapter we shall discuss the method of numerical calculations used in calculating thermal and electrical properties of some semiconductor materials such as silicon and germanium. Besides, we present our results for thermal and electrical conductivities and their corresponding relaxation-times. Our results are based on the RTA model developed for this purpose.

In section 2 we discuss the numerical method and the technique used. In the same section we summarize the major processes of the computation in order to calculate the required quantities. In section 3 we discuss thermal properties and results. In section 4 we present the electrical results.

6.2 Numerical method of calculations

In this study, the electrical and thermal properties for some semiconductor materials are followed for an initial system composed of a Fermi sphere of temperature zero. The Fermi sphere is chosen to have a radius of 1.36 Å. In order to simplify the calculations, we have chosen a cylindrical box to place the sphere in.

We start our calculations by generating the initial distribution function. This distribution function is defined as

$$f_i(\bar{k};t) = \begin{cases} \theta(k_F - k) & , \text{fork} \le k_F \\ 0 & , \text{ othrwise.} \end{cases} \tag{6.1}$$

where θ is the step function. The time evolution of the distribution in equation (6.1) is described by the collisional part of the Boltzmann equation, which is solved numerically. The three-dimensional integral appeared in the QBE is integrated numerically in momentum-space and the new distribution function is evaluated on the grid points. The angular integrations are calculated by using Gaussian numerical method (8 points Gaussian quadrature); while integration over momenta are done by using Simpson's rule. Range of the momenta are: $0< k_x, k_y, k_z \le 3$ Å, so that the array storing the distribution function has a dimension 21×21 words. The distribution function is assumed to be zero outside this region. A constant time step at (0.05×10^{-6}sec) is used. The numerical calculation of the collision term gives the change of the distribution function. By the end of the time step a small fraction of particles of the representative ones have then acquired new momenta and a new non-equilibrium distribution function is formed. This distribution is then used in the second time step for the calculations of the new distribution function at the next time step. This procedure is then repeated for several time steps until eventually the steady state case is achieved. That is, the initial sharp distribution

function of a Fermi sphere is now represented by a hot Fermi sphere characterized by its temperature and its Fermi-Dirac distribution for system in equilibrium. The characteristic temperature and Fermi energy (chemical potential) of the hot Fermi sphere are calculated using energy and density conservation. We do this numerically by setting up tables of density and energy of the Fermi distribution function $f^0(\vec{k})$ as a function of temperature and chemical potential.

The transition rate for charge carriers is calculated by assuming a screened Coulomb interaction of the form

$$V(\vec{r}) = Z_1 Z_2 \frac{e^{-\frac{r}{a}}}{r} \tag{6.2}$$

where a is the screening radius. The differential cross section according to Born approximation (Matthews, 1974) is of the form

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{m}{2\pi\hbar^2}\right)^2 \frac{k_f}{k_i} \left|\tilde{V}(K)\right|^2 \tag{6.3}$$

where V(K) is the Fourier transform of the screened potential and **K=k**$_f$-**k**$_i$. Thus

$$\tilde{V}(K) = \int e^{i\vec{K}.\vec{r}} V(r) d^3\vec{r} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{iKr\cos\theta'} Z_1 Z_2 e^2 \frac{e^{-\frac{r}{a}}}{r} r^2 \sin\theta' dr\, d\theta' d\varphi'$$

$$= \frac{4\pi\ Z_1 Z_2 e^2}{K^2}(1 + \frac{1}{K^2 a^2}) \tag{6.4}$$

Therefore, the transition rate according to Fermi-Golden rule writes

$$\omega = \frac{2\pi}{\hbar}\left(\frac{Z_1 Z_2 e^2 m}{4\pi\,\varepsilon_0 \hbar^2 K^2}\right)^2 \rho(E) \tag{6.6}$$

The above expression is used for calculating the transition rates.

The macroscopic parameters such as thermal conductivity, electrical conductivity and relaxation-times are calculated from the distribution function.

In any theoretical analysis of thermal conductivity the electronic contribution must be separated from the lattice component; the latter can then be analyzed in terms of phonon transport. The theoretical calculations of the thermal conductivity can be carried out within the frame of the relaxation-time approximation.

1. the components of the flow electrons (holes) and energy are given by

$$J_i = -\frac{1}{4\pi^3\hbar^3}\int \upsilon_i f\, d^3\vec{k} \tag{6.7}$$

$$W_i = \frac{1}{4\pi^3\hbar^3}\int E\upsilon_i f\, d^3\vec{k} \tag{6.8}$$

2. The distribution function f is obtained by solving the Boltzmann equation.

3. The coefficient L_{ik}^{m} can be expressed in terms of integrals of the type

$$I_{ij}^{(1)} = \frac{T}{4\pi^3\hbar^3}\int E^{l}\tau\, \upsilon_i \upsilon_j \frac{\partial f_0}{\partial E} d^3k \quad (6.9)$$

Therefore,

$$L_{ij}^{1} = -I_{ij}^{(0)}; L_{ij}^{(2)} = L_{ij}^{(3)} = I_{ij}^{(1)} \text{ and } L_{ij}^{(4)} = -L_{ij}^{(2)} \quad (6.10)$$

4. If a single spherical band with an isotropic effective mass is considered, the calculation of the transport coefficients is considerably simplified. The carrier energy E and the relaxation-time can then be taken to depend on $|\vec{k}|$,

$$d^3\vec{k}' = k'^2 dk \sin\theta \; d\theta \, d\varphi \quad (6.11)$$

the integral over all the coordinates is zero values i=j, in which case it becomes equal to $\frac{4\pi}{3}$. The integrals over the modulus k of **k** can be transformed to an integral with the variables $E = \frac{\hbar^2 k^2}{2m*}$, the energy being measured with respect to the band edge.

5. Introducing the following integrals

$$M_1 = -\frac{1}{m*}\left(\frac{2m*}{\hbar^2}\right)^{\frac{3}{2}} \frac{T}{4\pi^2\hbar^3} a \int E^{l} E^{\left(s+\frac{3}{2}\right)} \frac{\partial f_0}{\partial E} dE \quad (6.12)$$

An integration by parts further simplify M_L to

$$M_L = \frac{a}{m^*}\frac{T}{3\pi^2}\left(\frac{2m^* k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left(\ell + s + \frac{3}{2}\right)(k_B T)^{\ell_{Ts}} \Gamma_{s+\ell+\frac{1}{2}}(\xi) \tag{6.13}$$

where F are the Fermi integrals,

$$F_r(\xi) = \int_0^\infty \frac{\eta^r d\eta}{1 + e^{n-\xi}} \tag{6.14}$$

where

$$\eta = \frac{E}{k_B T} \text{ and } \xi = \frac{E_F}{k_B T} \tag{6.15}$$

The electrons thermal conductivity can be written in terms of the integrals M_l as

$$\kappa_e = \frac{M_0}{T^2}\left\{\frac{M_2 M_0 - M_{12}}{M_0^{\ 2}}\right\} \tag{6.16}$$

6.3. Results of thermal conductivity

Materials considered in this work are represented by a cylindrical bar with heat flowing across its length, which is assumed to align with z-direction. At moderate temperatures, the thermal transport behavior of an intrinsic semiconductor is similar to that of an insulator with heat conduction due to lattice waves (phonons). Controlled amounts of suitable impurities (dopants) can be added to a semiconductor producing

electrons or holes which gives rise to electronic contribution to thermal conductivity. However, apart from serving as heat carriers, electrons and holes may also act as scattering centers for phonons and cause a reduction in lattice thermal conductivity. At temperatures sufficiently high to excite carriers across the semiconductor energy band gap, electron-hole pairs transport heat and give rise to a bipolar contribution to thermal conductivity.

It was found experimentally that, pure diamond has a thermal conductivity of a bout $2000Wm^{-1}$ at room temperature (Slack, 1961). Only a small fraction of this thermal conductivity (about 1 or 2 percent) arises from the lattice contribution. $k_L(cal) = 5Wm^{-1}k^{-1}$ (Berman, 1976); the high concentration of electron being responsible for the large electronic contribution. Pure, undoped silicon, on the other hand, has a thermal conductivity of $145Wm^{-1}k^{-1}$ (Drabble, 1961), all of which is the lattice contribution.

6.3.1. Results of lattice thermal conductivity

Expressions used to calculate the thermal conductivity are (6.16) and (3.18). The model was applied to silicon and germanium. The general patterns of the variation of the lattice thermal conductivity of some of the calculated results of the thermal conductivity are shown in Figures 6.1-6.3. These figures are chosen to show the effect of temperature, concentration, and the effect of the type carriers on thermal conductivity.

The lattice thermal conductivity in these materials is the only important contribution to thermal conductivity and this depends on atomic mass, nature of binding and the perfection of the specimen under study which in turn depends upon the absence of any impurities and disorder boundaries.

Many thermal properties of semiconductors are described in terms of phonon behavior. In heavily doped semiconductors the scattering of phonons by electrons and holes may also contribute to the phonon scattering.

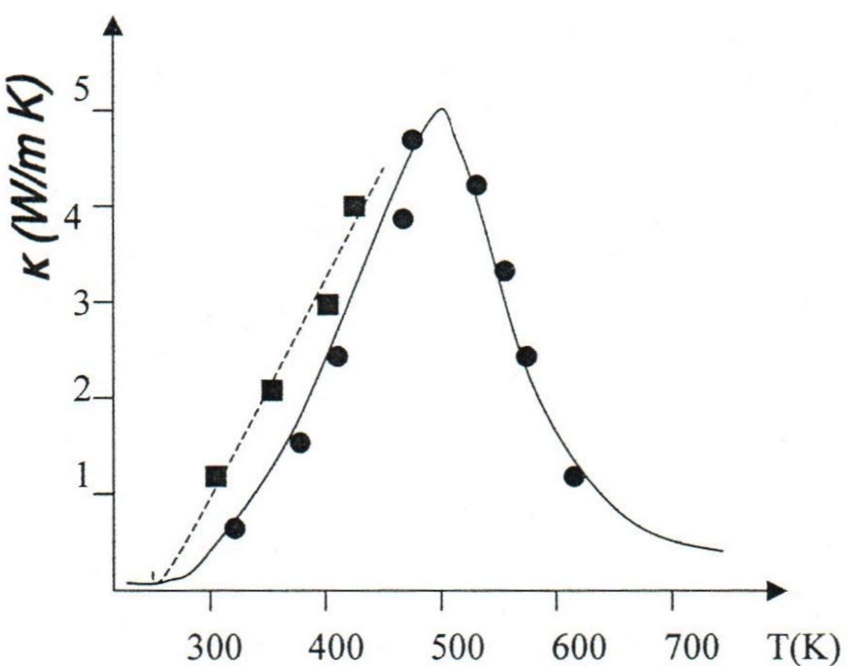


Figure 6.1.Schematic behavior of thermal conductivity for ideal semiconductor.-----Thermal conductivity versus temperature for silicon in the intrinsic range

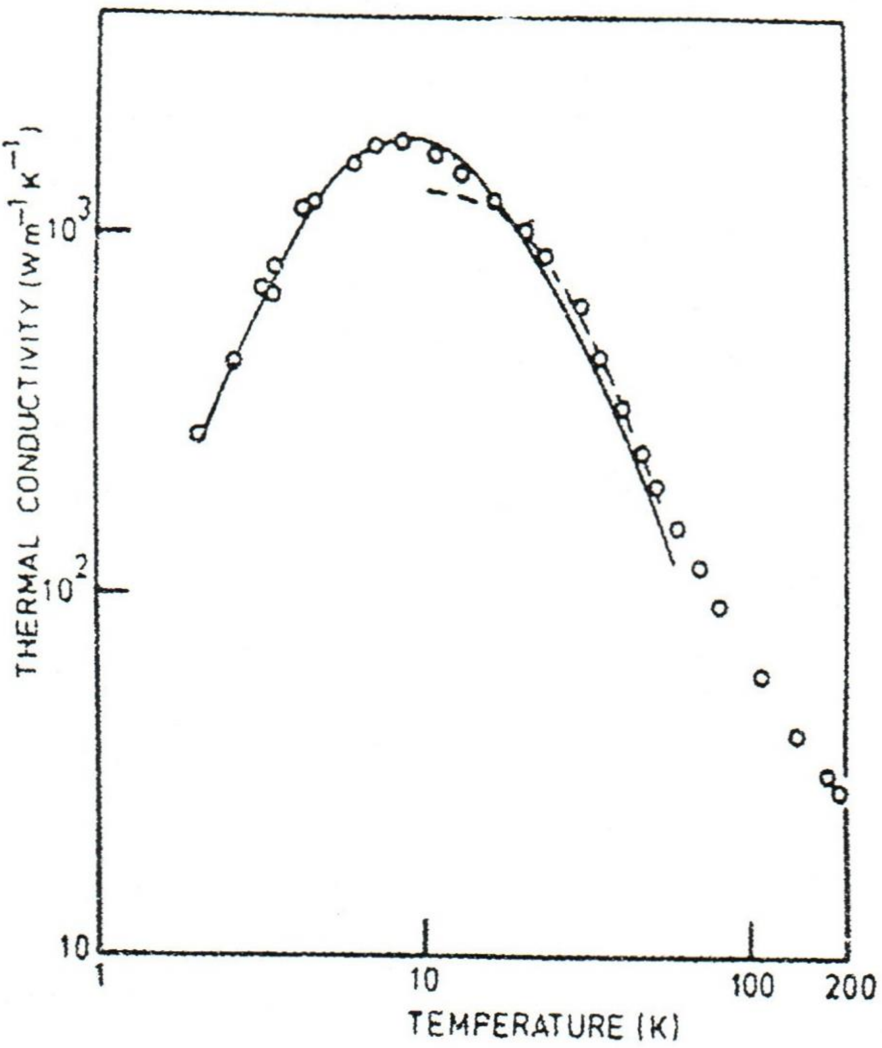


Figure 6.2. Temperature dependence of thermal conductivity for Si semiconductor

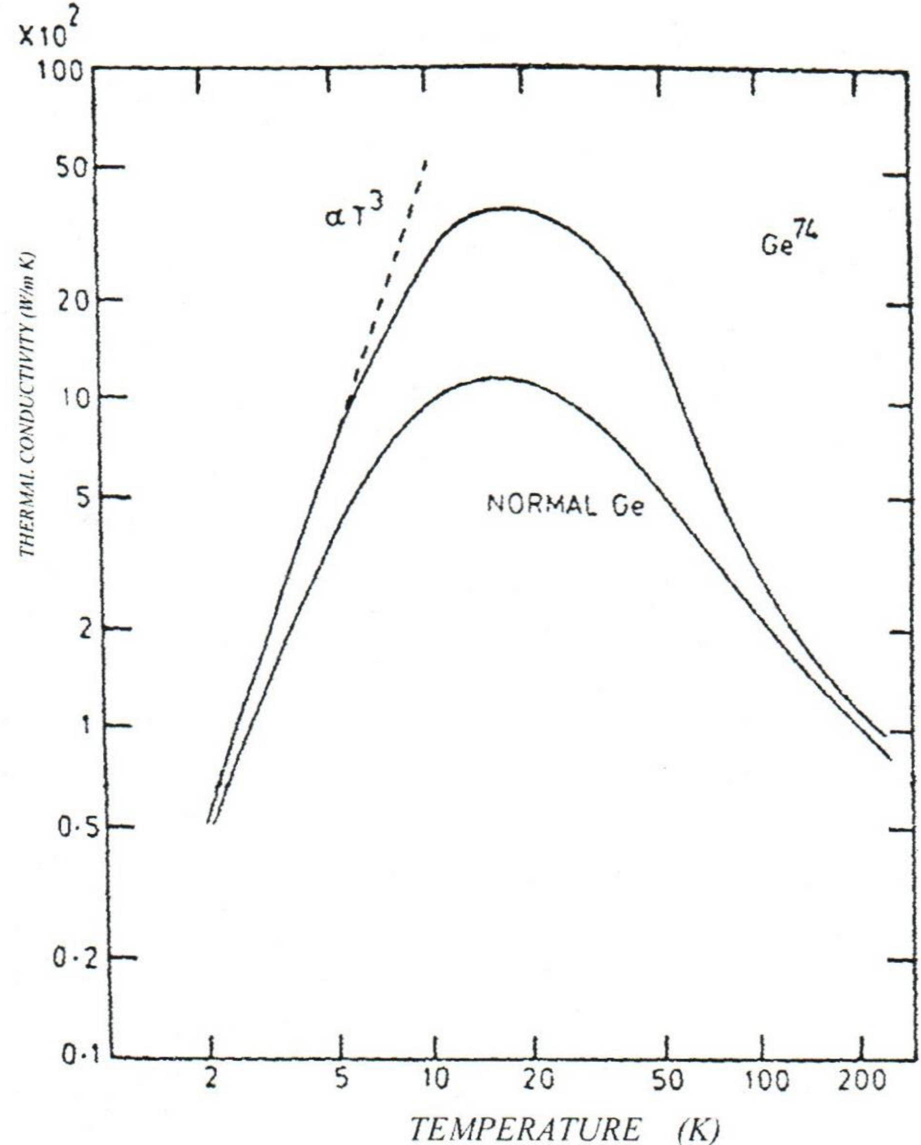


Figure 6.3. Thermal conductivity of normal germanium, Ge.

It was found that $\kappa \alpha$ T^{-1} above the Debye temperature in agreement of Eucken's experimental law (Bhandari et al, 1988). As the temperature is lowered κ rises more rapidly than it is predicted by T^{-1} law at somewhat lower temperatures and reaches a maximum at a temperature well below the Debye temperature. Slack (1972) pointed out that change in the volume with temperature can produce this departure from T^{-1} law. At temperatures well below the Debye temperature, the lattice thermal conductivity is dominated by an exponential form, that is

$$\kappa = \left(\frac{T}{T_D}\right)^3 e^{\frac{T_D}{bT}} \tag{6.17}$$

where b is a numerical parameter, T is the temperature and T_D is the Debye temperature.

With a further lowering in the temperature κ decreases rapidly and vanishes at absolute zero. A simple explanation of this behavior is as follows: As the temperature decreases the phonon mean-free-path increases rapidly, resulting in an increase in κ until it becomes comparable to the sample dimensions. The boundaries of the sample are usually poor reflectors to phonons and, consequently, their mean-free-path cannot increase any further. In this temperature range, the lattice thermal conductivity now decreases with a decrease in temperature following the same T^3 law as the specific heat do (Touloukain *et al*,

1970). This is because the lattice thermal conductivity can be written in terms of the mean-free-path as

$$\kappa = \frac{1}{3} C_v \upsilon_s \ell \tag{6.18}$$

where C_v is the specific heat per unit volume and υ_s is the sound (phonon) velocity.

At higher temperatures, the donor atoms are ionized and phonons scattered by electrons in the conduction band. However, at lower temperatures a significant fraction of electrons may still be trapped by donors, and in such a case scattering of phonons by electrons bound to donor atoms has to be taken into account.

The phonon relaxation-time for scattering by free electron in a parabolic band can be written as (Mahan, 1988)

$$\frac{1}{\tau_{pe}} = \frac{n\omega \in}{\rho\omega_L^2 k_B T} \sqrt{\frac{\pi m^* \omega_L^2}{2k_B T}} e^{-\frac{m^* \omega_L^2}{2k_B T}} \tag{6.19}$$

Where ρ is the density, n is the carrier density, and $\in$ is the strength of the electron-phonon interaction and is referred to as the deformation potential (Parrott, 1979). This relaxation-time was derived for longitudinal phonons although a similar expression is also taken to be valid for transverse phonons. Similar results were obtained by Parrott (1979).

A phonon may be scattered by one or more of the scattering mechanisms causing a reduction in lattice thermal conductivity. In some materials, scattering of phonons by dislocations may play an important role in limiting the phonon mean-free-path. The core of the dislocation constitutes a region of disorder and is expected to scatter phonons according to the relaxation-time $\tau_R^{-1} \propto \omega^3$. However, for randomly arranged dislocations, the phonon-relaxation time is fitted by the following expression

$$\tau_{pho}^{-1} = \frac{1}{27} N_d \omega \left[1 + \sqrt{2} \left(\frac{\omega_L}{\omega_T} \right)^2 \right] \qquad (6.20)$$

Here N_d is the number of dislocation lines through a unit area and ω_L, ω_T are referred to the longitudinal and transverse phonon frequencies. Similar expressions were obtained by Ziman (1960), Carruthers (1961) and Ohasi (1968), and these differ mostly in the numerical constants. The experiments of Anderson and Malinowski (1972) provided evidence of the effect of this type of scattering on thermal conductivity.

The total lattice thermal conductivity is shown in Figure 6.4 and can be written as

$$\kappa = \kappa_T + \kappa_L \qquad (6.21)$$

Where

$$\kappa_T = \frac{2}{3}\int_0^{\frac{\theta_T}{T}} \frac{C_T T^3 x^4 e^x (e^x - 1)^{-2}}{\tau_T^{-1}} dx \tag{6.22}$$

and

$$\kappa_L = \frac{1}{3}\int_0^{\frac{\theta_L}{T}} \frac{C_L T^3 x^4 e^x (e^x - 1)^{-2}}{\tau_L^{-1}} dx \tag{6.23}$$

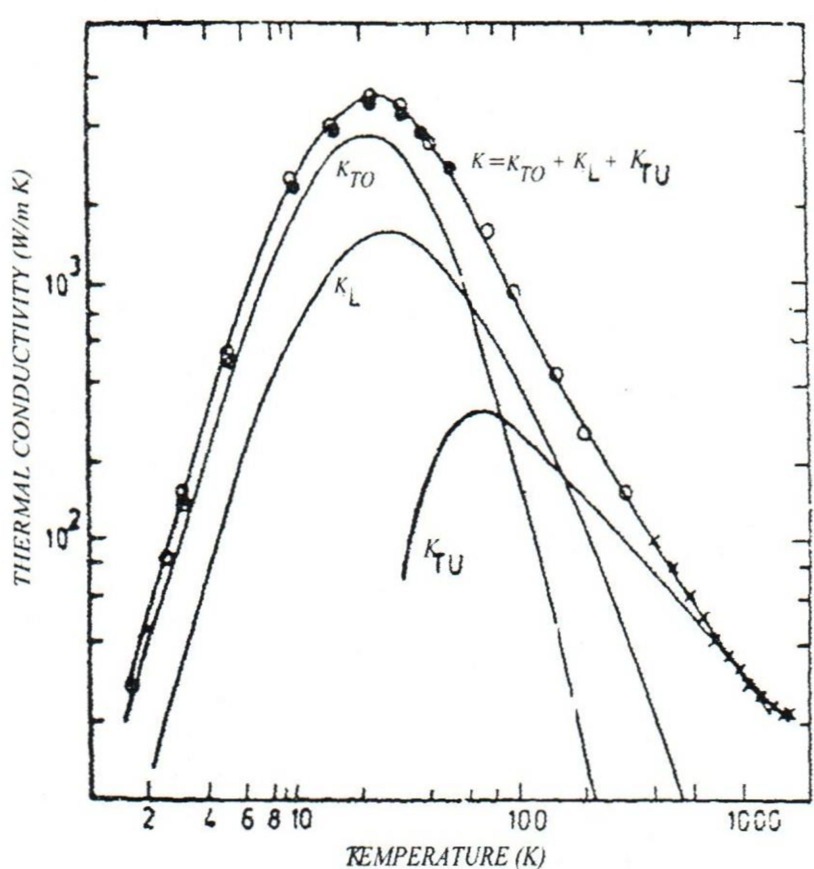


Figure 6.4. The thermal conductivity of silicon. Solid lines show the results of calculations for κ_L, κ_{TO} and κ_{TU} refer to the contribution from longitudinal phonons, low frequency transverse phonons and high frequency transverse phonons, respectively.

Here $x = \frac{\hbar\omega}{k_B T}, \theta_{T,L} = \frac{\hbar\omega_{T,L}}{k_B}$, and $C_{T,L} = \frac{k_B}{2\pi^2 \upsilon_{T,L}}\left(\frac{k_B}{\hbar}\right)^3$. Suffixes T and L are referred to the transverse and longitudinal branches, respectively. Similar results were obtained by Parrott (1971). The thermal conductivity can be written in terms of transverse and longitudinal relaxation-times (τ_T and τ_L) as

$$\kappa = \frac{1}{3} C_v \upsilon^2 \frac{\langle \tau_L \rangle}{\langle \tau_L \rangle + \langle \tau_T \rangle} \left[\langle \tau_T \rangle + \frac{1}{\langle \tau_T^{-1} \rangle} \right] \tag{6.24}$$

For $\tau_T \gg \tau_L$ the above expression is reduced to the usual expression for the thermal conductivity.

It was found that the thermal conductivity depends on concentration. At low carrier concentrations, the thermal conductivity of semiconductors can be described in terms of phonon conduction where the phonon mean-free-path is limited by other phonons, various impurities and crystal boundaries. The results of thermal conductivity of the low temperature thermal conductivity of germanium are shown in Figure 6.5. The results agree with experiment in the range 100-400 K (Callaway, 1959).The thermal conductivity general behavior was explained by Holland (1963) by considering the longitudinal and transverse phonon contribution separately with a strong dispersion of transverse acoustic branch.

The relaxation-time dependence on temperature and concentration is found to fit the following empirical relation

$$\tau = \frac{850}{T^2} n^{\frac{4}{3}} \left(1 + \frac{0.05T}{n}\right) + \frac{80}{n\sqrt{T}\left(1 + \frac{60}{T^2}\right)} \qquad (6.25)$$

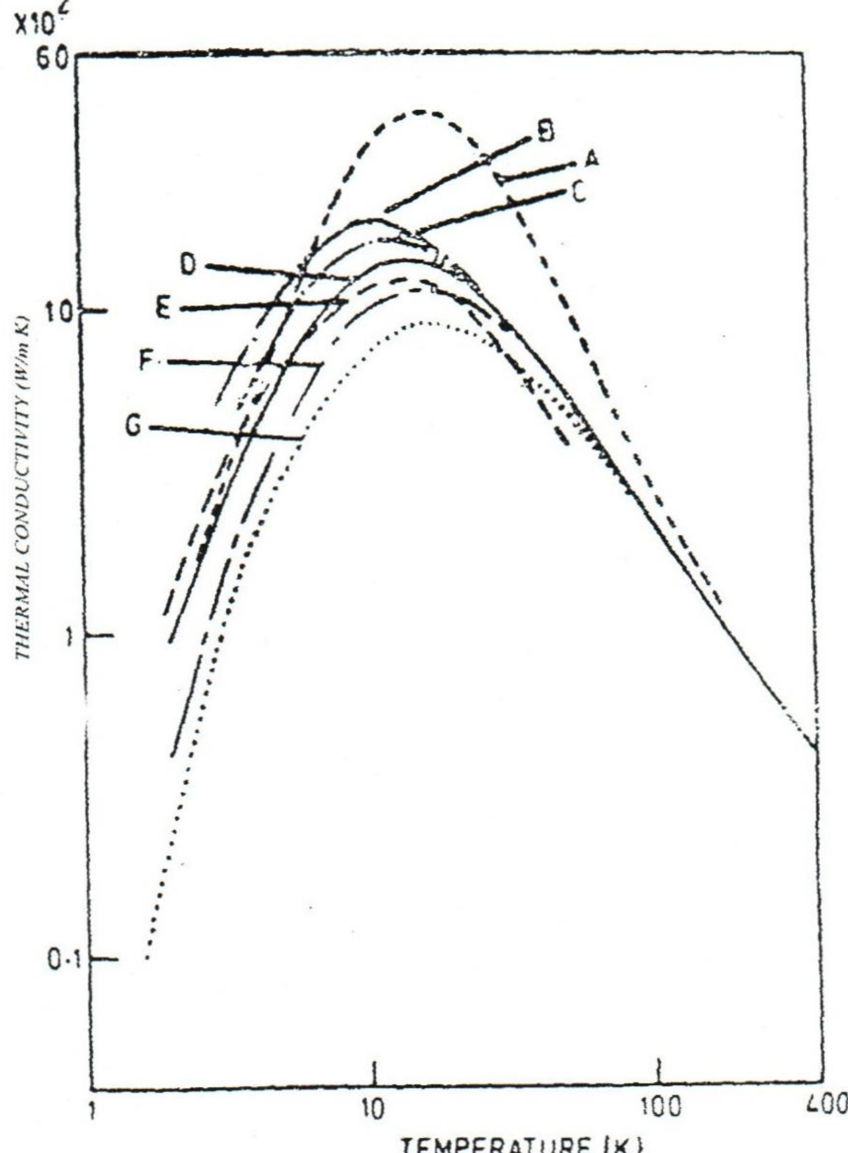
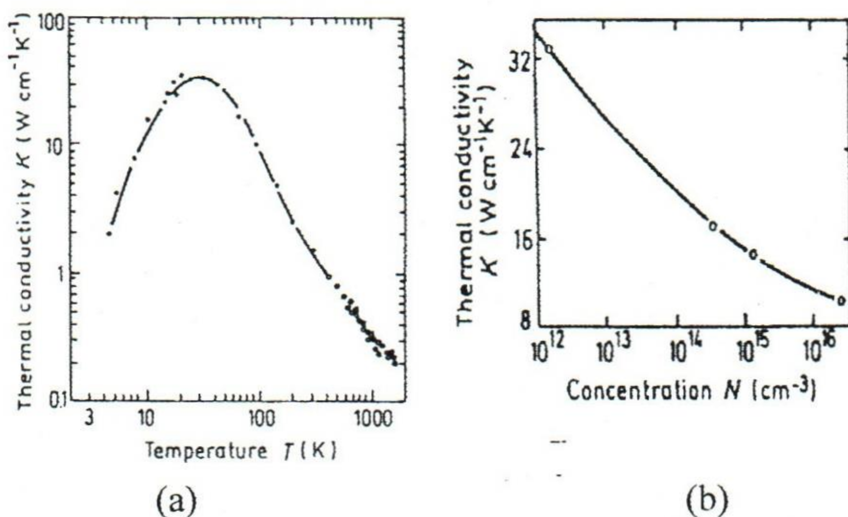


Figure 6.5. The low temperature thermal conductivity of germanium for different concentrations: Curve A, carrier concentration 1.3 $\times 10^{19}$ m^{-3}(n-type); B carrier concentration 1.1 $\times 10^{20} m^{-3}$(p-type); C carrier concentration 1.3 $\times 10^{19}$ m^{-3}(n-type); D carrier concentration 1.2 $\times 10^{19}$ m^{-3}(n-type); E carrier concentration 6.3 $\times 10^{19}$ m^{-3}(n-type).

The general behavior of the relaxation-time as a function of temperature and density is displaced in Figure 6.10.

Doping has a significant effect on thermal conductivity (Figure 6.6).



(a) (b)

Figure 6.6.(a) Temperature dependence of thermal conductivity for high purity Si semiconductor.(b) The dependence of thermal conductivity versus doping level at 20 K.

The lattice thermal conductivity of doped semiconductors shows a number of interesting features. There is a substantial reduction in the lattice thermal conductivity below the conductivity maximum even for dilute concentrations. Besides, the lattice thermal conductivity versus temperature curve sometimes shows a variation faster than T^3. In both germanium and silicon, the increase in the doping level causes a reduction in the maximum thermal conductivity, κ_m, and a shift of κ_m towards higher temperatures (Figure 6.5). Theoretical curves obtained

show a good agreement with experimental data (Bhandari *et al*, 1988). The effect of doping on thermal conductivity can be understood in terms of the scattering of phonons by electrons bound to impurity atoms and also by free carriers. In some cases the curves may show dips as shown in Figure 6.7.

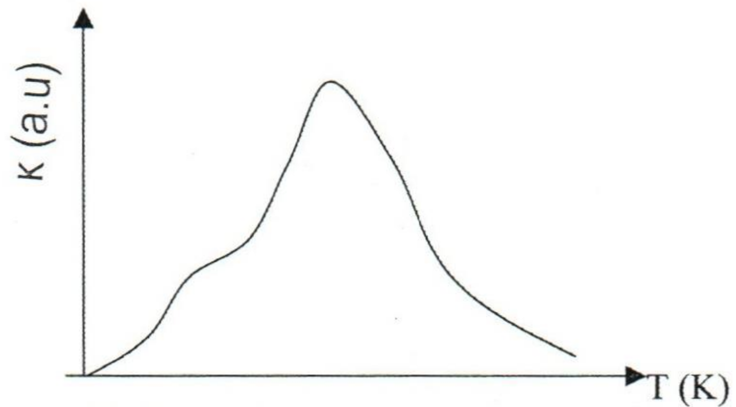


Figure 6.7. Thermal conductivity curve showing a dip.

An explanation for such observations were suggested by Keyes (1961). We shall discuss the germanium case. The ground state of a donor in germanium is four-fold degenerate in the effective mass approximation. Due to valley-orbit interaction the ground state is split into a singlet and a triplet separated by 4Δ (the energy shift). Keyes obtained for the relaxation-time

$$\frac{1}{\tau} = C\,\zeta_4^2\,(4\Delta)^2\,\omega^4\left(1+\frac{q^2 r_0^2}{4}\right)^{-8} n_{ex} \qquad (6.26)$$

Where ζ_4 is the shear deformation potential and n_{ex} is the concentration

of uncompensated donor electrons. In the acoustic approximation: $\omega=\upsilon_s q$, r_0 is the mean radius of the localized state. When q increases to more than $1/r_0$, the scattering decreases very quickly. This cut-off could explain the steep of the slope of the lattice thermal conductivity versus T curve below the conductivity maximum.

The electron-phonon scattering relaxation-time can be expressed in the form

$$\frac{1}{\tau_{pe}} = \Omega(q)\, F(q) \tag{6.27}$$

where F(q) is a cutoff function which takes into account of the fact that not every phonon can be scattered by electrons. For the situation in which an electron in state $\vec{k}$ is scattered into a state $\vec{k}'$, by absorbing a phonon as

$$\vec{k}' = \vec{k} + \vec{q} \tag{6.28}$$

Both $\vec{k}$ and $\vec{k}'$ can take the upper limiting value k_F and this sets a limit $q \le 2k_F$ on $\vec{q}$. This may yield a cutoff function F(q)=1 for $q \le 2k_F$ and F(q)=0 for $q \rangle 2k_F$. The scattering function $\Omega(q)$ takes the form

$$\Omega(q) = \frac{m^{*} \in^{2}}{2\pi \rho \hbar^{3}} q \tag{6.29}$$

This expression taken along with other phonon-scattering processes gives

a relatively good fit to the observed thermal conductivity at the highest temperatures. At low temperature the simple relationship in equation (6.29) overestimates the scattering of low q phonon. When the phonon wave length is of the order of or greater than the carrier mean-free-path a decrease in the strength of electron-phonon interaction is expected. On the basis of the RTA, the electron-phonon scattering predicts the relaxation-time to be proportional to $\tau_{pe} = \frac{\sqrt{E}}{T}$ at high temperatures.

Following the suggestion by Crosby and Grenier (1971), the scattering of the hole-phonon interaction for the low frequency phonons in heavily doped p-type semiconductor was examined. The hole-phonon scattering relaxation-time has the following form

$$\frac{1}{\tau_{ph}} = \frac{2ql}{\pi\left(1+3\left(\frac{q_F}{q}\right)^2\right)^2} \frac{\tan^{-1}(ql)}{ql - \tan^{-1}(ql)} \Omega(q)F(q) \tag{6.30}$$

Here l is the carrier mean-free-path, $q_F = \frac{\omega}{\upsilon_F}$ is the Fermi wave vector, υ_F is the Fermi velocity. Sota and Suzuki (1982) derived an expression for τ_{ph} in heavily doped semiconductors and applied their theory to n-type germanium and silicon at 0 K. The theory was extended by (Sota and Suzuki, 1984) to p-type material which takes into account the inter-band hole-phonon interaction. Their results are close to our results within 8%.

In general the role of electrons (or holes) as carriers of heat and also as scattering centers for phonons appears to be of great importance. For one type of carriers (electron or hole) a polar contribution to thermal conductivity arises which increases with an increase in a carrier concentration. The lattice thermal conductivity falls with increasing weight (Lee et al, 1976). Figure 6.8 shows this variation for three different semiconductor elements.

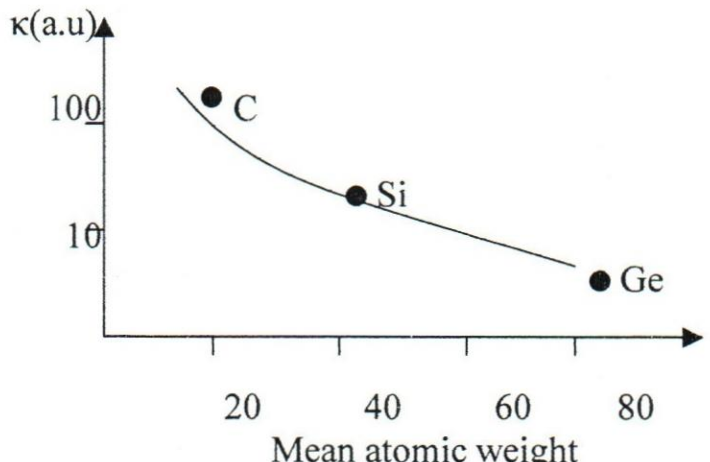


Figure 6.8. Lattice thermal conductivity versus atomic weight for various semiconductors.

6.3.2. Results of electronic thermal conductivity

The definition of thermal conductivity must be supplemented with the condition of zero current flow. The charge carriers (electrons and holes) contribute significantly to the total heat flux in semiconductors. In this description of flow of heat, the thermal current density can be expressed in terms of the electric current and the temperature gradient. The lattice

thermal conductivity in general is found to decrease with increasing the carrier concentration. This reduction in the lattice contribution may arise due to the scattering of phonons by electrons or holes.

In a large number of theoretical calculations the parabolic nature of the energy-momentum relationship described by $E = \frac{\hbar^2 k^2}{2m^*}$ This assumption gives a reasonable good description of the electronic behavior and shows good agreement between theory and experimental data except for materials of narrow energy gap (Ravich *et al*, 1970). This is, however, not applicable to small energy gap semiconductors and may lead to a serious error in the electronic transport coefficients including electronic thermal conductivity. The carrier effective mass is usually low for small energy gap materials and relatively higher values of the carrier energy even for moderate concentrations of carriers. At these energies ($E \cong E_g$) the proximity of the valence band is strongly felt and the non-degenerate nature of the energy momentum relationship comes into play (Bhandari and Rowe, 1988).

Somewhat similar considerations apply to the flow of electrons under the influence of a temperature gradient. For one type of carriers (either electrons or holes) a polar contribution to the thermal conductivity arises which increases with increasing carrier concentration. The electronic

polar contribution to thermal conductivity is usually written as (Kittle, 1995)

$$\kappa_e = L\,\sigma\,T \tag{6.31}$$

The parameter, L, is similar to the Lorentz number for metals and acquires a value of $2\left(\frac{k_B}{e}\right)^2$ in the non-degenerate region (if the electrons are assumed to be scattered by acoustic phonons only), whereas in the degenerate region limit L acquires a value of $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ (Christman, 1988). An approximate evaluation of this contribution to the conductivity is obtained at the Fermi surface. The relaxation-time of electrons on the Fermi surface is calculated from

$$\frac{1}{\tau(\vec{k})} = 4\pi\int_0^{\infty}\alpha_k^2(\omega)\,F_k(\omega)\left[\frac{1}{e^{\beta\hbar\omega}+1}+\frac{1}{e^{\beta\hbar\omega'}+1}\right]d\omega \tag{6.32}$$

Where $\frac{1}{\tau}$ is zero at zero temperature but is finite for a finite temperature. This lifetime is between scattering of the electron by a phonon emission or absorption. This lifetime is not the same as the relaxation-time which enters the calculation of resistivity.

In intrinsic semiconductors, the bipolar thermal conductivity becomes significant when electron-hole pairs across the energy band gap contribute to heat conduction as they flow down the temperature gradient.

In reasonably pure semiconductors (non-degenerate limit) the scattering of electrons by acoustic phonons leads to the relaxation-time $\tau = aE^{-\frac{1}{2}}$, where a is the energy independent parameter that has the given value (Fistul, 1969)

$$a = \frac{\hbar^4}{(8\pi)^3}\frac{\rho \upsilon_L^2}{k_B T}\frac{1}{(2m*)^{\frac{3}{2}} \in_1^2} \tag{6.33}$$

where ρ is the density and υ_L is the velocity of longitudinal phonons, $\in_1$ the deformation potential constant that can be determined from independent measurements, such as the changes of energy gap with pressure and temperature. The effective mass dependence on energy can be given by (Kane, 1957)

$$m_j^* = m_{jo}^*\left(1 + 2\frac{E}{E_g}\right) \tag{6.34}$$

Where m^*_{jo} is the effective mass near the band extremum.

Generally, the relaxation-time for various scattering mechanisms can be expressed as

$$\tau = aE^s \tag{6.35}$$

Where $b^2 = \frac{\tau_{ol}}{\tau_{oi}}$ is a measure of the relative strength of ionized impurity

where s takes values of $\frac{-1}{2},\frac{1}{2},\frac{3}{2}$ for acoustic scattering polar optical and scattering and impurity scattering, respectively. In heavily doped semiconductors, the electron scattering mechanism has a relaxation-time given by

$$\frac{1}{\tau_1}=\frac{z^2e^4N_i}{16\pi(2m^*)^{\frac{1}{2}}\in^2 E^{\frac{3}{2}}}\ln\left[1+\left(\frac{2E}{E_m}\right)^2\right] \qquad (6.36)$$

where $-E_m$ is equal to the potential energy of an electron distance r_m (half the mean distance between impurities). N_i is the number of ionized impurities per unit volume and $\in$ is the dielectric constant.

In the case of mixed scattering, where acoustic scattering and ionized impurity scattering act simultaneously, the associated relaxation-times τ_{ac} and τ_{imp} are given by

$$\left.\begin{aligned}\tau_{ac}&=\tau_{ol}\eta^{\frac{-1}{2}}\\ \tau_{imp}&=\tau_{io}\eta^{\frac{3}{2}}\end{aligned}\right\} \qquad (6.37)$$

Here η is the reduced carrier energy $\frac{E}{k_BT}$. The combined relaxation-time τ is obtained by adding the inverse relaxation-times for the two mechanisms. Thus, scattering and acoustic scattering relaxation-time can be written as

$$\tau = \frac{\tau_{ol}\eta^{\frac{3}{2}}}{\eta^2 + b^2} \quad (6.38)$$

Since the number of phonons of a given type are $\frac{k_B T}{\hbar\omega}$, the density of all phonons is proportional to T. Therefore, $\kappa \propto \frac{1}{T}$ for $T >> T_D$. At low temperatures ($T << T_D$), for the Umklapp-processes to occur, the phonons should have an energy larger than a certain minimum value, so that the sum of the energies of two phonons should exceed the Debye limiting energy $\hbar\omega_D$. This implies that, at low temperatures, each of the phonons should have a frequency of about $\frac{\hbar\omega_D}{2}$. The Debye theory has already provided the thermal conductivity proportional to T^3. Therefore,

$$\kappa \propto T^3 e^{\frac{T_D}{2T}} \quad (6.39)$$

The typical variation of phonon thermal conductivity with temperature is exhibited in Figure 6.1. At low temperatures, it was found that thermal conductivity do not increase without limit as the temperature is decreased, but it reaches a maximum value, usually about $\frac{T_D}{20}$. At further lower temperatures, the thermal conductivity is found to vary as T^3 only. It is found that the value of the thermal conductivity at low temperatures

for semiconductors is less than the observed value if the only the contributions due to lattice vibrations and sample boundaries are accounted. This is, of course, because of the additional scattering of phonons by various imperfections and dislocations.

When electrons and holes are present in almost equal concentrations they flow down a temperature gradient carrying all their energy and yet give rise to a vanishing small electric current. Each electron-hole pair can effectively transport a quantity of energy equal to the energy gap and this would give rise to a very large thermal conductivity according to $\kappa_e = L_e \sigma_e T$ and $\kappa_h = L_h \sigma_h T$ (Barrott, 1979). Electron-hole pairs are created at the hot end by the absorption of energy from the source. These pairs then move down the temperature gradient and recombine releasing the recombination energy. This process is sometimes called bipolar thermal diffusion (Price, 1955).

The thermal conductivity versus temperature for silicon in the intrinsic range is displayed in Figure 6.3. Similar results were reported for magnesium oxide by Touloukain and Klemens (1970). Thus, the total electronic thermal conductivity κ of a semiconductor can generally be represented by

$$\kappa = \kappa_L + \kappa_e + \kappa_b \tag{6.40}$$

Where, κ_L, κ_e and κ_b refer to the lattice, electronic (polar) and bipolar

contributions, respectively. The general behavior of the electronic thermal conductivity as a function of temperature for silicon in the intrinsic range is displaced in Figure 6.9.

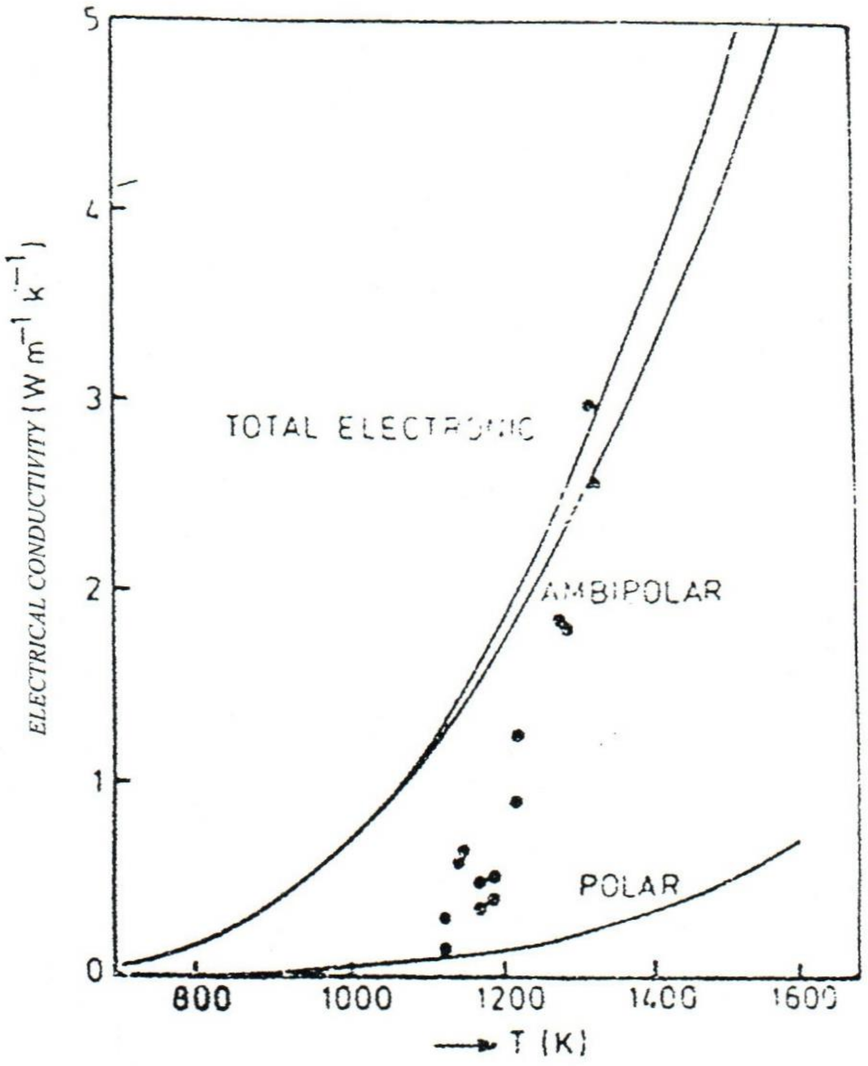


Figure 6.9. Electronic thermal conductivity versus temperature for silicon in the intrinsic range.

6.3.3. Inter-valley Scattering

The thermal conductivity is sensitive to the nature of the concentration of impurities and imperfections. In many-valley semiconductors inter-valley scattering of carriers, the transition of an electron from one valley (in **k**-space) to another, a large change in momentum is involved. This momentum may be taken up either by an impurity atom or a phonon near the Brillouin zone boundary where acoustic and optical branches are not far from each other. The case of impurity scattering is limited to low temperature and very impure semiconductors. Regarding the scattering by phonons the intra and inter-valley scattering by that most of the phonons emitted or absorbed in intra-valley scattering have energies considerably lower than the energy of charge carriers; whereas this does not apply to phonons involved in inter-valley scattering. Taking into account acoustic deformation potential scattering in addition to inter-valley scattering the total relaxation-time is given by

$$\frac{1}{\tau}=\frac{1}{\tau_{ac}}+\frac{1}{\tau_{iv}} \qquad (6.41)$$

Where τ_{iv} refers to inter-valley scattering.

The acoustic scattering and impurity scattering act simultaneously, the associated relaxation-times τ_{ac} and τ_{imp} are given by

where the Legendre expansion is used for $f(\vec{k})$. Then one takes the first two angular moments. That is, one first integrates the above equation over all solid angle 4π. This step removes all of the angular factors. Next, one multiplies the above equation by p and integrates again over all the solid angle. These steps produce the two equations:

$$\frac{\partial f_s}{\partial t} - \frac{e\varepsilon}{3\hbar k^2}\frac{\partial}{\partial k}\left(k^2 f_1\right) = -\frac{\left(f_s - f^0\right)}{\tau_1} \tag{6.45}$$

$$\frac{\partial f_1}{\partial t} - e\,\varepsilon\frac{\partial f_s}{\hbar \partial k} = -\frac{f_1}{\tau_1} \tag{6.46}$$

The above equations are of the first-order differential equations having the general form

$$\frac{\partial a(t)}{\partial t} + \frac{a}{\tau} = b(t) \tag{6.47}$$

which has the solution

$$a(t) = a(0)e^{\frac{-t}{\tau}}\int_0^t dt'\, e^{-\frac{(t-t')}{\tau}}\, b(t') \tag{6.48}$$

Introducing $\delta f = f_s - f_0$ and assuming that the field is turned on at t=0, so f_1 and δf vanish at t=0. Accordingly, solutions to equation (6.45) and equation (6.46) can be written as:

$$f_1(k,t) = e\,\varepsilon\,\tau_1\left(1 - e^{\frac{-t}{\tau}}\right)\frac{\partial f^0}{\partial k} - e\,\varepsilon\int_0^t dt'\, e^{\frac{-(t-t')}{\tau}}\frac{\partial}{\partial k}\delta f(k,t') \tag{6.49}$$

$$\delta f(k,t) = \frac{e\,\varepsilon}{3k^2}\int_0^t dt' e^{-\frac{(t-t')}{\tau_1}}\frac{\partial}{\partial k}\left[k^2 f_1(k,t')\right] \tag{6.50}$$

The current is determined from the distribution f_1. After the field is switched on at t=0, the distribution f_1 reaches its steady state value of $e\varepsilon\tau_1 \frac{\partial f^0}{\hbar \partial k}$. The change in isotropic distribution δf grows in according to ε^2. The Joule heating of $O(\varepsilon^2)$ affects the isotropic part of the distribution. The effect on f_1 is $O(\varepsilon^3)$. The current is only affected by Joule heating through nonlinear terms giving $J\alpha\alpha^3$.

The elastic scattering by impurities determines the rate by which electrons in the f_1 distribution are scattered to the s distribution f_s. This determines the current, since it gives the steady-state occupation of f_1 distribution. Energy relaxation occurs in the f_s distribution as f_s tries to relax toward f^0. This process has a very different rate and it does not affect the current unless the f_s distribution heats up, and the temperature is changed.

The resistivity is calculated from impurity scattering. Electron scattering by acoustical phonons presents a hard problem in transport theory. The scattering is slightly inelastic. We can apply to this problem neither the elastic scattering nor the inelastic scattering theory. Instead we derive and solve an integral equation for the energy dependence of the scattering process.

The potential energy of the electron scattering from impurities of R_i is

$$V(\vec{r}) = \sum_i V_{ei}\left(\vec{r} - \vec{R}_i\right) = \frac{1}{v}\sum_{iq} V(\vec{q})e^{i\vec{q}.(\vec{r}-\vec{R}_i)} \tag{4.51}$$

The force $\vec{F}$ is the gradient of the potential. The formula for the resistivity from impurity scattering is (Gupta, 1995)

$$\rho = \frac{n_i\, m^2}{6\pi\, n^2\, e^2}\int \frac{d^3\vec{q}}{(2\pi)^2}\, q\left|\frac{V(q)}{\varepsilon(q)}\right|^2 \tag{6.52}$$

This formula is the exact result for the zero temperature resistivity from impurity scattering when the scattering is calculated in the second Born approximation. If $\frac{V(q)}{\varepsilon(q)}$ is replaced by the scattering T-matrix, then it is the exact result. It is the formula $\rho = \frac{m}{n_0 e^2 \tau}$, where τ_1 is defined in equation (4.23). It even includes the $(1-\cos\theta)$ factor. One has to perform the angular integral in equation (4.23) which eliminates the delta function, in order to show the equivalence with the above formula for the resistivity.

The resistivity relation for the electron scattering by phonons is given by the equation (Ziman, 1960)

$$\rho(t) = \frac{3\hbar\omega}{M e^2 16 \upsilon_F^2 k_F^4}\sum_\lambda \int q d^3\vec{q}\,|\omega(q)|^2 (\vec{\varepsilon}_\lambda.\vec{q})^2\left[-\frac{\partial n_B(\omega)}{\partial\omega}\right] \tag{6.53}$$

where $\omega(q)$ is the screened electron-ion interaction $\omega_\lambda(\vec{q})$ is the phonon

frequency and ε_λ is the polarization vector.

6.4.1. Results of electrical properties

The relaxation-time τ_1 of electrons on the Fermi surface is calculated from equation (4.23). The general behavior of τ_1 is similar to the results shown in Figure 6.10, that is, $\frac{1}{\tau_k}$ is zero at zero temperature but is finite for a finite temperature (See Figure 6.4). The relaxation is between scattering of the electron by a phonon emission or absorption. It is not the same relaxation-time for energy which enters the calculation of resistivity.

The electrical conductivity is calculated from equation (4.31) and the result is shown in Figure 6.11. The conductivity is proportional to the relaxation-time τ_1, where $\frac{1}{\tau_1}$ is defined as the scattering probability weighted by the $1-\cos\theta'$ factor.

The conductivity is relatively insensitive to the temperature as long as the density of states of the metal is smooth function of energy near the Fermi surface. The resistivity $\rho = \frac{1}{\sigma}$, which is the inverse of the conductivity, is proportional to the concentration of impurities, that is,

$\sigma \alpha \tau_1$ and $\tau_1 \alpha \frac{1}{n_i}$, so that $\sigma \cong \frac{1}{n_i}$, and $\rho \cong n_i$.

This proportionality is experimentally verified.

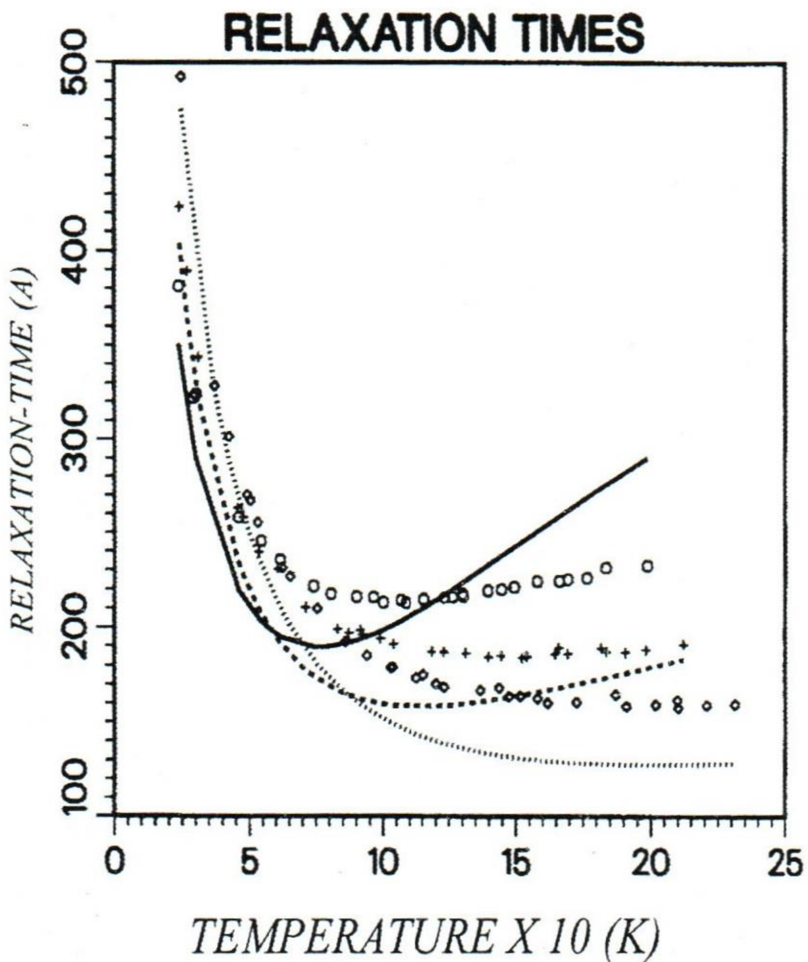


Figure 6.10. Relaxation-time dependence on temperature and density

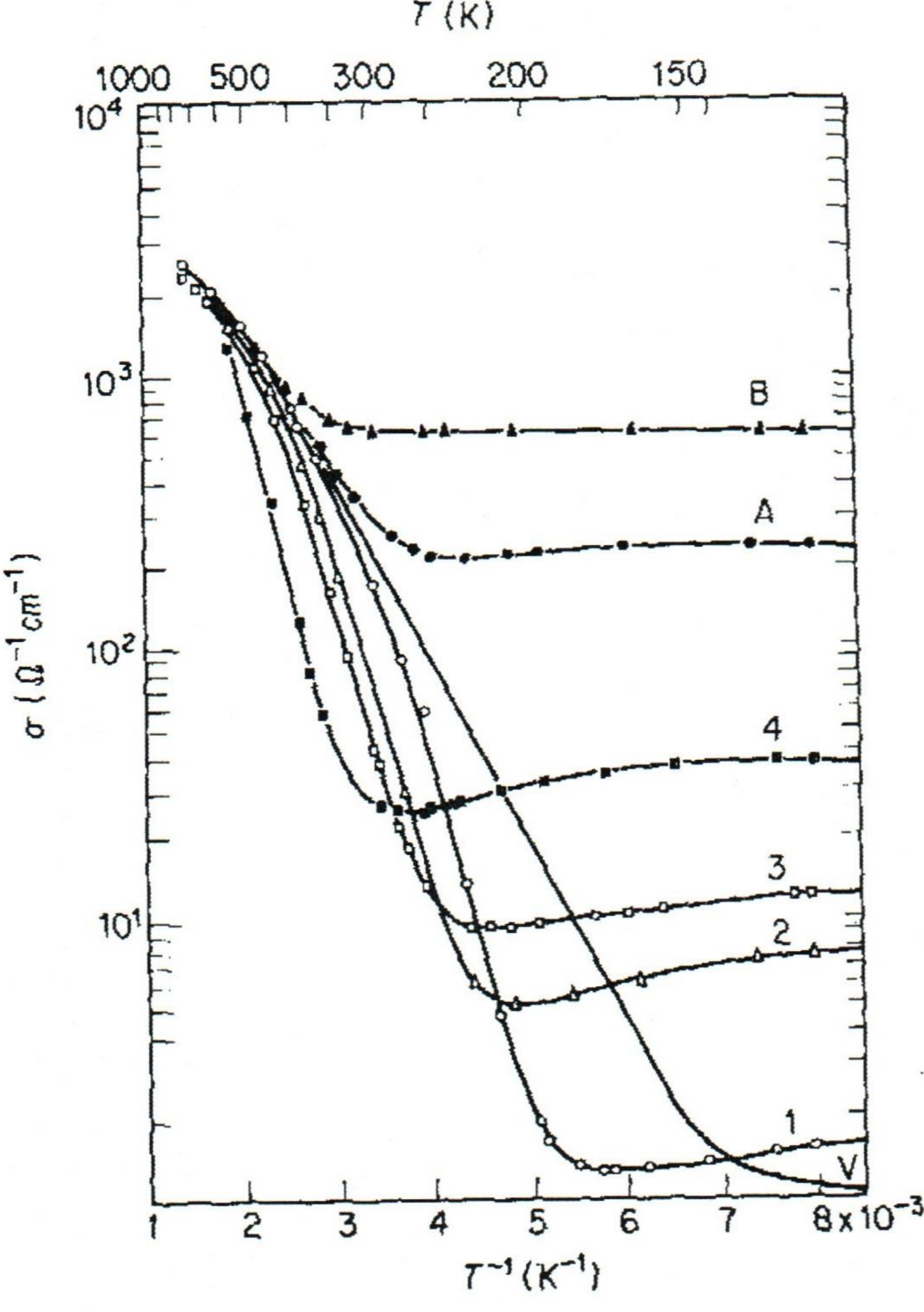


Figure 6.11. The temperature dependence of conductivity, σ, of indium antimonide semiconductor. Samples A, B, and V are n-type; 1 to 4 are p-type.

The electrical conductivity of an intrinsic semiconductor increases dramatically with temperature as electrons are thermally excited from valence to conduction bands. Since electron and hole concentrations are proportional to $e^{-\frac{E_g}{2k_BT}}$, a plot of ln(σ) as a function of $\frac{1}{k_BT}$ is nearly a straight line with a negative slope equal in magnitude to half the energy gap. An example is shown in Figure 6.12 for intrinsic germanium.

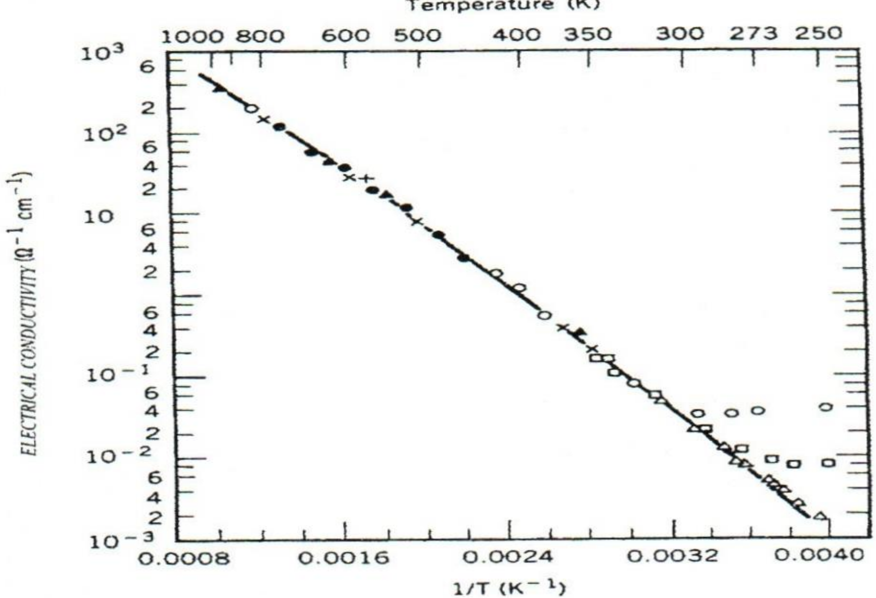


Figure 6.12. The natural logarithm of the electrical conductivity of intrinsic germanium as a function of 1/T.

The other important electrical quantity is usually the mobility of electrons. Typical experimental results of CdTd mobility are found in (Segall *et al.(*1963), and Delvin, 1967). The general behavior is shown in Figures 6.13 and 6.14. This behavior may be explained as follows: at

lower temperatures the mobility saturates because of the scattering from impurities. Impurity scattering varies from sample to sample, depending on the concentration and type of impurity.

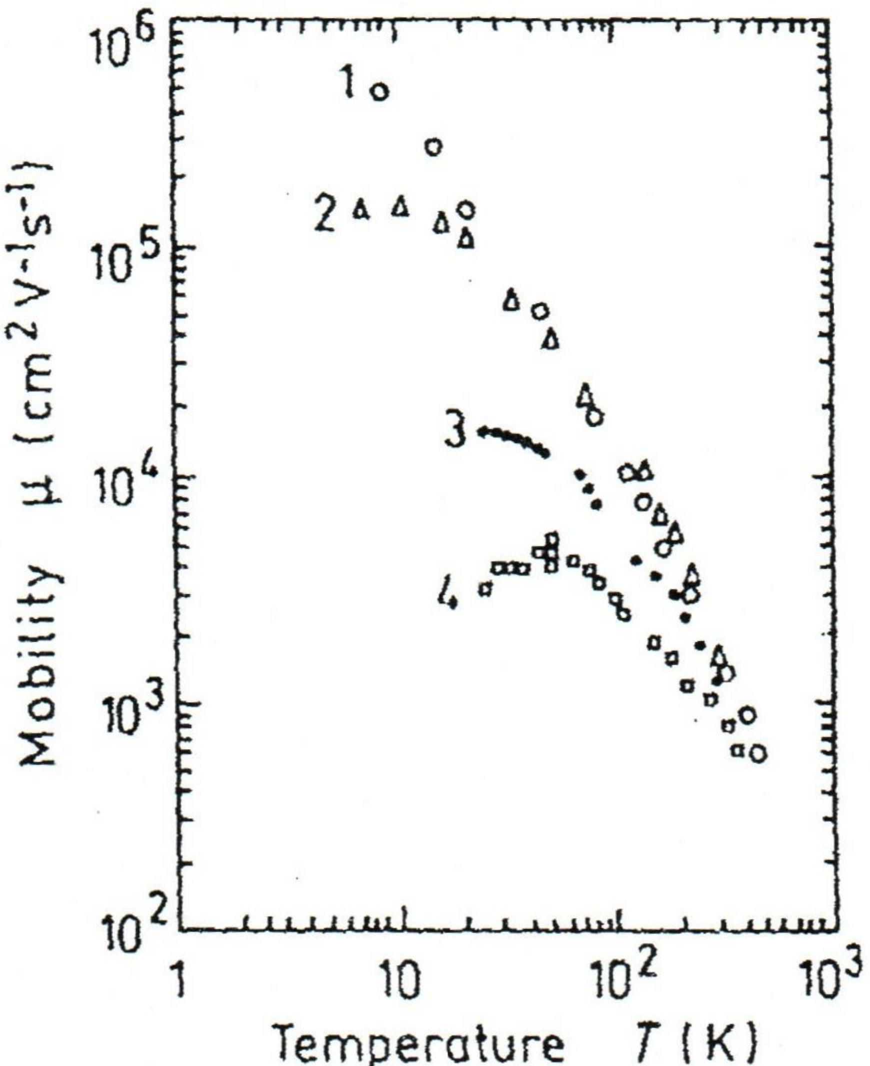


Figure 6.13. Electrons mobility versus temperature for different doping levels for Si semiconductors.(1) $n_d=10^{12}$ cm^{-3}; (2) $n_d=4\times10^{13}$ cm^{-3};(3) $n_d=1.75\times10^{16}$ cm^{-3} ; (4) $n_d=1.3\times10^{17}$ cm^{-3}.

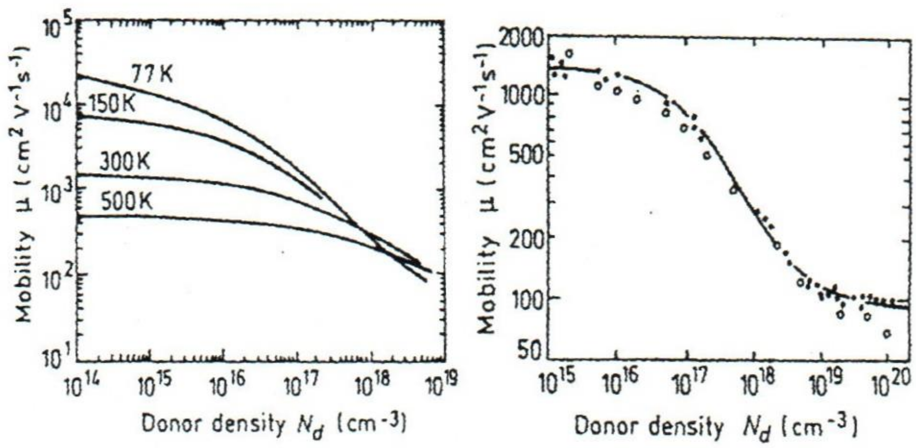


Figure 6.14. The mobility versus donor concentration electrons in silicon semiconductor.

The mobility usually has a temperature dependence which effectively cancels $T^{3/2}$ temperature variation, in the bracket in equation (4.67), leaving behind mainly the exponential term for the temperature dependence. The general behavior of mobility is found to be proportional to T^{-n}, where n is usually larger than 1.5. For example, the value of n is 2.42 for electrons in silicon and 2.2 for holes (Slack, 1961). The calculated mobility values for Si semiconductor are plotted in Figure 6.13. Similar results can be obtained for Ge semiconductor.

The electron mobility as a function of donor density at different temperatures is plotted in Figure 6.14. The calculated mobility measured

in cm^2/Vs for n-type (or for electrons) semiconductor is fitted by the following expression

$$\mu_n = \frac{1450\times\left(\frac{300}{T}\right)^{2.5}\left\{\frac{4.61\times10^{17}T^{3/2}}{N_d\left[\ln\left(1+\frac{1.53\times10^{15}T^{2.2}}{N_d}\right)-\frac{1.53\times10^{15}T^{2.2}}{N_d+1.53\times10^{15}T^{2.2}}\right]}\right\}}{1450\times\left(\frac{300}{T}\right)^{2.5}+\left\{\frac{4.61\times10^{17}T^{3/2}}{N_d\left[\ln\left(1+\frac{1.53\times10^{15}T^{2.2}}{N_d}\right)-\frac{1.53\times10^{15}T^{2.2}}{N_d+1.53\times10^{15}T^{2.2}}\right]}\right\}} \quad (6.54)$$

Similarly, for holes the mobility can be written as

$$\mu_h = \frac{490\times\left(\frac{300}{T}\right)^{2.45}\left\{\frac{1.0\times10^{17}T^{3/2}}{N_a\left[\ln\left(1+\frac{6.53\times10^{14}T^{2.5}}{Na}\right)-\frac{6..53\times10^{14}T^{2.5}}{N_d+6.53\times10^{14}T^{2.5}}\right]}\right\}}{490\times\left(\frac{300}{T}\right)^{2.45}+\left\{\frac{1.0\times10^{17}T^{3/2}}{Na\left[\ln\left(1+\frac{6.53\times10^{14}T^{2.2}}{N_a}\right)-\frac{6.53\times10^{14}T^{2.5}}{Na+6.53\times10^{14}T^{2.5}}\right]}\right\}} \quad (6.55)$$

Equations (6.54) and (6.55) are similar to those derived by Levinshtein and Rumyantsev (1990). The mobility of injected electrons in p-type germanium at 300 K as a function of concentration are displaced in Figure 6.15. The points represent the experimental results; while the curve represents the calculated values. As seen, there is a good agreement

between theory and experiment.

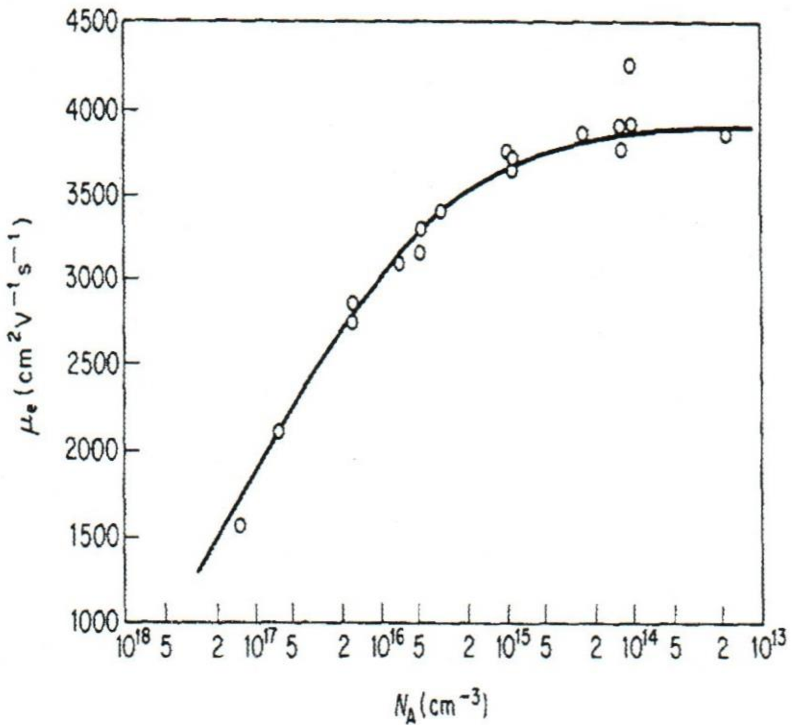


Figure 6.15. The mobility of electrons in p-type germanium at 300 K as a function of impurity concentration. Points experimental, curve calculated using equation (6.57).

Theories of the electron mobility in insulating material, such as II-semiconductors, treat the mobility as a property of a single electron. The electron lifetime (relaxation-time) is calculated for the scattering from impurities and by acoustical and optical phonons. The electron-electron interactions can be ignored in the limit when the concentration of electrons is very low. The theories predict

$$\lim_{T\to 0}\mu = \frac{-e\,\tau_0}{m_B} = \frac{-e}{2\alpha\, m_B\omega_0}\left(e^{\beta\omega_0}-1\right) = \mu_0 \tag{6.55}$$

$$\frac{1}{\tau_0} = 2\alpha\, N_0\omega_0 \tag{6.56}$$

$$n_0 = \frac{1}{e^{\beta\omega_0}-1} \tag{6.57}$$

This limit is appropriate, since at very low temperatures the electrons are in states within $k_B T$ from the bottom of the band. These low-energy particles can not emit phonons, since this event is prevented by energy conservation. They can only absorb them, and the rate of absorption is proportional to the thermal average density of phonons n_0. The factor n_0 makes the mobility increase exponentially with decreasing temperature, since the electron scattering becomes less likely as the number density of phonons declines. The exponential increase in the mobility is evident in the experimental results. The behavior of large polarons is opposite to that of small polarons, whose mobility increases with increasing temperature. The mobility is mostly limited to optical phonon scattering in the temperature region $\frac{\omega_0}{k_B T} \cong \frac{1}{2}$, so we need to calculate the mobility for higher temperatures. The electron lifetime $\tau(k)$ is inversely proportional to the temperature, so that the mobility is inversely proportional to T.

The electrical and thermal resistivities are calculated from impurity scattering. Electrons scattering by acoustical phonons present a hard problem in transport theory. At low-temperatures the electrical resistivity is provided by the scattering of the electron with impurities and phonons and found to have acoustical term ρ_0 from impurity scattering, plus a T^5 term from scattering by phonons. The T^5 term is often never observed experimentally, at any temperature. The most general way to represent the theoretical results is:

$$\rho(t) = AT^2 + \rho_0\left(1 + BT^2\right) + \delta\rho(t) \tag{6.58}$$

The ρ_0 term is from impurity scattering, and is proportional to their concentration. The T^2 term is given by the coefficients A and B. The term $\delta\rho$ is from a variety of effects: phonon drag; dislocation and size effects.

The first term of equation (6.58), AT^2, is intrinsic and comes from electron-electron scattering from the crystal potential which is known as the UmKlapp scattering. Normal electron-electron scattering conserves electron momentum and does not contribute to resistivity. This Bragg scattering provides crystal momentum, and gives finite contribution to the resistivity. The term B is due to inelastic scattering of the electrons by impurities [Koshino 1960 and Taylor, 1962]. Since the impurities are part

of the lattice, the scattering by the electron can excite phonons. The calculated resistivity is displaced in Figure 6.16.

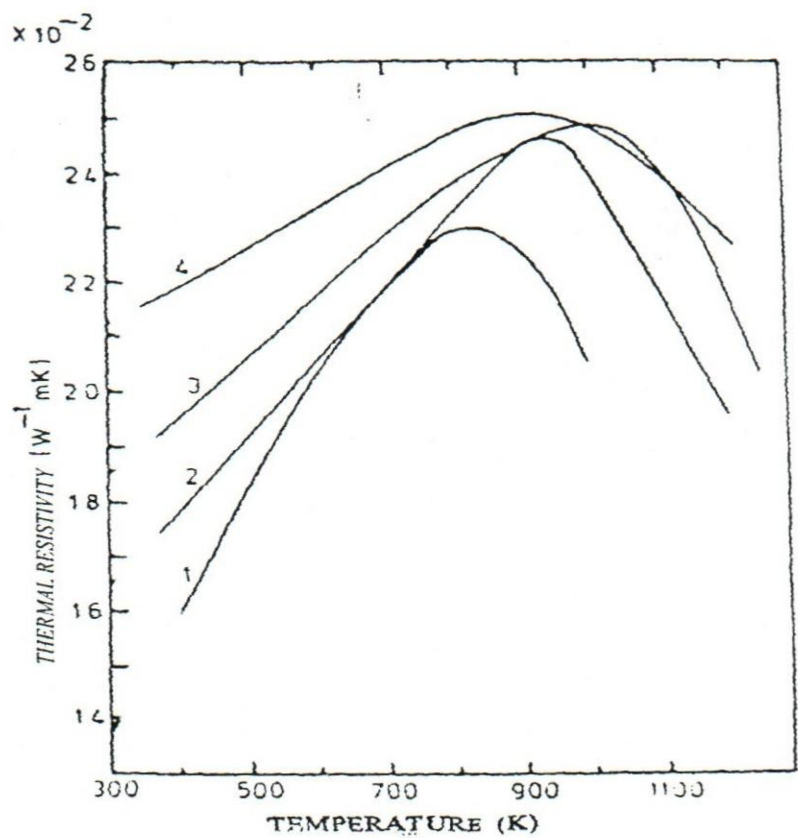


Figure 6.16. Thermal resistivity versus temperature in n-type Si-Ge alloys for different concentrations: curve 1, 1.25×10^{24} m^{-3}; curve 2, 2.25×10^{26} m^{-3}; curve 3, 6.65×10^{25} m^{-3}; curve 4, 1.5×10^{26} m^{-3};

The results are found to fit an expression of the form

$$\rho_{th}(T) = \rho_0 + AT^2 + BT^5 \tag{6.59}$$

The above result is obtained by using a screened Coulomb interaction. The calculated values for A and B are found to be 0.01 and 0.0025,

respectively. These values are too small compared with experiment.

In comparison with experiment, the best experimental results in a good agreement are Si and Ge semiconductors. The theoretical results are slightly high, which suggests that electron polaron scattering is actually important in the scattering process. At T=1 K the factor BT^2 is of $O(10^{-5})$ which shows that these terms are a small correction to there resistivity.

The AC conductivity results are shown in Figure 6.17 as a function of frequency and energy at 300 K.

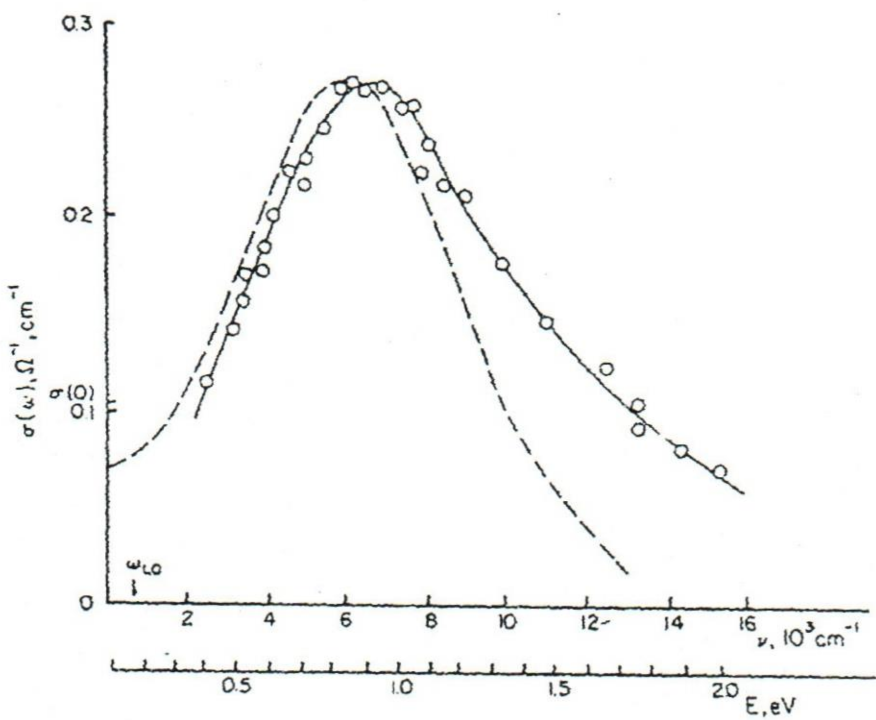


Figure 6.16. The AC conductivity at 300 K.

Chapter Seven

Conclusion and Future Work

7.1 Introduction

In this chapter we summarize our achievements of this work and outline fruitful paths for future work.

7.2 Conclusion

The RTA model, in which the conservation of energy and momentum are expressed as delta functions in the QBE collision term, has been used to investigate thermal and electrical properties of semiconductors. It has been found that the results obtained agree fairly well with the experimental results as well as the theoretical ones.

This work may shed some light on the thermal and electrical behavior of some semiconductor samples. The overall behavior of these systems was found to be consistent with the previous reported results. This statement is based on our attempt to determine some parameters, such as, thermal conductivity, electrical conductivity and mobility. We can say this method is good enough to rely on it when investigating semiconductor transport properties using distribution functions having small disturbances from their equilibrium ones. The following conclusions may be withdrawn:

1) Thermal conductivity shows temperature, concentration, and carrier dependence.

2) The lattice thermal conductivity is resulted from several mechanisms such as: phono-phonon scattering, electron-phonon scattering, impurity scattering and scattering by dislocations.
3) The electrical contribution to thermal conductivity depends on the charge carriers and the electron plays the most important role.
4) The electrical properties are followed by considering the dc conductivity as well as the AC conductivity. Both of them are found to temperature dependent.
5) The Hall coefficient is used to determine the type of charge carrier.
6) The relaxation-times are found to be energy, temperature and density dependent. The characteristic relaxation-time of the system decrease with increasing temperature. This is because of the Pauli blocking depends on temperature. In an expansion at low temperature, the relaxation-time is found to be proportional to T^{-2}.

7.3 Future work

To shed more light on the general behavior of thermal, electrical, optical and magnetic properties of semiconductors, we suggest the following work to be done in future:

1) The relaxation dependence on position, momentum energy is needed in order to form a general theory for the relaxation-time.
2) General distribution function in phase-space such as Wigner distribution may be appropriate approximation for future work.

3) Effect of different mechanisms involved in transport problems must be included and followed simultaneously.

4) Three-dimensional studies are needed for the development of the general theory.

5) Investigations of bands other than parabolic bands. In many situations the energy of electrons (or holes) is expressible in the simple quadratic form, $E(k)= (\hbar k)^2/2m^*$. This simplification arises from the utilization of the first term of a more general expansion of E(k) about the band edge. A more rigorous theoretical model would require the inclusion of higher order terms; this is true for all types of energy surfaces- spherical and spheroidals or otherwise.

6) Magnetic properties. The effect of a magnetic field on thermal conductivity and thermal mobility. The magnetic field can be used to suppress the electronic components and thus enable tit to be separated from the lattice thermal conductivity.

7) Thermal conduction of heat at low temperature by magnons (quanta of spin waves), as well as photon thermal conduction especially at higher temperatures. The photon thermal conduction may by appreciable in materials such that telurium, selenium, and silicon germanium alloys (Bhandari and Rowe, 1988).

8) Investigation of the electron-phonon drag. The theory of heat transport by phonons electrons play the role of the scattering centers

whereas they themselves are assumed to be in equilibrium. Similarly, the phonon system is assumed to be in equilibrium while describing electronic transport although they act as scattering centers for electrons. Those assumption are studied but there are situations have to be taken onto account such as the "phonon-drag" on electrons and the "electron-drag" on phonons. Parrott (1957) discussed the contribution of phonon-drag to thermal conductivity. The thermal conductivity of semiconductors which is made up of contributions from phonons and electrons is likely to be affected by the electron-phonon drag. For low concentrations, the phonon contribution dominates and the change in the electron distribution produced by the phonon flow is expected to be small.

9) Relativistic kinematics should also be investigated.

10) Investigations of photon scattering contribution to thermal and electrical properties.

We think investigating the mentioned problems will be in favor of the RTA model used in this work.

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