1.1 Introduction

A perfect crystal is a solid, in which the atoms or group of atoms are arranged in a pattern that repeats periodically in three dimensions to an infinite extent. An imperfect crystal is one, which possesses defects such as vacancies, interstitial foreign atoms or dislocations. Strictly speaking, most crystals are imperfect. On the other hand, non-crystalline or amorphous materials possess randomness or disorder in the arrangement of their atoms. Randomness or disorder can occur in several forms, of which topological (or geometrical), spin, substitutional and vibrational disorders are the most important. These types of disorders are illustrated in Fig. 1.1. Disorder is not a unique property. It must be compared with some standard, and that standard is the perfect crystal.

Topological disorder is that form of randomness in which there is no translational periodicity whatsoever (Fig. 1.1a). Certain amorphous materials have considerable short-range (or local) order, while others have little. However, both have no long-range order. So amorphous solids are therefore distinguished by their lack of periodicity and long-range translational order. This thesis deals with materials that possess topological disorder.
Another variety of randomness is spin or magnetic disorder, in which the underlying crystalline lattice is preserved, but each atomic site possesses a spin or magnetic moment oriented randomly (Fig. 1.1b). Materials possessing randomness in spin are called spin glasses. A further kind of randomness is substitutional disorder in which, although the underlying crystalline lattice is preserved, the material is in fact an alloy with one type of atom randomly substituting the other in the lattice (Fig. 1.1c). The final category of randomness is vibrational disorder of a crystalline lattice (Fig. 1.1d). The concept of a perfect crystal is only valid at absolute zero of temperature, and at any finite temperature, the random motion of atoms about their equilibrium positions destroys the perfect periodicity. However,
vibrational disorder is not another form of topological disorder, since although the atoms are vibrating, they do so about their equilibrium crystalline positions, which are not topologically disordered.

The terms amorphous and non-crystalline are synonymous and can be used interchangeably, whereas the term glass is more restricted. The definition of glass is that, it is an amorphous solid, which exhibits a glass transition, even though the term has conventionally been used for an amorphous solid prepared by quenching the melt. If the randomness in a liquid is frozen we get a solid, which is a glass. For a solid glass, the shear viscosity exceeds $10^{14.4}$ poise.

1.1.1 The glass transition

Materials that can be quenched from a melt to form an amorphous solid are represented by all the major types of bonding interactions found in solids viz., covalent, ionic, metallic, van der Waals' and hydrogen bonds. Consequently, they can be insulating, semiconducting or metallic in nature.

When a vapour is cooled, it forms a liquid and when the liquid is cooled further it solidifies. A liquid may solidify in the following two ways, (i) discontinuously to a crystalline solid or (ii) continuously to an amorphous solid. These are shown in Fig. 1.2. This figure should be read from right to left, since time runs in that direction during the course of temperature lowering. A sharp break or bend in $V(T)$ marks a change of phase occurring with decrease of temperature. The first occurs when the gas condenses to the liquid phase at the boiling temperature $T_b$. Continued cooling decreases the liquid volume in a continued fashion, the slope of the smooth $V(T)$ curve defining the liquid's volume coefficient of thermal expansion. Eventually, when the temperature is bought low enough, a liquid $\rightarrow$ solid
Fig. 1.2 The two general cooling paths by which an assembly of atoms can condense into the solid state. Route (1) is the path to the crystalline state. Route (2) is the rapid quench path to the amorphous solid state.

transition takes place following any one of the two ways cited above and as indicated in Fig. 1.2.

The liquid $\rightarrow$ crystal transition is marked by a discontinuity in $V(T)$, an abrupt contraction to the volume of the crystalline solid at temperature $T_f$. This is usually the route taken to arrive at the solid state if the quenching experiment is carried out at a sufficiently low cooling rate. But at sufficiently high cooling rates, it is found that most materials alter their behaviour and follow route (2) to the solid phase. Temperature $T_f$ is bypassed and the liquid phase persists until a lower temperature $T_g$ is reached. The liquid $\rightarrow$ glass transition occurs in a narrow temperature interval near $T_g$, the glass transition temperature. There is no volume
discontinuity as such; instead \( V(T) \) bends over to acquire a small slope characteristic of the low thermal expansion of a solid.

Experiments show that the observed glass transition temperature \( T_g \) depends upon the cooling rate at which the experiment is carried out. This dependence is very small in most solids. Typically, changing the cooling rate by an order of magnitude causes \( T_g \) to shift by a few degrees Kelvin. The reason that \( T_g \) shifts to lower temperatures when the cooling process is extended over longer times resides in the temperature dependence of a typical molecular relaxation time \( \tau \). The quantity \( 1/\tau \) characterizes the rate at which the molecular configuration (atomic scale structure) of the condensed system adapts itself to a change in temperature. This quantity varies enormously during the cooling process as indicated in Fig. 1.2. As soon as the temperature of the liquid is lowered to \( T_f \), it may take route (1) to the solid state and crystallize. But crystallization takes time. Crystalline centres must form by nucleation and then grow by outward propagation of the crystal / liquid interfaces. With the liquid being cooled at a finite rate, the liquid may be taken below \( T_f \) along the \( V(T) \) trajectory, which smoothly continues the curve from higher temperatures. In the temperature interval between \( T_f \) and \( T_g \), the liquid is referred to as supercooled liquid. If its temperature can be taken below \( T_g \) before crystallization has had time to occur, the liquid solidifies as the glass and remains in this form essentially indefinitely. Therefore, glass formation is a matter of bypassing crystallization.

The thermodynamic variables, volume, entropy and enthalpy are continuous through glass transition, but exhibit a change of slope there. This implies that at \( T_g \), there should be a discontinuity in derivative variables such as coefficient of thermal

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expansion, compressibility and heat capacity. This is indeed the case in all glasses. Even though a number of theories have been put forward to explain glass transition, it still remains a phenomenon, which is not yet completely understood.

1.2 Preparation and classification of amorphous solids

1.2.1 Preparation

The glass forming ability of solids vary considerably, but, in principle, all solids can be prepared in the amorphous state, provided the required necessary physical conditions are satisfied. Nearly all materials can, if cooled fast enough and far enough, be prepared as amorphous solids. Thus, the essential ingredient in the preparation of an amorphous solid is speed and the formation of amorphous state is a process of bypassing crystallization [1]. Usually cooling rates of $10^2-10^6$ K sec$^{-1}$ are required to freeze the disorder. For pure metals, cooling rates of $10^9$ K sec$^{-1}$ are required. Details of glass formation and related processes are discussed in many review articles [2-6].

There exists a number of ways for the preparation of materials in the amorphous state. Thermal evaporation, sputtering, chemical vapour deposition and melt quenching are the most commonly used techniques to prepare amorphous materials [7]. Amorphous thin films are usually prepared by vapour deposition or sputtering. Bulk glasses having a well-defined $T_g$ are usually prepared by the melt quenching technique.
1.2.2 Classification

As already stated, amorphous solids are characterized by different kinds of bonding, and consequently they can be insulating, semiconducting or metallic in nature. Amorphous semiconductors can, in general, be divided into two groups as tetrahedrally coordinated silicon type materials and two-fold coordinated chalcogenide glasses [8]. Chalcogenide glasses contain one or more of the chalcogen elements, sulphur, selenium or tellurium of the sixth group of the periodic table. The distinction between these two classes can be well accounted for on the basis of chemical considerations. The four-fold coordination in Si leads to symmetrical bonding and the formation of rigid structures. In this case a continuous random network with tetrahedral bonds can be constructed with negligible density deficit and very little possibility for local reorganization of atoms. On the other hand, the two-fold coordination in chalcogens is highly asymmetrical and the structure gives rise to greater degree of flexibility. A major distinction comes from the fact that, in chalcogens, but not in Si, the valence band is formed from non-bonding lone pair p electrons and is very important when we consider the defect chemistry and various properties of chalcogenide glasses that differentiate it from Si type materials.

Out of these two classes of materials, chalcogenide glasses can be prepared in the bulk, as well as thin film forms, but a direct comparison of the properties of thin film and bulk glasses may not be possible. However, Si type materials cannot often be prepared in the bulk form by the melt quenching technique. These materials are usually prepared in the thin film form. The reason why certain materials can be prepared in the thin film as well as bulk forms, while others can only be prepared in the thin film form can be explained by the nature of chemical bonds present in these
materials. This difference has its origin in the mismatch between constraints and the number of degrees of freedom in three dimensions and the flexibility required to accommodate the mismatch. The flexibility of covalent bond angles is largest for the two-fold coordinated Se type materials and least for the tetrahedrally coordinated Si type materials. The reason for this is the greater variety of admixture from other atomic orbitals to the covalent bond when the coordination number is less than the number of valence electrons. Therefore, based on chemical considerations and the average coordination number $Z$, a classification of amorphous solids can be made as shown in Fig. 1.3. According to this, glasses are restricted to $3 \geq Z \geq 2$, and materials with higher connectivity, i.e., $4 \geq Z \geq 3$ are over constrained amorphous, while those with $Z < 2$ are under constrained amorphous. The average coordination number $Z = 4$ separates non-crystalline metals from semiconductors or insulators.

![Fig. 1.3 Classification of non-crystalline solids based on the average coordination number.](image)

Fig. 1.3 Classification of non-crystalline solids based on the average coordination number.
1.3 Structural properties

Even though amorphous materials lack long-range periodicity of constituent atoms, the disorder is not complete on the atomic scale [9]. Short-range order similar to that present in crystalline materials is also present in these disordered materials. In chalcogenide glasses, the covalently bonded atoms are arranged in an open network with order extending up to 3rd or 4th nearest neighbours and they are also referred to as network glasses [10]. The semiconducting nature of chalcogenide glasses is however, a direct consequence of the covalent bonding that exists in these materials.

The structure of an amorphous solid can never be determined unambiguously. The absence of periodicity in a glass makes the unit cell concept invalid or one can consider unit cell is infinite which implies that the coordinate of each and every atom should be known. The uncertainty in the structure of an amorphous solid is compounded by the fact that the structure of a non-crystalline material, at both microscopic and macroscopic levels, often depends on the details of method of preparation. Furthermore, in general, more than one experimental structural probe must be used to obtain as complete a picture as possible of the structural arrangement in an amorphous solid. The best information one can get from the diffraction methods for a glass is the radial distribution function (RDF), which expresses the probability of finding another atom at a given distance from an arbitrary point.

In both amorphous and crystalline materials, the chemical forces holding the atoms together are the same. Therefore the amorphous state is always defined with reference to a crystalline state [7, 11]. From a comparison of radial distribution functions of amorphous and crystalline films of silicon, it has been revealed that
Covalent glasses exhibit some ordering in their atomic structure. The structural ordering in covalent glasses can be classified into two types depending on their length scale [12, 13]. They are of short-range order in the range 2-5 Å and of medium-range order in the range 5-20 Å.

Since there is no unique structure for an amorphous material, structural modeling is very useful in determining the structure of amorphous solids. The structure of amorphous semiconductors is developed by the repetition of one or more basic molecular units in a way that cannot be identified topologically with any known crystalline structure or with any periodic array. The atomic order within a molecular unit might be similar within small bond angle distortions in both crystalline and amorphous phases. This reveals the importance of short-range order in describing the structural behaviour of a non-periodic network. The most important aspects of the short-range order are the number and type of immediate neighbours, and their spatial arrangement about a given reference atom. Given the short-range order, with three parameters viz., the number of bonds, the bond length and the bond angle having well defined values in a narrow range, it is possible to construct a model for the amorphous structure. Such models are known as random network models. The continuous random network (CRN) model, the first model of an ideal glass proposed by Zachariasen [14] is the basis for all structural models. A number of structural models have been proposed to explain the various structure related properties of amorphous materials.
1.4 Structural models of amorphous solids

1.4.1. Network models

Covalent random network (CRN) model proposed by Zachariasen is more applicable for covalent glasses. He imposed some rules to be followed while building the model, based on the local similarity between crystalline and amorphous materials. A definite short-range order is imposed as each atom fulfills its chemical valence requirements according to Mott's (8-n) rule [15], where $n$ is the number of valence electrons of the particular atom. The underlying principle of this model is that a closed outer shell of eight electrons is the most stable structure. Small variations introduced in bond lengths and bond angles lead to disorder in the glassy matrix. The variation in bond length is much less and they are within 1% to those found in crystals. The major source of randomness comes from the variation in bond angles. The flexibility of covalent bond angles is largest for the two-fold coordinated chalcogens and least for tetrahedrally coordinated group IV elements. CRN model generates amorphous structure without taking into account structural defects such as dangling bonds and voids and it is not adequate to account for features observed in medium-range order.

The structure of chalcogenide glasses can be more appropriately described by the random covalent network (RCN) model or chemically ordered covalent network (COCN) model [16, 9].

Chalcogenide glasses can be prepared over a wide range of compositions. This means that glasses with non-stoichiometric compositions can also be prepared which will contain bonds between like atoms. It is essential to estimate the fraction
of different kinds of bonds present in a system, as it determines a number of physical properties. RCN and COCN models differ in their approach to the distribution of bonds.

Consider a simple binary system $A_x B_{1-x}$ where $A$ and $B$ atoms belong to say column ‘a’ and ‘b’ of the periodic table respectively and $x$ is the normalized concentration variable. We have to estimate the fractions of $A-A$, $B-B$ and $A-B$ bonds present. RCN model estimates these fractions purely statistically, i.e., different types of bonds are considered to be equally probable and neglects the relative bond energies. The bond distribution is determined by the local coordinations of $A$ and $B$ and their concentration $x$. So $A-A$, $B-B$ and $A-B$ bonds are equally preferred at all compositions except at $x = 0$ and $x = 1$. On the other hand, in COCN model, bond energies are also taken into account. Thermodynamically, $A-B$ bonds are preferred over $A-A$ and $B-B$ bonds. So at all compositions, $A-B$ bonds are maximized first and then $A-A$ and $B-B$ bonds are favoured depending on the concentrations of $A$ and $B$. So according to COCN model, there exists a critical composition defined by $x_c = \frac{Z_B}{Z_A + Z_B}$ where $Z_A$ and $Z_B$ are the coordinations of $A$ and $B$ atoms respectively. For example, in $\text{Ge}_x\text{Se}_{1-x}$ system, the critical composition is $\text{GeSe}_2$, while in $\text{As}_x\text{Se}_{1-x}$ system, the critical composition is $\text{As}_2\text{Se}_3$. At these compositions, anomalous variations are reported in many physical properties. The bond statistics obtained on the basis of RCN and COCN models for V-VI and IV-VI alloys are shown in Fig. 1.4.
1.4.2 Mechanical Threshold model

The models proposed by Phillips and Thorpe [17-20] and Tanaka [21] interpret the dynamical properties of chalcogenide glasses, in terms of the average coordination number $Z$. Phillips constraint model, also called mechanical threshold model, examines the constraints governing the random network structure of chalcogenide glasses which are covalently bonded. This model attempts to relate the glass forming tendency with the constraints acting on the network. The glass structure is maximally optimized when the number of degrees of freedom ($N_d$) available for the atoms equals the number of constraints ($N_c$) in the network

i.e., \[ N_c = N_d \] (1.1)
The total number of constraints acting on the system is the sum of bond stretching
constraints and bond bending constraints. Consider a glassy network with N atoms
of which \( N_z \) atoms have \( Z \) bonds per atom. Then the total number of constraints
acting on the system can be written as,

\[
N_c = \left( \frac{Z}{2} \right) + (2Z-3)
\]  

(1.2)

Here the first term \( \left( \frac{Z}{2} \right) \) denotes the bond stretching constraints since a bond is
shared between two atoms. The term \( (2Z-3) \) represents the bond bending
constraints. Two bonds with the central atom will have one bond angle constraint.
For each of the remaining \( (Z-2) \) bonds, two bond angles (one each with the two
existing bonds) have to be specified. \( N_d \) can be 1, 2 or 3 for 1-dimensional, 2-
dimensional or 3-dimensional space respectively. Phillips considered \( N_d = 3 \) for the
cross-linked network structures. Now,

\[
3 = \left( \frac{Z}{2} \right) + (2Z-3)
\]  

(1.3)

This gives \( Z = 2.41 \). This is the critical average coordination number at which a
floppy to rigid structural transition occurs. If \( N_c > 3 \), the structure is over constrained
while if \( N_c < 3 \), the network is under constrained.

The transition from an under constrained to an over constrained network has
been interpreted by Thorpe [19, 20] as the percolation of rigidity in an
inhomogeneous medium containing both rigid and floppy regions. According to
him, there are glassy regions (or islands), which are rigid and spread out in a soft or
floppy region. This is shown in Fig. 1.5(a). As the average coordination number is
increased, these regions grow in size and become interconnected. In other words, the
Fig. 1.5 Rigid and floppy regions in the network of (a) polymeric glass and (b) amorphous solid.

Rigid regions start percolating and at $Z = 2.4$, the system transforms into a mechanically rigid amorphous solid (Fig. 1.5(b)). The point at which this threshold occurs is termed mechanical or rigidity percolation threshold.

Tanaka modified the concept of Phillips and Thorpe, by arguing that medium-range order should also be considered in the constraints balancing conditions as evidenced by characteristic features in the composition dependence of certain physical properties at $Z = 2.67$ [21]. He assumed a hypothetical material
having a plane lattice laid in a 3-dimensional space. As per this modification, the bond bending term \((2Z - 3)\) in Eq. (1.2) reduces to \((Z - 1)\). Now Eq. (1.2) becomes.

\[ N_c = \left( \frac{Z}{2} \right) + (Z - 1) \]  

(1.4)

This gives \(Z = 2.67\), i.e., the coordination number of glasses having stable layer structure becomes 2.67. This means a 2-dimensional glass possessing a layered structure appears to be stably fixed in a 3-dimensional space if the coordination number of the glassy network is 2.67.

The experimental reports on a wide range of physical properties of various binary glasses indicate the threshold behaviour at \(Z = 2.4\) [22-32]. Some results have been reported, indicating a shift in \(Z\) value at which the threshold occurs. Photodarkening, molar volume, X-ray diffraction, elastic constants, optical band gap values etc. of ternary glasses show a threshold behaviour around \(Z = 2.67\) [33-36].

1.5 Band Models

In a crystalline solid, the discrete energy levels of the atoms are broadened into bands of allowed energy levels, separated by forbidden energy regions. At very low temperatures, electrons will occupy the lowest possible energy levels and will exactly fill a certain number of bands. The highest of these occupied bands is known as the valence band and the empty band immediately above this is known as the conduction band. The separation between the top of the valence band and the bottom of the conduction band is called the energy gap \(E_g\). Experimental investigations reveal that many of the fundamental properties such as optical absorption spectra, Arrhenius nature of electrical conductivity etc. of amorphous semiconductors and
their crystalline counterparts look similar. The existence of different classes of materials (metallic, semiconducting and insulating) indicates that electronic structure of these materials should also possess energy gap similar to that of crystalline materials. This shows that these physical properties are largely associated with the short-range order rather than the translational periodicity. To account for these features, various models have been proposed.

According to Anderson's theory [37], the spatial fluctuations in the potential caused by the configurational disorder in amorphous materials, lead to the formation of localized tail states above and below the normal bands. These stats are localized in the sense that an electron in these regions will not diffuse away at zero temperature to other regions. Since localized and extended states cannot coexist at the same energy, a sharp boundary called 'mobility edge' separates the extended and localized states. All these models of the band structure of amorphous semiconductors use the concept of localized states in band tails and mobility edges.

The models tried to explain the features that are common to most of the glasses like the insensitivity of electrical conductivity to the added impurities, pinning of the Fermi level near the midgap etc.

1.5.1 Cohen-Fritzsche-Ovshinsky (CFO) model

This model [38] assumes that extensive tailing of the band edges occurs due to the compositional and topological disorders. The extensive tailing makes the conduction and valence band tails to overlap in the midgap, leaving an appreciable density of states (Fig 1.6a). As a consequence, there are filled states in the valence band that have higher energies than the unfilled states in the conduction band. A redistribution of charges takes place, forming negatively charged filled states in the conduction
Fig. 1.6 Schematic density of states for amorphous semiconductors (a) CFO model (b) Davis-Mott model showing a band of compensated levels near the middle of the gap (c) modified Davis-Mott model (d) the 'real' glass with defect states.

band and positively charged empty states in the valence band. This ensures self-compensation and pinning of Fermi level near the mid gap as required by the experimental observations [39, 40]. The tail states will be localized due to disorder and are separated from extended states in the band at critical energies called the mobility edges, marked by $E_c$ and $E_v$. 
This model has certain drawbacks. According to this model, the elemental semiconductors like a-Si, a-Ge etc. should not have the extensive band tailing as they are free from compositional disorder [41]. The high transparency of amorphous chalcogenides below a well-defined absorption edge indicates that, the extent of tailing is only a few tenths of an eV into the gap [42].

1.5.2 Davis and Mott (DM) model

According to this model [41-43], the tails of the localized states should be narrow and extend a few tenths of an eV into the gap as shown Fig. 1.6b. A band of compensated levels exist near the middle of the gap originating from the defects in the random network like dangling bonds, vacancies etc. The gap states act as deep donors and acceptors with single and double occupancy conditions leading to two bands separated by an appropriate correlation energy. As a consequence of this, the Fermi level is pinned between the bands, which is an essential requirement. In the Figure, $E_r$ and $E_b$ represent the energies that separate the ranges where the states are localized and extended.

Transition from extended to localized states drops the mobility by several orders of magnitude producing a mobility edge. The interval between $E_C$ and $E_A$ act as a pseudo gap and is called the mobility gap. The model explains three processes, which deal with electrical conduction in amorphous semiconductors.

According to CFO and DM models, a large number of densities of unpaired electrons should exist. However, in chalcogenide glasses, no electron spin resonance has been observed [46, 47]. Also, there is no Curie paramagnetism [48, 50].
1.6 Properties of amorphous semiconductors

1.6.1 Electrical properties

The d.c. conductivity of amorphous semiconductors can be well understood within the framework of Davis-Mott model. The model predicts three regions of conductivity, (i) conduction in extended states, (ii) conduction in band tails and (iii) conduction in localized states at Fermi energy $E_F$.

Conductivity in extended states is characterized by large mobility that decreases sharply at the mobility edge. Assuming a constant density of states and constant mobility, the conductivity is shown to vary as

$$\sigma = \sigma_0 \exp \left(-\frac{E_c - E_F}{kT}\right)$$  \hspace{1cm} (1.5)

where the pre exponential factor $\sigma_0$ is given by

$$\sigma_0 = eN(E_c)kT\mu_c$$  \hspace{1cm} (1.6)

Here $N(E_c)$ is the density of states at the mobility edge $E_c$, and $\mu_c$ is the mobility. Electrons at and above $E_c$ can move freely, while electrons below it can move through activated hopping [51]. Mobility in this region is of the order $10 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$.

Conduction via band tails takes place by exchange of energy with a phonon. If the current is carried mainly by holes and conduction is by hopping, then conductivity

$$\sigma = \sigma_h \exp \left\{ \frac{-(E_F - E_B + \Delta W)}{kT} \right\}$$  \hspace{1cm} (1.7)

where $\Delta W$ is the activation energy for hopping and $E_B$ is the energy at the band edge. $\sigma_h$ is expected to be less than $\sigma_0$ by a factor of $10^2$ to $10^4$. 

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In the third region (conduction in localized states), carriers move between states located at $E_F$ via phonon assisted tunneling process, which is analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. Conductivity in this region is given by

$$\sigma_1 = \sigma_2 \exp \left( -\frac{\Delta W_2}{kT} \right)$$  \hspace{1cm} (1.8)

where $\sigma_2 < \sigma_1$ and $\Delta W_2$ is the hopping energy of the order of half the width of the defect band shown in Fig. 1.7. As temperature is lowered, and the carries tunnel to more distant cites, conductivity behaves as,

$$\ln \sigma = A - \frac{B}{T^{-1/4}}$$  \hspace{1cm} (1.9)

This variable range hopping at low temperatures is one of the interesting properties of amorphous semiconductors. As one goes from extended to localized states, mobility decreases by a factor of $10^3$. This drop in mobility is called the mobility shoulder.

The three mechanisms for charge transport that contribute to d.c current can also contribute to a.c conductivity. The first is due to carriers excited to extended states near $E_c$ or $E_v$. Conductivity could be given by a formula of Drude type,

$$\sigma(\omega) = \frac{\sigma(\omega)}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (1.10)

where $\tau$ is the relaxation time. The second is due to transport by carriers excited to localized states at the edges of the valence or conduction bands. Since transport here is by hopping, conductivity increases with frequency as $\omega^{0.8}$. The third is transport by carriers with energies near the Fermi level. This again increases with frequency in the same manner as in the second case.
Fig. 1.7 Density of states and mobility as a function of energy in amorphous semiconductors.

Measurement of thermoelectric power as a function of temperature provides the most direct way of determining the temperature coefficient of activation energy for conduction. Measurement of thermoelectric power in chalcogenide glasses have shown the to be $p$-type in most cases. Hall measurements are used to determine the mobility of carriers. Hall coefficient yields a sign for carriers that is frequently in contradiction with thermoelectric power measurements, which are explained by the theory of Friedman [51].

1.6.2 Thermal properties

For amorphous materials, the phonon mean free path is shorter than that in crystals and correspondingly, thermal conductivity is low. At low temperatures, amorphous
materials exhibit a markedly different behaviour from their crystalline counterparts in phonon related properties such as heat capacity, thermal conductivity and acoustic absorption. The thermal properties of crystalline solids at low temperatures are well understood in terms of Debye’s theory in which it is assumed that the distribution of phonons is cut off at some frequency to which a characteristic temperature $\Theta_D$ may be associated. The specific heat of glass decreases much more slowly with temperature than the Debye $T^3$ prediction at low temperatures ($0K < T < 1K$) [52, 53]. Thermal conductivity decreases slowly and monotonically with decreasing temperature [54, 55]. Near 10 K, thermal conductivity is only weakly temperature dependent, showing a plateau like region. Below 10 K, it shows a $T^2$ dependence. The magnitude of the temperature dependence appears to depend on the amorphous structure of the material, rather than the chemical composition. Hence, the thermal transport below 10 K is provided by phonons. Acoustic and dielectric absorption in amorphous solids is strongly enhanced at low temperatures and in many glasses large absorption peak is found around liquid nitrogen temperature. The anomalous features observed in specific heat, thermal conductivity, acoustic and dielectric absorption below 4 K etc. are interpreted using the two level system (TLS) model proposed by Phillips [56] and Anderson et al. [57]. At high temperatures, atoms forming the TLS change the configuration by means of thermally activated hopping over barriers while at low temperatures, tunneling through the barrier dominates.

The process of glass transition is another aspect that has been receiving continuous attention all the time. Glass transitions are always characterized by a phenomenological value $T_g$ of the critical temperature and by a width $\Delta T_g$ of the so called glass transition around $T_g$. In this region, the diffusive motion of the melt
begins to freeze in before a glass structure is achieved, with viscosity values typical of solids. Both $T_g$ and $\Delta T_g$ depend smoothly on cooling rate [51]. $\Delta T_g/T_g$ provides a rough estimate of the non-equilibrium effects occurring at glass transition; $\Delta T_g/T_g << 1$ is a necessary condition for any thermodynamic approach. For good glass formers this condition is fulfilled at relatively low cooling rates.

Non-isothermal heating studies such as differential scanning calorimetry (DSC) could provide great deal of information about thermal properties of glasses like kinetics of crystallization and thermal stability of glasses against crystallization, apart from being an indispensable characterization tool to investigate glass transition.

1.6.3 Optical properties

The sharp structure observed in the fundamental optical spectra of crystals, both vibration and electronic, can be interpreted by symmetry arguments based explicitly on the existence of long-range order. In the case of amorphous materials, no sharp features are present even at low temperatures. They lack any special directions associated with crystallographic axes and are optically isotropic. The spectral fine structure is a consequence of band structure of k conservation in the crystalline state. Translational periodicity demands that only k conserving transitions contribute to reflectivity spectra. Amorphous solids do not possess the long-range order and so do not show this fine structure in their comparatively blank spectra. Also the vibrational modes are no longer plane waves unlike in the case of crystalline solids in which they are plane waves. Though k is not a valid concept in glasses, the concept of vibrational density of states retains its validity.
Optical absorption in amorphous semiconductors can be separated into three regions, with absorption coefficient $\beta \geq 10^4 \text{ cm}^{-1}$, $1 \text{ cm}^{-1} < \beta < 10^4 \text{ cm}^{-1}$ and $\beta \leq 1 \text{ cm}^{-1}$ as shown in Fig. 1.8. Regions B and C are created by transitions within the fully coordinated system, perturbed to some extent by defects, while region A arises from transitions involving the defect states directly. The absorption edge has a defect induced tail at lower energies, an exponential region at intermediate energies and a power law region at higher energies. The defects occur in a number of ways like voids arising from preparation techniques, occurrence of like bonds, or occasional occurrence of coordination variation. In the high absorption region, the absorption is governed by a power law of the type

$$\beta = \text{const.} (h\nu - E_g)^\rho$$

(1.11)

where $\rho = 2$ for amorphous semiconductors, under the assumption of parabolic bands and $E_g$ defines the optical band gap. Amorphous semiconductors continue to absorb strongly beyond the fundamental absorption edge also. All pairs of extended states with energy difference $h\nu$ can contribute to optical absorption, since the $k$ conservation rule is relaxed. A plot of $\beta^{1/2}$ vs $h\nu$ yields a straight line and the extrapolated $h\nu$ at which $\beta^{1/2}$ tends to zero gives the value of $E_g$.

The exponential tail in $\beta$ is associated with the intrinsic disorder in amorphous semiconductors in the intermediate range of absorption coefficient. It has been suggested that it is due to disorder induced potential fluctuations [58, 59] and strong electron-phonon interaction [60]. In chalcogenide glasses, defects due to coordination variation explain many of the optical properties. In the weak absorption region, the shape of the absorption tail is found to depend on the preparation, purity and thermal behaviour of the material [52]. The mobility gap in many amorphous
Fig. 1.8 Schematic representation of the absorption spectrum of amorphous semiconductors showing three different regions A, B and C.

semiconductors corresponds to a photon energy at which the optical absorption coefficient has a value approximately $10^4$ cm$^{-1}$. Here the assumption is that the mobility gap is twice the activation energy for electrical conduction. From the measurements made using UV diffraction grating reflectometer, the optical constants can be derived from Kramers-Kronig analysis of reflectivity.
1.7 Photoconductivity in chalcogenide glasses

Photoconductivity is the enhancement in dark electrical conductivity of a material due to the absorption of electromagnetic radiation, especially in the visible region. This phenomenon was first observed by Willoughb Smith in 1873 with a selenium resistor. Thereafter, extensive research had been carried out on different materials to understand this phenomenon and use it for various applications. Different models were suggested to account for the characteristics of photoconductivity in materials [61-64]. In the dark under conditions of thermal equilibrium, the thermally generated carriers are distributed among the available energy states in accordance with Fermi-Dirac statistics. These electrons and holes occupying the conduction band determine the dark electrical conductivity of the material. When the sample is illuminated, a steady state is reached, in which the rate of photogeneration is balanced by the various recombination processes, through which the carriers tend to relax to the normal equilibrium distribution. Thus, the phenomenon of photoconductivity involves absorption, photogeneration, recombination and transport processes and an intimate relationship exists between them.

Amorphous solids have a disordered structure, and the disorder has profound effect on their photoelectronic properties. There are large densities of state within the band gap due to translational and compositional disorders. Due to this, the carrier lifetime and photosensitivity are greatly reduced. Also, carrier mobilities in amorphous solids are typically much smaller than those in crystalline state, reflecting reduced mean free paths.

In the discussion of photoconductivity, generally two simplifying assumptions are made,
(i) Conductivity is dominated by one of the carriers so that the contribution of the other can be neglected

(ii) The system remains electrically neutral during photoconduction process without a build up of appreciable space charge so that $\Delta n = \Delta p$. The excess conductivity due to the light absorption is given by,

$$\Delta \sigma = \Delta n \mu_n + \Delta p \mu_p$$  \hspace{1cm} (1.12)

where $\mu$ represents the mobility of corresponding carriers. The increase in conductivity is due to the increase in the densities of positively and negatively charged carriers compared to their values at thermal equilibrium. At low temperatures, the values of $\Delta n$ and $\Delta p$ may be considerably higher than the corresponding equilibrium densities $n_o$ and $p_o$. Under steady state conditions, the excess densities are equal to the product of their generation rate $g$ and lifetime $\tau$. Generation rate is the number of carriers generated per unit time in unit volume. It is governed by the quantum yield $\eta$, which is the number of electron-hole pairs generated by the absorption of a photon.

The non-equilibrium charge carriers exist until they disappear by recombination of a free electron by a centre in which a hole is localized and capture of a hole by a centre in which there is a bound electron. In steady state, the rates of generation and recombination of carriers are equal. Since the band structure of a real amorphous semiconductor exhibits discrete energy levels associated with defect states, analysis of experimental data becomes complex. A variety of models have been proposed to explain different experimental findings satisfactorily [65-68]. Of these, the most important one is the ABFH model [69-72], outlined below.
1.7.1 The ABFH model for photoconductivity

Based on their photoconductivity behaviour, amorphous chalcogenides can be broadly divided into two groups namely, Type I and Type II. Type I photoconductivity has the following characteristics. (i) Photoconductivity shows a maximum at a temperature $T_m$, and it has defined activation energies above $(E^+)$ and below $(E)$ the maximum. (ii) It shows a linear variation with light intensity and an exponential increase with $1/T$ at temperatures above $T_m$. (iii) It has a square root variation with light intensity at high intensities, a linear variation at low intensities and an exponential decrease with $1/T$ at low temperatures. (iv) Dark conductivity more than photoconductivity for $T > T_m$ and less for $T < T_m$. In the case of Type II photoconductors, the photoconductivity maximum is absent. Photoconductivity increases slowly and monotonically with increasing temperature, and in general, photoconductivity is much less than dark conductivity. Also, there are materials, which show an intermediate behaviour between Type I and Type II.

Although a number of models exist that try to describe this behaviour [65-68], the model proposed by Arnoldussen, Bube, Fagen and Holmberg [70-72], known as the ABFH model could describe this phenomenon adequately. The ABFH model incorporates the standard carrier recombination statistics applicable to semiconductors and a generalized distribution of localized states within the mobility gap of amorphous semiconductors. In addition to the traditional non-localized to localized state recombination transitions, localized to localized state recombination transitions are also included in this model, in order to establish consistency with experimental observations.
The basic energy parameter and transition processes are shown in Fig. 1.9. Here the localized states extend into the gap from the conduction and valence edges. With increasing energy above the valence edge, the density of effective recombination centres decreases sharply as the energy exceeds $E^*_v$ for valence states and increases sharply as the energy exceeds $E^*_c$ for conduction states.

Different types of possible electronic recombination transitions are shown in Fig. 1.9b. Transitions 1 correspond to electron (hole) capture by a positively charged valence state below $E^*_v$ (negatively charged conduction state above $E^*_c$) with rate coefficient $C^+$ ($C^-$). Transitions 4 are similarly defined as capture of mobile electrons (holes) by a neutral conduction state above $E^*_c$ (neutral valence state below $E^*_v$) with rate coefficient $C^0$. Transitions 2 correspond to recombination between electrons localized in conduction states above $E^*_c$ and holes localized in valence states above $E^*_v$, with rate coefficient $K$. Transitions 3 represent recombination between an electron (hole) localized in a conduction state (valence state) above $E^*_c$ (below $E^*_v$) and holes (electrons) localized at energies near the equilibrium Fermi level with rate coefficient $K'$ ($K''$). In this model, it is assumed that for Type I photoconductors, transitions 1 or 2 dominate in the high temperature range. In the intermediate temperature range, transitions 2 dominate at high intensities and transitions 3 at low intensities and in the low temperature region, transitions 4 dominate. On the other hand, Type II photoconductivity can, in principle, be described under the assumption that transitions 3 dominate the photoconductivity over the whole measurable range without transforming to a transition 2 dominant region.
Fig. 1.9 Simple photoconductivity model for Type I photoconductivity in chalcogenide amorphous semiconductors, (a) schematic energy level diagram for the model (b) typical recombination transitions considered in the photoconductivity model.

1.8 Electrical switching in chalcogenide glasses

Electrical switching is a very interesting phenomenon exhibited by certain chalcogenide glasses. It is the rapid and reversible transition between a highly resistive OFF state and a conducting ON state driven by an external electric field.
and characterized by a threshold voltage. This has been an area of intense research, ever since Ovshinsky reported reversible switching in amorphous semiconductors [73-83]. Electrical switching could find applications in areas like information storage, electrical power control etc. Several tellurium containing chalcogenide glasses such as Cd-Te, Ga-Te, As-Te, As-Te-Se, Al-Ge-Te, Ge-As-Te etc. are reported to exhibit electrical switching [84-91].

While analyzing the OFF state $V$-$I$ behaviour of a material possessing switching property, it can be seen that the $V$-$I$ characteristics is linear only for a small region at low electric fields. Then the material goes into a quasi-equilibrium state where $V$-$I$ behaviour shows exponential dependence of the form $I \propto V^n$ where $n > 2$. In this region, the material switches to a highly conductive state.

Electrothermal instability [92] seems to explain reasonably well the switching phenomenon in chalcogenide glasses. This is a combination of purely electronic and thermal effects. Electronic effect is caused by the deviation of the carriers from equilibrium by the electric field while the thermal effects are due to the lattice heating because of Joule effect. Joule heating causes the lattice temperature to rise locally above the ambient temperature, which could result in a large increase in conductivity owing to the thermal generation of carriers [93].

1.8.1 Threshold and memory switching

In general, there are two types of switching behaviour exhibited by chalcogenide glasses, (i) threshold switching and (ii) memory switching.

In threshold switching, the ON state persists only while a current flows, whereas in memory switching the ON state is permanent until a suitable reset pulse
is applied. The $V-I$ characteristics of threshold and memory switchings are shown in Fig. 1.10. In threshold switching materials, the ON state requires a small holding current ($I_H$) and voltage ($V_H$) to sustain it. Once the switching current is removed, the material reverts back to the low conducting OFF state. On the other hand, in memory type switching, the ON state is permanent, even after the removal of the applied field. A suitable reset pulse has to be applied to bring it back to the OFF state. In both cases, switching occurs with a delay time reaching values of the order of $10^{-9}$ sec, when the voltage across the sample is about 50% higher than the threshold voltage [74].

It is seen that the crystallization of glasses from the melt state is very important in determining the switching mechanism, rather than from the glassy state. Very easy glass formers may not exhibit switching under normal conditions, as they prefer to go to glassy state upon cooling. On the other hand, glasses that can be prepared only under high cooling rates, may exhibit switching [86, 87, 94-100].

1.8.2 Switching models

In order to account for the electrical switching process in chalcogenide glasses, different models have been proposed [96-98]. These models based on electronic, thermal and electrothermal mechanisms assume that threshold switching is electronic in origin, while memory switching is thermal in origin.

The model proposed by Adler and Petersen [101, 102] is one of the most successful explanations of threshold switching phenomenon in chalcogenide glasses. Chalcogenide glasses contain large densities ($10^{18}$-$10^{19}$ cm$^{-3}$) of positively and negatively charged defect states called valence alternation pairs (VAPs) [103]. When sufficiently large electric fields are applied, carriers are excited and these defect
centers are filled. When all the traps are filled, the life time of the carriers increase sharply to a value, much larger than that needed to cross the thickness of the sample. This leads to a drop in the voltage and the associated switch to the conducting state. This process is clearly reversible.

In threshold type switching, a redistribution of charge carriers having very different mobilities and transition rates occur through the electrode interfaces. This gives rise to a space charge and field enhancement near one electrode and to a small
value for the holding voltage after switching \((V_H)\). In general, the temperature being steady, the threshold voltage is not affected significantly upon the creation of high density of electron-hole pairs by photon or electron bombardment, even though current is considerably increased. However, with increase in temperature, threshold voltage is found to decrease with an increase in current [104-108].

It is believed that memory switching occurs in those chalcogenide glasses in which the cross-linking atoms are too few. Such glasses have lesser thermal stability [102] and consequently, crystallize easily when heated. It is proposed that memory switching phenomenon is caused by the phase transition of the material from the glassy to the crystalline state due to Joule heating [109]. In the crystalline state, conduction is higher compared to the non-crystalline state, since the disorder is significantly less. Clearly, this process is irreversible. The formation of a crystalline conducting channel in a memory glass during switching has been confirmed by electron microscope and optical reflectivity investigations [109].

According to Boer and Ovshinsky [98], electrothermal instability is the cause for electrical switching. They solved the thermal balance equation,

\[
c \rho \frac{dT}{dt} = K \nabla^2 T + \sigma E_A^2
\]

(1.13)

to calculate the break down temperature for switching [108, 110, 111], where \(c\) is the specific heat capacity, \(\rho\) is the density, \(K\) is the thermal conductivity, \(\sigma\) is the electrical conductivity and \(E_A\) is the applied electric field. According to them, the actual switching transition cannot be a simple thermal run away. It would require temperature in the current channel far in excess of those which can be reached without material destruction, and one should be able stabilize the transition with sufficiently large load resistor.
1.9 Carrier type reversal in chalcogenide glasses

It has been known for a long time that bulk chalcogenide glasses, prepared by the melt quenching technique are $p$-type semiconductors [42, 112, 113], with a positive Seebeck coefficient describing thermoelectric power. This is the case not only for chalcogenide elements themselves, but also for binary, ternary and multicomponent glass forming alloys of S, Se and Te with elements like Ge, As, Sb, Si, Sn etc. Further, addition of impurities to them does not alter the nature of conductivity.

In the case of chalcogenide glasses, the valence band is constituted by the chalcogen lone pair orbitals [114]. The effect of structural disorder is less on the lone pair band compared to that on the antibonding orbitals that constitute the conduction band [112]. Therefore, the range of localized tail states at the valence band edge is smaller in comparison to the localized states at the conduction band edge. As a consequence, the number of electrons excited above the conduction band mobility edge is less than the number of holes excited below the valence band mobility edge. This is one of the reasons for the $p$-type conductivity found is chalcogenide glasses.

As mentioned in the previous section, chalcogenide glasses contain a large number of positively and negatively charged defect states, known as valence alternation pairs (VAPs) [103]. During thermal excitation, the life time of free holes excited from the positively charged defect states are higher than the life time of free electrons from negatively charged defects, which also account for $p$-type conductivity of amorphous chalcogenides.

In general, chalcogenide glasses are insensitive to the addition of impurities. This is because of the fact that the Fermi level in these materials is pinned near the
middle of the band gap by valence alternation pairs [108, 115]. However, of late, it has been found that, the addition of certain heavy elemental metallic impurities like Bi or Pb could change the conduction to \( n \)-type in certain chalcogenide glass systems. These impurities enter the network as charged species, and change the ratio of valence alternation pairs to such an extent that the Fermi level gets unpinned. When the concentration of charged additives exceeds that of the valence alternation pairs, chalcogenide glasses can exhibit the phenomenon of carrier type reversal (CTR) or \( p \) to \( n \) transition.

This phenomenon was first observed in bismuth doped germanium selenide glass [116, 117]. \( \text{Bi}_{2}\text{Ge}_{20}\text{Se}_{80-x} \) system of glasses, where the subscript is the normalized concentration variable, exhibits CTR around \( x \approx 8 \). This discovery has led to extensive research on these materials [118-124] and to a reconsideration of the existing theories of electronic structure of chalcogenide glasses [125]. Since a significant amount of Bi has to be incorporated for CTR to occur, it is desirable to use the term ‘chemical modification’ rather than doping [126]. Continued efforts to understand CTR, led to the discovery of this phenomenon in other chalcogenide glassy systems like Pb-Ge-Se, Pb-In-Se, Pb-Ge-Se-Te, Bi-Ge-Te-etc [127-130]. Electrical transport measurements clearly show the occurrence of CTR at certain specific compositions. For example, \( \text{Pb}_{20}\text{Ge}_{x}\text{Se}_{80-x} \) \((x = 17-24)\) system shows CTR at \( x \approx 21 \), \( \text{Pb}_{3}\text{Ge}_{42-y}\text{Se}_{58} \) \((y = 0-20)\) system exhibits CTR around \( y \approx 8 \), \( \text{Pb}_{x}\text{In}_{25-x}\text{Se}_{75} \) \((x = 0-15)\) system exhibits CTR around \( x \approx 5 \), \( \text{Pb}_{2}\text{Ge}_{42-x}\text{Se}_{48}\text{Te}_{10} \) \((x = 0-20)\) system exhibits CTR around \( x \approx 8 \), while \( \text{Bi}_{x}\text{Ge}_{20}\text{Te}_{80-x} \) \((x = 0-6)\) system exhibits CTR around \( x \approx 3.5 \).
In all these systems, the sign of the thermo power changes from positive to negative at the respective critical compositions. In this thesis, we report the results of our measurements on Pb-Ge-Se, Bi-Ge-Se and Pb-In-Se systems. We have measured the thermal parameters viz., thermal diffusivity ($\alpha$), thermal effusivity ($e$), thermal conductivity ($k$) and heat capacity ($c_p$) of these systems as a function of composition, using an improved photopyroelectric (PPE) technique [131]. It is found that the thermal parameters show anomalous variations at critical compositions [132, 133]. We also report the results of photoconductivity measurements on Pb-Ge-Se [134] and Pb-In-Se systems.

There is a vast scope for technological exploitation of the phenomenon of carrier type reversal observed in chalcogenide glasses such as preparation of a new class of p-n junctions [135] based entirely on glasses, since it offers several manufacturing advantages [136].

### 1.10 Applications of amorphous materials

Amorphous materials have got a wide range of applications. For many applications, they are more suitable than crystalline materials. Until recently, silicate glasses were the only type of amorphous materials commonly used. However, the relatively recent discovery that many other types of materials can be produced in the amorphous form, either as bulk glasses or as thin films has led to a rapid expansion in the use of such materials in electronic, magnetic and optical applications.

One of the main advantages of amorphous materials over crystalline materials is that, they are relatively easy to prepare. Large area homogenous
amorphous thin films can be prepared for solar cell applications. Bulk glasses can often be prepared easily by melt quenching technique.

A number of amorphous semiconductors are used as passive and active elements in electronic devices [137, 138]. These applications are in the fabrication of solar cells, thin film transistors and in electro photography. The ability of certain ions to diffuse readily in oxide or chalcogenide glasses in the presence of a concentration gradient or an electric field opens up a range of electrochemical applications such as solid state batteries, electrochemical sensors and electrochromic optical devices [139, 140]. The most wide spread use of an electrochemical sensor is in the so called ‘glass electrode’ commonly used to monitor proton activity.

Amorphous materials find applications in infrared optical communication systems also. They are extensively being tested and used for the fabrication of optical fibers, prisms and optical windows. Near the glass transition temperature, the material remains workable over a range of temperature, so that it can be easily fashioned into fibers. Further, amorphous materials, particularly bulk glasses, are often structurally homogeneous and isotropic over a macroscopic length scale, as a result of which their physical properties are also isotropic. Since these materials have ultra low optical loss characteristics in the IR region, they are extensively used for optical communication applications, both for long distance and local area networks. There have also been reports on active optical devices like LEDs [141, 142].

The phenomenon of electrical switching exhibited by certain tellurium rich glasses finds applications in switching devices. Switching materials find applications in electrical power control also. Amorphous semiconductor thin films are used as
storage targets in electron beam memory devices [143]. Chalcogenide glasses are also used as IR filters and in other IR optical elements [144]. This is possible because chalcogenide glasses have very good transmittance reaching up to the far IR region. Chalcogenide glasses have found several applications relating to their photoconducting property. Two major applications are in xerography and photo detection [144].

Another advantage of amorphous materials over crystalline materials is that, they can be prepared over a wide range of compositions, and not restricted to stoichiometric values. Because of this, physical properties of such amorphous materials can often be varied continuously by varying the composition. This allows one to design materials for specific requirements.
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