# CHAPTER 5

# THERMOELECTRICITY

There are two very basic methods for investigating the properties of electrical conductors. We may apply an electric field, a temperature gradient, or both, and observe what occurs. If we apply only the electric field, an electric current will result and the ratio of current density to electric field when no temperature gradient is present defines the electrical conductivity ( $\sigma$ ) of the material. On the other hand, we may apply a temperature gradient and measure the flow of heat which results when no electric current is allowed to flow; under these conditions the ratio of heat flow per unit area to the temperature gradient defines the thermal conductivity ( $\kappa$ )of the material. Both $\sigma$ and $\kappa$ are, generally speaking, bulk properties of any individual substance.

There is however, a third phenomenon which, at least until rather recently has received less attention. This is thermoelectricity or Seebeck effect. When we apply a temperature gradient to a conductor without an electric field, this of itself tends to produce not only an energy flow ( i.e., essentially the heat flow ) but also an actual electric current, which is a thermoelectric current; under these conditions the ratio of voltage developed per unit temperature gradient is defined as the Seebeck coefficient ( $\alpha$ ) of the material. But in order to observe an electric current one must have a closed circuit of some kind. Further, it is necessary to have a circuit composed of two different materials ( or perhaps the same material in two different states, for example, one under strain, the other not ), and we can then measure the net difference between their thermoelectric properties.

The single parameter which determines the usefulness of any semiconductor as a thermoelectric material is the "figure of merit" Z, defined by[1]

$$Z = \alpha^2\sigma / \kappa$$

where $\alpha$ is Seebeck coefficient/ thermoelectric power,

$\sigma$ is electrical conductivity,

and $\kappa$ is thermal conductivity.

It has been shown in [1,2] that the maximum figure of merit for a material depends on the mobility $\mu$ and the effective mass $m^*$ of the electrons or holes and the lattice component of the thermal conductivity $\kappa_l$ :

$$\mathbf{Z} \propto \mu m^{*3/2} / \kappa_l$$

To evaluate a semiconductor as a thermoelectric material, measurements of the Seebeck coefficient, the total thermal conductivity and the resistivity may be made on the specimens with different impurity types and concentrations. The maximum figure of merit can then be found. Another method is to determine the fundamental properties, $\mu$, $m^*$ and $\kappa_l$, of any specimen of the semiconductor and then to predict what the maximum figure of merit would be in material with optimum doping. While the second method provides more basic information about the material, it is an indirect method and the determination of these quantities requires a detailed study of the band structure of the semiconductor. Hence in the present case the first procedure has been used to evaluate the figure of merit of the materials under study. The figure of merit Z is defined in this way as a function of electrical conductivity, thermal conductivity and square of Seebeck coefficient because of the fact that it is in this form that the three parameters appear in the expression for the efficiency $\varepsilon$ of a thermoelectric generator, which is the important quantity on which the suitability of a thermoelectric material is based. Obviously, the efficiency of a thermoelectric generator should be as high as possible for practical applications.

## THERMOPOWER

Thermoelectric power determination yields information concerning the nature of the conduction process in the solid. In metals, i.e., substances having large positive Fermi energies, the thermoelectric power is a relatively small second-order phenomenon. According to the Lorentz-Sommerfeld theory, the expression for the absolute thermoelectric power of a metal is

$$S = \frac{\pi^2 k^2 T}{3e}\left\{ \partial \log \sigma(E) / \partial E \right\}_{E=\zeta}$$

where k is the Boltzmann constant, e the electronic charge, $\sigma(E)$ the electrical conductivity due to conduction electrons of kinetic energy E and $\zeta$ is the Fermi energy. The thermoelectric power of a metal is influenced by any change in carrier density or scattering mechanism. The thermoemf of a metal is extremely sensitive to small addition of impurities[3], strain[4], defects produced by irradiation[5] or cold work[6], especially at low temperatures. The thermoelectric power of alloys is very different from that of the constituting metals, often considerably larger.

In semiconductors, solid electrolytes and insulators, i.e., materials in which the conduction electrons obey classical statistics, the thermoelectric power is a first-order effect with magnitudes substantially greater than in metals and with a relatively strong temperature dependence. In general, thermoelectric power depends upon the scattering mechanism, carrier density, carrier sign, and effective mass and perhaps the forbidden energy gap, mobility ratio and other aspects of the band structure.

Hence measurement of thermoemf in semiconductors is a useful tool in the investigation of the properties of materials, like density and the sign of free carriers. Like the Hall effect, the sign of the thermoelectric power is an indication of the type of current carrier dominating the conduction.

The electronic component of thermoelectric power (TEP) for a mixed semiconductor is given approximately by[7]

$$P_e = -k/e \left\{ \frac{n\mu_n[2+\ln(N_c/n)] - p\mu_p[2+\ln(N_v/p)]}{n\mu_n + p\mu_p} \right\}$$

where n and p are the densities of free electrons and holes, respectively, $\mu_n$ and $\mu_p$ are the mobilities of electrons and holes respectively, and $N_c$ and $N_v$ are the effective density of states in the conduction band and valence band, respectively. There is, therefore, a change in the sign of $P_e$ from positive to negative when

$$n\mu_n \approx p\mu_p$$

This criterion for change in sign may be compared with that for the small magnetic field Hall effect, for which the Hall voltage changes sign when

$$n\mu_n^2 \approx p\mu_p^2$$

Thus, TEP measurement should be more sensitive to two carrier effects than the Hall effect. Furthermore, the TEP measurement does not have the disadvantage of requiring balancing out of mismatch voltages as is the case with the dc Hall effect measurement and can therefore be used with varying temperature more conveniently.

## THERMOPOWER MEASUREMENTS

The measurement of the thermoelectric power of one conductor with respect to another requires the establishment of a temperature difference $\Delta T$ between two junctions, the determination of $\Delta T$ which may be accomplished by finding the junction temperatures $T_1$ and $T_2$ and the measurement of the voltage $\Delta V$ developed between the two junctions. Ideally, the thermoelectric power S is given by the ratio $\Delta V/\Delta T$ for $\Delta T \to 0$. In practice, S is found as a function of temperature by using $\Delta T$-values as small as the over-all accuracy the measurement allows; the temperature difference should, however, never be more than a few percent of the ambient temperature of the sample.

The different methods used to measure the thermoelectric power are (i) the integral method and (ii) the differential method.

If we keep the temperature of one end of the sample constant and vary that of the other end continuously and measure the developed thermal emf as a function of temperature difference between the constant temperature cold end and the varying temperature hot end, then the method is termed the integral method.

The thermoelectric power at a given temperature is measured as the slope of the thermal emf vs temperature plot at the corresponding hot-end temperature.

In the differential method, the difference between the hot end and the cold end temperatures is kept constant and small and the temperature of the sample as a whole is varied and the developed thermal emf at different average specimen temperatures is measured for this constant temperature difference between the hot and the cold ends. The slope of the thermal emf plot against the average temperature at the (average) temperature of interest gives the thermoelectric power at that temperature.

The details of the differential method used in the present study of the $Sb_2Te_3$ and $Sb_2Te_3$ based alloys are given in Chapter 10.

## ELECTRICAL CONDUCTION

Electrical conduction is an important property of all solids. The electrical conductivity of different types of materials varies over a wide range from values of the order of $10^6$ $(\Omega cm)^{-1}$ for metals to less than $10^{-16}$ $(\Omega cm)^{-1}$ for insulators. Semiconductors usually have a room temperature conductivity of the order of $1(\Omega cm)^{-1}$, although this value is strongly dependent on both the temperature and the purity of the semiconductor. While metals have only one type of charges to support conduction, i.e. electrons, the semiconductors have electrons and holes as charge carriers.

When the conductivity of a semiconductor is due to the formation of equal number of electrons and holes as a result of thermal excitation, then it is known as an intrinsic semiconductor. The expression for electrical conductivity of intrinsic semiconductor can be represented as the sum of two terms: $\sigma = en_i\mu_n + ep_i\mu_p$ where $n_i$ is the electron number density in an intrinsic semiconductor, $p_i$, the hole concentration and $\mu_n$ and $\mu_p$ the mobilities of electrons and holes, respectively. In the intrinsic temperature region $\sigma = \sigma_o \exp(-E_g/2KT)$ where $\sigma_o$ is constant ( the conductivity at absolute zero ), K is the Boltzmann constant and $E_g$ is the energy band gap.

Any material in which conduction is due to charge carriers associated predominantly either with donor or acceptor atoms is called an impurity or extrinsic semiconductor. In the case of extrinsic semiconductor, new energy states are created in the band gap region by either incorporating impurity atoms into the semiconductor or due to the presence of various types of defects such as imperfections, disorders etc., as a result of which there may be a large change in their conductivities. The expression for electrical conductivity is given by $\sigma = ne\mu$ where n is the charge carrier concentration that determines the conductivity of a given substance and $\mu$ is the mobility of these carriers and $\sigma = \sigma_o \exp(-\Delta E/2KT)$ where $\Delta E$ is the thermal activation energy for the excitation of donor or acceptor atoms. $\Delta E$ for an extrinsic semiconductor is very low, of about the order of KT and in some cases even much less and hence conductivity is often observed to be high even at room temperature. If the majority charge carriers are holes, it is p-type semiconductor and if the majority charge carriers are electrons, it is n-type semiconductor.

The temperature dependence of electrical conductivity is determined by the temperature dependence of the free carrier density and the temperature dependence of the free carrier mobility defined as the velocity due to an electric field per unit electric field.

In the case of metals, the free carrier density is independent of temperature and therefore the temperature dependence of conductivity for a metal arises totally from the temperature dependence of the mobility. On the contrary, the charge carrier concentration in semiconductors strongly depends on temperature, while temperature variations of the mobility are insignificant. However, in the temperature regions where the carrier concentration is constant ( in the depletion region and the impurity saturation region ), the temperature dependence of conductivity is fully determined by the temperature variation of the mobility of carriers. The temperature dependence of the mobility is determined by the type of scattering process operative in the semiconductor. There are several processes by which the charge carriers can be scattered and these also affect the semiconducting parameters. The scattering agents are primarily (a) lattice vibrations, (b) ionized impurities, (c) neutral impurities such as defects, vacancies, interstitials, etc., (d) dislocations, (e) grain boundaries, (f) phonon drag, etc. The most important is the interaction between carriers and the ionized atoms of various impurities and the thermal vibrations of the crystal lattice. Scattering processes determined by these interactions have different effects in different temperature regions. At low temperatures, when the thermal vibrations of atoms are so small that they can be neglected, the scattering by ionized impurity atoms plays the major role. On the other hand at higher temperatures the atoms at the lattice sites are considerably displaced from their equilibrium position in the crystal due to the thermal vibrations and so thermal scattering predominates.

For many purposes it is desirable to be able to separate the effects of carrier density and carrier mobility in the electrical conductivity. One way to do this is by the use of Hall voltage, a voltage difference, proportional to the carrier mobility, induced in the y-direction in the presence of an electric field in the x direction and a magnetic field in the z-direction.

## ELECTRICAL CONDUCTIVITY MEASUREMENTS

The electrical conductivity of crystals can be carried out using one of the following techniques:

1) Van der Pauw Method
2) Two Probe Method
3) Four Probe Method

### Van der Pauw Method

The room temperature electrical conductivity measurements can be easily carried out using Van der Pauw method[8]. This method is convenient when the crystal size is greater than 5×5×0.3 mm$^3$. The basic requirements of the method are as follows: The contacts should be at the circumference of the sample, the size of the contacts should be negligibly small as compared to that of the sample, the contacts should be ohmic, the sample should be very thin as compared to its area, the surface of the sample should be singly connected, i.e., the sample should be free from steps and discontinuities, the sample should be flat so that the sample surface and contacts lie in the same plane and the applied field should be low so that breakdown does not occur. If the contacts are not taken perfectly, the observed results may be associated with some error which will be proportional to the dimensions of the contact.

**Two Probe Method**

When the single crystals are very thin, two probe method can be used to measure the resistivity. In this method, voltage and current are measured between the same contacts where the voltage is applied. With an accurate measurement of the dimensions of the sample, the conductivity can be determined as $\sigma = IL/VA$ where I is the current measured in ampere, V is the voltage drop in volts and L and A are the length and area of cross-section of the sample, respectively. The above equation holds true only if the number of carriers is sufficiently large so that the thermal variations in the carrier density are negligible. Unless this is so, there will be random fluctuations in the conductivity as a function of time and only the time average can be specified accurately. In the case of thin films, the length (L), breadth (B) and thickness (d) of the rectangular sample are to be determined accurately since unlike bulk material, the conductivity of the films are dependent on its thickness. The conductivity is then determined by $\sigma = IL/VBd$[9].

In the electrical study carried out on the thin films of $BiSbTe_3$, the author has used the two probe method. The results are given in Chapter 13.

**Four Probe Method**

Of special interest for rapid routine measurements, particularly for semiconductors, is the four point probe method[10]. In this method, all the current and potential probes are point-contacts, usually mounted on a special holder. This arrangement permits a rapid testing of resistivity or conductivity by simple application of the four points to a specimen and, within limits, the results are independent of the size or shape of the specimen.

In the in-line arrangement of the four contacts as depicted in Fig. 1, the simplest case is to have the distance between successive points of contact equal. Considering the area of contact of each point to be small, the conductivity is given by

$$\sigma = I / 2\pi V s$$

where I is the current through the current leads and s the separation between successive points. If this separation is not the same for each successive pair of contacts, it can be replaced with s given as

$$1/s = 1/s_1 + 1/s_3 - 1/s_{1+}s_2 - 1/s_{2+}s_3$$

where $s_1$, $s_2$ and $s_3$ are corresponding probe separations. Then

$$\sigma = \frac{I \ (1/s_1 + 1/s_3 - 1/s_{1+}s_2 - 1/s_{2+}s_3)}{2\pi V}$$

These results apply only if the distance between probes is small compared to the smallest dimension of the sample and provided none of the probes is too close to an edge of the sample.

Several departures from these assumptions are of interest for practical work:

1) The thickness of the specimen is not large compared to the distance between the probes.

   The results must be corrected by using correction curves such as given in Fig. 2 and Fig. 3, which is applicable to a thin slice of thickness $\omega$ with a conducting bottom surface and non conducting bottom surface, respectively. The true conductivity is the conductivity calculated from the above equation multiplied with $G_6(w/s)$ or $G_7(w/s)$ factor for conducting or non-conducting bottom surface, respectively, as the case may be.

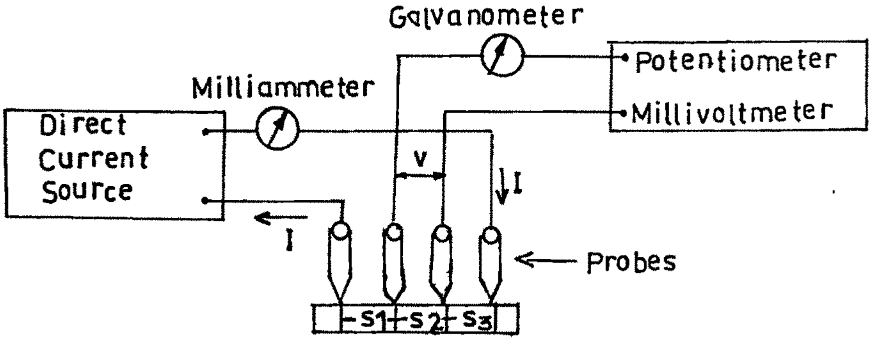

**Fig. 1. Schematic diagram For Resistivity Measurements**

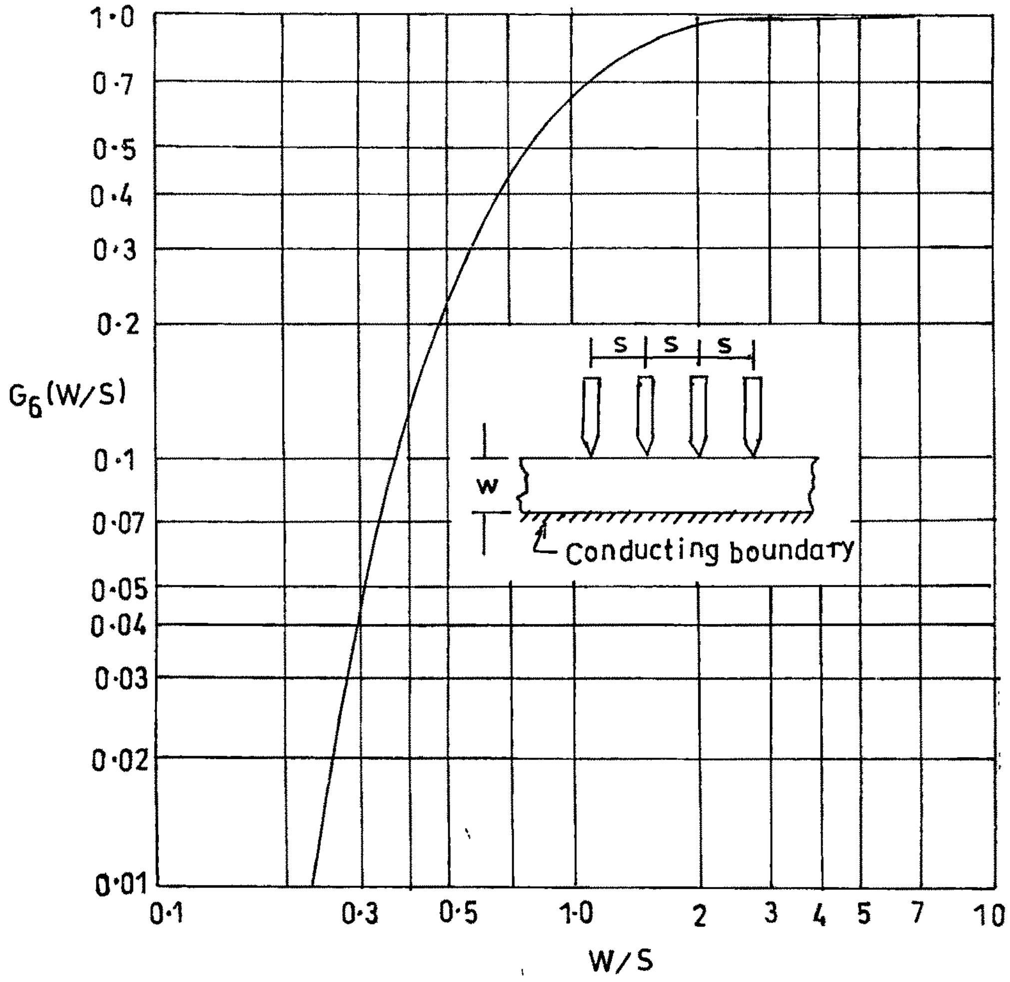

Fig. 2. Correction Divisor For Probes On A Slice With A Conducting Bottom Surface

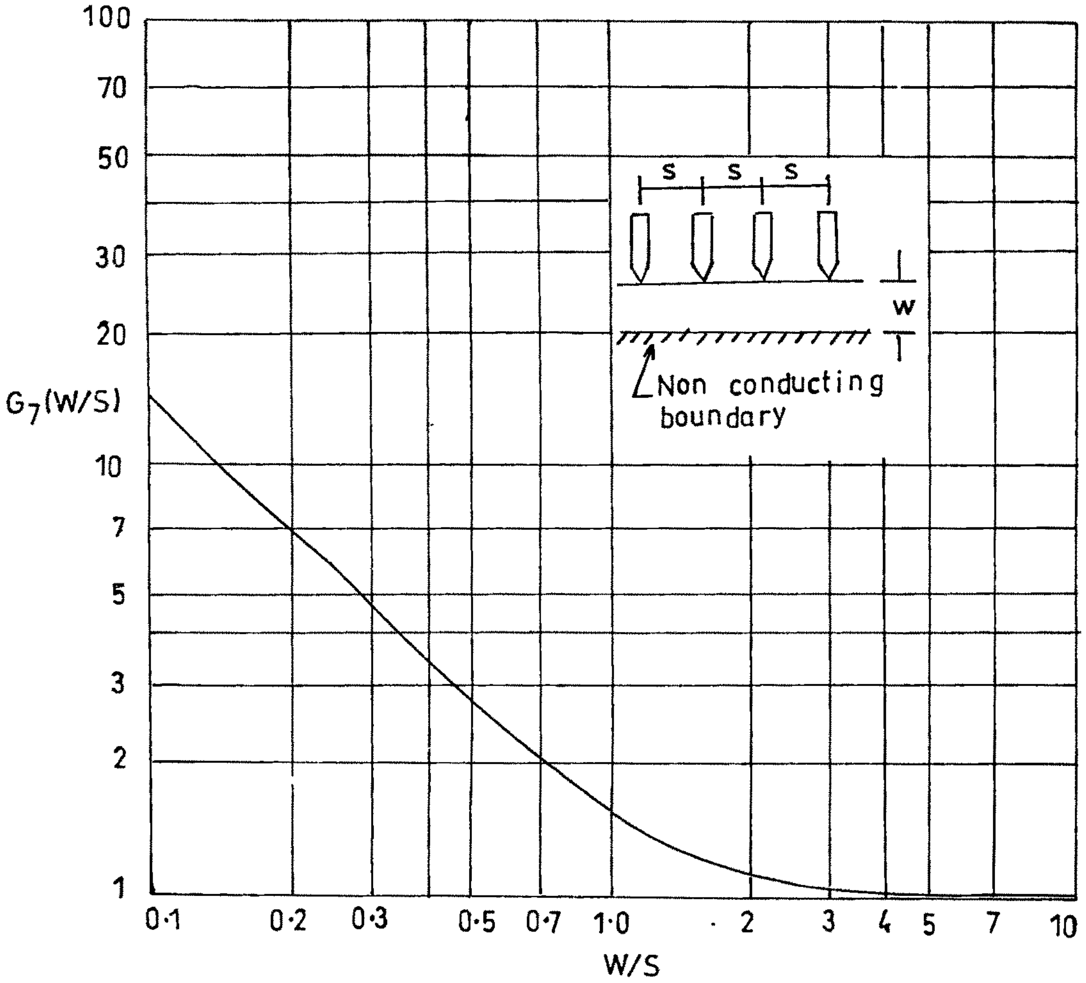

Fig. 3. Correction Divisor For Probes On A Thin Slice With A Non-Conducting Bottom Surface

2) The lateral dimensions of the plate are not large compared to the distance between the probes. The possible errors are smaller in this case than in case 1.

The four point probe technique is widely used in both laboratory and industrial evaluation of semiconductors. Results obtained by the use of the technique are probably accurate to 5% if the apparatus is carefully constructed.

An extremely important aspect of conductivity measurements is the making of suitable contacts to the specimen. Among the important types of contact are: (a) pressure contacts, (b) soldered or brazed contacts, (c) spot-welded contacts, (d) alloyed contacts, (e) diffused contacts, (f) evaporated and sputtered contacts, (g) plated contacts and (h) painted contacts.

Pressure contacts are usually made by pressing needle points on to the specimen surface, usually in a holder designed to maintain the points rigidly in place. However, such contacts are not suitable for semiconductors, especially at low temperatures because they develop high contact resistance Hence at low temperatures, painted contacts are favourable since they are moderately strong and stable and if the contacts are baked at high temperature, such contacts become quite hard. In the case of thin films, evaporated contacts are to be used.

## THERMAL CONDUCTION

Thermal conduction on a microscopic scale is a diffusion process. Heat can be transported by a number of entities. The entities diffusing are capable of absorption and release of heat energy and, consequently, enable heat energy to diffuse through the solid. Some of these heat transporting entities are the following: 1) phonons (quantized lattice vibrations), 2) free electrons and / or holes, 3) electron-hole pairs, 4) excitons (bound electron-hole pairs) and 5) photons (radiant energy). The motion of these entities is limited by various scattering mechanisms. Except for this scattering, the thermal conductivity would be infinite. Study of various scattering mechanisms have been reviewed by Klemens[11,12]. If several heat conducting entities are present, their contributions to the conductivity are additive. Usually the contribution of an entity to the thermal conductivity is given by the kinetic formula

$$\kappa = Cvl / 3$$

where C is the specific heat per unit volume of the entity, v is the velocity and l is the mean free path. If an entity is scattered by several mechanisms, the scattering probabilities are additive. The additivity of scattering probabilities implies approximate reciprocal additivity of the mean free paths. The most important scattering mechanism is the one with the shortest mean free path. If the mean free path of one is very much shorter than all the others, the scattering by the others is effectively negligible.

The thermal conductivity $\kappa$ for extrinsic conduction is the sum of a lattice conductivity $\kappa_{ph}$ and an electronic component $\kappa_{el}$ given by the Wiedemann-Franz law[13]

$$\kappa = \kappa_{ph} + \kappa_{el}$$

Since $\kappa_{ph}$ may be regarded as independent of n, the carrier concentration and $\kappa_{el}$ is directly proportional to n, the total thermal conductivity increases with an increase in the density of carriers.

However, for the more general case, which includes intrinsic conduction, there is an additional term $\kappa_{amb}$, which is the ambipolar contribution due to the diffusion of electron hole pairs[14]

$$\kappa = \kappa_{ph} + \kappa_{el} + \kappa_{amb}$$

Hence in the intrinsic range, where the density of thermally excited electron hole pairs is large, $\kappa_{amb}$ is appreciable.

## Electronic Conduction:

Conduction of heat by electrons can be divided into two general categories; one in which the electronic states form a band of the usual type with properties which can be treated by the effective mass approximation and free electron theory, and another in which states are not distributed continuously in energy and processes of an activated type are involved.

The free electronic conduction refers to the transport of kinetic energy by the electrons which carry the electric current. The electronic conduction is given by Wiedemann Franz relation $\kappa_{el} = L\sigma T$, where L is the Lorentz number, $\Upsilon(k/e^2)$. The value of $\Upsilon$ depends on the degree of degeneracy of the material and the nature of scattering mechanism. The scattering of electrons, however, also determines the electrical conductivity and hence the theories of the two effects are closely related.

In case there are gaps in the energy distribution of electronic states, various types of excitation energy can be transported by the electrons[15,16]. A particularly important case of this type is the intrinsic semiconductor. However, in the thermoelectric application, extrinsic semiconductors are usually used and no thermal conduction due to the intrinsic effect is present.

## Lattice Conduction:

In lattice conduction, the heat transporting entities are the vibrational modes of the lattice, or phonons. In a perfect lattice with a rigorously harmonic potential the phonon mean free path l would be infinite. The scattering of the phonons results from deviations from the idealized description of a crystal.

- Phonon-phonon scattering:

This is usually most important phonon scattering at high temperatures. It arises from the fact that the normal modes of the lattice are weakly coupled to one another by the anharmonic part of the lattice potential. Thus the anharmonic terms can cause transitions between phonon modes. The theory of these transitions was originally developed by Peierls[17]. In the phonon-phonon scatterings vibrational energy is conserved and the wave vector is conserved to within a reciprocal lattice vector. That is, if, for example, phonons 1 and 2 interact to form phonon 3, then

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \text{ and } q_1 + q_2 = q_3 + Q$$

where ω's are the phonon angular frequencies and Q is a reciprocal lattice vector.

- Scattering by Static Imperfections:

Another important source of phonon scattering is static defects of the crystal lattice. The common types of defects which have significant effects on the thermal conductivity are structural imperfections, such as crystallite boundaries and dislocations and randomness in the distribution of different kinds of atoms in the crystal, such as occur in alloys and solutions of impurities. The effects of these defects may be prominent in thermoelectric materials, as foreign atoms and polycrystallinity are frequently deliberately introduced and dislocations can be reduced to a low concentration only by very careful growth techniques. Scattering by defects is most conveniently studied at low temperatures. The different types of defect scattering are 1) Impurity scattering b) Isotope scattering c) Alloy scattering d) Dislocation scattering e) Boundary scattering f) Scattering of phonons by electrons.

The effect of changes of composition and structure on thermal conductivity :

1) Thermal conductivity decreases wit increasing atomic weight. This is true for a series of covalent materials of similar structure, e.g., C, Si, Ge and As, Sb, Bi. However, among the noble gases the order is inverted. The material of highest (C) and lowest (Ne) thermal conductivity are the two lightest materials.
2) A large mass difference between the two components of a compound is favourable to low thermal conductivity. However, the dependence on the mass difference is complicated and is discussed in more detail by Keyes[18]. The ionic crystals tend to be below the covalently bonded crystals with respect to thermal conductivity. Some of the semiconducting crystals have relatively low thermal conductivities; however, in most such cases some of the bonds are probably not of the covalent type ( e.g. Te, $Bi_2Te_3$ ).

## METHODS OF THERMAL CONDUCTIVITY MEASUREMENT

In order to obtain the figure of merit of a thermoelectric material it is necessary to measure its Seebeck coefficient, electrical conductivity and thermal conductivity. Of these three measurements, the determination of thermal conductivity is time consuming and also difficult to accomplish with accuracy. The problem originates from the fact that thermal insulation can never be as good as electrical insulation. Thus, whereas in electrical conductivity measurements one can ignore the possibility of current flowing other than through the sample, in thermal conductivity measurements one must allow for heat exchange with the surroundings by radiation and usually, to a greater or lesser extent, by conduction and convection as well.

There are two different methods to evaluate the thermal conductivity of the material. 1) Static method and 2) Dynamic method

The most direct way of finding the thermal conductivity of a material is by means of a static, absolute method. However certain precautions are desirable.

1) In practical apparatus the enclosure that contains the sample is usually evacuated to reduce the rate of heat transfer to the walls since the thermal conductivity of a gas does not fall as the pressure is lowered until the mean free path of the atoms becomes comparable with the dimensions of the enclosing vessel.
2) The rate of heat loss from the source other than through the sample has to be determined by conducting separate experiment without the sample.
3) The thermal resistance at the contacts can be found by inserting samples of different lengths but of the same material.

A number of workers[19,20] have used the static absolute method for measuring thermal conductivities at room temperature and down to liquid helium temperature. However, the absolute method becomes rather inaccurate as the temperature is raised because of excessive heat losses from the source by radiation. Still it is generally agreed that, for the highest accuracy, this method should be used, in which observations are made after equilibrium has been reached. However, nonequilibrium or dynamic method can be adopted to speed up the measurements and is regarded as being less accurate than those in which equilibrium is reached. Ioffe and Ioffe[21,22] devised a dynamic method in which the errors are claimed to be rather less than 5%. The author has used this method and the details of the apparatus are given in Chapter 10.

**Sample Preparation:**

The shape of the sample used bears an important influence on the thermal conductivity measurements. If the thermal conductivity is high, the ratio of length to cross-section area should also be high and when the thermal conductivity is low it is necessary to reduce the ratio since this minimises the rate of heat exchange between the surroundings and the exposed surfaces of the source and the sample. The use of a short sample also allows equilibrium to be reached reasonably quickly. It is essential that the thermal contact between the sample and the source and sink should be exceptionally good. This can be done by polishing the surfaces, after grinding or machining them flat, and then interposing layers of glycerine to reduce the thermal resistance.

The results obtained in the measurements of electrical conductivity, thermal conductivity and thermopower of $BiSbTe_3$ crystals are discussed in Chapter 10.

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