CHAPTER 1.

AMORPHOUS SEMICONDUCTORS

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CHAPTER I

AMORPHOUS SEMICONDUCTORS

1.1. Structure of Amorphous solids

1.1.1. SOLID STATE THEORY

A. General Approach:

After the development of quantum mechanics, it became possible to understand the properties of atoms, molecules, and solids, in a much more fundamental manner than was previously imagined. In principle, the physics could be determined from the solution of a partial differential equation, which could be symbolically written

H Ψ (r_1 , ..., r_n) = E Ψ (r_1 , ..., r_n) ...(1) In Eq.(1), E represents a number which gives the energy of the state characterized by the wave function, Ψ (r_1 , ..., r_n) a complex function of the positions of the N particles in the system. The physical significance of the wave function is that magnitude squared, $|\Psi(r_1, \ldots, r_n)|^2$ yields the probability density for finding the particles near $r_1, r_2, ...$ r_n , respectively. The symbol in Eq.(1), called the Hamiltonian of the system, is a differential operator which can always be determined provided the forces between the particles are known. H can be written:

$$H = \sum_{i=1}^{N} \left(\frac{h^{2}}{2m_{i}} \nabla_{i}^{2} \right) + V (r_{1}, \dots, r_{n}) \qquad ...(2)$$

Where ∇_i^2 is the Laplacian operator corresponding to particle i, m_i is mass of the particle i, and $V(r_1, ..., r_n)$ is the potential energy corresponding to the forces

between the particles, h is the Plank's constant divided by 2π , and is equal to 1.05 X 10^{-34} joule-seconds in the MKS system of units.

The great simplification which enables the solution, in principle, of all nonrelativistic problems involving atoms, molecules, and solids is the fact that the only important forces are the electrostatic interactions between the positively - charged nucli and the negatively - charged electrons. For example, if there are N nuclei of charge +Ze and ZN electrons of charge -e present then:

$$V (R_{1}, \dots, R_{N}; r_{1}, \dots, r_{ZN}) = \frac{1}{2} \sum_{\alpha, \beta}^{\beta} \frac{Z^{2} e^{2}}{|R_{\alpha} - R_{\beta}|} + \frac{1}{2} \sum_{i,j}^{\beta} \frac{e^{2}}{|r_{i} - r_{j}|} - \sum_{\alpha=1}^{N} \sum_{j=1}^{ZN} \frac{Ze^{2}}{|r_{j} - R_{\alpha}|}$$

where the R_{α} represents the positions of the nuclei, the r_i represents the position of the electrons, and the primes on the summation symbols mean that the terms $\alpha=\beta$ and i=j are omitted from the double sums (since particles do not interact with themselves). The first set of terms of Eq.(3) represent mutual repulsions between the nuclei, the second set the mutual repulsion between the electrons, and the third set the attraction between the nuclei and the electrons.

The quantitative mathematical problem represented by equations (1)-(3) can be solved to a high degree of accuracy for atoms and simple molecules, but is much more difficult for solids, which typically contain ~ 10^{23} nuclei and 10^{24} electrons in 1 cm³. Ideally, we should like to calculate the lowest possible energy levels for any system, together with their corresponding wave functions, since these would yield the electrical, optical and thermal properties of the system.

We know that by defination, solids retain their shape physically, this means that the nuclei possess equillibrium position in which the forces on them vanish. Since all materials (except helium, a very anomalous case because of its light mass and very weak interatomic forces) become solids at sufficiently low temperature, the lowest energy state of any collection of atoms must possess equillibrium position for the nuclei. This set of equillibrium positions for the lowest energy state is called the structure of the solids. It is very difficult to calculate the structure of solids from the nature of the constituent atoms. Instead, an empirical approach is used. in which structure is determined or inferred from experimental observations.

B. Structure:

X rays, whose wavelengths are of the order of interatomic separations were used to study the structure of solids. In 1922, Von Laue suggested that periodic crystals would act as a diffraction grating for X-rays, and the next year Bragg was the first to use this effect for determining crystal structures. More recently, the diffraction of electrons and neutrons with similar wavelength have also been used to study the structure of crystals, whose long range periodicity makes the interpretation of such experiments relatively straightforward. Or the other hand, the structure of amorphous solids is much cifficult to determine. Diffraction experiments can be used to discover the interatomic separations of the neighbouring atoms from a central atom, from which a structure can often be inferred. This procedure can be ambiguous in complex materials. However in an elemental solid, the results are relatively straight forward.

1.1.2. STUDIES OF THE STRUCTURES OF AMORPHOUS MATERIALS

An amorphous solid is one in which three dimensional periodicity is absent. The arrangement of atoms, however will not be entirely random as in a gas. The binding forces between atoms are very similar to those in the crystal and although long range order is excluded, short-range order of a few lattice constants will generally be present.

A complete theoretical discription of the properties of an amorphous solid would need a full knowledge of the structure. Even within the restraints imposed by forces between individual atoms and the tendency towards short range order, there are an infinite number of allowed structures for any amorphous material. If no features greater than 50°A (which would indicate crystallization or phase separation) are observable, then the techniques used for a more microscopic investigation include electron and X-ray diffraction, infrared absorption and Raman spectroscopy. Diffraction patterns from an amorphous solid consists of broad haloes or rings, without any evidence of spots, which would indicate some degree of crystallinity, Fig.(1.1).

From the angular dependence of the scattered radiation, the radial or pair distribution function $4\pi r^2 \rho(r) dr$ can

be obtained by a Fourier inversion. This gives the average number of pairs of atoms separated by a distance lying between r and r+dr. Several approximations are involved in obtaining this function, only two of which are mentioned here. First it is normally assumed that the atomic density is uniform over a sphere of a given radius. This is probably a good approximation for liquid metals, it may not be for amorphous semiconductors, in which the presence of voids and cracks is quite likely. Secondly, termination errors in the Fourier integrals can distort the radial distribution function and introduce spurious structure. Considerable care and skill is needed in generating and interpreting plots of $4\pi r^2 \rho(r) dr$ against r, i.e. radial distribution curves(r.d.c.).

Fig.(1.2) represents radial distribution curve for amorphous Ge. The first peak of the r.d.c. is well separated from the following ones, measurement of the area beneath the maximum gives the number of atoms contained in the first coordination sphere. The position of the peak gives the average separation between nearest neighbours. The curve is seen to be distributed about a parabola, which represents the r.d.c. of a hypothetical amorphous solid of the same density but with matter uniformally distributed in space. Although first few coordinations are well defined, the width of the peaks indicate some spread in the interatomic distance, and the decreasing amplitude of the oscillations with r shows the lack of long range order. In the case of germanium, the first two coordination numbers are 4 and 12



2345678910 r(A°) Fig. 1.2. Radial distribution function of

Arrorphous Ge.

as in the crystal. The average interatomic distances are increased, by about 3%. In crystalline InSe for example, the first coordination sphere is occupied by atoms of both kinds. Thus each In atom is surrounded by one In and three Se atoms as first neighbours, and each Se atom by three In atoms. In amorphous InSe the first maximum of the r.d.c. is split in to two peaks; and the short range configuration present in the crystal is retained.

Structural models of amorphous solids or liquids can be constructed to give the best fit to the experimental r.d.c., together with any other conditions required by the nature of the bonds surrounding each atom. In most cases knowledge of the structure of material in its crystalline form, where this exist, is used to determine the basic unit, z, the number of bonds, a, the bond length, and θ , the bond angles. These basic units are then stacked or mixed in an appropriate manner to satisfy experimental observations. When the three parameters, z, a and θ have well determined values in a narrow range, the material is said to exhibit short range order. Given the short range order it is not difficult to construct a model for the structure which does not have any long range crystalline periodicity. Such models are called random networks.

The hypothesis that an amorphous solid could be modelled by a random network of atoms with near-perfect shortrange order was first proposed by Zachariasen[4] over 50 years ago, with reference to oxide glasses. Many years later,

Polk[5] constructed such a model for tetrahedral amorphous semiconductors. However this approach to the structure of amorphous solids has remained controversial and alternative models based on microcrystalline arrays have continually been suggested[6].

1.1.3. CHEMISTRY OF COVALENT AMORPHOUS SEMICONDUCTORS

The three parameters z,a, and θ simply reflect the nature of the chemical forces which characterize the constituent atoms. These chemical forces are themselves just parameterizations of the complex interactions given in Eqs.(2) and (3), and arise from the balance between the kinetic energies of the electrons and the nuclei and the electrostatic coupling between them. The strongest chemical forces are ionic, covalent or a resonant admixture of both of them. In the presence of large number of atoms, there can be a contribution from a slightly weaker force called metallic, which basically has the same crigin as that of an unsaturated covalent bond.

Icnic bonding takes advantage of the attractions between oppositely-charged atoms and tends to predominate whenever at least one type of atom with a relatively low ionization potential (i.e. ninimum energy necessary to remove an electron) and another type of atom with a relatively high electron affinity (i.e. the maximum energy reduction from forming the negatively-charged ion) are both present. The lowest energy ionic solid maximizes the electrostatic attraction between the positively and negatively charged ions while minimizing the mutual repulsions among similarly charged ions. For two similar sized ions, the optimal value of z is 8 and an optimal value for the bond length, a, also exists. As the ratio of ionic redii begins to deviate from unity, lower values of z (six or four) become optimmal for geometric reasons. In any case the only constraints on the bond angles are that maximize the distance between similarly charged second neighbouring ions.

Covalent bonding places strong constraints on all three parameters, z, a, and θ . Consequently it is not difficult to form covalent amorphous structures even from single elements or simple binary compounds. All of these exhibit a great deal of short range order, as expected. In some covalent amorphous solids, there is evidence for intermediate -range order, in which third and sometimes fourth neighbour peaks in the correlation function resemble those in the corresponding crystal.

In addition to a determination of the local environments of the constituent atoms, other issues are important in describing the structure of amorphous solids. For example, a-Si and a-Ge appear to contain significant regions of microvoids and samples may resemble swiss cheese in that respect. In addition to this possibility, many other types of inhomogeneties may exist in perticular materials. The inhomogeneties include the disorders,

a) Translational disorder,

b) Topolcgical disorder and

- c) Compositional disorder.
- a) <u>Translational disorder</u>: The long range order is complete absent, while short range order is responsible for observable properties.
- b) Topclogical disorder : This is attributed to
 - i) Crowding of atoms at one place forming clusters

ii) Missing planes from the structure and

iii) Atoms not occupying regular sites. This causes potential fluctuations inside the structure, giving rise to localised states in the forbidden gap.

c) <u>Compositional disorder</u>: While forming multicomponent system, the composition of elements in amorphous material may not be in the same ratio and it will give rise, localized states in the forbidden zone.

These may take the forn of density fluctuations, of which voids represent an extreme example, or compositional variations, including, e.g., phase separation or more local clustering. When amorphous solids are deposited in thin film form on a substrate, the region near the substrate may have a different structure than the bulk of the material and that the properties of the interface region can depend strongly on the nature of the substrate. Furthermore, the free (i.e., upper) surfaces of films can exhibit structures which differ from those of the bulk. Finally, the possibilies of the incorporation of unintentional impurities in significant concentrations should not be overlooked.

1.1.4. ELECTRONIC STRUCTURE

Using one electron approximation, we can write the electronic problems as one involving the positions of only single electron r_i :

where the effects of all the other ZN-1 electrons are included in the operation H_i . The solution to equation (4) give the one electron energies,(E $_i$)_n . The lowest energy of state of the solid is then the one in which the lowest ZN energy state, (E,)n, are filled and all higher ones are empty. Excited states can be analysed by transferring electrons from lower energy-filled to higher energy-unfilled states. Since there are so mary $(\sim 10^{23} \text{ cm}^{-3})$ electrons in a typical solid, the energy levels (Ei) in)are closely spaced $(\sim 10^{22} \mbox{ cm}^{-3} \mbox{ev}^{-1}$). Consequently, it is preferable to treat them as essentially continuous, replacing the discrete levels (E_i) by a function, g(E), which gives the number of one-electron states per unit Jolume per unit energy, g(E) is called the density of one electron states. If q(E) is known, we can ordinarily deduce the electrical and optical properties of the solid from it.

Fermi Energy :- Fermi energy is very useful and convenient parameter for expressing the properties of semiconductor crystal. In case of metals E_F is the highest level occupied by electrons when the metal is at absolute zero of temperature. At room temperature E_F is defined as that energy for

1.

which just one-half the levels are occupied by electrons.

In case of semiconductors and insulators E_F may be defined as the energy that is as far below an energy level which has a certain fractional filling as it is above another level of the same fractional emptyness.

Rule for locating the Fermi Energy :

If we want to determine $E_{\rm F}$ for any system, we can do it as follows:

1) Go to $T = 0^{\circ}K$

2) Determine the highest occupied state, Eoccupied

3) Find the lowest state empty, E_{empty}.

Then Fermi Energy $E_{\mathbf{F}}(0) = \frac{E_{\text{occupied}} + E_{\text{empty}}}{2}$

Above T = 0 °K as T rised, E_F drops. An exception occurs when holes are involved. E_F rises with T when hole action dominates.

In perticular the Fermi energy, ${\rm E}_{\rm F}$, is obtained from the relation:

$$ZN = \int_{-\infty}^{\infty} g(E) f(E) dE \qquad ..(5)$$

where f(E) is Fermi-Dirac distribution function. For weakly interacting particles in thermal equillibrium at a temperature, T :

$$f(E) = \frac{1}{\exp[E - E_F / kT] + 1}$$
 ...(6)

where k is Boltzman's constant, equal to 1.38×10^{-23} j/k in units. The electrical conductivity can be obtained from the expression :

$$\sigma = \int_{-\infty}^{\infty} g(E) f(E) \varrho \mu(E) dE \qquad ..(7)$$

where $\mu(E)$ gives the mobility (velocity attained per unit

applied electric field) of an electron in a state at energy E under the condition that the other electrons are in their lowest-energy states. The mobility is controlled by the scattering process that affect the motion of the excited electron as it moves in the presence of the applied field. The scattering can be due to the phonons, the other electrons, or, in some cases, even the ion cores at their equillibrium positions.

1.1.5 CRYSTALLINE SOLIDS

A) Conventional Viewpoint :

The conventional approach to understanding the electronic structure of crystalline solids is well known. The key element is to simplify the problem by making use of the fact that the one electon potential energy must exhibit the periodicity of the lattice, Fig 1.3(a),. Group-theoretical methods can then be applied to reduce the problem to one involving only the small number of electrons contained in a single primitive cell from which the crystal can be generated. It can easily be shown that all electronic states are extended throughout the sloid, in fact having the same probability of being found in each of the primitive cells. The one-electron density of states, g(E), can be calculated by solving the one electron problem in a single primitive cell and applying periodic boundary conditions. Eecause of the periodicity, the density of states of any crystalline solid takes the form of alternating regions of energy with large densities, typically

CRYSTAL STRUCTURE



Fig .

 $g(E) > 10^{22} \text{ cm}^{-3} \text{eV}^{-1}$, called pands separated from regions where no states are possible, called gaps. The states with E < 0 form the valence band which is ordinarily filled at low temperatures. The conduction band, ordinarily empty at low temperature lies at higher energies. The Fermi energy lies in a gap. The sharp structure that is evident in g(E) Fig 1.3(c), at many different energies arises directly from long range periodicity and these energies are called Van Hove singularities [7]. It can easily be shown that the density of states near a Van Hove singularity has the behavior,

$$g(E) = A |E-E0|^{\frac{1}{2}}$$
 ...(8)

either above or below the critical energy, E_0 . The valence and conduction band edges, E_V and E_C , respectively, are important examples of Van Hove singularities.

B) Alternative Viewpoint :

This type of approach, in its simplest form employs the tight-binding approximation [8], in which the electronic wave functions are antisymmetric linear combinations of atomic orbitals centered on nearest neighbouring ion cores. Schrodingers equation is then solved for the oneelectron energy levels. Although this method is very crude, it provides a good starting point for analyzing g(E), one which does not lose sight of the chemistry. More recently the method has been modified and an empirical tight binding (ETB) approach has become pcpular [9]. In this technique, the matrix element of the Hamiltonian and the overlap integrals between electrons centered on neighbouring atoms are treated as adjustable parameters to obtain good fits to experimentally measured quantities such as energy gap. Since the short-range order of corresponding crystalline and amorphous solids is ordinarily identical, it is useful to set the parameters by their crystalline values and keep them the same in their amorphous counterparts.

1.1.6 EFFECTS OF DISCRDER

The density of states, g(E), of an amorphous solid should not be very different from that of its corresponding crystalline solid, provided the short range order is identical. As a rough guide, we may again use a tight-binding approach, now asking how the analysis would be modified if we introduce bond angle and perhaps even bond-length distortions. Fig(1.4) shows a sketch of the energies of the bonding and antibonding orbitals as a function of bond lenght and bond angle. It is clear that either the stretching or the bending of the bord tends to increase the energies of the valence-band states and decrease the energies of the conduction-band states.

1.1.7 LOCALIZED STATES

Either bond stretching or bond bending could introduce localized states into energy gap. This is consistent with the fact that the band edges are just one type of Van Hove singularity, which, as we previously disussed, arises only because of long range periodicity. In the absence of long-range order, we expect these singularities be disappear and be replaced by more gradually



- Fig. 1.4 (a) Energy as a function of interatomic Separation for the Lowest-energy bonding and antibonding orbitals of a hydrogen molecule.
 - (b) Sketch of the energies of the lowest energy bonding and antibonding orbitals as a function of bond angle for H20.



decreasing densities of states, Fig.(1.5). These regions of gradually decreasing g(E) are called band tails.

We have already indicated that a range of energies may exists in which g(E) is finite but states are localized, and the mobility of an electron with such an energy is zero at T=0. $\sigma_E(0)$ vanishes for these energies. The vanishing of $\sigma_E(0)$ can serve as a defination of localization for electrons with energy E. Other definations of localization are possible. One is trat all eigen function of the one electron Schrodinger equation decay exponentially in space outside regions in which the eigen function is localized Fig.(1.8). The defination of localization is that, for a Fermi gas of non-interacting electrons with Fermi energy E,

$$\lim_{N \to \infty} \langle \sigma_{\mathbf{E}}(0) \rangle = \mathbf{0} \qquad ..(9)$$

1.1.8. ANDERSON LOCALIZATION

Anderson takes the potential of Fig.(1.7) and ask the following questions. Suppose at time t=0 an electron is placed on one of the wells. What happens then as $t \rightarrow \infty$? Is there a finite probability that the electron will have diffused to large distances, at the absolute zero of temperature, or does change that an electron will be found at a large distance r vary as exp $[-2\alpha r]$, in which case there is no diffusion?

The first approach to this problem is contained in Anderson's important paper, 'Absence of diffusion in certain random lattices' [1958]. Anderson finds that there is no





Fig. 1-8, Form of the wave function in the Anderson model:
(a) when Los a; (b) when states are just non-localized
(E≥ Ec); (c) when states are just localized (E≤ Ec);
(d) Strong localization.

diffusion if Uo/J is greater than a constant that depends on the coordination number z, and which for z=6 is about 5. Where Uo gives measure of disorder, and J is band width. This means that if Uo/J>5 all the wavefunctions for an electron in the system are of the type shown in Fig 1.8(c), decaying exponentially with distance r from some well n. The initial state is of the form

}a_m Ψm

and the coefficient a_m will fall off exponentially with distance between wells m and n. Some more recent work on Anderson localization has concentrated on the quantity $\sigma(0)$. If there is no diffusion the conductivity σ too must vanish for all energies in the band. Alternatively we can say, following Anderson(1958) that states are localized if an electron with energy E±dE placed in a volume 1³, large enough to satisfy the uncertainty principle, will not diffuse away.

1.1.9 DENSITY OF STATES

In science of semiconductors, we wish to know = (a) the energies of all the electrons in the semiconductor, and (b) all the possible energies electrons can attain after they have been given some additional energy, for instance, by absorption of sunlight or by heating the material.

There are three principle avenues that may lead to the solution of this problem. The first is to carry out a number of experiments and measurements, and to infer from them the electron energies. A second important way is to use our knowledge of the electron energies in individual atoms and of chemical bonding, and to duduce what the electron energies should approximately be in the solid. The third method involves the theoretical solution of the powerful equations of quantum mechanics and quantum statistics, found successful in crystalline semiconductors.

Chemical Approach :

In atoms the available energy are discrete quantum levels, or energy eigenstates, which are labelled with numbers and letters which signify conserved quantities (quantum numbers) like angular momentum. Only two electrons with cpposite spins can occupy a state characterized by a given set of quantum numbers. There are many unoccupied states at higher energy in to which electrons can get excited by absorbing, for instance, a photon of light of just the right energy. In a Se atom, the four electrons of highest energy are in 4P states. We are principly interested in the electrons of highest energy (the valence electrons) because these are far away from the nucleus and therefore from the chemical bonds between atoms. Imagine that we form a solid by slowly decreasing the interatomic distance, a, of a large number, N, of Si or Se atoms. Fig 1.9, shows what we expect to happen: the N individual and discrete atomic energy states will interact and broaden in to bands. As the atomic separation is further decreased, the stand p states of Si will mix and lose their identity because

covalent bonding occurs with four neighbours in tetrahedral direction. These mixed states are called SP³ orbitals and they form the strong tetrahedral bonds typical for diamond, Si and Ge. Once formed, it costs energy to pull them apart. Hence the band of bonding states lies lower than the average energy of the atomic 3s and 3p states. The equillibrium atomic distance is the one for which the energy of the solid is lowest. All important properties of semiconductors are govern by the electron states near the top of the uppermost filled band (the valence band) and near bottom of the first empty band (the conduction band) and, of course, by any states which lie in the gap in between on account of defects and other causes.

Thermal excitations or optical excitation can only lift electrons across the gap, which is 1.7 eV wide in amorphcus Si and 2.2 eV wide in Se. The widths of the valence and conduction bands are about 5 eV. We, therefore, can forget about the more distant bands of energy states. It is well known that amorphous Si and chalcogenide glasses are, in many ways very different noncrystalline semiconductors. The major reason for this was first explained by M.Kastner [10], who pointed out that the uppermost filled band in Se and other chalcogenide glasses is not the bonding band but a band of states formed by electrons which do not participate in bonding (or antibonding). This is illustrated in Fig 1.9(b). Se has four p electrons of which only two are needed for covalent bonding to two neighbours.

The remaining two p-electrons remain an unused lone pair. The filled band formed in the solid by these lone-pair electrons is the valence band. This fact is the origin for the rather unusual defect chemistry in chalcogenide glasses [11-14] a negative effective correlation energy, self compensation, pinning of Fermi level, and other defect related phenomena that are absent in a tetrahedral semiconductor such as amorphous Si.

Figure (1.10) sketches the density of electron energy states g(E). This is essentially the distribution of energy states of the CFO Model [15] that has been proposed by Cohen, Fritzsche, and Ovshinsky in 1969. Let as make an order of magnitude estimate of the densities of states and describe the main features of Fig (1.10), as one moves from the bands progressively deeper in to the gap.

Si contains about 5 x 10^{22} cm⁻³ atoms. There are four valence electrons per atom; hence, the valence band and conduction band contain approximately 2 x 10^{23} cm⁻³ states. Since the bands are approximately 5 eV wide, the average density of states (number of states in 1 cm³ and leV energy range) is

$$g(E) = 4 \times 10^{22} eV^{-1} cm^{-3}$$

Both the conduction band and valence band have tails of states, and deeper in the gap there are states originating from structural and coordinal defects as well as from impurities. Hence, in contrast to crystal, g(E) is no where zero. The tail states are unavoidable because they are







Fig 1.10, Band model of a noncrystalline sumiconductor. Evand Ec are the mobility edges, of the valence band and of the conduction hand. intimately associated with the disorder in the noncrystalline structure. The valence band tail states are covalent bonds that are weaker than normal. This can happen, for instance, when the covalent angle is bent from its equillibrium value, when the bond is stretched due to internal strains, or when some antibonding orbital is mixed in. That occurs, for instance, when atoms bond together in odd-numbered rings containing 5,7, and 9 atoms (instead of the 6 atoms in crystal). Mcreover, it was recently found, both theoretically and experimentally, that there are net static charges on some atoms or groups of atoms [16]. These produce potential fluctuations which push states up and down and prevent any sharp feature in g(E). All these effects are expected to produce also a tail of states extending down in energy from the conduction band.

The total number of tail states is approximately 10^{-3} of the number of states in one band, and the number of defect-related gap states varies between 10^{-5} and 10^{-7} band states. One wishes, ofcourse, to have as few gap states as possible in order to control the electronic properties by intentional additions of donor and acceptor atoms. Furthernore, the gap states act as recombination centres of photoexcited charge carriers, and thus limit the photoconductivity and life time of electronically injected carriers.

The tail states, as well as the defect related states, are localized to a region of a few atoms. A charge carrier occupying them has, therefore, no chance of moving away (zero mobility) at low temperatures. Carriers in extended band states, in contrast, have a finite mobility.

Non crystalline semiconductors have bands of electron energy states which are extended throughout the materials, and hence provide a finite mobility. The highest filled band (valence band) is separated in energy from the lowest empty band (conduction band) by a mobility gap. There are localized tail states extending from the top of the valence band and from the bottom of the conduction band in to the gap. These localized tail states are weakened or modified band states. They do not conduct -a charge carrier trapped in such a state has zero mobility.

1.1.10 MOBILITY EDGE

The mobility of charge carriers, μ (E), affects the electrical conductivity via Eq.(7). Even if all states are localized to a distance r_0 , electrons can still tunnel from an occupied to an unoccupied state at equivalent energies, with a probability proportional to $\exp(-2d/r_0)$, where d is the distance between the two states. Thus we can write [17].

$$\mu$$
 (E) = $\mu_0 \exp(-2d/r_0)$...(10)

Where μ_0 is a constant of proportionality. If all states with in an energy range Δ are equivalent, then the average separation between equivalent states is :

$$d = [g(E) \Delta]^{-1/3} ...(11)$$

Substitution of Eq. (11) into Eq. (10) yields :

$$\mu(E) = \mu_0 \exp(-2/[\mathbf{g}(E)\Delta]^{1/3}r_0). \quad ..(12)$$

It is not yet clear how g(E) varies in a band tail, and both gaussian and exponential [18] behavior has been inferred theoretically. For the later we may write

$$\mathbf{g}(\mathbf{E}) = \mathbf{A}^3 \exp[-(\mathbf{E}_{o} - \mathbf{E})/\mathbf{KT}_{o}],$$
 ...(13)

where T_{O} is a parameter describing the extent of the tail. In this case Eq. (12) yields :

$$\mu(E) = \mu_0 \exp\{-(2/Ar_0 \Delta^{1/\xi})\exp [(E_0-E)3kT_0]\} ..(14)$$

Equation (14) is essentially a step function, in which
 $\mu(E)$ increases sharply from very small values to μ_0 near
the value of E at which point the term in the curly brack-
ets is unity.

Thus we can define a critical energy, E_{c}^{+} , by :

$$E_{c}^{\prime} = E_{o}^{-} KT_{o} \ln (Ar_{o} L^{1/3}).$$
 ..(15)

 E_{C}^{\prime} is called the conduction-band mobility edge, and it plays the same role in disordered solids that the band edge, E_{C} does in crystals. The critical density of states at a mobility edge is :

$$g_{c} = 8/(\Delta r_{o})^{3}$$
 ..(16)

For example, if we take $\Delta = 0.027$ eV (kT at room temperature) and $r_0 = 100 \text{ A}^\circ$, then $g_c = 3 \times 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$.

The conductivity is an integral over the prodect $g(E) f(E)\mu(E)$ [see Eq.7], and is not simply given by the value of the product at E_c . This can be significant when g(E) is such a rapidly varying function of E as is commonly

believed [19].

Of course the valence band should also have a mobility edge, E'_v . The difference between E'_c and E'_v is called the mobility gap, E'_a :

$$E'_{q} = E'_{c} - E'_{v}$$
 ..(17)

Mott [20] was the first to suggest the idea of a mobility edge. Mott suggested that at the transition from extended to localized states the mobility drops by several orders of magnitude producing a mobility edge. Cohen [21] proposed a slightly different picture for the energy dependence of the nobility. He suggested that there should not be an abrupt but rather a continuous drop of the mobility occuring in the extended states just inside the mobility edge.

1.1.11 EAND MODELS

Several models were proposed for the band structure of amorphous semiconductors, which were the same to the extent that they all used the concept of localized states in the band tails. Opinions vary, however, as to the extent of this tailing. Experimental data of electrical transport properties can only be properly interpreted if a model for the electronic structure is available. Figure (1.11) illustrates, schematically, the main features of these various nodels.

The Cohen-Fritzsche-Ovshinsky Model :

The CFO model [22] shown in Fig. 1.11(a), assumes that the tail states extend accross the gap in a structure-

less distribution. This gradual decrease of the localized states destroys the sharpness of the conduction and valence band edges. The CFO model was specifically proposed for the multicomponent chalcogenide glasses, used in switching devices. The authors suggested that in the chalcogenide alloys, the disorder is sufficiently great that the tails of the conduction and valence bands overlap, leading to an appreciable density of states in the middle of the gap. A consequence of the band overlapping is that there are states in the valence band, ordinarily filled, that have higher energies than states in the conduction band that are ordinarily unfilled. A redistribution of electrons must take place, forming filled states in the conduction band tail, which are negatively charged, and empty states in the valence band, which are positively charged. This model therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap.

The essential features of the CFO model are

band tails,

2) mobility edges,

3) density of states at the Ferni energy $g(E_{\rm F})$ and

4) local satisfaction of valence requirements.

Most of these feature involves the shape of g(E), perticularly within the gap, so that modern spectroscopy techniques should prove to be extremely useful.

Naive application of the CFO model would suggest that simple amorphous semiconductors, e.g., a-Si, a-As, a-Se, should not exhibit extensive band tails.

Davis-Mott Model :

Fig. 1.11(b) sketches the Davis-Mott model; here E_C and E_V represents the energies which separate the ranges where the states are localized and extended. According to Davis and Mott [23] the tails of localized states should be narrow and should extend a few tenths of an electron volt into the forbidden gap. They proposed furthermore the existance of a band of compensated levels near the middle of the gap, originating from the defects in the random network, e.g., dangling bonds, vacancies, etc. This band may be split in to a doner and an acceptor band, which will also spin the Fermi level, Fig.l.ll(c). The concept of localized states implies that the mobility is zero at T=0 K. The interval between the energies E_C and E_V acts as a pseudogap and it is the mobility gap.

In recent years experimental evidence, mainly coming from luminescence, photoconductivity and drift mobility measurements, has been found for the existance of various localized gap states, which are split off from the tail states and are located at well-defined energies in the gap. These states are associated with defect centres, the nature of which is not always known.

It is clear now that the density of states of a real amorphous semiconductor does not decrease monotonically in to the gap but shows many peaks which can be well separated from each other, as in the case of some chalcogenide



glasses. The position of the Fermi level is largly determined by the charge distribution in the gap states, Fig. 1.11(d).

The interpretation of electrical transport data is closely interwoven with the energy distribution of the density of states. On the basis of Davis Mott model, there can be three processes leading to conduction in amorphous semiconductors. Their relative contribution to the total conductivity will predominate in different temperature regions.

1.1.12 DEFECTS IN AMORPHOUS SOLIDS

In crystalline solids, the equillibrium position of each atom is ordinarily one in which its coordination number. z, its bond length a , and its bond angles, θ , are all optimal. In amorphous solids, no crystalline constraints are present, and the concept of lattice defects such as vacancies, interstitials, dislocations, etc. has little value. However the same chemical interactions that control the structure of crystals are present, and they provide strong dividing forces for optimization of z,a, and θ , i.e. the short range order. Furthermore in multicomponent alloys, a hierarchy of bonds strength can exist, favouring some local environments over others.

The amorphous solids are not ordinarily the lowest energy structure for any large collection of atoms. Most of the amorphous materials are Metastable (i.e. locally rather than globally stable), and they are generally be processed using non ideal techniques such as by quenching from the liquid phase or by direct deposition from a vapour phase onto a relatively cool substrate. The atomic mobility diminishes rapidly with decreasing temperature below the melting point, and long-range motions which would normally induce crystallization are retarded. A softning point or glass transition temperature, Tg, usually exist below which the visocity of the material increases by many orders of magnitude and the material becomes an amorphous solid. Ovshinsky pointed out that the connectivity of the network is a major factor in controlling the overall strain in the material, and this in tern is determined by the chemical composition.

Consider a localized defect centre that is neutral when occupied by a single electron. Let us call the neutral centre D°. We set the zero cf energy at that of an unoccupied centre, D⁺. A, D⁺ centre has two states available at the one-electron energy E_d , one with spin up and the other with spin down. Here E_d can be set by the energy it takes to remove the electron from D° and place it at the conduction band mobility edge, E_c' leaving a D⁺ defect behind -this energy must be $E_c' - E_d$. If both a spin up and a spin down electron are present, the defect centre is negatively charged, D⁻. Since the two electrons repel each other, the second electron is not at E_d but at E_d +U. Only an energy of $E_c' - E_d - U$ is needed to excite it beyond the conduction band mobility edge. However, we cannot neglect the electronphonon interations either. The three states D^+ , D° , and D^- all possess a minimum-energy local configuration which is necessary distinct.

The correlation energy, U, can be defined as the energy required for the reaction,

$$2 D^{\circ} \rightarrow D^{\dagger} + D^{--} \qquad \dots (18)$$

without any local atomic relaxation. However, in reality, the local environments around both D^+ and D^- will relax, lowering the energy of both the states. If we take these relaxations into account, the energy required will be lower than U. We define the minimum energy to create an oppositely charged $D^+ - D^-$ pair from 2 D° centres as the effective correlation energy, U_{eff} . The value of U_{eff} is of importance in characterizing defect centres.

Fig. (1.12) represents two dangling bonds at the end of Se chain, for which the reaction (18) is exothermic. On the configurational co-ordinate diagram, Fig (1.13), the positive correlation energy U associated with the two electrons at D⁻ in the absence of configurational changes become nagative (U_{eff}) after lattice relaxation. The "chemical" reason for the exothermic nature of the reaction is that, at D⁺, an extra bond with neighbouring chain can be formed by utilizing the normally non-bonding loan-pair electrons. The co-ordination of Se atoms at D⁺ is therefore three, in contrast to that at D⁻ where it is one and at a normally bonded Se atom where it is two. MDS proposed that the lattice distortion at D^- is negligible, at D^+ it is considerable and at D° it is intermediate.

In a chemical-bond description of these defects given by Kastner et al. [24], the charged states of the defect are disignated C_1^- and C_3^+ , C standing for the chalcogenide and the subscript indicating the atomic coordination. The neutral centre is labelled C_3° since these authors believe that an extra electron placed on C_3^+ is shared equally between the three bonds of the atom, which therefore remains threefold coordinated. In this respect the description of the neutral center differs from that proposed in [25], in which it was suggested that the extra electron is located primarily on only one of the three bonds.

The structures and energies of several simple bonding configurations for a chalcogen, as given by Kastner et al. [26], are displaced in Fig. (1.14). The normal bonding configuration is C_2° ; the straight lines representing bonds (σ states) and the dots the lone-pair (LP), nonbonding electrons. In this configuration the antibonding (σ^*) states are empty and the energy, relative to the LP level, is -2 E_b as shown. Antibonding states are pushed up from the LP energy more than bonding states are pushed down. Thus the next configuration shown, C_3° - a neutral three fold coordinated atom with an extra electron placed in the antibonding orbital has a higher energy than C_2° by an amount Δ .
The C_3^+ configuration, with an energy of $-3E_b$, is the defect having the lowest energy. The energy of C_3^- is $-E_b^+ 2 + U_{6*}$, the positive correlation term U_{6*} arising because two electrons are in the antibonding state. The extra electron at a normal dangling bond C_1° is indistinguishable from the two lone pair electrons at the site and so the energy of this defect is $-E_b$. Finally a negatively charged dangling bond, $C_{\overline{1}}$, has four electrons in the lone-pair state, its energy is $-E_b^+ U_{LP}^-$, the second term arising from the correlation energy in this level. The reaction corresponding to (18), in Kastner's notation, is

$$2 C_3^{\circ} \neq C_3^{+} + C_1^{-}$$
, ...(19)

which can be seen to be exothermic if

$$-4 E_{\rm b} + 2 \Delta > -3 E_{\rm b} - E_{\rm b} + U_{\rm LP}$$

i.e., if

$$2 \Delta - U_{I,P} > 0.$$
 ...(20)

Here, relaxation effects around the configuration shown in Fig. 1.14 which would change the energy of electrons on near neighbours, have not been included. Finally there is an implicit assumption in the model that the lattice is infinitely soft, i.e. the configuration illustrated are assumed to form without steric hinderance from the surrounding network; introduction of lattice stiffness would be expected to make the reaction less exothermic.

The charged defects C_3^+ and C_1^- have been called by



Kastner a valence alternation pair (VAP). Their creation, starting from a fully bonded network in which all atoms are in the C_2° configuration can be described by

$$2 C_2^{\circ} \rightarrow C_3^+ + C_1^-$$
 ...(21)

which costs an energy

$$-3E_{b} - E_{b} + U_{LP} + 4E_{b} = U_{LP}$$
. ..(22)

The concentrations of VAPs present in a sample prepared by cooling a melt, assuming equilibration at the glass transition temperature T_g , is then N exp(-U_{LP}/2kTg) where N is the concentration of lattice sites.

The energy to create VAPs may be reduced if they form close to each other because of the coulomb energy of attraction. Such bound pairs have been called by Kastner, intemate valence-alternation pairs (IVAPs). Although certain configurations of IVAPs are self-annihilating, others may not be.

Another way of looking at the negative corelation energy which makes reaction (18) exothermic, is as follows. Let the addition of an electron from, say, valence band to D+ cost an energy E_1 and the addition of an electron to the resulting D° an energy E_2 . Then we can write

$$D^{+} + e(+E_1) \rightarrow D^{\circ}$$
 ..(23)

$$D^{\circ} + e(+E_2) \rightarrow D^{-}$$
 ..(24)

Thus

$$2 D^{\circ} \rightarrow D^{+} + D^{-} + (E_{1} - E_{2})$$
 ..(25)

If the addition of the second electron to D^+ costs less energy than the first (i.e., $E_2 < E_1 -$ which is what a negative correlation energy means), then $E_1 - E_2$ is positive and the total reaction is exothermic.

1.2 Transport Properties

1.2.1. ELECTRICAL PROPERTIES OF NON-CRYSTALLINE SEMICONDU-CTORS :

In most semiconductors, the dc transport properties are very well understood. Electrical conductivity, Hall effect, and thermo-electric power (or thermopower) measurements as functions of temperature can be interpreted to yield the position of the Fermi energy, the effective mass of the carriers, the band mobility, and the predominant carrier scattering mechanism. Intrinsic and extrinsic regions can be distinguished and investigated separately. Small polaron formation and hopping transport can be identified if present. The most remarkable feature of the electricalconductivity data in amorphous chalcogenide alloys is the strong pinning of the Fermi energy.

1.2.2. DC ELECTRICAL CONDUCTIVITY :

The essential features of the Davis-Mott model for band structure of amorphous semiconductors are the existance of narrow tails of localized states at the extremities of the valence and conduction bands, Fig. 1.11(b), and furthermore of a band of localized levels near the middle of the gap. This leads to three basically different channels for conduction.

a) Extended State Conduction :

Conduction due to carriers excited beyond the mobility edges in to non localized or extended states.

The conductivity for any semiconductor can be expressed in the form

$$\sigma = -e \int g(E) \mu(E) kT \frac{\partial f(E)}{\partial E} dE \qquad ..(26)$$

where f(E) is the Fermi-Dirac distribution function,

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/kT]}$$

Using this relationship

$$\frac{\partial f(E)}{\partial E} = - f(E)[1 - f(E)]/kT$$

 σ can be written as

$$\sigma = e \int g(E) \mu(E) f(E) [1 - f(E)] dE.$$
 ...(27)

In the Davis-Mott model, the Fermi level E is situated near the middle of the gap and thus sufficiently far from E , the energy which separates the extended states from the localized states, so that Boltzmann statistics can be used to describe the occupancy of states,

 $f(E) = \exp[-(E - E_F) / kT].$

According to Mott's view the mobility drops sharply at the critical energy E_C (or E_V) but at present it is not exactly known how the mobility depends on the energy in both conduction regimes.

In the nondegenerate case and under the assumption of a constant density of states and constant mobility, the conductivity due to electrons excited beyond the mobility edge in to the extended states is given by

$$\sigma = e g(E_c) kT \mu_c exp[-(E_c - E_F) / kT] \qquad ..(28)$$

Where $\mu_{\rm C}$ is the average mobility. The number of electrons is given by

$$n = \int_{E_{C}}^{\infty} g(E_{C}) \exp[-(E - E_{F}) / kT] dE$$

= g(E_C) kT exp.[-(E_C - E_F) / kT] ...(29)

In order to get an idea of the order of magnitude of $\mu_{\rm C}$, we shall follow Mott's treatment. We define

 $\sigma(E_C)$ = eg(E_C) μ_C kT. If g(E_C) \simeq < g(E) > /3, where < g(E) > is the average density of states over the band, then

 $\sigma(E_{C}) = e < g(E) > \mu_{C} kT/3.$

Mott calculated the lowest value of the electrical conductivity before the start of an activated process, i.e. just at E_c . This quantity he called the "minimum meta-llic conductivity". He derived the expression

$$\sigma_{\min} = \text{Const. e}^2/\hbar a, \qquad ..(30)$$

Where the constant lies in the range between 0.026 and 0.1; $\sigma_{min.is}$ usually of the order 200-300 Ω^{-1} cm⁻¹. Taking Const.= 0.026, one finds for the mobility

 $\mu_{\rm C} = 0.078 \, (e/ha)/\langle q(E) > kT.$

In the nearly free electron model, g(E) is given by

$$q(E) = km / 2\pi^{2}h^{2}$$

On the other hand, the maximum energy E_{max} of the band, which also yields the width B of the band, is expressed by

$$E_{max} = \frac{\hbar^2 \pi^2}{2ma^2}$$
 and $k_{max} = \frac{\pi}{a}$

This yields $c(E) \simeq 1/a^{3}B$.

Introducing this result in the expression for $\boldsymbol{\mu}_{_{\mathbf{C}}}$ one gets

$$\mu_{a} = 0.078 \text{ ea}^{2} \text{B}/\text{fkT}.$$
 ...(31)

Taking a = $2A^{\circ}$, E = 5 eV one finds at room temperature that $\mu_{C} \approx 10 \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}$. This value corresponds to a mean free path comparable or less than interatomic distance. Cohen [21] suggested that conduction in this case would be more properly described as a diffusion or Brownian-type motion. In this regime the mobility can be obtained with with the help of Einstein relation,

 $\mu = e D/kT$

The diffusion coefficient D may be written as

$$D = (1/6) v a^2$$
,

where v is the jump frequency and a the interatomic separation. The mobility in the Brownian-motion regime is then given by

$$\mu_{c} = \frac{1}{6} \frac{ea^{2}}{kT} v \qquad ..(32)$$

This expression yields the same temperature dependence as (31) derived by Mott. Since $\mu \propto 1/kT$, one expect that the expression for conductivity is of the form

$$\sigma = \sigma_{\tilde{c}} \exp \left[-(E_{c} - E_{F}) / kT \right].$$
 ...(33)

Optical absorption measurements made on amorphous semiconductors have shown that the band gap decreases with increasing temperature. The energy distance $E_c - E_F$ there-

fore will show a similar behavior, and, under the assumption of a linear temperature dependence,

$$E_{C} - E_{F} = E(0) - \gamma T,$$
 ...(34)

the expression for the conductivity becomes

$$\sigma = \sigma \exp \left(\frac{\gamma}{k}\right) \exp \left[-E(\sigma)/kT\right]. \qquad ..(35)$$

Here E(o) is energy distance at T = OK.

We can write this formula in the form

$$\sigma = c_{exp} [-E(o)/kT],$$
 ...(36)

Where $C_0 = eg(E_c) kT \mu_c exp.(\gamma/k)$. (37)

As seen before μ_c is proportional to 1/T, so that the preexponential factor C_0 is temperature independent. Mott [27] has made an estimate of the preexponential σ_0 . In general σ_0 may lie between 10 and 10³ Ω^{-1} cm⁻¹ in most amorphous semiconductors. An estimate of γ can be obtained from the temperature dependence of the optical gap. In chalcogenide glasses the temperature coefficient of optical gap generally lies between 4 x 10⁻⁴ and 8 x 10⁻⁴ eV deg⁻¹. As the Fermi level is situated near the middle of the gap, values of γ of approximately half this magnitude are expected and hence values of $\exp(\gamma/k)$ in the range 10-100 are most probable.

b) Conduction in Band Tails

The conduction take place due to the carriers excited into the localized states at the band edges i.e., at E_A or

 E_B . Conduction can only occur by thermally activated hopping. Every time an electron moves from one localized state to another it will exchange energy with a phonon. It may be expected that the mobility will have a thermally activated nature,

$$\mu_{hop} = \mu_0 \exp[-W(E)/kT].$$
 ..(38)

The preexponential μ_0 has the form

$$\mu_0 = (1/6)v_{bh} eR^2/kT,$$
 ...(39)

Where $\nu_{\rm ph}$ is the phonon frequency and R the distance covered in one hop.

For a typical phonon frequency $v_{ph} = 10^{13} \text{ s}^{-1}$ and $W \simeq kT$, (38), yields a mobility of the order $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. Comparison of this value with the one calculated for conduction in the extended states suggest, as postulated by Mott, that the mobility may drop by a factor of at least 100 at the energy which separates the localized and non-localized states.

The conductivity, being an integral over all available energy states, will depend on the energy distribution of the density of localized states. If one assumes that the density of states g(E) behaves as some power s of E,

$$g(E) = \frac{g(E_C)}{(\Delta E)^S} (E - E_A)^S \dots (40)$$

with $\Delta E = E_{\rm C} - E_{\rm A}$, then the conductivity $\sigma_{\rm hop}$ due to electrons can be easily calculated starting from (27) :

$$\sigma_{\text{hop}} = \sigma_{\text{ohop}} (kT/\Delta E)^{S} C \exp[-(E_{A} - E_{F} + W)/kT]$$
...(41)

Where

$$\sigma_{ohop} = (1/6) v_{ph} e^2 R^2 g(E_C).$$
 ...(42)

and

$$C = s! - (\Delta E/kT)^{S} \exp \left(-\frac{\Delta E}{kT}\right) \left[1 + s\left(\frac{kT}{\Delta E}\right) + s\left(s+1\right)\left(\frac{kT}{\Delta E}\right)^{2} + ...\right]$$

For the specific case of s=1 (linear variation), the condu-
ctivity is given by

 $\sigma_{\rm hop} = \sigma_{\rm ohop} \; \frac{kT}{\Delta E} \; C_1 \; \exp\left[-(E_{\rm A} - E_{\rm F} + W)/kT\right], \; \ldots (43)$ with

$$C_{1} = 1 - \exp\left(\frac{\Delta E}{kT}\right) \left[1 + (\Delta E/kT)\right] \qquad ..(44)$$

C) Conduction in Localized States at the Fermi Energy

If the Fermi energy lies in a band of localized states, as predicted by the Davis-Mott model, the carriers can move between the states via phonon assisted tunneling process. This is the transport analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. An estimate for the temperature dependence of the hopping conductivity at E has been given by Mott [28]. We shall follow his original derivation. Let us consider an electron that is scattered by phonons from one localized states to another. The mjump probability between the states is donated by three factors, which are the following :

I) The probability of finding a phonon with an excitation energy equal to W, given by a Boltzmann expression exp (-W/kT).

- II) An attempt frequency v_{ph} , which can not be greater than the maximum phonon frequency (in the range $10^{12} - 10^{13} \text{ s}^{-1}$).
- III) The probability of electron transfer from one state to another.

This factor depends on the overlapping of the wave functions and should be given by $\exp(-2\alpha R)$. Here R is the jumping distance, which at high temperatures equals the interatomic spacing, and α is the quantity which is representative for the rate of fall-off the wave function at a site. If overlapping of the wave functions is important, the factor $\exp(-2\alpha R)$ becomes of the order of one.

The probability p that an electron jumps will then be expressed by

 $p = v_{ph} exp (-2_{\alpha}R - W/kT)$(45) By making use of the Einstein's relation

$$\mu = eD/kT$$
 with D = (1/6) pR², the conductivity can be written as

$$\sigma = (1/6) e^2 p R^2 g(E_F).$$

Here $g(E_F)$ is the density of states at the Fermi level and $g(E_F)$ kT is the number of electrons that contribute to the conductivity.

Using (45) the conductivity is represented by

$$\sigma = (1/6) e^2 R^2 v_{\text{ph}} g(E_F) \exp(-2\alpha R) \exp(-W/kT).$$
..(46)

As the temperature is lowered the number and energy of phonons decrease, and the more energetic phonon-assisted hops will progressively become less favourable. Carriers will tend to hop to large distances in order to find sites which lie energetically closer than the nearest neighbours. This mechanism is the so-called variable range hopping. The factor $\exp.(-2\alpha R - W/kT)$ will not have its maximum value for the nearest neighbours. In order to find the most probable hopping distance, Mott used an optimization procedure. This is as follows. If g(W) is the density of states per unit volume per unit energy, then the number of states with energy difference W within a distance R from a perticular atom is given by

$$\frac{4\pi}{3} R^3 g(W) W.$$

The electron can leave its site only if the number of accessible sites is at least one. Taking this into acccunt one gets for the average energy spacing between states near the Fermi level

$$W = \frac{3}{4\pi R^{3} g(E_{F})} ...(47)$$

and for the jump probability

 $p = v_{ph} \exp \left\{ -2\alpha R - \left[(4\pi/3) g(E_F) R^3 kT \right]^{-1} \right\} ...(48)$

The most probable distance is found by minimizing the exponent of the above expression as a function of R :

$$R = \left[\frac{9}{8\pi\alpha g(E_{F}) kT}\right]^{1/4} ...(49)$$

This gives a jump frequency of the form

$$p = v_{ph} \exp((-\frac{A}{T^{1/4}}))$$
 ...(50)

where

A = 2.1
$$[\alpha^3/kg(E_F)]^{1/4}$$

Mott's treatment of variable range hopping leads to a temperature dependence for the conductivity of the form

$$\sigma = (1/6) e^2 R^2 v_{\text{ph}} g(E_F) \exp((-\frac{A}{T^{1/4}}))$$
 ..(51)

or

$$\sigma = \sigma_0 (T) \exp \left(-\frac{A}{T^{1/4}}\right)$$
 ...(52)

In the recent literature many experimental studies, especially on the tetrahedral bonded materials, dealt with variable range hopping. In many cases, unreasonable high values were calculated for $g(E_F)$, very often by use of the preexponential factor $\sigma_0(T)$. Although the $\overline{T}^{1/4}$ dependence of $\ln\sigma$ is widely observed, these findings seem to indicate that the above expression do not describe in an exact quantitative way the conductivity. A review article on hopping condutivity in disordered solids has recently been published by overhof.

1.2.3. THERMO ELECTRIC EFFECT IN SEMICONDUCTORS.

Fundamental information about the mechanism of conduction in solids can be obtained from studies of the thermoelectric effect. In 1821, Thomas Seebeck found that if a metal is connected at its two ends with a second metal, and if one of the juctions is heated, a voltage is developed across the open ends of the second metal. The schematic circuit for the measurement of thermoelectric voltages for a semiconductor is given in fig. (1.15). If the metal contacts are applied to the two ends of a semiconductor rod and if one of the junction is maintained at a higher temperature than the other, a potential difference will be developed between the two electrodes. This thermoelectric or Seebeck voltage is produced partly because of the majority carriers in semiconductor defused from hot to cold junction per second, thus giving a potential difference between the two ends. This voltage builds up a value such that the return current just balances the diffusion current, when a steady stage is reached.

In the experimental arrangement of Fig. (1.15), if the charge carriers in semiconductors are predominantly electrons, the cold junction becomes negatively charged, if the carriers are positive holes, the cold junction becomes positively charged. The magnitude of the voltage Vs is proportional to the difference in temperature between the hot and cold junction.

From the sign of the thermoelectric voltages, it is thus possible to deduce whether a specimen exhibits n-type or p-type conductivity; further from the magnitude of the thermoelectric voltage one can determine the concentration of charge carries in the specimen.

Semiconductors exhibit thermoelectric behavior in circuits with metals, the magnitudes of the thermoelectric quantities exhibited by semiconductors are often much larger than those exhibited by metals. The thermoelectric properties of semiconductors can be used to know the position of Fermi level with respect to band edges.

A typical thermoelectric circuit containing a semiconductor in the form of long thin rod, with metal contacts at its two ends is shown in Fig. (1.16). One end of the rod is kept at a reference temperature T_0 , while the other end is placed at $T_0+\Delta T$. Let us suppose that a linear temperature gradient exists along the rod, which is p type. Under these conditions, the Fermi level in the metal and semiconductor and the edges of the semiconductor band assume the position shown in the lower part of Fig. (1.16). The semiconductor band edges become titled as indicated; while the Fermi level also becomes titled, with a somewhat different slope. The Fermi level in the semiconductor is continuous with the Fermi levels in the metals at two contacts. The Fermi level in metal wires leading away from the contacts do not change with temperature as compared

to the magnitude of change in Fermi level in semiconductor; hence the Fermi level in metal wires are shown horizontal in Fig (1.16). The Seebeck voltage of the circuit is essentially given by the difference in the Fermi level from one end of the semiconductor rod to the other end. In the case of uniform p-type semiconductor taken as an example, the right end of rod becomes negative with respect to left hand side. The tilting of the energy levels in the Fig(1.16) is greatly exaggerated in order to illustrate the arguments to be presented.

If the temperature difference is small the effects depicted in Fig. (1.16) will be linear with temperature and hence linear with horizontal distance across the diagram. The quotient between Vs and ΔT is called the "thermoelectric power." Its physical dimensions are volt per degree, it is disignated by a symbol S. If both the hot and cold junctions are raised or lowered in temperature keeping T same, it will be found that S varies with mean temperature. The variation of S with temperature can just be well observed by keeping the cold juction at temperature T and plotting the thermoelectric voltage Vs against the variable temperature $T_0 + \Delta T$ of the hot junction. The slope of this plot at temperature T gives the value of S at that temperature.

The tilting of the energy bands and Fermi level in the semiconductor sustaining a temperature gradient can be explained as follows.

Because of the temperature gradient, there will be a diffusion of positive holes down the temperature gradient from right to left. The cooler end of the specimen, therefore becomes positively charged and a steady state potential difference just counter balances the diffusion flow. The potential difference in question is given by the vertical distance d on the diagram.

Even if there were no concentration gradient of majority carriers, there would still be a small potential difference generated between the two ends of the specimen. This difference would result from the fact that those holes crossing an imaginary cross section of the specimen by random thermal motion would be going alightly faster in the right to left direction than in left to right because they come from a warmer region of the specimen, and hence have higher thermal kinetic energies. For semiconductor in the impurity dominated and intrinsic temperature range, however this effect is small compared with the effect of diffusion and may be neglected in approximate theory.

1.2.4 SEEBECK EFFECT AND THERMOELECTRIC POWER

The Fermi level in p-type semiconductor rises with temperature towards the middle of the forbidden gap. Hence the total rise of the Fermi level in Fig. (1.16) from cold end of the speciment to the warm end is given by the sum of rise in the upper edge of the valence band and the additional increase due to the rise of the Fermi level above







the valence band edge. In other words,

$$V_{\rm S} = d + \frac{dV_{\rm F}}{dT} \Delta T \qquad ..(53)$$

where Vs is voltage which would be indicated by a high resistance voltmeter in the metallic part of the circuit.

The calculation of the thermoelectric quantity Vs in terms of basic physical quantites is straight forward for simple cases of semiconductors in which only one type of conducting particles need be considered. In the p-type sepcimen indicated in Fig.(1.16) the right to left current density due to diffusion is,

$$I_{RL} = D_p q \frac{dp}{dx} \qquad ..(54)$$

where Dp is diffusion constant, dp/dx is rate of change of holes with distance and q is charge on the hole.

The left to right return current due to electricfield set up by this process is,

$$I_{RL} = p \mu_p q E_x$$

where $E_{\rm X}$ is electric field, p-number of holes and $\mu_{\rm p}$ is hole mobility.

In steady state, these two currents are equal giving

$$D_p q \frac{dp}{dx} = p \mu_p q E_x \qquad \dots (55)$$

Using Einstein relationship, we may write

 $D_p = kT\mu_p/q$ and assuming the electric field to be uniform (as it will be for a small temperature difference and uniform gradient) we may set d/L for E_X where L is the length of the specimen; with these substitutions, and rearranging above equation we get

$$\frac{dp}{dX} = \frac{pq}{kT} \frac{d}{L}$$
 (56)

However

where

$$\frac{dp}{L} \cdot \frac{dp}{Tb} = \frac{Tb}{xb} \cdot \frac{dp}{Tb} = \frac{dp}{xb} \cdot \frac{dp}{Tb}$$

Therefore above equation becomes

$$\frac{dp}{dT} = \frac{pq}{kT} \cdot \frac{d}{\Delta T} \qquad \dots (57)$$

From the Fermi statistics,

$$p = 2 U T^{3/2} e^{-\mathbf{q} V_F / k T}$$
$$U = 2.42 \times 10^{15} \text{ cm}^{-3} \text{ Ab s}^{-3/2}$$

Differentiating with respect to T, and substituting the result in to equation (57), and simplifying we get,

$$d = \left(-\frac{dV_{T}}{dT_{-}} + \frac{V_{F}}{T} + \frac{3 k}{2 q}\right) \cdot \Delta T \qquad ..(58)$$

Combining equations (57) and (58)

$$V_{S} = \left(\frac{V_{F}}{T} + \frac{3k}{2q}\right) \Delta T$$
 ...(59)

Since $S = V_S / \Delta T$, we have

$$S = \frac{V_F}{T} + \frac{3 k}{2 q}$$
 ...(60)

These last two equations for Seeback voltage and thermoelectric power are only approximate. Their derivation neglected the effect described earlier in which a small contribution to S comes from the difference in mean thermal kinetic energy of particles diffusing randomly in two directions in the specimen. The correction to take account of this effect yields for Vs and S,

$$V_{\rm S} = \left(\frac{VF}{T} + \frac{2k}{T} \right) \Delta T$$

and

$$S = \frac{VF}{T} + \frac{2k}{q}$$

therefore

$$S = \frac{k}{q} \left(2 + \frac{E_F}{k_T} \right)$$
 ...(61)

A similar derivation holds for n-type semiconductor leading to equations similar to the two above except that the signs of Vs and S will be negative and that (Vg- VF) will appear instead of V_F .

Equation (61) gives us an independent method for determining V_F in a p type semiconductor sample and hence for obtaining by calculation a value for the hole concentration p. Therefore we have,

$$p = 2 U T^{3/2} e^{-q Q/k + 2} ...(62)$$

In case of an n-type semiconductor above formula becomes,

$$S = \frac{-k}{q} (2 + \frac{E - E_F}{kT})$$
 ...(63)

1.2.5 THERMOELECTRIC POWER

Important information about the transport mechanism in amorphous semiconductors has been obtained from thermopower data. In this section we shall derive the formulas for the thermopower associated with the three possible processes of conduction.

Fritzsche [29] has given a general expression for the thermopower S,

$$S = -\frac{k}{q} \frac{\int \mu(E) g(E) [(E - E_F)/kT] f(1 - f) dE}{\int \mu(E) g(E) f(1 - f) dE} ...(64)$$

Where f is the Fermi-Dirac distribution function. For nondegenerate semiconductor classical Boltzmann statistics are appropriate. In this case the factor f(1 - f)in (64) reduces to a Boltzmann factor $f = \exp[-(E - E_F)/kT]$. a) Conduction in Extended States :

Under the assumption of a constant density of states and an energy-independent mobility the thermopower can be readily found by intergrating (64). This yields an expression for the familiar form for band conduction of electrons

$$S = -\frac{k}{q} \left(\frac{E_{C} - E_{F}}{kT} + A \right)$$
 ... (65)

with A=1.

In crystalline semiconductors it is well known that the kinetic term A depends on the scattering machanism.

Comparison of (33) and (65) shows that a plot of lng and of S vs. 1/T should have the same slope if conduction takes place in the extended states. Hindley [30] has found a similar expression for S using the random phase model.

If both electrons and holes contribute to the conductivity then the thermopower is the algebraic sum of the individual contribution Se and Sh but each weighted according to the ratio of its conductivity to the total conductivity. Thus we have

$$S = \frac{S_e \sigma_e + S_h \sigma_h}{\sigma_e + \sigma_h} \qquad ..(66)$$

b) Conduction in localized States Near the Mobility Edge. The thermopower built up by the carriers conducting in the localized states of a band tails will be given by

$$S = -\frac{k}{q} \frac{\int [(E - E_F) / kT] \exp [-(E - E_F) / kT] g(E) dE}{n}$$

If it is again assumed that the density of localized states behaves like some power s of the energy E,

$$g(E) = \frac{g(E_c)}{(E_c - E_A)^s} (E - E_A)^s$$

then we have

$$S = -\frac{k}{q} \left(\frac{E_A - E_F}{k_T} + \frac{C^*}{C} \right),$$

where C is defined as before, in dc conductivity,

$$C^{*} = \int_{0}^{\frac{\Delta E}{kT}} e^{-x} x^{s+1} d_{x}$$

Here $\Delta E = E_C - E_A$ is the width of the tail and $X \equiv (E - E_A) / kT$.

If the carriers move by hopping in the localized states, the conductivity varies nearly exponentially with temperature, and the measured activation energy is the sum of the activation energies for carrier creation and for hopping. The activation energy for hopping does not appear in the expression for S and, therefore, one expects a difference in slope between the conductivity and thermopower curve. c) Conduction in Localized States at the Fermi Energy

At low temperature, charge transport can arise from electrons tunneling between states at E_F . Cutler and Mott suggested that the thermopower in this regime should be identical to the equation used for metallic conduction,

$$S = \frac{\pi^{2}k^{2}T}{3q} \left[\frac{d \ln \sigma(E)}{dE}\right]_{EF}, \quad ...(67)$$

Since the Fermi level lies in a region where the density of states is finite. The thermopower is expected to be small. Its sign may be positive or negative, depending on whether the major contribution to the current will lie below or above the Fermi energy.

1.2.6. CONDUCTION BY SMALL-POLARON MOTION

In contrast to the CFO and Davis-Mott ideas, a different approach to the understanding of the electrical properties of amorphous semiconductors has been put forward by Emin [31]. He suggested that the charge carriers in some amorphous materials might be small polarons. It is generally accepted that hopping of small polarons is the Mechanism responsible for electrical transport in oxide glasses, in which the major constituent is a transition-metal oxide.

Emin argued that the probability of small polaron formation in the disordered state is largely increased as compared to the crystalline state. It may be remembered that Davis-Mott model postulates the existance of mobility edges at the energies which separate the localized tail states from the extended states. The existance of such tail states does not appear in the small-polaron picture where it is assumed that the electronic states form a small polaron band.

If the charge carrier remains in the vicinity of a perticular atomic site over a time interval long enough for displacement of the surrounding atoms to take place, a potential well may be created which can lead to trapping of the carrier. The unit built up by the trapped carrier and its induced lattice deformation is called a polarom. The polaron has a lower energy than the free electron but has a larger effective mass, since it must carry its induced deformation with it as it moves through the lattice. The decrease in energy of a small polaron relative to that of the electron binding energy.

In paper on 'small polaron motion' Holstein [32] introduced the fundamental concept called coincident event which characterizes the hopping mechanism. In 'adiabatic' regime, the electron goes backwards and forwards several times during the period that the two potential wells have equal depth. The carrier will possess a high probability to hope to the adjacent site. In 'nonadiabatic' regime

the electron can not follow the lattice vibrations and the time required for an electron to hop is large compared to the duration of a coincident event. In this case carrier will have many coincident events before it hops, its probability for transfer being much smaller than in the adiabatic case.

The dc conductivity for small polarons, being proportional to the probability for hopping, is geiven by

$$\sigma = (ne^2 a^2 / kT) P.$$
 ...(68)

The jump probability p, can be written as a product of two terms: the probability P_1 for the occurance of a coincidence event and the probability P_2 of charge transfer during this event. The probability for a configuration with equal potential can be expressed by

$$P_1 = \frac{\omega_0}{2\pi} \exp((-W/kT))$$
 ...(69)

where $\omega_0/2\pi$ is an average phonon frequency and W is the minimum energy necessary to obtain two equivalent sites. The total probability P becomes

$$P = \frac{\omega_0}{2\pi} \exp\left(-W/kT\right)P_2. \qquad ..(70)$$

In the adiabatic regime, where the carrier can follow the motion of the lattice, the probability for jumping during coincidence is high, and one can put P_2 = 1. In the non adiabatic regime where the carrier is slow, one expects $P_2 << 1$. Holstein [32] derived the following expression for P_2 :

$$P_2 = \frac{2\pi}{\hbar\omega_0} \left(\frac{\pi}{W\,k\,T}\right)^{1/2} \,J^2 \,...(71)$$

The electronic transfer in integral J is a measure of the overlapping of the wave functions.

The transport proerty thermoelectric power S, received special attention in the experimental studies on small polarons. For small polaron hopping, S was found to be expressed by a formula of the classical form:

$$S = \frac{-k}{e} \left(\frac{E}{kT} + A \right) \qquad ..(72)$$

Where E is the energy associated with the thermal generation of the carriers.

1.2.7. SWITCHING

Amorphous chalcogenide alloys were among the first and certainly have been the most investigated materials which exhibit the phenomenon of "threshold switching" discussed by Ovshinsky in his landmark paper [33]. When electric field in excess of about 10^5 V/cm are applied to this materials, a metastable state of high conductance appears, in which of the order of 10^{19} cm⁻³ free electrons move with mobilities of approximately $10 \text{ cm}^2/\text{V-s}$ [34]. When the current is reduced below a critical value, the material returns to its original low-conductance state.

The detailed experimental observations of switching in chalcogenide can be explained by VAP model [35]. Near equillibrium, the charged centers, e.g., C_3^{\ddagger} and P_2^{-} , act as efficient traps for field-generated as well as photogenerated carriers, and the trapping time is considerably shorter

than the transit time. However, beyond the critical value of the applied field, sufficiently free-carrier generation takes place so that the charged traps are all occupied and thus neutral. Since the concentration of the positively and negatively-charged centers were originally equal, the material remains neutral after charged trap saturation. Only neutral traps remain, so that the trapping time increases sharply. If it becomes large compared to the transit time, the current rises dramatically, initiating the switching. Note that it is essential that a sufficiently high barrier to neutral defect interconversion exist to retard this posibility over the time necessary for the switching transition, since such interconversion would tend to pin the quasi-Fermi energies. When the current is reduced below the values necessary to sustain sufficient carrier concentrations to keep the charged traps filled, the material quickly transforms to the nonconducting state.

1.3. Magnetic Properties

1.3.1. CLASSIFICATION OF MATERIALS :

From atomic physics we know that electrons have an intrinsic magnetic moment associated with the spin angular momentum, and an orbital magnetic moment associated with the crbital angular momentum. There is also a magnetic moment and angular momentum associated with the nucleus.

It has been realized that all substances possess magnetic properties, i.e. all substances are affected by the application of magnetic field. If a substance is placed in a field of H oersteds then the magnetic induction B, is given by H plus a contribution, $4\pi I$ to the substance itself.

$$B = H + 4^{\pi}I,$$
 ...(73)

Where I is the intensity of magnetization. Dividing Eq.(73) by Howerget,

$$p = 1 + 4\pi k$$
, ...(74)

Where p and k are permeability and susceptibility per unit volume respectively and which may be considered dimensionless.

In practice susceptibility, is usually more convenienlty expressed per unit mass (gram susceptibility) than per unit volume.

$\chi = k/density$

The molar susceptibility, $\chi_m = \chi_X$ molecular weight.

Eg. (74) leads to a most fundamental magnetic classification of substances.

(a) p<l i.e. I, K and X negative.

In this case the substance is said to be diamagnetic and causes a reduction in the density of lines of force Fig. (1.17).

Experimental values of χ are negative and are found to be very small ($\simeq -1.0 \times 10^{-6}$) and generally independent both of field strength and temperature. (b) p>l i.e. I, k, and χ positive.

In this case the substance is said to be paramagnetic and causes an increase in the density of lines of force, Fig. (1.18). Experimental values of χ are positive and are found to be rather larger than in diamagnetic case (1 to 100 x 10⁻⁶). Though independent of field strength, χ is markedly dependent on temperature.

1.3.2. DIAMAGNETISM :

Diamagnetism is the occurrence of a negative magnetic susceptibility. In a case of negative susceptibility, the magnetization is opposite in direction of field. There is no electrical counterpart to negative susceptibility, although it is somewhat vaguely analogous to the induced or deformation polarization. It arises from Lenz's law. We consider the Bohr model of the atom a central nucleus with electrons revolving about it with some frequency ω_0 . The moving electrons are equivalent to current; and there is flu

where there is current, there is flux. If an external field is applied, the current changes so as to oppose the change in flux. This appears as a change in the frequency of revolution.

Let us consider the forces on an electron in a circular orbit. In the absence of an external field we have

$$F = m \omega_0^2 r = e^2 / r^2$$
 ..(75)

Or

$$\omega_0 = \left(\frac{e^2}{mr^3}\right)^{\frac{1}{2}}$$

In the presence of a magnetic field H there is the additional Lorentz force

$$F = \frac{e}{c} v x H = \frac{e}{c} r \omega H \qquad ..(76)$$

if Hlr. Then the force equation is

$$m\omega^2 r = \frac{e^2}{r^2} - \frac{e}{c} r \omega H$$

the minus sign representing the negative charge.

Thus

$$\omega^2 + \frac{eH}{mc}\omega - \frac{e^2}{mr^3} = 0$$

and solving for ω we have

$$\omega = \pm \omega_0 - \underline{e H}_{2mc}$$

if

$$\frac{e H}{2 mc} << \omega_0 \qquad \dots (77)$$

The \pm sign on ω_0 means that those electrons whose orbital moments were parallel to the field are slowed down

and those whose moments were antiparallel are speeded up, by the amount eH/2mc. This frequency change gives rise to a magnetic polarization or magnetization. The reason for this is that the frequency change is equivalent to an additional current, and this current component in every atom is in the same direction, where as the original circulating currents were in random direction and canceled each other.

In the field we can write a current for each electron due to its frequency change eH/2mc

$$I = -\frac{Ze}{2\pi c} \frac{e H}{2\pi c} \dots (78)$$

The magnetic moment is defined from μ = IA, where A is the area enclosed by the current I

$$\mu = -\frac{z e^2 H}{4 m c^2} \pi \bar{p}^2 \qquad ..(79)$$

Where $\overline{\rho}$ is the average radius of the electron from the field axis. If the field is in the Z direction

$$\overline{\rho}^2 = \overline{X}^2 + \overline{Y}^2$$

If \bar{r}^2 is the average radius from the nucleus, then $\bar{r}^2 = \bar{X}^2 + \bar{Y}^2 + \bar{Z}^2$. If the atom has spherical symmetry, $\bar{X}^2 = \bar{Y}^2 = \bar{Z}^2$. Then $\bar{\rho}^2 = 2/3 \bar{r}^2$

Thus

$$\mu = -\frac{Z e^2 H r^2}{6m c^2} \qquad ..(80)$$

If $M = \lfloor N \text{ and } \chi = M/H$, then

$$X = -\frac{Z e^2 N}{6 m c^2} \bar{r}^2 \qquad \dots (81)$$

This expression of χ indicates that all materials should be diamagnetic - and bigger the atom the bigger the magnitude of diamagnetism.

1.3.3. PARAMAGNETISM :

Paramagnetism is a positive magnetic susceptibility. It is the magnetic analogue of the electrical orientational polarizability and is due to the permanent magnetic moment of the atoms.

Sources of Paramagnetism :

1) All atoms having an odd number of electrons.

2) Atoms with unfilled inner shells.

- 3) Free radicals
- 4) Metals

Paramagnetic susceptibility is calculated using Curie

$$\chi = \frac{N \mu^2}{3 k_B T} \qquad ..(82)$$

Where $N \mu^2/3 k_B T$ is called Curie constant.

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