Chapter 1

Introduction and Literature Review
1.1 Introduction

Crystals are the unacknowledged pillars of modern technology. The modern technological developments depend greatly on the availability of suitable single crystals, whether it is used for lasers, magnetic devices, optical devices, telecommunication, etc. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering Physics, Chemistry, Material Science, Chemical engineering, Metallurgy, Crystallography, Mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological application. Crystal growth is one of the fascinating fields where the atomic nature of matter clearly shows itself to the observation made in research laboratories. Crystals have since long been appreciated by mankind for their symmetry, structural simplicity and purity. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline materials and extra effort is justified because of the outstanding advantages of single crystals. The reason for growing single crystal is, many physical properties of solid are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystal in the present day technology is evident from the recent advancements in the above mentioned field \([1, 2]\).

During the last decade, considerable effort has been directed towards understanding the chemistry and physics of metal chalcogenides. As a result of these investigations, a variety of new materials with interesting properties have been discovered. Metal chalcogenides form an important class of inorganic materials, which includes many technologically important semiconductors which range from common
oxides and sulphides, selenides and tellurides, to complex compound or solid solution systems containing different metal or chalcogen elements in various oxidation states and varying proportions. Because of their broad range of properties, these materials relate to a large variety of existing and potential applications in optics, electronics, solar energy conversion, catalysis, passivation, ion sensing, fuel cells and batteries [3].

1.2 Existing Literature on Metal Chalcogenides

1.2.1 Transition Metal Dichalcogenides

For decades, layered transition-metal dichalcogenides (TMDCs) have attracted considerable interest of researchers in different fields of physics and materials science. Besides, the various anisotropic properties, TMDCs have been also intensively investigated because of their unique crystal structure as well as their interesting electronic properties. Semiconducting two-dimensional (2D) layered transition metal dichalcogenides like MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, and WSe$_2$ are emerging as promising materials for a wide range of applications, including applications in optoelectronics and transistor technology. After they were possibly prepared by the same exfoliation technique as was applied to graphene, there were a number of reports that have led to an enormous amount of research in this area [4]. TMDCs are inorganic compounds with the chemical formula MX$_2$, where M is a transition metal and X = S, Se, Te in a hexagonal structure with space group $P6_3/mmc$ [5]. The bulk TMDCs are semiconductors having indirect band gaps in the range of 1.0–1.4 eV and direct band gap of about 1.6–2.5 eV. Depending on the combination of metal and chalcogen, TMDCs offer a wide range of 2D materials: metals, superconductors, charge-density-wave systems, Mott insulators, and semiconductors [6]. In addition to its role as a catalyst in dehydrosulfurization, the layered structure of TMDCs allows its use as a dry lubricant [7, 8] and it functions effectively as a lubricant in air and inert gases as well as in high vacuum over a temperature range from cryogenic ($\sim$190°C) to over 450°C in air and up to 800°C in inert environments. So, it overcomes the limitation problem in graphite whose low friction property depends on the presence of condensable vapors such as hydrocarbons or water [9, 10]. On the other hand, high pressure properties of MX$_2$ (M = Mo, W; X = S, Se) can
be especially useful in industrial applications since lubrication directly affects the service life, energy consumption and reliability. High pressure studies are very useful to understand materials properties and design new materials because the increase in pressure allows us to reduce the interatomic distances and to finely tune the materials properties. It has been verified that the thermoelectric properties of semiconductor chalcogenides improve with increasing pressure and that the study of the properties of these materials could help in the design of better thermoelectric materials by applying external pressure [11].

Figure 1.1 Shows the crystal structure of the hexagonal MX$_2$ layered semiconductors

The compounds of MX$_2$ (M = Mo, W; X = S, Se) are formed by a layer of transition metal atoms between two layers of sulphur or selenium atoms as shown in figure 1.1. Interactions between atoms in a layer are mainly covalent, but a weak van der Waals bonding between the layers and have many polytypes in terms of various stacking arrangements [12]. Stacked layers in these compounds consist of six-fold-bonded metal atoms sandwiched between two three-fold-bonded chalcogenide atoms with the intralayer
atoms. One layer of the crystal unit cell is rotated and translated with respect to the other layer in such a way that a line drawn parallel to the c-axis and passing through the metal atom in the first layer will pass through the two chalcogen atoms of the second layer [13]. These molecules lined up to form a hexagonal crystal structure in which the adjacent molecules along c-direction interact through weak van der Waals bond. The unit cell includes two adjacent layers and thus has hexagonal symmetry with 2H arrangement having two geometries are possible: trigonal prismatic and trigonal antiprismatic (commonly referred to as octahedral, although distorted). The octahedral coordination can be obtained from the trigonal prism structure by rotating one of the chalcogen basal planes by 60° around c-axis. The preferred coordination is determined by the bond ionicity as given by the electronegativity difference between metal and chalcogen. Octahedral coordination is preferred in more ionic compounds, since it maximizes the distance between negatively charged chalcogens. On the other hand the overlap between metal and chalcogen wave functions is optimized in a trigonal prismatic coordination [14], which is typically found for more covalent compounds.

1.2.2 Tin Mixed Chalcogenide

Over the last two decades a great deal of interest has been developed in the group IV–VI layered compounds, since their electrical and optical properties make them technologically useful. Tin dichalogenide belongs to a class of intermetallic compounds of the form MCh₂, where M represents an element of group IV (Sn, Zr, Hf, Tl, etc.) and ‘Ch’ an element of group VIB (S, Se, Te) possess many semiconducting properties. [15, 16]. Among these, SnS₂ and SnSe₂ belong to the interesting group of isomorphic materials that are in many ways between two-dimensional systems and three-dimensional crystals, and it exhibits a strong anisotropy of optical properties. SnS₂ and SnSe₂ are known as "layered compounds" in which the bonding within the layer is considerably stronger than the bonding perpendicular to it. The curiosity in these materials is mainly due to their quasi-two dimensional structure and the resulting anisotropy which is revealed in their diverse physical properties and various technological applications [17]. A characteristic feature of these layered crystals is their polytypism, arising due to the infinite number of possible layer alternations which differ in the sequence of the
constituent atoms. The lattice dynamics and electronic properties of these materials are of attention because of their two dimensional nature and as well wide application such as solid solution in solid state batteries. Apart from this, broad band gap leads to photoconductance [18], and makes it possible to be a candidate in solar cells and opto-electronic devices [19]. It can be used as cathodic material in lithium intercalation batteries and as antireflective layers in solar cell and is also of interest in holographic recording systems and electrical switching [20, 21].

![Figure 1.2](image)

Figure 1.2 Shows the crystal structure of the hexagonal SnCh$_2$

Tin dichalcogenide crystals with the hexagonal closed packed CdI$_2$–type structure is shown in figure 1.2. The individual tightly bonded layer in SnCh$_2$ (Ch = S, Se) is an Ch–Sn–Ch sandwich and the adjacent sandwiches are held together along the c-axis by
weak van der Waals forces because the primary valencies of constituent atoms are almost fully satisfied within the layer. Each chalcogen atom is nested at the top of a triangle of Sn atoms. The different possibilities of packing these Ch–Sn–Ch slabs are the origin of the polytypism. There are many different polytypes, the most common being the polytype denoted by 2H, which contains only one slab in the elementary unit cell. Within this structural unit, for all polytypes, metal atoms are covalently bonded (sp$^3$d$^3$) to six chalcogen atoms in an octahedral configuration. The stacking sequence along the c axis is thus Sn–Ch–Ch–Sn and the layer character of the solid arises from weak interlayer interaction, and the relatively weak Ch–Ch interaction results in the compound having layer-like character with the Ch–Sn–Ch sheets constituting a layer [22, 23].

1.2.3 Group V$_2$–VI$_3$ Chalcogenide

The metal chalcogenides of the group V$_2$–VI$_3$ are useful semiconductors, which find application in thermoelectric devices, television cameras with photoconducting targets, humidity sensors, electronic and optoelectronic devices [24–27]. At ambient conditions, the M$_2$X$_3$ (M = Sb, Bi; X = S, Se, Te) family is divided into two structural classes: the heavier Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ compounds adopt a rhombohedral structure (space group: R$\bar{3}$m, Z=3), which is composed of layers of AB$_6$ octahedra stacked perpendicular to the long c-axis; the lighter Bi$_2$S$_3$, Sb$_2$S$_3$, and Sb$_2$Se$_3$ materials on the other hand, crystallize in an orthorhombic phase (space group: Pnma, Z=4), made up of AB$_7$ and AB$_{7+1}$ polyhedra [28]. It is an important class of semiconductors with extensive applications in photovoltaics and optoelectronics. They hold great promise as photovoltaic converters and thermoelectric cooling devices due to their small direct bandgaps, high thermoelectric power, and high absorption coefficient in the visible region.

Bismuth Selenide (Bi$_2$Se$_3$)

Out of M$_2$X$_3$, bismuth selenide (Bi$_2$Se$_3$) is a conventional thermoelectric material which has been extensively investigated because of its good thermoelectric cooling ability at room temperature and its high coefficient of performance [29–32]. It ranks among the family of layer-type semiconductors having narrow band gap of 0.2–0.3 eV
which is suitable for applications in optical and photosensitive devices, in photoelectrochemical cells, in solar-selective decorative coatings, and in the fabrication of an ideal Hall effect magnetometer [35–37]. Bi$_2$Se$_3$ has been shown to be an ideal candidate for studying room temperature topological insulating behavior as it has a topologically nontrivial band gap of 0.3 eV, much larger than the room temperature energy scale [38, 39]. Because of this, it has regenerated great interest by being predicted to be a three-dimensional topological insulator, i.e. insulators with conductive surface states shaped in a Dirac cone that are robustly protected against any time-reversal perturbation, such as crystal defects and nonmagnetic impurities [40]. These topological insulators are attractive for both fundamental research and for potential applications in spintronics, quantum computing, magnetic memory, low-energy dissipation electronics, etc. Because of the broad range of promising potential applications, research attention on this material has increased dramatically in recent years [41]. Therefore, Bi$_2$Se$_3$ is considered to be a promising topological system toward unique applications in next generation electronics.

Figure 1.3 Shows the crystal structure of Bi$_2$Se$_3$
The primitive unit cell of Bi$_2$Se$_3$ has two Bi and three Se atoms, and the atomic plane arrangement is Se(1)–Bi–Se(2)–Bi–Se(1), where Se(1) and Se(2) indicate the two different types of selenium atom in the crystal. Therefore, as shown in Figure 1.3, the system has a layered structure with five atomic layers as a basic unit (cell), named a quintuple layer (QL). The inter-layer bonding within the QLs is strong because of the dominant covalent character, but the bonding between the QLs is much weaker due to the van der Walls-type interaction.

**Bismuth Sulfide (Bi$_2$S$_3$)**

At ambient conditions, Bi$_2$S$_3$ adopts an orthorhombic structure (Pnma, Z=4, U$_2$S$_3$-type) with mixed sevenfold [Bi(1)] and eightfold [Bi(2)] cationic coordinations. Figure 1.4 shows the crystal structure of Bi$_2$S$_3$ which can be described as a layered structure, with alternating blocks of Bi–S polyhedral units stacked perpendicular to the short b-axis [42]. The structure of Bi$_2$S$_3$ was originally determined by Kupcˇik & Vesela´-Nova´kova´ [43] and refined by Kyono & Kimata [44]. High-pressure structural data up to 10 GPa were reported by Lundegaard et al. [45]. The interatomic distances of Bi(1)–S are 2.70 and 2.67Å, those of Bi(2)–S are 2.60, 2.76, and 2.97 Å. In this case clustering into three shorter and two longer distances justifies (even better than in stibnite) treatment as trigonal pyramid plus two more remote S ligands.

**Figure 1.4** Shows the crystal structure of Bi$_2$S$_3$
Among the Group V metal chalcogenides ($M_2 \, ^{\text{V}}X_3^{\text{VI}}$), bismuth sulfide ($\text{Bi}_2\text{S}_3$) is considered to be one of the attractive materials for photoanode in photoelectrochemical (PEC) solar cells and also exhibits promising applications in photovoltaic converters and thermoelectric cooling technology based on the Peltier effect. This is due to its forbidden energy gap lying between 1.25 and 1.70 eV, near to the range of theoretically maximum attainable energy conversion efficiency [46, 47]. $\text{Bi}_2\text{S}_3$ semiconductor with the direct band gap has been suggested to be useful material for photodiode arrays or photovoltaic converters and also exhibits promising applications in photovoltaic converters and thermoelectric cooling technology based on the Peltier effect. This is due to its forbidden energy gap lying between 1.25 and 1.70 eV, near to the range of theoretically maximum attainable energy conversion efficiency [46, 47]. $\text{Bi}_2\text{S}_3$ semiconductor with the direct band gap has been suggested to be useful material for photodiode arrays or photovoltaic [48]. Recently, $\text{Bi}_2\text{S}_3$ nanostructures have been used in X-ray computed tomography imaging [49], gas sensing [50] and biomolecule detection [51]. Thus far, studies on $\text{Bi}_2\text{S}_3$ have focused mainly on the synthesis and applications of its physical and chemical properties.

**Antimony Sulfide ($\text{Sb}_2\text{S}_3$)**

Antimony sulfide, $\text{Sb}_2\text{S}_3$, a mineral, silvery gray in color, with a metallic luster. It crystallizes in the orthorhombic structure. There is also a surge of interest in using $\text{Sb}_2\text{S}_3$ as a solid-state semiconductor-sensitized solar cell to replace the inorganic dye in dye-sensitized solar cells [52, 53].

![Figure 1.5 Shows the crystal structure of $\text{Sb}_2\text{S}_3$](image)

Figure 1.5 Shows the crystal structure of $\text{Sb}_2\text{S}_3$
The structure of stibnite as shown in figure 1.5 has been determined by Hofmann (1933) and has been refined by several authors (e.g., Šćavnicar, [54]; Bayliss & Nowacki, [55]; Makovicky, [56]; Lukaszewicz et al., [57]; Kyono & Kimata, [44]). Structural data determined in the temperature range 293–128 K have been provided by Kyono et al. [58] and at pressures up to 10 GPa by Lundegaard et al. [59]. The structure of stibnite, which crystallizes in space group $Pnma$ ($Z = 4$), is formed of infinite $[\text{Sb}_4\text{S}_6]_n$ ribbons running parallel to the $b$ axis. Each ribbon consists of two $\text{Sb}(1)\text{S}_3$ “trigonal pyramids” at the rims and two distorted $\text{Sb}(2)\text{S}_5$ “square pyramids” in the center. Weak $\text{Sb–S}$ and $\text{S–S}$ bonds link each unit to four neighboring ribbons. The $\text{Sb}(1)\text{S}_3$ pyramid is slightly distorted as indicated by the interatomic $\text{Sb–S}$ distances of 2.52 Å and 2.54 Å, and also by the $\text{S–Sb–S}$ bond angles of 87.5° and 98.0° (Kyono & Kimata [44]). The $\text{Sb–S}$ distances around $\text{Sb}(2)$ are 2.46, 2.68 and 2.85 Å, and are therefore best described as a $[1 + 2 + 2]$ coordination. Hence, the shortest three $\text{Sb–S}$ bonds also form a distorted trigonal pyramid with $\text{S–Sb–S}$ angles of 88.1° and 91.4°.

**Antimony Selenide ($\text{Sb}_2\text{Se}_3$)**

Antimony selenide is the chemical compound with the formula $\text{Sb}_2\text{Se}_3$. The material exists as the sulfosalt mineral antimonselite, which crystallizes in an orthorhombic space group [60]. In this compound, antimony is assigned the oxidation state 3+ and selenium 2−, but in fact the bonding in this compound is highly covalent. Antimony selenide ($\text{Sb}_2\text{Se}_3$) belongs to $\text{V}_2\text{–VI}_3$ family with orthorhombic crystal structure, in which each $\text{Sb}$–atom and each $\text{Se}$–atom is bound to three atoms of the opposite kind that are then held together in the crystal by weak secondary bonds [61]. $\text{Sb}_2\text{Se}_3$ crystallizes in the orthorhombic $Pnma$ structure as shown in figure 1.6 at ambient conditions ($\text{U}_2\text{S}_3$-type). In this phase, there exist two non-equivalent $\text{Sb}$ cation sites, labeled as $\text{Sb}(1)$ and $\text{Sb}(2)$. The $\text{Sb}(1)$ cation is coordinated by seven $\text{Se}$ anions; these $\text{Sb}(1)\text{Se}_7$ polyhedra are interconnected along the short $b$-axis by two edge sharing equatorial $\text{Se}$ ions [$\text{Se}(1)$ and $\text{Se}(2)$]. The second $\text{Sb}(2)$ cation is similarly coordinated by seven $\text{Se}$ ions, forming a monocapped trigonal prism. There exists, however, a second capping $\text{Se}(3)$ an ion [$\text{Se}(3)/\text{long}$] at a distance of ~4.3 Å, which can be considered far-off with respect to the first coordination sphere of $\text{Sb}(2)$. Therefore, the coordination of the
Sb(2) cation can be described as of (7+1) with respect to the Se anions. The height of the Sb(2)Se trigonal prism equals to the length of the orthorhombic b-axis.

\[
\text{Sb}_2\text{Se}_3
\]

Figure 1.6 Shows the crystal structure of \(\text{Sb}_2\text{Se}_3\)

\(\text{Sb}_2\text{Se}_3\) is a layered chalcogenide with great interest for applications owing to its good photoconducting and thermoelectric power properties which allow possible application to optical devices and thermoelectric cooling devices [62]. In the last few years, \(\text{Sb}_2\text{Se}_3\) has received a great deal of attention due to its switching effects [63] and its excellent photovoltaic properties and high thermoelectric power [64], which make it possess promising applications in solar selective and decorative coating, optical and thermoelectric cooling devices [65]. Optical band gaps due to both direct and indirect transitions in the range 1–1.2 eV are reported [66]. This makes it an alternative material for use as an absorber in solar cells. Also, it is used for optical coatings in thermophotovoltaic applications due to its high refractive index [67].

Considering these aspects, it is essential to understand the dynamics of phonons in these materials, particularly the phonon-phonon and electron-phonon interaction, in order to achieve the best device performance. In this regard, Raman scattering spectroscopy is a powerful and sensitive technique to study phonons in such technological important materials. Therefore, knowledge of their structural stability range under conditions of variable temperature or pressure is important for such applications.
1.3 Existing Literature of Raman Spectroscopy carried out on Metal Chalcogenides

1.3.1. Transition Metal Dichalcogenide MX$_2$ (M=Mo, W; X=S, Se)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of work carried out by them</th>
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<tbody>
<tr>
<td>Verble et al. (1970)</td>
<td>The observed degeneracy of mutually exclusive infrared- and Raman-active modes in MoS$_2$ is traced by means of group theory to the weak van der Waals interaction between layers [68].</td>
</tr>
<tr>
<td>Wieting et al. (1972)</td>
<td>Infrared and Raman measurements of lattice vibrations in hexagonal MoS$_2$ have been made over the combined range 20–4000 cm$^{-1}$. Two infrared-active modes at 384 and 470 cm$^{-1}$ and three Raman-active modes at 287, 383, and 409 cm$^{-1}$ have been observed. All 15 optical modes are assigned to irreducible representations and their frequencies tabulated or predicted [69].</td>
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<tr>
<td>Bagnal et al. (1980)</td>
<td>The frequencies of the Raman active $A_{1g}$ and $E_{2g}^1$ phonon modes of 2H–MoS$<em>2$ have been measured as a function of applied hydrostatic pressure from atmospheric pressure to 50 kbar, using an opposed diamond anvil pressure cell. An approximately linear relationship is found for both modes. The pressure coefficient of the $A</em>{1g}$ mode (+0.37 cm$^{-1}$ kbar$^{-1}$) is nearly twice that of the $E_{2g}^1$ mode (+0.18 cm$^{-1}$ kbar$^{-1}$). The results are discussed in terms of a simple force constant model [70].</td>
</tr>
<tr>
<td>S. Sugai et al. (1981)</td>
<td>Lattice vibrations under hydrostatic high pressure, up to 180 kbar, were investigated in the layered materials, 2H–MoS$_2$, 2H–MoSe$<em>2$ and 2H–MoTe$<em>2$ by Raman scattering. Including the rigid layer mode, one $A</em>{1g}$ and two $E</em>{2g}$ modes were observed in each material. The energy of the rigid layer mode rapidly increased with pressure, but the increase became slow above 50 kbar. The pressure dependences of the interlayer shear force constant and intralayer shear force constant were obtained using a linear chain model [71].</td>
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Stacy et al. (1985)  
Raman spectra of ZrS$_2$, HfS$_2$, MoS$_2$ and WS$_2$ using laser energies near the energies of the absorption edges. The Raman spectra probe the properties of the first-excited electronic state and the nature of the electron-phonon coupling. The spectra of the IVB disulfides are independent of the laser excitation energy, suggesting weak electron-phonon interaction. In contrast, additional Raman bands appear in the spectra of the VIB disulfides as the laser energy approaches the band gap energy. The new modes in the spectra of MoS$_2$ and WS$_2$ cannot be assigned as first-order processes nor as combination bands of the phonons with zero momentum [72].

Sandoval et al. (1991)  
A valence-force-field model has been used to study the lattice dynamics of MoS$_2$ single molecular layers. This study indicate that the strong 383cm$^{-1}$ Raman mode that is present in spectra obtained from crystalline 2H–MoS$_2$ should also be Raman active in single layer trigonal-prism-coordinate T-MoS$_2$ but inactive in single-layer octahedrally coordinated Ω-MoS$_2$ [73].

Sourisseau et al. (1991)  
The resonance Raman spectra of 2H–WS$_2$ single crystals are investigated in detail in the region of low-energy indirect transitions including two direct transitions characterized by A and B exciton peaks. The spectra reveal the activities of first-order resonance Raman signals as well as of second-order Raman processes due to coupling phonons with a non-zero momentum. The direct gap nature of the A and B excitons in 2H–WS$_2$ is responsible for the enhanced intensity of first order Γ-point phonons (A$_{1g}$), whereas the K-point phonons, which contribute to the indirect gap absorption edge, are enhanced in the two-phonon resonance Raman spectra: distinct and simultaneous first and second-order resonance Raman scattering mechanisms are thus taking place in this material [74].

Marko Virsek et al. (2009)  
The Raman spectrum of the MoS$_2$ microtube closely resembles that of a MoS$_2$ single crystal. For the first order A$_{1g}$ and E$_{2g}$ Raman modes, the same frequencies can be observed for both MoS$_2$ microtubes and single crystals, respectively, while line widths are slightly larger in the
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The microtube spectrum, which can be attributed to defects [75].

Changgu Lee et al. (2010) MoS$_2$ of single- and few-layer thickness was exfoliated on SiO$_2$/Si substrate and characterized by Raman spectroscopy. Two Raman modes, $E_{2g}^1$ and $A_{1g}$, exhibited sensitive thickness dependence, with the frequency of the former decreasing and that of the latter increasing with thickness. The results provide a convenient and reliable means for determining layer thickness with atomic-level precision. The opposite direction of the frequency shifts, which cannot be explained solely by van der Waals interlayer coupling, is attributed to Coulombic interactions and possible stacking-induced changes of the intralayer bonding [76].

Livneh et al. (2010) Raman scattering spectra of 2H–MoS$_2$ were measured at room temperature under hydrostatic pressures up to 31 GPa and under ambient pressure in the temperature range of $T = 95$–573K. Pressure and temperature-dependent intensity ratio analysis of the resonant $A_{1g}$ phonon and $E_{2g}^1$ phonon is complemented by the calculation of resonance Raman probability profiles of the former, which well agree with experiments [77].

Windom et al. (2011) Molybdenum disulfide (MoS$_2$) and molybdenum trioxide (MoO$_3$) are investigated using Raman spectroscopy with emphasis on the application to tribological systems. The Raman vibrational modes were investigated for excitation wavelengths at 632.8 and 488 nm using both microcrystalline MoS$_2$ powder and natural MoS$_2$ crystals. Differences are noted in the Raman spectra for these two different wavelengths, which are attributed to resonance effects due to overlap of the 632.8 nm source with electronic absorption bands. In addition, significant laser intensity effects are found that result in laser-induced transformation of MoS$_2$ to MoO$_3$. Finally, the transformation to molybdenum trioxide is explored as a function of temperature and atmosphere, revealing an apparent transformation at 375 K in the presence of oxygen [78].
Lanzillo et al. (2013) They present a combined experimental and computational study of two-dimensional molybdenum disulfide and the effect of temperature on the frequency shifts of the Raman-active $E_{2g}$ and $A_{1g}$ modes in the monolayer. While both peaks show an expected red-shift with increasing temperature, the frequency shift is larger for the $A_{1g}$ mode than for the $E_{2g}$ mode. This is in contrast to previously reported bulk behavior, in which the $E_{2g}$ mode shows a larger frequency shift with temperature. The temperature dependence of these phonon shifts is attributed to the anharmonic contributions to the ionic interaction potential in the two-dimensional system [79].

Berkdemir et al. (2013) The Raman scattering of single and few-layered WS$_2$ is studied as a function of the number of S–W–S layers and the excitation wavelength in the visible range (488, 514 and 647 nm). For the three excitation wavelengths used in this study, the frequency of the $A_{1g}(\Gamma)$ phonon mode monotonically decreases with the number of layers. For single-layer WS$_2$, the 514.5nm laser excitation generates a second-order Raman resonance involving the longitudinal acoustic mode (LA(M)). This resonance results from a coupling between the electronic band structure and lattice vibrations. First-principles calculations were used to determine the electronic and phonon band structures of single-layer and bulk WS$_2$. The reduced intensity of the 2LA mode was then computed, as a function of the laser wavelength, from the fourth-order Fermi golden rule. Their observations establish an unambiguous and nondestructive Raman fingerprint for identifying single- and few-layered WS$_2$ films [80].
1.3.2. Tin Mixed Chalcogenides (SnS$_{x}$Se$_{2-x}$ where $0 \leq x \leq 2$)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of work carried out by them</th>
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<tr>
<td>Agnihotri et al. (1975)</td>
<td>We report the Raman spectrum of a layer type semiconducting compound SnSe$<em>2$ with one Sn atom surrounded by six selenium atoms of the layer in an octahedral configuration. A correlation chart relating the irreducible representations of the site groups with those of the factor group has been established. Two Raman active modes at 320 and 399 cm$^{-1}$ have been observed and assigned $E_g$ and $A</em>{1g}$ representations respectively. Mode degeneracy observed in MoS$_2$, MoTe$_2$ and MoSe$_2$ was not observed in SnSe$_2$ [81].</td>
</tr>
<tr>
<td>Mead et al. (1976)</td>
<td>The first order Raman spectra of the Group IVa layer compounds SnS$_2$ and SnSe$_2$ are presented. The two Raman active modes of each compound have been identified and on the basis of their observed symmetry assigned in accord are with group theoretical predictions. The SnSe$_2$ spectrum is compared to the results of a previous investigation and poor agreement is obtained. The present results are also compared to spectra previously obtained from Group IVb dichalcogenides [82].</td>
</tr>
<tr>
<td>Smith et al. (1977)</td>
<td>The Raman spectra of 2H and 4H–SnS$_2$ and 6Hb–SnSe$_2$ have been studied at room and liquid nitrogen temperatures. Interpretation of the observed Raman modes is given in terms of the different symmetries of these polytypes and the more important short-range forces involved in determining the energies of the higher-energy phonon modes are identified by the use of a simple force-constant model [83].</td>
</tr>
<tr>
<td>Jandl et al. (1978)</td>
<td>We report the first order Raman spectra of layer type semiconducting compounds SnS$<em>{1.75}$Se$</em>{0.25}$ and SnS$<em>{1.5}$Se$</em>{0.5}$. The two Raman active modes of each compound have been identified and on the basis of their observed symmetry assigned in accord with group theoretical predictions. The frequencies of the observed phonons show that the behaviour of these two solid solutions is of the two-mode type [84].</td>
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The Raman spectra of the mixed crystal SnS$_{2-x}$Se$_x$ show a two-mode behavior with local and gap modes developing for concentrations of 25% for S and Se respectively [85].

They have measured the Raman scattering spectra of 4H and 18R polytypes of SnS$_2$ crystals. The dispersion curve for the shear type acoustic phonon (TA) propagating along the c-direction is deduced from the frequencies of the rigid layer modes. The dispersion curve is in agreement with that calculated by applying a one-dimensional model. The effect of hydrostatic pressure on intralayer and interlayer modes has been measured. The mode-Grüneisen parameter determined for these modes show a remarkable difference which is the characteristics of layer compounds having anisotropic bonding forces [86].

The combinations of the Raman scattering and X-ray diffraction experiments under high pressures have given the relationship between the bond-length and the bond strength for the interlayer bonding in CdI$_2$ and SnS$_2$. The pressure dependence of the interlayer forces in CdI$_2$ and SnS$_2$ have been analysed in terms of the 6-exp type potential. The experimental determination of three parameters in the 6-exp type potential yields reasonable values for CdI$_2$. It is concluded from this result that the van der Waals force dominates the interlayer force in CdI$_2$ and that forces other than the van der Waals force contribute to the interlayer force in SnS$_2$ [87].

Large single crystals of semiconducting layer compounds with composition SnS$_x$Se$_{2-x}$ where, 0 ≤ x ≤ 2 have been successfully grown by a vertical Bridgman technique. The series forms a complete range of solid solutions and follows Vegard’s law. Long wavelength optical phonons have been studied experimentally for SnSe$_2$, SnS$_2$ and seven different solid solutions SnS$_x$Se$_{2-x}$ by laser Raman scattering and far-IR absorption and reflection measurements in the region up to 500 cm$^{-1}$. The frequencies of the vibrational modes for SnSe$_2$ (SnS$_2$) do not tend towards
the corresponding values for SnS₂ (SnSe₂) with increasing (decreasing) ‘x’ and the intensity decreases. This rules out any possibility of one mode behaviour in the series. A two-mode behaviour is indicated; however, no local or gap modes are observed [88].

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cingolani et al. (1988)</td>
<td>The second order Raman scattering and infrared absorption spectra of 2H–SnS₂ are reported. The temperature, excitation wavelength and polarization dependence Raman spectra are studies; resonance effect are put in evidence. The assignment of the second-order bands is discussed on the basis of the applicable selection rules [89].</td>
</tr>
<tr>
<td>Gupta et al. (1988)</td>
<td>The optical phonons in mixed-layer crystals of the series SnSₓSe₂₋ₓ (0 ≤ x ≤ 2) are calculated theoretically utilizing the effect of the interlayer and intralayer coupling parameters. A two-mode type of behavior is predicted. Long-wavelength optical phonons have been studied for SnSe₂, SnS₂, and dilertent solid solutions of SnSₓSe₂₋ₓ. A satisfactory agreement has been found between theory and experiment [90].</td>
</tr>
<tr>
<td>Scamarcio et al. (1989)</td>
<td>The explanation of the two-phonon spectrum of SnS₂ is achieved in terms of sum and overtone modes of the A and Γ points by comparing the observed polarization properties of the IR and Raman structures with those predicted by the selection rules [91].</td>
</tr>
<tr>
<td>Julien et al. (1994)</td>
<td>Details of resonant Raman scattering (RRS) in SnS₂ single crystals are presented. A detailed investigation of some newly observed features has been carried out using far-IR (FIR) absorption spectroscopy. A comparison of RRS and FIR data shows that the new features are IR active modes, and second-order or combinations modes which become allowed under the resonant Raman condition. The resonant behaviour of non-polar modes is explained using a quasi-two-dimensional approach. Our experimental data provide a good fit to the theory of RRS at the M1 critical edge [92].</td>
</tr>
<tr>
<td>Julien et al. (1996)</td>
<td>They report on the vibrational properties of lithium-intercalated SnS₂ single crystal. Raman scattering and infrared absorption spectra have</td>
</tr>
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</table>
been recorded as a function of temperature in the frequency range 50–600 cm$^{-1}$. The new bands are interpreted such as modes due to vibrations of lithium atoms located in the van der Waals gap against the nearest neighbouring chalcogen atoms [93].

**Wang et al. (2002)**

The optical property of SnS$_2$ nanocrystallites has been investigated by Raman scattering, far infrared spectrum and photoluminescence at room temperature. The Raman and far infrared spectrum of the SnS$_2$ nanocrystallites have a shift in comparison with that of the SnS$_2$ single crystals. The shift is mainly attributed to nanosize effect. The intralayer and interlayer force constant of SnS$_2$ nanocrystallites have been calculated by using a linear chain model [94].

**Chanchal et al. (2006)**

The Modified random-element-isodisplacement (MREI)-model have been found appropriate to calculate the frequencies of IR active and Raman active modes in SnS$_{2-x}$Se$_x$ ($0 \leq x \leq 2$) mixed series. The model confirms the two mode behavior exhibited experimentally by the series over the whole range of composition. The calculated values of optical phonon mode frequencies for the series are found to be in good agreement with the corresponding experimental values. The values of local and gap modes are their theoretically predicted values. The order of magnitude of various force constants determined from MREI-model are consistent with reported earlier [95].

**Utyuzh et al. (2010)**

The 2H polytype of a SnS$_2$ layered crystal has been studied using Raman spectroscopy at pressures of up to 5 GPa in a diamond anvil cell. The Raman frequency of the intralayer mode increases linearly with increasing pressure at baric coefficients of 5.2 cm$^{-1}$/GPa for P < 3 GPa and 3.4 cm$^{-1}$/GPa for P > 3 GPa. This change in the baric coefficient for Raman scattering and the available data on X-ray measurements of the compressibility of 2H–SnS$_2$ up to 10 GPa suggest that the crystal structure undergoes a transformation at about 3 GPa [96].

**Hadjiev et al.**

They present a combined Raman spectroscopy and density functional perturbation theory (DFPT) study of phonon variation with composition...
The experimentally observed two-mode behavior of the $A_{1g}$ and $E_{g}$ vibrations involving Se(S) atoms is shown to arise from the lack of overlapping of the corresponding phonon dispersion bands in SnS$_2$ and SnSe$_2$ [97].

### 1.3.3 Group V$_2$–VI$_3$ Chalcogenide

<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of work carried out by them</th>
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<tbody>
<tr>
<td>Richter et al. (1977)</td>
<td>The Raman-active lattice vibrations of Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$<em>3$, and their solid solutions, whose symmetries correspond to the R3m space group, are investigated by Raman scattering. Three of the four expected Raman modes, $E_g$ and $A</em>{1g}$, could be determined. The results for Bi$_2$Te$_3$ are compared to the predicted frequencies from the lattice dynamical model. The frequency shifts of the Raman-active modes in the mixed crystals show single-mode and two-mode behaviour which is in agreement with simple models for the substitution of antimony and selenium atoms for bismuth and tellurium respectively in Bi$_2$Te$_3$ [98].</td>
</tr>
<tr>
<td>Trentelman et al. (2009)</td>
<td>Raman spectra of bismuth metal powder, bismuth (III) sulfide (Bi$_2$S$_3$) and bismuth (III) oxide ($\alpha$-Bi$_2$O$_3$) are presented. The influence of excitation laser wavelength is explored, along with the laser-induced oxidation of bismuth to $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$. In the work presented here, the dependence of the Raman spectrum of bismuth and bismuth oxides on excitation wavelength is explored with spectra acquired using 488, 514, 633, 785 and 1064 nm excitation. In addition, conditions leading to laser-induced oxidation and laser-induced phase transformations are reported [99].</td>
</tr>
<tr>
<td>Kharbish et al. (2009)</td>
<td>Oriented single-crystals of stibnite (Ag$_5$SbS$_4$), bismuthinite (PbCuSbS$_3$), kermesite (Sb$_2$S$_3$), stephanite (Sb$_2$S$_2$O) and bournonite (Bi$_2$S$_3$) were investigated by polarized Raman spectroscopy. The obtained spectra were compared to those of the sulfosalt minerals tetrahedrite and</td>
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Sandip V. Bhatt/Ph.D. Thesis/Department of Physics/Sardar Patel University/May-2014
pyrargyrite. The latter showed isolated SbS$_3$ groups with ideal trigonal symmetry, the former showed distorted XS$_3$ ($X = \text{Sb, Bi}$) groups with lower symmetry [100].

**Kondrat et al. (2010)**

The comparative analysis of the calculated and experimental Raman spectra of non-crystalline As$_2$S$_3$, Bi$_2$S$_3$ and Sb$_2$S$_3$ films (i.e. with exchanging As to Sb, Bi) obtained by flash evaporation on glassy and silicon substrates was performed. The spectra were interpreted and analysed using the results of molecular modelling and ab initio calculations. The structural models used for calculations include both basic building blocks and other types of atomic clusters known for As–S, Bi–S, and Sb–S binary systems. The influence of atomic substitution on the nanostructure of flash evaporated As(Sb,Bi)$_2$S$_3$ films were investigated, observed photo-induced phenomena and related peculiarities were analysed using results of ab initio calculations and discussed in detail [101].

**Sereni et al. (2010)**

Polarization-dependent Raman spectroscopic measurements have been performed on single crystal samples of Stibnite (Sb$_2$S$_3$), a naturally occurring sulfide mineral with semiconducting properties and an energy band gap of approximately 1.72 eV, using both a visible and an infrared laser excitation line (532 and 1064 nm respectively), and the results have been compared with density functional theory calculations [102].

**Gnezdilov et al. (2011)**

The topological insulator Bi$_2$Se$_3$ shows a Raman-scattering (RS) response related to topologically protected surface states amplified by a resonant interband transition. Most significantly this signal has a characteristic Lorentzian lineshape and spin-helical symmetry due to collision-dominated scattering of Dirac states at the Fermi level $E_F$ on bulk-valence states. Its resonance energy, temperature, and doping dependence points to a high selectivity of this process [103].

**Zhang et al. (2011)**

They report on Raman spectroscopy of few quintuple layer topological insulator bismuth selenide (Bi$_2$Se$_3$) nanoplatelets (NPs) synthesized by a polyol method. The as-grown NPs exhibit excellent crystalline quality,
hexagonal or truncated trigonal morphology, and uniformly flat surfaces down to a few quintuple layers. Both Stokes and anti-Stokes Raman spectroscopy for the first time resolve all four optical phonon modes from individual NPs down to 4 nm, where the out-of-plane vibrational \( A_{1g} \) mode shows a few wavenumbers red shift as the thickness decreases below \( \sim 15 \) nm. This thickness-dependent red shift is tentatively explained by a phonon softening due to the decreasing of the effective restoring force arising from a decrease of the van der Waals forces between adjacent layers [104].

Vilaplana et al. (2011) They performed XRD and Raman scattering measurements at room temperature in Bi\(_2\)Se\(_3\) up to 20 and 30 GPa, respectively, that were complemented with ab initio total-energy and lattice dynamics calculations. XRD measurements show that the layered-compound \( \alpha \)-Bi\(_2\)Se\(_3\) undergoes an electronic topological transition (ETT) in the range 3–5 GPa, in which the bulk modulus changes as a consequence of the change of the layer compressibility. In addition, a phase transition toward a \( C2/m \) structure (\( \beta \) phase) is observed between 10 and 12 GPa. However, Raman scattering measurements indicate that \( \alpha \)-Bi\(_2\)Se\(_3\) undergoes an ETT near 5 GPa and confirm the transition from the \( R\bar{3}m \) to the \( C2/m \) phase near 10 GPa, with an increase in coordination of Bi from 6 to 7. In addition, two other phase transitions were observed near 20 and 28 GPa, where Bi\(_2\)Se\(_3\) is suggested to transform into a \( C2/c \) structure (\( \gamma \) phase) and a disordered bcc structure (\( \delta \) phase) respectively [105].

Kim et al. (2012) Inelastic light scattering spectra of Bi\(_2\)Se\(_3\) and Sb\(_2\)Te\(_3\) single crystals have been measured over the temperature range from 5 K to 300 K. The temperature dependence of dominant \( A_{1g}^2 \) phonons shows similar behavior in both materials. The temperature dependence of the peak position and linewidth is analyzed considering the anharmonic decay of optical phonons and the material thermal expansion. This work suggests
that Raman spectroscopy can be used for thermometry in Bi$_2$Se$_3$ and Sb$_2$Te$_3$-based devices in a wide temperature range [106].

Bera et al. (2013) They used a combination of Raman experiments on single crystal Sb$_2$Se$_3$ and first-principles density functional theory of electronic structure to establish the presence of an ETT in Sb$_2$Se$_3$ as a function of pressure. Vibrational anomalies in Raman spectra of the bulk that signify changes in electronic topology: an E$_{2g}$ phonon softens unusually and its linewidth exhibits an asymmetric peak at the pressure induced electronic topological transition (ETT) in Sb$_2$Se$_3$ crystal [107].

Makreskia et al. (2013) Photoinduced transformation/degradation of stibnite (Sb$_2$S$_3$) by the use of micro-Raman spectroscopy is explained. The transformation products were compared with those obtained by the thermal degradation of stibnite carried out in independent experiments. The proposed mechanism of photodegradation of Sb$_2$S$_3$ also found to occur in other related SbS$_3$-pyramid-containing sulfosalts helps to overcome the future erroneous interpretation of the bands in the Raman spectra of this important group of minerals as well to stress particular concern on the adjustment of the laser-excitation intensity when using micro-Raman and FT-Raman spectroscopy instrumentation in the study of other photosensitive and photodegradable compounds (including minerals) [108].

1.4 Raman Spectroscopy at High Pressure and Low Temperature

In classical thermodynamics, pressure is one of the fundamental thermodynamic variables, which can be varied over a range of more than sixty orders of magnitude from vacuum of outer space ($10^{-32}$ bar) to pressures in the interior of neutron stars ($10^{32}$ bar). In the same way, another thermodynamic variable temperature ranges from about $10^9$ K, the temperature at center of the hottest stars and necessary to form or destroy atomic nuclei, to $2\times10^{-6}$ K, the lowest temperatures accessible today in the laboratory in condensed matter physics experiments. The exploration of matter at extreme conditions is
a central theme in a broad range of scientific disciplines (e.g. material science chemistry, physics, and Earth and planetary science). In recent years, there has been considerable interest in the study of the high pressure behavior of solid because of academic, technological and geophysical reasons. The academic interest owes its origin to the fact that the most basic effect of high pressure in materials is compression, which in turn brings about a reduction in the inter-molecular distance. The reduction in the intermolecular distance affects and can, in fact, be used to tune intermolecular forces operative in the materials. With large and reproducible compression achievable in the laboratories, one can change the intermolecular forces by almost two orders of magnitudes higher than that of what is possible by the variation in temperature. Therefore, it follows naturally that high pressure investigation provide a very stringent test for the theoretical understanding of condensed matter. In addition the high pressure studies are also of great importance to visualize the mechanism governing the structures. The associated large decrease in volume provides a wealth of opportunities to observe basic changes in bonding character, magnetic or electronic structure or chemical state. Such experiments have become possible with the development of ultrahigh-pressure diamond anvil cell techniques (e.g., Ref. [109]). In particular, high-pressure spectroscopy provides crucial and often unique information on bonding properties and excitations of metals, semiconductors and superconductors [110, 111]. Ultrahigh-pressure research, by its very nature, imposes substantial requirements on experimental technique. The extremely small amount of the material (e.g., down to picoliter volumes) brought to megabar pressures demands extremely sensitive and versatile equipment. Thus, the quality of information obtained critically depends on the development of new techniques and improvement of the existing methods [112].

High pressure are now very widespread both as a means of studying the nature of substances and phenomena occurring in them and even more so as means of obtaining new materials (synthesis under high pressure) and processing of the already know materials. Since the pioneering studies at high pressure by P. Bridgman, the range of organization and individuals involved in research in this area has been unusually expanded. High pressures are widely used in research in solid state physics, chemistry, geophysics, and geochemistry. This is an independently, rapidly developing area of
science and technology [113]. Historically high pressure research has been an area heavily dependent on the availability of the experimental equipment. In fact, many of the discoveries in high pressure science followed promptly breakthroughs in instrumentation development which provide researchers with higher pressure limits or larger sample volume [114]. The introduction of the diamond anvil cell (DAC) has changed the field of vibrational spectroscopy at high pressures and, at the present time, the DAC represents a well-established and important high pressure technique. However, the application of high pressure covers many industries from basic material production, mechanical engineering, energy management, chemical engineering to bio-processing and food processing [115].

Considering interest has also been shown by the geophysicists in high pressure studies to explore the inner mantle of the earth where most of the matter is expected to be confined under very high pressures and temperatures. Under normal conditions, solids exhibit a particular crystal structure for which the total energy is minimum. However, on application of high pressure the atomic arrangement in solid changes resulting into change in interatomic distance and crystal structure. The pressure at which such structural change occurs is call phase transition pressure. Under the high pressure condition, the atoms rearrange themselves and assume a new stable structure for which again the total energy of the solid is a minimum. Such a structural phase transition can be noticed experimentally by observing the X–ray diffraction pattern, electrical resistivity and optical properties at different pressures. In the present thesis measurement of Raman spectroscopy and resistivity have been used to studies the possibility of structural phase transition in metal chalcogenides single crystals.

Low temperature physics and technology are not possible without knowledge of the relevant properties of matter of liquid and solid matter at low temperatures. Many fundamental properties of matter were only found and understood after matter had been cooled to the Kelvin range or to even lower temperatures. Among these properties are the quantization of lattice vibration (phonon), the electronic excitations leading to the linear temperature dependence of the specific heat of conduction electrons, superconductivity, superfluidity and many aspect of magnetism. Once these processes are understood, it will be possible to predict responses of materials under thermomechanical extremes using
advanced computational tools. Further, this fundamental knowledge will open new avenues for designing and synthesizing materials with unique properties. Using these thermomechanical extremes will allow tuning the atomic structure and the very nature of chemical bonds to produce revolutionary new materials [116].

Subjecting various types of matter to high external pressure, and utilizing a spectroscopic technique as the diagnostic tool to determine the change that have occurred, has proven very successful. Raman spectroscopy has been the most useful of the diagnostic tools utilized. Valuable information about intermolecular interaction, phase transition, structural changes, vibrational assignments and conversion of insulators (semiconductors) to metals is obtained when matter is subjected to pressure [117]. Raman spectroscopy is ideally suited for studying the evolution of the bond character in diatomic molecules under compression because measurements of their vibrational properties provide a powerful diagnostic of this process. The electronic density function changes with compression to minimize the total energy of the system. For the molecular materials, pressure tends to destabilize the intramolecular bonds as the kinetic energy of the participating electrons increases steeply with compression (e.g., [118]). Raman spectroscopy is a powerful technique to study numerous solid-solid phase transitions and metastability phenomena as it is very sensitive to minor changes in the crystal structure. This is because of the sensitivity of the Raman selection rules to the presence of atomic sites with different symmetry, and also to the vibrational coupling and the orientational ordering [119-121]. Accurate measurements of vibrational mode frequencies over a broad range of pressures and temperatures in conjunction with a well-defined equation of states allow a precise separation of the frequency changes arising from pure volume effects from those related to temperature effects at constant volume. Intrinsic anharmonic effects can thus be tracked in materials [122].
1.5 The Effect of Pressure on the Electrical Conductivity of Materials

The conductivity is defined by Ohm’s law relating the current density to the applied field. It may be expressed in term of the density of the charge carriers (n), their mobility (µ), the charge carried by them (q) and is related to the resistivity (ρ) by,

\[
\sigma = n|q|\mu
\]  \hspace{1cm} (1.1)

It is convenient to divide types of material conduction into (a) metallic (b) semi-metallic (c) semiconductor and (d) ionic.

The essential, distinguishing, feature between metals, semi-metals and semiconductors concerns the manner in which the electronic energy levels broaden as the atoms are brought close together into the condensed phase. Electrons from neighboring atoms overlap and their interaction broadens the original atomic levels into energy bands. The plot of density of electronic states for semiconductors materials with band-gap \(E_g\) is shown in figure 1.7.

The distribution of energy levels in different materials can be explained as follows:

(a) Monovalent metal: The energy band is half-filled. [maximum filled energy is called the Fermi energy, \(E_F\)]

(b) Divalent metal: The valence and conduction bands overlap appreciably, so that the valence band is not completely filled.

(c) Semimetal: The overlap between conduction and valence bands of divalent materials is very small [e.g. \(\leq 0.1\) eV]

(d) Semiconductor or insulator: The valence of an elemental semiconductor is even so that the valence band is filled and separated from the conduction band levels by an energy gap \(E_g\).

In the case of the semiconductors, empty valence states, or filled conduction band states, can only be created by thermal excitation across the band gap or from impurities or other lattice imperfections.
Figure 1.7 A sketch of the density of electronic state for (a) monovalent metal (b) divalent metal (c) semi metal (d) semiconductor with band-gap $E_g$

Elemental Metals

At ambient temperature the conductivity of the metal is given by the Bloch-Gr neisen formula (Mott and Jones, 1936 [123])

$$\sigma = \text{constant} \left( \frac{\theta_D^2}{T} \right) \quad (T \ \theta_D) \quad (1.2)$$

where $\theta_D$ is the Debye temperature and the constant includes terms that express the coupling between the electrons and lattice vibration that produce the resistance to the passage of electrons.

Then, $\sigma = \Gamma K_T = 2 \Gamma K_T \quad (1.3)$
where, $\Gamma$ is Grüneisen’s parameter and $K_T$ the isothermal compressibility, as before. This is the “normal” effect of pressure on resistivity. As pressure increases, it stiffens the lattice, so that the amplitude of thermal vibration decreases. This is turn lead to an increase in the mobility and thus in the conductivity. For divalent metals another important contribution the pressure derivative $\frac{\partial \ln \mu}{\partial p}$ can arise from the relative shifting of the bands with respect to each other. However, the high density of states increases the scattering probability for the s or p band electrons, so that the conductivity is relatively low and the pressure coefficient complicated. The complicated nature of the electronic states and scattering mechanisms in metals [124, 125].

$$\frac{\partial \ln \theta}{\partial p} = K_T \left( \left( 2 + \frac{\theta^2}{9r^2} \right) \Gamma + C \right)$$  \hspace{1cm} (1.4)

where, the parameter $C$ may take a value between $-4/3$ and $+2/3$ depending on the model assumed for the binding of electrons in the materials.

Above equation (1.4) predicts an increase in conductivity with increasing pressure, hence a decrease in resistance. This type of behaviour is in fact observed for a large number of metal i.e. Be, Na, Mg, Al, K, Mn, Cr, Fe, Co, Ni, Cu, Zn, Ga, Rb, Zr, Cb, Mo, Rh, Pd, Ag, Cd, in, Sm, Te, Cs, ba, La, Ce, Pr, nd, Ta, W, Hf, Nb, Ir, Pt, Au, Hg, Th, Pb, U at moderat pressures, the observed values falling generally between those calculated by equation (1.4) within the external values of the constant $C$.

**Semimetal**

The typical semimetal are Bi, Sb, As, graphite. Graphite is an interesting case in which these two terms approximately cancel one another out at ambient temperature for basal conduction in crystalline material [126, 127]. The decrease in the mobility with pressure arises from the change in the density of states with pressure. That conductivity is a tensor property. The polycrystalline materials are sample dependent and normally the pressure coefficient of the conductivity is very different for this type of material than for crystalline. The resistance can largely be attributed to inter-crystalline effects which are strongly dependent on pressure.
Alloys

Effects similar to those encountered in pure metals are also found in alloys, with the added feature of more complex scattering mechanisms, a larger number of high pressure phases and ordering or clustering effects that may occur in alloys. Several alloys with low temperature coefficient of resistance have been proposed for secondary pressure gauges.

Semiconductors

The main effect of pressure on the conductivity of pure semiconductors arises from the change of the energy band gap ($E_g$) with pressure, which therefore influences the number of electrons ($n$) in the conduction band and empty states (i.e. holes, $p$) in the otherwise filled valence band. For an “intrinsic” semiconductor, $n = p$, given by the mass-action formula

$$n = p A_C A_V \exp\left(-\frac{E_g}{2kT}\right)$$

(1.5)

where $A_C$ and $A_V$ are parameters related to the density of electronic states in the conduction and valence bands. Thus,

$$\frac{\partial \ln \theta}{\partial p} = \frac{\partial \ln A_C}{\partial p} + \frac{\partial \ln A_V}{\partial p} - \left(\frac{1}{2kT}\right) \left(\frac{\partial E_g}{\partial p}\right) + \frac{\partial \ln \mu}{\partial p}$$

(1.6)

In some semiconductors the band gap is reduced by the application of pressure, in other (e.g. Ge) it increases.

The study of the variation of band gaps with pressures has been of technological importance in furthering our understanding of the electronic energy states in semiconductors.

Semiconductors may also contain defects (e.g. impurities, point defect, dislocation etc.) which either donate electrons to the conduction band (donors) or accept electrons from the valence band (acceptors). In this case the number of electron and holes are not equal ($n \neq p$) and may not be used to estimate ‘$n$’ or ‘$p$’ [128]. In this case the conductivity and its pressure dependence is similar to that of a semimetal. Thus, the main effect of
pressure on the conductivity will be through the term \( \frac{\partial \ln \mu}{\partial p} \), since ‘n’ or ‘p’ will usually be insensitive to pressure. Consequently, the pressure coefficient of resistance will be much smaller. More detailed review of the effect of pressure on semiconductor behavior has been given by author [129–131].

1.6 The Effect of Temperature on the Electrical Conductivity of Materials

Near room temperature, the electrical resistivity of most pure metals decreases monotonically with temperature following an approximately linear relationship. This trend is the result of electron–phonon scattering and is the dominant temperature-dependent contribution to the resistivity \( R(T) \). At low temperature, the resistivity trends to a constant value, which is approached when the metal is near liquid helium temperature. The constant value of low temperature is referred to as the residual resistivity \( \rho_0 \) and is strongly dependent on the purity and amount and distribution of lattice imperfections in the metal. Generally, these two effects are additive, obeying what is known as Matthiessen’s rule that the total resistivity is the sum of two contributions,

\[
\rho = \rho_0 + \rho(T)
\]  

(1.7)

The theoretical interpretation of electrical conductivity of metals associates the loss mechanism with scattering processes between the electrons and the lattice. Considering a low-frequency transport of electrical current in a metal, we can relate the conductivity to the mean scattering time, \( t \approx \frac{l}{v_F} \), where \( l \) is the mean free path between electron scattering events and \( v_F = (2E_f/m)^{1/2} \) is the Fermi velocity. Elementary theory of electrical conductivity gives \( \sigma \) as,

\[
\sigma = \frac{n e^2 \tau}{m_e}
\]  

(1.8)

where \( n = N_e/V \) is the number of conduction electrons per unit volume and \( m_e \) is the electron mass. As mentioned above, there are two principal types of electron-lattice
scattering that determine the magnitude of the electrical conductivity. For fairly high
temperatures, \( T \approx \Theta_D \), the dominant mechanism is due to electron scattering by quantized
lattice vibrations i.e. phonons. A simple way to see the temperature dependence of this
effect is to relate the magnitude of the phonon scattering with the mean square
displacement of the molecules in the lattice, \( <x^2> \). In a simple harmonic solid, this
quantity is proportional to \( k_B T \), the thermal energy of the lattice. Assuming that the
electrical resistivity is proportional to the magnitude of phonon scattering, near room
temperature the resistivity of metals should also be proportional to \( T \), a fact borne out at
least approximately by the data.

For low temperatures, \( T<<\Theta_D \), the phonon scattering decreases with \( T \) giving way
to scattering dominated by lattice imperfections. In this domain the resistivity approaches
a temperature-independent value determined primarily by the amount of impurities and
imperfections in the lattice. For metallic elements, a few parts per million of impurities
can have a profound effect on electron transport as can the amount of cold work
generated imperfections. At the lowest temperatures with the purest samples, the mean
free path of the electrons can become very large approaching the sample size, such that
scattering off the surface of the sample can contribute a size effect dependence to the
resistivity.

At intermediate temperatures, \( T<<\Theta_D/3 \), the resistivity varies smoothly between
the two regions. Many metals have roughly \( T^5 \) dependence in this regime which can be
attributed to the phonon population being proportional to \( T^3 \) and the probability of
scattering through large angle having a \( T^2 \) dependence. The resistivity is therefore
proportional to the product of these two factors [132].
Temperature Dependence of Conductivity for a Semiconductor

The conductivity for a semiconductor depends on both carrier concentration and mobility, so there are variety of possible temperature dependencies for conductivity. For instance, at fairly low temperatures (less than 200 K), the dominant scattering mechanism might be impurity scattering (\( \mu \propto T^{3/2} \)) while the carrier concentration is determined by extrinsic doping (\( n = N_D^+ \)), therefore, conductivity would be seen to increase with temperature (\( \sigma \propto T^{3/2} \)). Other possibilities, depending on the material, doping, and temperature will show different temperature dependence of conductivity. One particularly interesting case occurs at high temperatures (above 400 K or higher) when carrier concentration is intrinsic and mobility is dominated by lattice scattering (\( \mu \propto T^{-3/2} \)). In such cases, the conductivity can easily be shown to vary with temperature as:

\[
\sigma \propto \exp\left(\frac{E_g}{2kT}\right)
\]  

(1.9)

In this case, conductivity depends only on the semiconductor bandgap and the temperature. In this temperature range, measured conductivity data can be used to determine the semiconductor bandgap energy, \( E_g \).
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