# UNIT 7 ELECTRICAL PROPERTIES OF SOLIDS

## Structure

## 7.1 INTRODUCTION

In this unit we are going to see the effect of an external electric field on a solid. We should remember that every solid is composed of a positively charged core, i.e. the ion and a negatively charged "cloud" of electrons surrounding it. The ions form the lattice and the electrons provide the binding force which holds the solid together. In an earlier unit we had classified solids according to the binding mechanisms as follows: in metals the binding (or valence) electrons are not confined to any single atom and so the energy required to make them move is very small; in ceramics and polymers, the electrons are more or less confined to specific regions with respect to the ions and so require a lot of energy to make them mobile. This has great consequence in understanding the response of a solid to an external electric field.

### Objectives

At the end of this unit, you should be able'to

* understand the general behaviour of metals, ceramics and polymers under external electric fields, and

* estimate the conductivity of metals, ceramics and semiconductors.

## 7.2 ELECTRICAL CONDUCTION IN METALS

When an electric field, $E$, is applied to a metal, a current flows. One can visualise this as due to the fact that an electron in the solid would experience a force on it equal to $-eE$, where $|e|$ is the electronic charge and is negative. Under this force there would be a

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movement of the charge and hence result in a current. Experimentally it is seen that a steady state results the moment we apply a small voltage to a wire. The current per unit cross-section area, i.e. the current density, by definition is $j = nev$, where $n$ is the number of electrons per unit volume and $v$ is the linear velocity of the electron. This is because $nv$ is the number of electrons crossing a unit area in one second. Note that $j$ is positive as, for an electron, v is also negative. The ratio of the current density and the electric field is the conductivity, $\sigma$. The value of $\sigma$ ranges from $10^{-20}$ to $10^{+6}$ siemens in engineering solids. The reciprocal of the conductivity is called the resistivity, which has the units of ohm-meter. Some representative values of the resistivity in solids, at room temperature, are given in Table 7.1.

Table 7.1 : Resistivities of Some Materials

| Material | Resistivity (ohm-m) | Material | Resistivity (ohm-m) |
|---|---|---|---|
| Silver | $1.61 \times 10^{-8}$ | Nichrome | $1.2 \times 10^{-6}$ |
| Copper | $1.70 \times 10^{-8}$ | Germanium | $10^{-1}$ |
| Gold | $2.20 \times 10^{-8}$ | Silicon | $10^{3}$ |
| Aluminium | $2.74 \times 10^{-8}$ | Silicon Carbide | $10^{-1}$ |
| Tungsten | $5.30 \times 10^{-8}$ | Lead glass | $10^{10}$ |
| Zinc | $5.92 \times 10^{-8}$ | Diamond | $10^{12}$ |
| Nickel | $7.00 \times 10^{-8}$ | Quartz | $10^{13}$ |
| Cadmium | $7.26 \times 10^{-8}$ | PTFE | $10^{16}$ |

Can we understand this large variation in the values of resistivity? The clue lies in the fact that metals have low resistivity and ceramics and polymers have high values of resistivity. This means that the bonding plays a role in the electrical properties also. We must then try to see what is the part played by the valence electrons in the response of the solid to the external electric field.

## 7.2.1 The Role of the Valence Electrons

We have seen in an earlier unit that in the case of a metal, the outermost electrons are shared by all the atoms and so for practical purposes can be considered to be "delocalised" or "free". These free electrons would then respond to an external field by being physically displaced, so that the motion of electrons would constitute the current. In order to calculate the current, we should know the electron density, i.e. the number of electrons per unit volume that would be displaced by the external electric field. One way to calculate this number is to determine the number of atoms per unit volume and multiply this by the valence. If the number of electrons per unit volume is $n$, then the current density is given by $j = nev$. The question is what is the velocity.

If we assume that electrons can be considered as particles with mass m, then, when the force -eE acts on it , it should cause the electron to suffer an acceleration, so that :

$$m \frac{dv}{dt} = -eE \text{ , and}$$

on integrating we would see that the velocity

$$v = -\frac{eE\,t}{m},$$

i.e. the velocity increases linearly with time. But this would mean that the current per unit area, j would increase with time. This is contrary to our experience as the current in any circuit, when measured by the best m e t e r s or oscilloscopes, is found to be "steady". One way out of this difficulty is to define a quantity mobility, $\mu$, as the velocity per unit electric field, or

$$\mu = \frac{|v|}{|E|}.$$

You should remember that both $v$ and $E$ are vectors and $\mu$ can be defined only provided the two vectors are in the same direction. With this assumption we can write the current to be:

$$j = ne\,\mu E .$$

This equation is a statement of Ohm's law, which postulates the linear relationship between the current and the voltage applied across a device. The product ne $\mu$ is a constant for a given material and is called the conductivity. As the conductivity of a solid can be measured, one can get an estimate of the mobility and hence of the velocity of the electron in moderate electric fields.

## SAQ 1

Using the data in Table 7.1, determine the velocity of electrons in a metal like copper when a field of 1 V/cm is applied.

The assumption that the velocity of an electron is linearly proportional to the electric field implies that the electrons are not free to move in a solid (as then they should be accelerated) but that there is a viscous or damping force also experienced by them. The origin of this force is purely quantum mechanical in origin and governs the time taken for the system of electrons to reach equilibrium once an external force is switched on or off. Experimentally this would mean the time taken for a steady state current to be set up in a conductor and it is faster than any measuring device, such as an oscilloscope, can offer. Quantum calculations give values in the range of $10^{-16}$ seconds, for metals. This time is called the relaxation time, $t$ , and is a characteristic of the material. One can get a feel for the calculations by a simple derivation of the quantities involved. The equation of motion of the electron can be written under the condition of damped motion as:

$$m\frac{dv}{dt} + m\frac{v}{\tau} = -eE.$$ ...(7.1)

The second term on the left is the damping term. Under steady state conditions, no force acts on the electron. Hence the first term would become zero. We would then have

$$v = -\frac{eE\,\tau}{m}.$$

One would then get the mobility,

$$\mu = -\frac{e\,\tau}{m}$$

Using the value of the resistivity, you can calculate the time $\tau$.

This simple picture has one major problem. It postulates that the conductivity is directly proportional to the valency of the atom. Divalent metals like Ca or Mg should show higher conductivity than monovalent metals like copper and silver. This is simply not true. Our picture of conduction in solids must be altered to take into account the wave nature of the electron.

### 7.2.2 The Free Electron Approximation

In Unit 2 we had seen that the electron obeys Schröndinger's equation and has the energies $E_n$ given by:

$$E_n = \frac{h^2\kappa^2}{8\pi^2 m}$$

wherein $\kappa = p\,\pi/L$ , for the case of an electron which is confined to a length L, but is free, i.e. V = 0. We should remember that p can take integral values from 1, 2, 3 and so on. This means that an electron which is confined to remain within a definite region in space should have energy levels that are discrete. But then there are N electrons inside a volume V. What levels should these electrons occupy? To get an answer, let us assume that there is no interaction between the electrons. Now, no more than two electrons (with opposite spins) can occupy a given energy level. The lowest energy level would be occupied by the first two electrons, the next higher level by two more and so on. Remember that $n = N/V$ is a very large number. It makes a good approximation to assume that the electrons would occupy levels so that all the occupied $\kappa$ levels lie within a sphere of volume $(4\pi/3)\,\kappa_F^3$ ,

where $\kappa_F$ is the highest occupied $\kappa$ level. This level is called the Fermi level. This volume should contain all the N electrons. But each electron occupies a region in $\kappa$ space equal to $8\pi^3 / V$; we get this by recalling that in one dimension, there is a single $\kappa$ state in a linear $\kappa$ region of $2\pi/L$, and so in three dimensions the region occupied by a single $\kappa$ state would be $(2\pi/L)^3$, or $\dfrac{8\pi^3}{V}$. It is then easy to see that :

$$\frac{N}{2} = \frac{[(4\pi/3)\,\kappa_F^3]}{8\pi^3/V}$$

This gives us

$$\kappa_F = [3\pi^2 N / V]^{1/3},$$

and the Fermi energy

$$E_F = \left(\frac{h^2}{8\pi^2 m}\right)\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Now we should remember that an electron can only be excited from an occupied state to an unoccupied state, so as not to violate the exclusion principle. Then, only those electrons near the Fermi level, which can be excited by the electric field to the unoccupied levels would give rise to the current. Electrons with energies lower than this threshold would not be able to contribute to the current. The Fermi level, then, holds the key to understanding the electrical behaviour of solids.

## SAQ 2

Calculate the Fermi energy for copper. Compare this energy with the thermal energy, What would be the velocity of the electron if it has energy equal to
i)   thermal energy, and

ii)   the Fermi energy.

## 7.2.3 Drift Velocity

In the previous section we have seen that the electrons which contribute to the current in a solid when an electric field is applied to it, are very energetic. Why then is it that, when no field is applied to it, the current is zero? This is because there are electrons moving randomly and this random movement cancels out the current so that there is no net displacement of the electrons. But when a field E is applied, electrons near the Fermi level are raised in energy to higher $\kappa$ values. Now, $\dfrac{h\,\kappa}{2\pi}$ is the momentum of the electron. So there is a change in momentum and therefore a change in the velocity. The net velocity of the electron would then be $v_F + v_D$, that is the Fermi velocity plus the additional velocity due to the field. The latter is called the drift velocity and is very small compared to the Fermi velocity. The current density $j$ is then $n.e. <v_F + v_D>$, where the brackets denote an averaging. The Fermi velocity does not contribute to the current and so we get as before that $j = n.e.\,v_,$. The mobility $\mu = \dfrac{|v_D|}{|E|}$ as defined earlier. Only now we have a clearer idea about the velocity term. In metals, the drift velocity is of the order of a meter per second per kilovolt of field; as if the electrons are taking a walk down the metal! We will see later that in semiconductors this velocity can be two or three orders of magnitude higher. It is the speedier response of electrons in semiconductors that is exploited in modem day electronics.

Don't electrons experience electron - electron interaction in solids? Well they do and this results in two ways: one, the damping term in the equation of motion is a result of this interaction and two, the strong manifestation of the exclusion principle is a result of this e - e interaction. So, next we should consider the interaction of electrons with the ions or the

lattice. The regular periodic array of atoms would interact with the electron wave like a grating, leading to diffraction effects if the interatomic spacing and the wavelength of the electron wave satisfy the Bragg condition, i.e.,

$$n \lambda = 2 d \sin \theta$$

where $n$ is an integer giving the order of diffraction, $\lambda$ is the wavelength, $d$ is the interatomic spacing and $\theta$ is the angle of diffraction.

## SAQ 3

Calculate the velocity of an electron in copper which would be Bragg diffracted. Compare this velocity with the Fermi velocity.

## 7.2.4 Phonon Scattering

Bragg diffraction is easy to visualise when the ions occupy fixed positions. But we know that as temperature increases, lattice vibrations set in and these would also interact with the free electrons. It is difficult to visualise this interaction and we need to solve this problem quantum mechanically. Quantum theory tells us that the thermal energy in a solid is just a manifestation of lattice vibrations; the energy of these vibrations is also quantised and only discrete energy levels are possible for the lattice vibrations. This is something like a clamped string in a musical instrument, which can vibrate only with fixed frequencies. All the ions participate in these vibrations and such quantised lattice vibrations are called phonons. The interaction of electrons and the lattice ions can be considered as electron - phonon interactions or scattering.

## 7.2.5 Dependence of Conductivity on Temperature

One of the nice methods to check our understanding of theory is to test it against experimental observation. The temperature dependence of conductivity in metals is a well known result. In metals the conductivity decreases linearly with temperature, i.e. $\sigma \propto \dfrac{1}{T}$.

According to our theory, $\sigma$ is a product of $n, e$ and $v$. In metals, the number of electrons per 'unit volume does not change much with temperature, it certainly does not decrease, and e is a constant. So the temperature dependence should arise only from $v$. We have seen that it is the electrons near the Fermi level which are the ones to consider, i.e., $v$ is really $v_F + v_D$. With this velocity the electron moves for a small time $\tau$, before it is scattered. The distance that it covers in this time is called the mean free path, and the time $\tau$ is called the relaxation time. The mean free path is usually denoted as $\Lambda$ and is equal to $(v_F + v_D) \cdot \tau$, which is approximately $v_F \cdot \tau$, as $v_D$ is small. The conductivity is then given as:

$$\sigma = n.e.\mu = \left(\frac{n e^2}{m}\right) . \tau = \left(\frac{n e^2}{m}\right) . \frac{\Lambda}{v_F} .$$

The temperature dependence of $\sigma$ is really due to the temperature dependence of $\Lambda$. This is visualised as follows. As the temperature increases, more phonons are excited. In fact the number of phonons excited is directly proportional to the temperature. AS the number of phonons increases, lhe probability of electron - phonon scattering increases. With the increase in scattering probability, the mean free path decreases. As the scattering probability is directly proportional to T, the mean free path $\Lambda$ is inversely proportional to T. The resistivity, $\rho$, which is $1/\sigma$, in metals increases linearly with the temperature. This fact is a direct manifestation of the electron - phonon scattering. The variation of $\sigma$ with T at very low temperatures is more complicated. Experiments show that the dependence is approximately as $T^5$, and at T = 0 K the resistivity attains a finite value. What happens if there are impurity atoms in the crystal? These should also scatter the electrons and the resistivity should increase. The temperature behaviour, however, would remain unaltered. This is also shown in the figure. The resistivity of a metal, at T = 0 K then can be written as:

$$\rho (T) = \rho_i (T = 0) + \rho_{impurity}$$

This is known as Matthiessen's rule and states that for small impurity concentrations, the increase in resistivity is proportional to the impurity concentration.

If our model is correct then the resistivity should also depend on the charge of the iinpurity atom. That is the increase in resistivity should be higher for a higher valent impurity.

### 7.2.6 Dependence of Conductivity on Structure

In metals, one can add one metal to another to form an alloy. The ions of the additive element may dissolve in the parent and be distributed randomly. It is also possible to give the alloy a heat-treatmentin order to develop crystalline ordering. In a disordered material, the impurity atoms would act as scattering centres and the resistivity would increase. But once ordering sets in, the electron wave would possibly have some phase relationship with the phonon reducing the probability of scattering. The resistivity would show a decrease. The minima in the resistivity match the formation of ordered phases in the Cu-Au phase diagram. In general, we can say that with careful measurements we can map the phase diagram details by Studying the electrical resistivity in metals.

To summarise then, metals are good conductors and have very low electrical resistivity. Metallic wires are often used to carry electric currents, the most common materials bemg wires of copper or aluminium. In electrical circuits, the resistance of the wire is important. But the resistance is not a material constant. It depends on the cross-sectional area, the amount of defects generated due to cold working etc. On the other hand, the resistivity is an intrinsic property of the material independent of the material geometry. It however depends on the amount of scattering of the electrons by lattice vibrations, or the phonons when an external field is applied. Since electrons get scattered by any impurity that changes the lattice potential, impurity atoms, lattice defects and imperfections do greatly alter the resistivity of the pure metal. The resistivity can be written as :

$$\rho = \rho_I + \rho_T + \rho_D$$

where the contribution from impurity atoms is $\rho_I$, $\rho_T$ is the temperature dependent component and $\rho_D$ arises from lattice defects such as dislocations, strains etc., normally produced in the act of drawing the metal into wires. The temperature independent portion of the resistivity is called the "residual resistivity" and is simply $\rho_I + \rho_D$. Consequently it is customary to deduce the purity of a metal by measuring the ratios of the resistivity at room temperature ($300^\circ$ K) and at liquid helium temperature ($4.2^\circ$ K). Commercial high purity copper has large resistivity ratios, often of the value of 1000 or more. All impurity atoms adversely affect the resistivity and those impurities that dissolve in the metal affect the most. Often heat treatments have to be given to see that the impurity is removed from the matrix and gets deposited at the grain boundary.

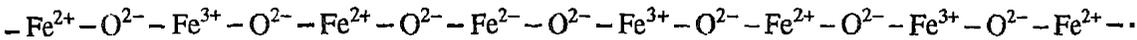## 7.3  ELECTRICAL CONDUCTIVITY IN CERAMICS

Historically, the use of ceramics has been for electrical insulation, and even today the largest electrical grade ceramic material is the one used for outdoor insulating supports for high tension cables. In the more common ceramics, the bonding is highly ionic and so there are no free electrons to participate in conduction. However, the resistivities of magnetite, $Fe_3O_4$, and alumina, $Al_2O_3$, are widely different. Does this difference arise because of the crystal structure? The answer is no. The difference is a natural consequence of the electronic structure of the ions in the two solids.

If we refer back to the periodic table of elements, we find that the lighter elements have a well &fined valence and this arises from the inherent stability of a completely filled electronic shell. We had called an element a cation if it readily gave up its electrons to achieve the filled shell structure; and we called an element an anion if it gained electrons to complete the octet structure. In ceramic materials, such elements would give rise to high insulation as there would be no possibility of electron movement. Hence oxides of the lighter elements make good insulators such as MgO, $Al_2O_3$ or $SiO_2$. One comes across elements with more than one valence state in the transition series in which the inner electrons also sometimes participate in the bonding. In ceramics containing such elements we come across the possibility of moving the electron from ion to ion, constituting charge movement. Let us discuss this and see how this gives rise to conduction in ceramics.
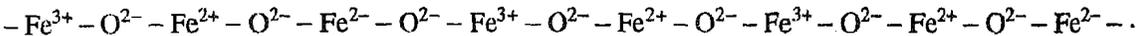
## 7.3.1 Electron Hopping

The possibility of charge transfer from one cation to another through the intermediate anion explains the low resistivity in ceramics containing ions such as Mn and Fe. Such ceramics show semiconducting behaviour. Let us see how this occurs.

Consider a hypothetical one-dimensional chain of atoms containing O and Fe ions as shown:

$$- Fe^{2+} - O^{2-} - Fe^{3+} - O^{2-} - Fe^{2+} - O^{2-} - Fe^{2-} - O^{2-} - Fe^{3+} - O^{2-} - Fe^{2+} - O^{2-} - Fe^{3+} - O^{2-} - Fe^{2+} - \cdot$$

If, due to some interaction, an electron from each $Fe^{2+}$ ion goes over to the $Fe^{3+}$ ion , then tlie chain would look as follows:

$$- Fe^{3+} - O^{2-} - Fe^{2+} - O^{2-} - Fe^{2-} - O^{2-} - Fe^{3+} - O^{2-} - Fe^{2+} - O^{2-} - Fe^{3+} - O^{2-} - Fe^{2+} - O^{2-} - Fe^{2-} - \cdot$$

You can quickly see that the two ion arrangements are the same and therefore the lattice energy for the two cases is the same. This means that the transfer of an electron can occur between two states of the same energy. Such a transfer would then have a large probability and so need low energy to initiate it. A small electric field would enable the transfer of charge and hence lead to a current. Such a material would show low resistivity. But what interaction would lead to such a transfer of charge'? Well the distance between the ferrous ion and oxygen would be larger than that between the ferric ion and oxygen. This is because of the larger ionic interaction if the charge is large. The distance between atoms would always fluctuaie due to lattice vibrations. A particular type of lattice vibration would make cations and anions vibrate against each other. When oxygen ions come closer to the ferrous ion, tlie electron would leave it to lower the energy and as the oxygen ions move oppositely the other ferrous ion would become ferric. This is a probable way in which charge transfer could take place. Such electron hopping has been used to explain the low resistivity in $Fe_3O_4$, in which a situation very nearly like the one discussed above occurs, as well as in ceramics containing both $Mn^{3+}$ and $Mn^{4+}$. Notice that when we have considered electron hopping we have assumed that both the cations are in identical sites. In $Mn_3O_4$, though we have both $Mn^{2+}$ and $Mn^{3+}$, the compound shows higher resistivity than the iron analogue as the manganous and manganic ions are on dissimilar sites.

## 7.3.2 Ionic Conduction

There is another possibility that cannot be discounted in ceramics and that is the actual movement of the ions leading to conduction. This is known to occur especially in those compounds in which there are a lot of vacancies or in which there is a small ion which can diffuse through tlie open structure. Hydrogen is an ion which diffuses through the ceramic easily and there are a lot of structures that show proton conductivity. This is also the dominant method of conduction in phosphate glasses. Also as the lattice contains charged ions, any long range movetnent of the ions would constitute conduction. In silicate structures like porcelain, a monovalent ion like $Li^+$ or $Na^+$ would lead to conduction. Again, in ceramics, there can be charged defects such as vacancies (wherein a site that should normally be occupied is not), interstitials (in which an ion occupies a site that it should not) and defects (in which the site is occupied by an ion with a different valency). It should not be difficult for you to appreciate that ionic conductivity would be more prominent at higher temperatures.

## 7.3.3 Dependence of Conductivity on Temperature

In ceramics, as tlie conductivity depends on the number of charge carriers created, if the charge carriers can be thermally generated, then the conductivity would show a strong temperature dependence. Normally the conductivity would increase with temperature exponentially. In fact ceramics are often used to measure temperature by determining their conductivity. A graph of logarithm of conductivity against the reciprocal temperature is often plotted. The slope determines a quantity called the activation energy for the conduction process. A general equation known as the Arrhenius equation is often written as follows lo represent the conductivity behaviour:

$$\sigma = \sigma_0 \cdot \exp\left(\frac{-Q}{P\kappa_B T}\right)$$

In this equation $\sigma$ is tlie conductivity, $Q$ is the activation energy and $\kappa_B$ is the Boltzmann constant with $T$ the absolute temperature.

It should be remembered that conduction can be a complex process in red system in which both electronic and ionic conductivities co-exist. In such cases, $Q$ would be made up of two quantities, shy $Q_{electronic} + Q_{ionic}$, and the graph of log (a) versus $(1/T)$ would exhibit a change of slope, the high temperature portion normally giving the ionic contribution, while the low temperature portion emphasising the electronic conduction. This is shown in the figure.

## 7.4 PHENOMENON OF SUPERCONDUCTIVITY

In some metals and ceramics, we see an unusual behaviour at low temperatures in which the resistance of the material becomes zero. The material can support a current without any heat generation showing that there is no electron phonon scattering. This phenomenon is called superconductivity and the material which shows this behavious is called a superconductor Superconductivity was first discovered in metals and about 26 metals show this behaviour, albeit at very low temperatures. Mercury becomes superconducting at 4.2 K, tin at 3.7 K, while niobium at 9.15 K. However there are hundreds of alloys and compounds that exhibit this behaviour.

The temperature at which a material's resistivity becomes zero is called the critical temperature, $T_c$. Above this temperature it has a finite resistivity and is said to be normal or exhibiting normal behaviour. Below $T_c$ the material is called superconducting. Besides temperature, a superconductors behaviour depends upon two more factors: one the magnetic field, H, and the other the current density, J, in the material. In both cases, there is a critical magnetic field and a critical current density above which superconductivity vanishes. For every superconducting material there exists a critical surface in the $T$, $H$, $J$ space.

### 7.4.1 Superconductivity in Metals and Alloys

We have seen that the electrical properties of metals can be easily understood on the basis of interaction of electrons with the lattice vibrations. This electron-phonon interaction was at the heart of the nearly increase in electrical resistivity with temperature in metals. Resistivity is also the cause of heat being generated in a current carrying conductor. A metal is called a perfect conductor if its resistivity becomes zero at zero K. In practice, however, there are always some impurities that give a metal a residual resistivity even at zero K. What then is the explanation of the phenomenon of superconductivity that is seen in some metals?

We had seen earlier in this section that in a metal there is no band gap. Electrons at the top of the Fermi level are essentially mobile that is they need very small energy to excite them to higher unoccupied levels. Such a situation would not give rise to superconductivity. We will see in a later section that in semiconductors, at the Fermi level, there is a band gap separating the bound electron states from the free electron states due to strong electron-lattice interactions. According to our current understanding, in a superconductor the electrons at the Fermi level develop a small band gap, because of an attractive electron - electron interaction. The band gap has a value, at zero K, ranging from 3 to 5 times $k_B T_c$, where $T_c$ is the superconducting transition temperature. The band gap continuously decreases as the temperature is raised and becomes zero at the transition temperature. In the superconducting state, the electron states are presumed to be occupied by pairs of electrons with opposite momenta (so that the total momentum is zero) and opposite spins (so that they can together be treated as a single quantum particle obeying different statistics, the Bose-Einstein statistics, instead of the more usual Fermi-Dirac statistics). This assumption is the basis of the Bardeen-Cooper-Schrieffer or BCS theory. The pairs of electrons are called Cooper pairs and they are spread in a narrow region of width called the coherence length, typically some 1000 nm wide. In a volume occupied by a single Cooper pair, there are about $10^6$ "normal" conduction electrons. One can visualise that all the electrons near the Fermi level with opposite momentum and opposite spins form Cooper pairs which move co-operatively in a crystal with no scattering due to phonons, i.e. the resistivity in the solid is zero. A current induced in such a solid would persist for an infinite time, without attenuation.

### 7.4.2 The Meissner Effect

As seen in the last section, a superconductor shows persistent currents. This would be possible only if the magnetic flux in the material is zero. A superconductor, then, behaves

like a perfect diamagnet. This can be seen as follows: The magnetic flux density in a metal is given by:

$$B = \mu_0 (H + M)$$

where H is the applied external field and M is the magnetisation induced in the material due to the response of the magnetic dipoles in the material under the influence of the external field. As $B$ must be zero this means that the magnetisation induced, M, is equal to $-H$. The susceptibility, $\chi$, of a material is defined as the ratio of $M/H$. For a superconductor this is $-1$. Compare this with the value of $\chi$ for a metal like copper, which is $10^{-5}$.

When a normal metal like tungsten is placed in a magnetic field, the magnetic flux lines pass through the metal relatively undisturbed as its permeability is close to that of free space. Below 0.01 K, tungsten makes a transition to the superconducting state. Its conduction electrons get ordered and the Cooper electron pairs can move in the solid without scattering. In this state the material is a perfect diamagnet and so the magnetic flux would be repelled from the solid. As the flux lines are repelled, the flux density in the vicinity of the superconductor is greatly increased. This would give rise to large magnetic fields and one major application of superconductors is in the generation of high magnetic fields. Another way of saying the same thing is that there would be a force of repulsion on a magnet when it is placed close to a superconducfor. This force of repulsion is very striking and is being considered very strongly for surface transport at very high speeds, there being no friction as a magnet levitates above a superconductor. This phenomenon of repulsion of flux lines in a superconductor is called the Meissner effect. It is also because of the attractive proposition of frictionless transport at high speeds that has made the search for high temperature superconductors so competitive.

### 7.4.3 Type I and Type II Superconductors

It has been observed that the behaviour of a superconductor in a magnetic field is varied. There are some materials in which the magnetic field is completely repelled and if the field value is increased above a critical field the superconductivity is destroyed and the flux lines penetrate inside the material. Such superconductors are called Type I superconductors. There are other materials, however, and these are more common, in which some magnetic flux lines do penetrate but are confined to a very narrow region and the transition to the normal state takes place with magnetic field more gradually, One can define two field values; one at which the flux lines begin to penetrate the material and a higher field value above, which superconductivity is destroyed. These field values, $H_{c1}$ and $H_{c2}$, are not intrinsic to the material and depend upon the purity level and metallurgical history as well as the stress state of the material. Materials showing such behaviour are termed as Type II superconductors. It is common to observe $H_{c1}$ to be about a few kilo amperes per meter and $H_{c2}$ to be a hundred time higher. In Type II superconductors much higher fields can be produced. Commercial magnets employing wire wound solenoids of NbGe alloy give flux densities exceeding 10 Teslas.

### 7.4.4 Superconducting Ceramics

In the last ten years, a new generation of superconducting materials has been discovered. These are ceramic materials which are mixed oxides of yttrium (or other rare earths), barium and copper, in which superconductivity is found to exist upto temperatures of 90 K. As the temperature is higher than the boiling point of liquid nitrogen, using liquid nitrogen to cool the ceramic to the superconducting state has become a very attractive proposition. These ceramic materials are not very pure and are known to possess both superconducting and non-superconducting phases. They exhibit Type II superconductivity. The exact mechanism by which such high temperature superconductivity is possible is not thoroughly understood. Nevertheless the possibilities of generating high magnetic fields and passenger trains using magnetic levitation has made this one of the most researched areas in recent times.

## 7.5   SEMICONDUCTORS

We have seen in Unit 2, how the band gap arises in some solids, especially when there are an even number of valence electrons participating in the bonding. In ionic solids there is a band gap as the ions generally have an even number of outermost electrons, which

completely fill up the band formed due to electron orbital overlap. In covalent solids, a similar band gap arises for the elements in the Group IV of the periodic table. The magnitude of the gap decreases as we go down the periodic table, as all the energies reduce and it should require less energy to excite an electron from one band to another. If thermal energy is enough to excite a sizeable number of electrons from the filled band to the empty band, the material is called a semiconductor. Let us see some more features of such materials.

## 7.5.1  The Band Gap in Semiconductors

Let us take a look at the energy band structure of the semiconductors. In a semiconductor, it is necessary to have covalent bonding. The average number of electrons per atom must be equal to four. The crystal structure of the solid is diamond cubic, which is a FCC structure with two atoms per lattice point, identified in positions $(0, 0, 0)$ and $(114, 114, 1/4)$. The E versus k curve shows energy gaps for those values of k that satisfy the Bragg diffraction condition. In the figure we have plotted the energy band structure showing the band gaps. If we consider the energy states available for the electrons in the First Brillouin Zone we get a scheme of levels called the reduced zone scheme, and the band picture becomes a little simplified. What we are saying in the reduced zone scheme is that an energy state outside the first Brillouin Zone is **equivalent** to another state within the First Brillouin Zone and changing the k value to give the equivalent state (a state with the same energy and same slope in the E -vs. - k curve) only means including Bragg diffraction in our consideration.

How many of these bands get occupied? Well, in the diamond structure, we have at least two atoms per unit cell and there are four electrons per atom. This means that the eight electrons per unit cell would fill up the first four bands completely. Note the following:

1)   The topmost filled band, also called the valence band, has a maximum at $k = 0$.

2)   The lowest unfilled band, also known as the conduction band, has a minimum at $k = 0$.

3)   There is a band gap between the highest occupied state and the lowest unoccupied state.

The above points are generally true for all semiconductors, with one difference. In materials with large band gaps, the conduction band minimum shifts away from the $k = 0$ point in the E versus k curve. Semiconductors in which the valence band maximum and the conduction band minimum both lie at $k = 0$ are called direct band semiconductors. Semiconductors in which the conduction band minimum does not lie at $k = 0$ are called indirect gap semiconductors. The reason for this classification stems from the strikingly different behaviour of the two types of semiconductors to optical absorption. Let us see this in some detail.

Interactions in solids to any external influence can be understood by considering that the electrons in the solid go from one allowed state to another. In the process, both energy and momentum should be conserved. The momentum is proportional to $k$ and so we may represent on the $E - k$ diagram the various processes that may take place by lines showing a transition from one state to another. A vertical line would depict a change in energy but no change in momentum; a horizontal line would show a transition in which energy is not changed but momentum is changed substantially. In semiconductors, the scale at which energy changes are considered are of the order of a few eV. Optical photons have this energy. Thermal energies are much smaller than this value. So, when an electron absorbs a photon, it changes its energy substantially. In fact the energy may be sufficient for an electron in the valence band to be excited to the conduction band. But what about the change in momentum? Remember that the $E - k$ diagram has been plotted with k values typically of the order of $\pi/a$. As a is of the order of $10^{-8}$ cm, $k$ is of the order of $10^8$ cm$^{-1}$. The k value of a photon is given by $2\pi/\lambda$, which for visible light gives a value about a thousand times smaller. Hence for all practical purposes, the absorption of a photon does not change the momentum of an electron. Photon absorption would then be represented by vertical lines in the $E - k$ diagram. What happens when an electron absorbs a phonon? Phonons are lattice vibrations having quantised energies and the order of magnitude of the energy is $k_B T$, or the thermal energies. Therefore the absorption of a phonon by an electron would essentially be a horizontal line in the $E - k$ diagram. In indirect gap semiconductors the photon of the lowest energy could be absorbed only with the help of a phonon which would give the necessary momentum. In direct gap semiconductors, the electron could absorb the photon without the need of a phonon, and so would be a very probable process.

## 7.5.2 The Dependence of Resistivity with Temperature

The temperature dependence of resistivity is strikingly different from that in conductors. The difference is a natural consequence of the energy band gap. Using simple statistics, the number of electrons, $n$, that can be excited to cross a band gap of $\Delta E$, at a temperature $T$, can be written as:

$$n = N_C \exp\left(\frac{-\Delta E}{k_B T}\right)$$

where, $N_C$ is the available number of states and $k_B T$ is the thermal energy.

The application of Fermi-Dirac statistics does alter this number and we have to replace $\Delta E$ by $E_C - E_F$. $E_C$ is the energy at the bottom of the conduction band and $E_F$ is the Fermi energy. This number would contribute to the conductivity and so we can see that the conductivity would increase exponentially with temperature. Can we calculate the increase in conductivity? As we have not yet defined the position of the Fermi level, this would be difficult. But we can see that for every electron excited to the conduction band, there would be a vacant energy level created in their valence band. As the valence band would no longer be completely filled, it also would contribute to the conductivity. The contribution from a single vacant site in the valence band can be calculated quite simply. We know that the current density due to one electron would be $e.v$. Consider a band with one vacant electron state. As it would be possible for another electron to be excited to this state, we should be able to see a contribution to conductivity due to the electron motion in this band. The net current would be:

$j = \sum e.v$, where the sum is over the $N-1$ electrons. We may also write this as:

$$j = \sum_{n=1}^{N} e.v - e.v.$$

Now we also know that the net current from a completely filled band is zero. Therefore the current due to a band with one electron state untilled is the same as $-e.v$ or equal to the current of a single charge but one with an opposite sign. Such a situation can be visualised as if the vacant electron state had a positive charge and contributed to current. This state with a positive charge is called a hole. Remember that the description of a hole contributing to a current is best suited for the valence band. This is because it is convenient to consider .the summation over fewer states and the hole states are fewer in the valence band just as the electron states that are occupied are the fewer states in the conduction band. The net contribution to the total conductivity, then, arises out of the motion of electrons in the conduction band and the holes in the valence band. One can then write the equation from conductivity as:

$$\sigma = n.e.\mu_e + p.e.\mu_h$$

where, $n$ and p are respectively the number of electrons and holes that contribute and $\mu_e$ and $\mu_h$ are the mobilities of the electrons and holes.

- Just as above we may write for p :

$$p = N_v \exp\left(\frac{-\Delta E}{k_B T}\right),$$

where $\Delta E$ is really equal to $E_F - E_v$. Taking the product of $n$ and p helps us to eliminate $E_F$ : $n.p. = N_C.N_v \exp-\left(\frac{(E_C - E_v)}{k_B T}\right)$.

The energy difference $E_C - E_v$ is the band gap, $E_G$. Again, if the electrons are excited due to the increases in temperature, both $n$ and p increase exponentially with T. You can also see that in a pure semiconductor $n = p$ ! Such a semiconductor is also called as an intrinsic semiconductor. Unlike a metal, in a semiconductor, the conductivity would increase rapidly with temperature. It can be easily seen that a graph of $\ln \sigma$ against $1/T$ would be a straight line with a slope of $-E_G/2k_B$. This is a convenient method of determining the band gap in a semiconductor.

### 7.5.3 Intrinsic and Extrinsic Semiconductors

Pure semiconductors, which we have studied above are called intrinsic semiconductors. A semi-conductor atom needs energy of the order of 1.1 eV to shake off the valence electron. This energy becomes available to the semi-conductor even at room temperature. Due to thermal agitation of the crystal structure, electrons from a few covalent bonds come out. The bond from which electron is freed, a vacancy is created. As there should have been an electron in this vacant space, this space in covalent bond is called hole. This hole can be filled by some other electron in a covalent bond. As the electron from a covalent bond moves to fill the hole, the hole is created in the covalent bond from which the electron has moved. In other words, one can say that hole shifts from one covalent bond to another in a similar way as an electron does in an attempt to fill the hole. Since the direction of movement of the hole is opposite to that of the negative electron, a hole behaves as positive charge carrier. Thus, at room temperature, a pure semiconductor will have electrons and holes wandering in random directions. These electrons and holes are called intrinsic carriers and such a semiconductor is called intrinsic semiconductor. Figure 7.1 shows an intrinsic semiconductor.
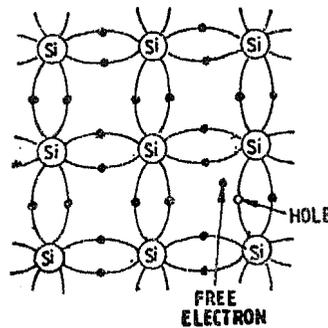


**Figure 7.1 : An Intrinsic Semiconductor**

We may change the property of the semiconductor by the addition of some appropriate impurity, called dopants. The process of the adding the required impurity is called doping. The doped semiconductors are called extrinsic semiconductors. In a pure semiconductor, the number of free electrons and the holes are equal. However, we can make them into predominantly electrons or predominantly holes by appropriate doping. Let us look at silicon. It has $1.45 \times 10^{10}$ electrons and equal number of holes per $cm^3$ at 300 K. Let us incorporate some phosphorous into it by diffusion. Let us accept that the phosphorous atoms take the place of some silicon atoms. While phosphorous has five valence electrons, silicon has only four. Once phosphorous forms covalent bonds like silicon with four adjacent silicon atoms, it is left with one extra electron. The higher dielectric constant of silicon compared to vacuum, makes the ionisation of phosphorous easy and the excess electron in the valence shell of phosphorous is released to the silicon lattice. This is an extra electron added by one added phosphorous atom to the silicon lattice. If we add $10^{15}$ atoms per $cm^3$ of silicon, we would have added so many electrons to the lattice. However, the product of the density of electrons and that of holes in silicon should be a constant at constant temperature. Hence the large number of electrons suppress the number of holes in the silicon, We essentially have a material with $10^{15}$ electrons per $cm^3$ with the same band gap as that of silicon. It is a n-type conductor as the material conducts electricity predominantly by the conduction of electrons. Here, phosphorous is called a donor. In a similar way, we can think of doping silicon with boron, which makes silicon a $p$-type conductor. Here, boron takes one free electron from the lattice to form the four covalent bonds and hence it is called an acceptor.

By the addition of impurities, the conductivity of Ge-crystal or Si-crystal can be remarkably improved. The process of adding impurity to pure Ge-crystal or Si-crystal is called doping.

The impurity atom are of two types.:

i) Pentavalent impurity atoms i.e., atoms having 5 valence electrons such as antimony (Sb) or arsenic (As).

Such atoms, when added to a pure semiconductor, will create excess of free electrons.

(ii) Trivalent impurity atoms i.e. atoms having 3 valence electrons such as indium (In) or gallium (Ga).

Such atoms on being added to a pure semiconductor, instead of producing free electrons, will make the crystal deficient in electrons and holes will be produced. The N-type (Extrinsic) semiconductors is shown in Figure 7.2.
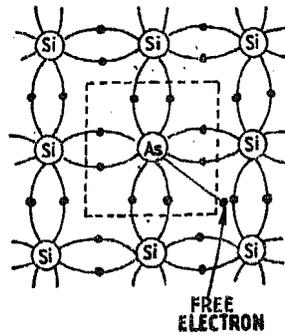


**Figure 7.2 : N-type (Extrinsic) Semiconductor**

**Table 2 : Ionisation Energies (eV) of Dopants in Silicon**

|  | Si | Ge | GaAs |
|---|---|---|---|
| Donors | P : 0.045 | P : 0.012 | Si : 0.006 |
|  | As : 0.054 | As : 0.03 | Se : 0.006 |
| Acceptors | B : 0.045 | B : 0.011 | Si : 8.035 |
|  | A1 : 0.067 | A1 : 0.01 | Zn : 0.031 |

In the above table, it is easy to note the way dopants behave in silicon and germanium, which are elemental semiconductors. You m y note that gallium arsenide is a compound semiconductor and silicon behaves as a donor as well as an acceptor. Here, depending on whether silicon takes the position of gallium or arsenide, it becomes a donor or an acceptor. The fermi level of a n-type semiconductor lies close to the bottom of the conduction band $E_c$ and that of a p-type semiconductor lies close to the top of the valence band.

## 7.5.4 The $p$ - $n$ Junctions

Semiconductors are used in devices which control the flow of electrons. Now let us see how they are controlled. The core of the control comes from making junctions between different types of semiconductors. Let us first make a junction between an n-type and a p-type semiconductor as shown in Figure 7.3. It is called a p-n junction,

P-type has excess holes and n-type has excess electrons. The fermi energy of electrons in n-type silicon is higher than that in p-type and hence the electrons will flow into the $p$-type silicon. While the electrons balance the charge of ions in a given material, when electrons are removed by the flow said above, the material is left with some positive ions. These ions resist the flow of electrons perpetually. These two opposing factors come to an equilibrium after the transfer of certain number of electrons. Under these conditions, the positive charge in the core elevates the $E_c$ and $E_v$ in the n-type semiconductor and the excess negative
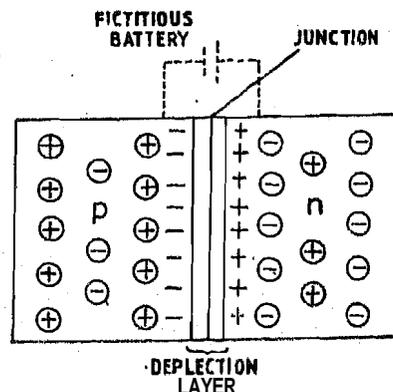


**Figure 7.3 : The $p$ - $n$ Junction**

charge in thep-type makes the said levels lower. A barrier is crated for the flow of electrons at the $p$-$n$ junction. This is a barrier for flow of electrons in one direction, while in the opposite directions electrons flow with ease. It is this barrier which allows the fabrication of a rectifier using the p-n junction. Such junctions are used in tandem to form a transistor and even a semiconductor light emitting diode.

## 7.6  SUMMARY

In this unit we have seen some electrical properties of materials. While a classification of materials could be done based on their conductivity, we could see the physical reason behind such a classification. We learnt about the nature of free electrons in metals, and semiconductors. We saw that the small bandgap in the semiconductor makes its conductivity low compared to that of metals. At the same time, the same gap could be used to explain the variation of conductivity with temperature. We saw that the conductivity of semiconductors could be changed by introducing some impurities known as dopants,

## 7.7  KEY WORDS

| Intrinsic Semiconductor | : | Pure semiconductor with the intrinsic properties of the pure material such as carrier concentration. It has equal number of electrons and holes as c. |
|---|---|---|
| p-type Semiconductor | : | A semiconductor doped with an acceptor type impurity. This material has holes as the predominant charge carrier. |
| n-type Semiconductor | : | A semiconductor with a donor type impurity. This material has electrons as the predominant charge carrier. |

## 7.8  ANSWERS TO SAQs

### SAQ 1

Calculate the density of electrons from the density (number of atoms per unit volume) and valence of copper. Use this to find mobility of electrons and then the velocity.

### SAQ 2

Use the density of electrons calculated above to find the $N/V$ and use it to calculate the $E_f$.