

## CHAPTER 1

### INTRODUCTION

Research at high pressures has developed into an inter-disciplinary area which has important applications in the field of materials science, condensed matter, engineering and technology. It has provided new insights into the behaviour of matter. One of the most important outputs of high pressure experiments is the pressure-volume-temperature relationship of materials, which leads to the equation of state (EOS) is one of the most fundamental properties of solid. The application of pressure alters the electronic energy states. These electronic energy levels are of prime importance in computing electronic, thermal, electrical, magnetic, optical, Fermi surface and superconducting properties of solids. Fermi surface and superconducting properties under high pressure were studied earlier by using band structure results by Dakshinamoorthy et al (1984). Such high pressure studies have improved our understanding of the properties of the materials near phase-transitions. Thus, an understanding of materials with their characteristic properties is of much importance to both the theoreticians as well as the experimentalists.

#### 1.1 STRUCTURE BASED PROPERTIES AND APPLICATIONS

Pyrite is the most common of the sulphide minerals. The pyrite structure  $\text{FeS}_2$  occurs mainly among the transition metal dichalcogenides. The pyrite structure is also used by other compounds  $\text{MX}_2$  of transition metals M and chalcogens X=O, S, Se and Te. Also certain dipnictides with X standing



for P, As and Sb etc. are known to adopt the pyrite structure. Pyrite structure has a variety of structural, electronic, magnetic, optical and thermal properties. Copper di-sulphide ( $\text{CuS}_2$ ) exhibits temperature-independent paramagnetism and is superconducting. Pyrite structure compounds find interesting applications in optoelectronics or photovoltaic material required to have excellent environment compatibility, high absorption coefficient suitable band gap, high quantum efficiency and low production cost for photocurrent generator (Bettahar et al 2009, Ding et al 2011, Meng et al 2003). The inter-metallic compounds having the general formula  $\text{A}_3\text{B}$  crystallize in the A-15 structure with space group  $\text{P}_m\bar{3}_n$ . Many of the A15 compounds show superconducting properties, i.e. high temperature and high critical fields. These have the potential, which is now being realized in the design and construction of magnets, electrical machinery, and other devices. The contemplated use of superconducting magnets in fusion devices as well as in other high energy physics applications is well known (Francavilla et al 1978).

Recently, several high pressure investigations have been carried out to understand the structural modifications induced by pressure. Some of the high pressure studies include XRD of powder and single crystal samples for characterization, studies at extreme condition (high pressure and high temperature), study of phase diagrams and determination of equation of state (EOS). More often, theoretical calculations are carried out using the X-ray diffraction experiments performed on systems keeping them at room temperature. Pressure induced transformation in crystalline materials can often be predicted on the basis of crystal structure by Kanchana et al (2003). The effect of pressure on the electronic energy levels tuning as a powerful tool for modern solid state science (Minomura 1985, Chandrashekar et al 2010).



## 1.2 STRUCTURAL PROPERTIES

High-Pressure Synthesis of the Copper dichalcogenides series  $\text{CuS}_2$ ,  $\text{CuSSe}$ ,  $\text{CuSe}_2$ ,  $\text{CuSeTe}$  and  $\text{CuTe}_2$ , as well as new  $\text{MX}_2$  compounds of Fe, Co and Ni, (X=S, Se, Te) all having pyrite-type structure have been reported by (Bither et al 1966). Dichalcogenides of Mn, Fe, Co, Ni and Cu having either pyrite, marcasite, or  $\text{CdI}_2$  type of structures are also listed. For a specific composition, the densities of these structures vary in the order  $\text{CdI}_2 < \text{marcasite} < \text{pyrite}$ . Thus, the formation of the pyrite structure should be favoured only by high pressure. Some of the new pyrite-type compounds at high pressure studies, such as,  $\text{MnS}_2$ ,  $\text{MnSe}_2$ ,  $\text{MnTe}_2$ ,  $\text{FeSe}_2$ -(semiconductor),  $\text{FeTe}_2$ -(metallic),  $\text{CoTe}_2$ -(metallic) and  $\text{NiTe}_2$ -(metallic) reported by (Bither et al 1966). The pyrite-type dichalcogenides  $\text{ZnS}_2$ ,  $\text{ZnSe}_2$ ,  $\text{CdS}_2$ , and  $\text{CdSe}_2$  have been synthesized at high pressure (65-89 kbar) (Bither et al 1968). Ternary pyrite phases containing Cu have been described by (Bither et al 1970). Structural properties of  $\text{CuX}_2$  dichalcogenides (X=S, Se, Te) from X-ray measurements at 300K show that only the pyrite structure is present in all the samples (Krill et al 1976). Preparation and properties of Magnesium, Copper, Zinc and Cadmium Dichalcogenides have been investigated and also reported the structural data for the  $\text{FeS}_2$ -pyrite type phases  $\text{MgO}_2$  and  $\text{MgTe}_2$ . Pressure induced structural phase transformation from the stable cubic phase to the orthorhombic phase has been reported earlier for  $\text{CuS}_2$  (Arne Kjekshus & Trond Rakke 1979, Gunnar Brostigen & Arne Kjekshus 1970). Disulphides of the transition elements Mn through Zn crystallize in the pyrite structure (Hubert et al 1979). The copper dichalcogenides, with one unpaired d electron, show metallic conductivity, weak temperature-independent susceptibility, and superconductivity with a maximum superconducting transition temperature of 2.4K occurring in the series at the composition  $\text{CuSe}_2$ .



Phase stability studies of FeS<sub>2</sub> by Vijay Kumar Gudelli et al (2013), marcasite FeS<sub>2</sub> is stable at ambient conditions, and it undergoes a first-order phase-transition to pyrite at around 3.7 GPa with a volume collapse of about 3%. Using the Right bind approximation (RBA) and constant scattering time approximation (CSTA), structural, mechanical, electronic and thermoelectric properties calculated by an ab-initio study. Lattice parameters, internal coordination of sulphur atom, bond lengths and bulk modulus at ambient condition and the mechanical properties of pyrite FeS<sub>2</sub> have been explored at different pressures using classical inter-atomic potentials. First principles studies of the structural and electronic properties of pyrite FeS<sub>2</sub> by Joseph Muscat et al (2002) B3LYP functional based on Becke's three parameter and DFT calculations give a good description of the occupied electronic states.

### **1.3 THERMOELECTRIC PROPERTIES**

Thermal conductivity is the property of a material that indicates its ability to conduct heat. Thermal conductivity is the one of the important physical properties necessary at elevated temperature structural applications of metallic materials Ashby (1989). Inter-metallic compounds for high temperature applications must be oxidation - resistant, and in most cases, the aluminides satisfying all these conditions are the strongly favoured candidates for high-temperature applications. Ordered inter-metallic compounds have attracted much interest for high temperature structural applications (Stoloff 1984, Sauthoff & Metallkde1986). The thermal conductivity composition relationship in binary compounds is characterized by a sharp maximum at stoichiometry. The thermal conductivity and temperature coefficient are inversely correlated for metallic materials including inter-metallic compounds (Terada et al 1997). The Debye temperature is an important parameter of a solid and several physical properties are expressed in terms of Debye temperature by (Blackman 1955, Alers 1965). Based on the Debye model, Liu et al



(2010) suggested that the theoretical minimum thermal conductivity can be calculated after replacing different atoms by an equivalent atom with a mean atomic mass (Bouhemadou et al 2011). Nano structured thermoelectric materials for achieving high figure of merit of thermoelectric materials (ZT) for practical applications (Jeannine Szczech et al 2011).

Interesting thermoelectric materials have been discovered more recently in pyrite structure (AuTlSb - a new pyrite superstructure) (McGuire et al 2006). Enhanced thermoelectric properties by iridium doping of PtSb<sub>2</sub> with pyrite structure were studied and measured electrical resistivity, Seebeck coefficient, and thermal conductivity (Ir doping in PtSb<sub>2</sub>) by (Nishikubo et al 2012). The results showed an abrupt change from semiconducting behaviour without iridium to metallic behaviour with iridium doping and it exhibited large Seebeck coefficient (S) and low electrical resistivity ( $\rho$ ) resulting in a maximum power factor at 400K. The peculiar 'pudding mold'-type electronic band dispersion could explain the enhanced thermoelectric properties in the metallic state. More recently, thermoelectric properties were studied on pyrite structure FeS<sub>2</sub>. The thermal conductivity of two single samples of pyrite FeS<sub>2</sub> are investigated by the method of stationary longitudinal heat flux in the temperature range 50-300K. The low electrical conductivity of the crystals with small impurity content causes an identical value of experimental lattice thermal conductivity. The temperature dependence of the phonon mean free path was established by Popov et al (2013). Calculated thermoelectric properties of the mineral FeS<sub>2</sub> (marcasite and pyrite) were reported through an Ab initio study by (Vijay Kumar Gudelli et al 2013), and they find that the thermopower at high pressure phase is relatively higher than that for the ambient phase. Marcasite FeS<sub>2</sub> can be used for low-temperature thermoelectric applications, whereas pyrite can be used for the high temperature applications (Vijay Kumar Gudelli et al 2013).

A15 Nb<sub>3</sub>X (X = Al, Ga, In, Sn and Sb) inter-metallic compounds (Sundareswari et al 2010), and strongly correlated inter metallic



semiconductors  $\text{TMGa}_3$  (TM = Fe, Ru, and Os) (Amagi et al 2004, Haussermann et al 2002, Hadano et al 2009). This group of materials possesses a small hybridization gap at the Fermi level, due to the mixing of the conduction band with narrow d- or f-bands. This is a very important characteristic for thermoelectric properties (Aeppli & Fisk 1992, Riseborough 2000). Heavy element compound semiconductors commonly used thermoelectric materials such as  $\text{Bi}_2\text{Te}_3$  (Gordiakova et al 1958, Wright 1958, Bulusu et al 2008)  $\text{Sb}_2\text{Te}_3$ ,  $\text{PbTe}$  and  $\text{BiSb}$ ,  $\text{PbSb}$  alloy, forming complex crystal structures by phonon-glass electron-crystal (PGEC) approach i.e. materials that have high electronic conductivity due to their periodic crystal structure but low thermal conductivity (Schmitt et al 2012), germanium based clathrates (Li et al 2011, Nolas et al 1998), Skutterudites (Leithe-Jasper et al 2008, Sales et al 1996), complex chalcogenides (Chung et al 2000), Zintl compounds  $\text{Yb}_{14}\text{MnSb}_{11}$  (Brown et al 2006) is an excellent material for high temperature thermoelectric applications.

#### 1.4 ELECTRONIC PROPERTIES

Electronic properties provide the useful information about the band structure, electron density, ionicity and bonding. The electronic structures of the pyrite-type transition metal disulphides extending from Mn to Zn and related studies show that they exhibit a rich diversity of physical properties (Temmerman et al 1993):  $\text{MnS}_2$ -antiferromagnetic semiconductor,  $\text{FeS}_2$ -a Van Vleck semiconductor,  $\text{CoS}_2$ -a ferromagnetic metal  $\text{NiS}_2$ -a paramagnetic Mott-Hubbard insulator,  $\text{CuS}_2$ -a (metallic) superconductor, and  $\text{ZnS}_2$ -a diamagnetic insulator (Temmerman et al 1993). The interesting properties of the charge-density waves and the transport properties were also studied earlier (McMillan 1975, Sugai et al 1981, Wilson et al 1975).

For the transition metals an important factor determining the stability is the extent to which the nine  $sp^3d^5$  orbitals can be used in the formation of bands (Linus Pauling 1978). The outer shell of transition metals



contains nine orbitals- $4s4p^33d^5$  for the iron sequence;  $5s5p^34d^5$  for the palladium sequence;  $6s6p^35d^5$  for the platinum sequence. It has been recently recognized that these orbitals can be hybridised into sets of nine good orbitals (McClure 1970, Pauling 1975a, 1975b). The best sets of nine bond orbitals are the McClure set, the tetragonal antiprism with one cap, and the trigonal prism with caps on the three prismatic faces. These structures are compatible with the electro neutrality principle when the partial ionic character of covalent bonds is taken into consideration. Careful high resolution X-ray studies of the electron-density distribution in pyrite-structured compounds were carried out by Stevens & Coppens (1978), Nesbitt et al (1998).

The behaviour of valence electrons in the iso-structural compounds  $V_3Ge$  and  $Cr_3Ge$  has been examined on the scale of Fermi momentum (Sharma et al 2008). The valence electron distribution seems to be dominated by the metallic constituents rather than Ge and two compounds show covalent nature of bonding which is larger in  $V_3Ge$  compared to  $Cr_3Ge$ . The electronic valence charge density is a useful probe for the understanding of the chemical bonding in materials (Hoffmann 1988, Charifi et al 2005). All A15-type compounds show electronic properties which are highly structure- dependent. In this sense,  $Nb_3Sn$  is an example of a material whose properties are uniquely linked with its structure, whereas for compounds such as, for example,  $Nb_3Os$  or  $Mo_3Ge$ , no such specific influence of the atomic arrangement is apparent Matthesiss & Weber (1982), Klein et al (1978), Pickett et al (1979). It is well known that particularly favourable conditions for superconductivity may be expected in metallic narrow band systems. But in an attempt to 'construct' superconductors this way, the Coulomb interaction may also become important and, in addition, stability may be affected. It is qualitatively conceivable that some of the niobium-based A15 compounds just represent a most favourable compromise. The high symmetry of the structure and the comparatively large unit cell for equivalent positions, combined with the right number of *d*-electrons, appear as some of the most important factors (Muller 1980). Much has been written about the unique



atomic arrangement in the A15-type structure, permitting the occupation of orthogonal linear chains by transition metal atoms. It is certainly important for many of the outstanding physical properties that these chains are independent in the crystallographic sense, i.e. that no crossing or branches occurs at lattice sites. However, it is clear that one has to take into account an interaction between atoms at chain sites and neighbouring body-centred sites as well as between atoms belonging to orthogonal chains.

The valence and conduction bands overlap considerably for inter-metallics in general, and there is no band gap at the Fermi level. This finding confirms the metallicity of these compounds (Bouhemadou et al 2011). Semi empirical methods have been used in an attempt to identify the sub-bands producing a sharp structure near the Fermi energy (Weger & Goldberg 1973, Goldberg 1975, Barak et al 1975, Mattheiss 1975). More recently, a set of several new *ab initio* calculations with impressive accuracy have become available. Jarlborg (1978a, 1979) used a particularly economic self-consistent method developed by O K Andersen (1971), and presented the partial and total density of states curves for 27 compounds. The accuracy is such that comparison with various experimental results should be meaningful. Confronting the calculated densities of states with those derived from electronic specific heat measurements (Spitzli 1971) may be too severe a test, but the general trend in the series of compounds appears to be correct. The comparison with experimental spectroscopic data can be used to check the energy scale of the calculated bands. Taking the example of  $V_3Si$ , for which both soft x-ray emission spectra (Kurmaev et al 1974) and x-ray photoelectron spectra (Riley et al 1976, Nilson et al 1977) have been measured, we conclude, following Jarlborg, that their agreement is quite satisfactory. In earlier non-self-consistent APW-LCAO calculations (Mattheiss 1975), ad hoc adjustments had to be made to scale with the x-ray emission data.



Considering the latest impressive band structure calculations, one is tempted to admit that they must be very close to the truth, although some more fundamental problems, such as the correct treatment of exchange and correlation, may remain. In relation to superconductivity, the existence of very narrow peaks in the density of states finally raises the question of electron lifetime effects (Marvin&Cohen 1964). This aspect has been occasionally discussed most recently by Ho et al (1978) and Mukherjee (1979) and it is likely that considerable broadening occurs even at low temperatures.

## 1.5 SUPERCONDUCTING PROPERTIES

The superconducting properties of several hundreds of intermetallic compounds (Miracle&Darolia 1995) possessing different crystal structures have been studied. As is evident from Table 1.1, the occurrence of superconductors with  $T_C > 10$  K is by no means a rare phenomenon in intermetallic compounds. There are recently found oxide superconductors, which are basically ceramics and not intermetallic, but still superconducting at higher transition temperatures of 90K and 120 K after the discovery of 40 K superconductors (Bednorz and Muller 1986, Chen et al 2000).

Before the advent of high temperature oxide superconductivity, several intermetallic compounds possessing A15 crystal structure (Testardi 1973a) have been known to be good superconductors; namely,  $V_3Si$  ( $T_C = 17.1$  K),  $V_3Ga$  ( $T_C = 16.8$  K),  $Nb_3Sn$  ( $T_C = 18$  K),  $Nb_3Al$  ( $T_C = 18.5$  K) and  $Nb_3Ge$  ( $T_C = 23.2$  K). The A15 groups of compounds are the only intermetallic materials known at present to possess transition temperatures in excess of 18K. In fact  $Nb_3Sn$  has been used in the development of superconducting magnets for fields in excess of 100 kOe, inspite of difficulties involved in fabricating long continuous leads of the brittle material (Weger& Goldberg1973). In addition to high transition temperatures, these materials frequently display anomalies in their electronic and elastic properties.



These anomalies manifest themselves as strong temperature dependence of properties, like electronic specific heat, magnetic susceptibility, knight shift etc. (Testardi 1973a, Weger& Goldberg1973). Mossbauer spectroscopy studies on A15 structure Nb<sub>3</sub>Sn compound by Ashok Razdan (2000). Anharmonicity is either a high temperature or a low temperature phenomenon. They have shown that Nb<sub>3</sub>Sn is a case of temperature dependent anharmonicity which may not arise due to presence of any potential. They have also proved that Mossbauer experimental data can be explained for the same value of Debye temperature  $\theta_D$  as obtained from X-ray Debye-Waller measurements. So there is no discrepancy between Debye temperature values of X-ray Debye-Waller factor data and Mossbauer data have been discussed by Ashok Razdan (2000).

**Table 1.1 Structure Type and superconducting transition temperatures of different inter-metallic substances**

Structure Type	Substance	T <sub>C</sub> (K)
A12	NbTc <sub>3</sub>	10.5
A13	Mo <sub>3</sub> Al <sub>2</sub> C	10.0
A15	IrTi <sub>3</sub>	5.4
B4	InSb	2.1
C18	CuTe <sub>2</sub>	<1.25 - 1.3
A15-Cp8(Cr3Si)	Cr3Os	4.68
C14	ZrRe <sub>2</sub>	6.8
C15	HfV <sub>2</sub>	9.4
C16	Zr <sub>2</sub> Rh	11.3
E9 <sub>3</sub>	Zr <sub>3</sub> Rh	11.8
Chalcogenides	PbMo <sub>6</sub> S <sub>8</sub>	15.2



The main reason for the application of superconductivity to large scale electrical devices is that superconductors are capable of handling extremely large current densities. The normally allowed maximum rating of uncooled copper is  $2 \times 10^6$  A/m<sup>2</sup> (Dew-Hughes 1973). Among the inter-metallic superconductors, the most favourable group is the one based on the A<sub>3</sub>B compound. In the cubic A15 structure, six binary compounds have T<sub>C</sub> over 17 K. The highest known T<sub>C</sub> prior to 1986, close to 23 K is obtained in Nb<sub>3</sub>Ge, stabilized by traces of oxygen or aluminium; it exhibits the upper critical field of 38T. The A-15 structure exists in about 70 binary compounds. The H<sub>c2</sub> (T) values for A 15 superconducting compounds are very high. The typical A15 compounds (Flukiger et al 1974) as V<sub>3</sub>Au show the strongest variation in T<sub>C</sub>. VanReuth & Poulis (1967) found for V<sub>3</sub>Au an increase of T<sub>C</sub> from T<sub>C</sub> < 0.012 K to 2.97 K influenced more or less by the degree of atomic long range ordering (LRO). The resistivity ρ (T) of the A15 compounds differs significantly from that of a metal at both low and high temperatures. For example, ρ (T) of Mo<sub>3</sub>Ge (T<sub>C</sub> = 1.5 K) (Gurvitch 1980) varies as T<sup>5</sup> dependence at low temperatures.

The magnetic properties are as interesting as the mechanical properties of the intermetallic. Most frequently, the intermetallic compounds are found to be non-magnetic, if one of the components is ferromagnetic. The reverse case of magnetic alloys from non-magnetic constituents identified by Heusler (Kouvel 1967) was also surprising. Moreover, other compounds like MnBi with extremely high coercivities, and SmCo<sub>5</sub> (Brooks et al 1991), were found to be useful as permanent magnets. Another important milestone in the magnetic behaviour of intermetallic was the antiferromagnetic ordering suggested by (Kouvel 1967). In fact, the magnetic properties ranging from para to ferrimagnetism in compounds, give a much better understanding of the nature of interactions and their influence on the macroscopic properties. The magnetic moments due to the spin polarization are estimated for each atom



The hardness of many intermetallic compounds was found to be higher than that of the unalloyed metal components (Dolgin 1988). The super-alloys provide high strength and toughness, but are limited to low temperatures. Ceramics are useful for high temperature applications, but they are inherently brittle because of the covalent atomic bonding. The intermetallic compounds are expected to fill the gap between the super-alloys and the ceramics not only with respect to the service temperature range (Liu 1989), but also with respect to properties; i.e., higher strength than super-alloys because of the strong atomic predominance.

A phase for high temperature applications must have sufficient strength at service temperature, which means a sufficient creep resistance. The creep resistance scales with the diffusion coefficient and with the shear modulus, and both parameters scale with melting temperature. The Al / Cu metal joints used for electrical connectors were joined by the friction welding method to limit the formation of an intermetallic compound, under optimum friction welding conditions. A thicker intermetallic compound layer could seriously degrade the electrical resistivity and tensile strength (Lee et al 2005). Current research is focused on the aluminides of nickel, titanium and iron:  $\text{Ni}_3\text{Al}$ ,  $\text{NiAl}$ ,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ ,  $\text{Fe}_3\text{Al}$  and  $\text{FeAl}$ , which serve as structural intermetallic compounds. But the major problem of these strong intermetallic compounds is their brittleness, which however, should be less severe than that of ceramics, because of the different type of bonding.

## 1.6 SEMI-METALLIC PROPERTIES

A semi-metal is a material with a small overlap between the valence and conduction bands. Bi, Sb and As are typical semimetals since there is a small overlap of the fifth and sixth bands. This results in the fifth band being not quite filled and in there being some electrons in the sixth band.



These electrons in the sixth band and holes in the fifth band carry the current, regardless of the temperature. Other examples of semimetals are graphite(C),  $\beta$ HgS, HgSe, HgTe and  $Mg_2Pb$ . There are several methods of preparative techniques for the semimetals and narrow band gap semiconductors (Lovett 1977) particularly for the alloys, depend on the form of relevant phase diagrams.

V –VI LAYERED STRUCTURE COMPOUNDS: **1. Phase diagrams**–In the preparation of binary and ternary compounds and alloys it is imperative that information on the possible phases which can exist for different composition and preparation conditions be available. This information is contained in the relevant phase diagram, and a particular state of equilibrium can be characterised by the number and the identity of the phases. **2. Crystal structure** of antimony chalcogenides: The first three compounds namely  $Sb_2Te_3$ ,  $Sb_2Te_2Se$ ,  $Sb_2TeSe_2$  belong to the trigonal system with space groups of R-3m (166), R-3m (166) and R3m (160) respectively, whereas the  $Sb_2Se_3$  is of orthorhombic family with the space group of pbnm(62). Their structure consists of zigzag chains- Sb (Bi)-S (Se)-Sb (Bi)-, oriented along the c-axis. **3. Compounds with the tetradymite structure** are usually non-stoichiometric. **4. Physical properties**–The electrical conductivity of  $Sb_2Se_3$  is about  $10^{-6} \Omega^{-1}.cm^{-1}$ , the thermoelectric power is  $+1200\mu V/deg$ , and the mobilities are  $\mu_n=15cm^2.V^{-1}.sec^{-1}$  and  $\mu_p= 45cm^2.V^{-1}.sec^{-1}$ . ( $Sb_2Te_3$ )–The compound always has the p-type conduction. The forbidden band width of this compound is 0.23eV (Ronnlund et al 1965). The best thermoelectric materials for applications at room temperature are compounds of antimony, bismuth and tellurium. **Anisotropy of properties** –A characteristic feature of compounds with the tetradymite structure is the anisotropy of their physical properties related to their crystal structure. **Thermodynamic properties**– The high vapour pressure of the chalcogens present in the V-VI compounds make it difficult to obtain stoichiometric compositions. The properties of alloys in



this range of compositions vary monotonically with the composition. An increase in the concentration of  $\text{Sb}_2\text{Se}_3$  reduces the electrical conductivity and thermal conductivity. **Optical properties**-These compounds have phase change property. It finds many applications in optoelectronics.

## 1.7 PRESENT WORK

Recent developments in materials science led to a comprehensive understanding of the basic science and engineering concepts that enable many developments in technologies and their applications (Sankey et al 1989) Computational materials science plays a vital role in an understanding and gain knowledge concerned with the fundamental properties of materials. Owing to the advent of computational methods and tools available in the present days, applications of density functional theory calculations, atomic and molecular dynamical simulations, Monte-Carlo simulations (Raty et al 2000) etc., in the studies of electronic structure of condensed matter are carried out with great ease.

The main objective of the present work is to study of the structural, electronic, thermal and superconducting properties of some compounds, namely, transition metal dichalcogenide pyrite structure metallic compound (copper disulphide)  $\text{CuS}_2$ , binary  $\text{A}_3\text{B}$  type A15 structure inter-metallic compounds (titanium-gold, titanium-platinum, titanium-iridium)  $\text{Ti}_3\text{M}$  ( $\text{M}=\text{Au}, \text{Pt}, \text{Ir}$ ), and semi-metallic compounds (V-VI) layered structure (antimony telluride, antimony selenide ditelluride, diantimony telluride diselenide, antimony selenide)  $\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$  ( $x=3,2,1,0$ ).

The present computational work has been carried out by using the results such as density of states (DOS), equation of states (EOS), Fermi energy ( $E_F$ ) etc., obtained from the first principles electronic band structure computations of these compounds. The electronic band structure of solids,



under the self-consistent field approximation (Slater 1953) has proved to be immensely successful, especially in the physics of materials and superconductors. The ab-initio self consistent calculations of electronic band structures have been carried out through the tight binding linear muffin tin orbital (TB-LMTO) technique within the atomic sphere approximation (ASA) (Andersen et al 1984, 1975) Within this method, the atom and orbital calculations are performed for the above mentioned compounds, in the compressed and expanded unit cell volumes by varying the relative volume ( $V$ ,  $V_0$  = Volume and equilibrium volume)  $V/V_0$  of the unit cell.

The electronic total energy values are obtained for various unit cell volumes and fitted to Murnaghan's equation of state (EOS) (Murnaghan 1944) to obtain the ground state properties such as equilibrium lattice constants and bulk modulus. Volume dependent studies have improved our understanding the properties of these materials such as superconductivity, structural phase stability, structural phase transitions etc. The computed values of the Fermi energy ( $E_F$ ), density of states at  $E_F$ , Wigner-Seitz radius ( $R_0$ ), bulk modulus ( $B_0$ ), etc., have been used to calculate the electronic and lattice specific heat coefficients, electronic and lattice thermal conductivities, Debye temperature ( $\theta_D$ ), electron-phonon coupling constant ( $\lambda$ ) and superconducting transition temperature ( $T_C$ ). To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Gruneisen model (Debye 1912). The electronic coulomb pseudo potential parameter,  $\mu^*$ , has been obtained from the empirical relation given by Bennemann and Garland by using the DOS at  $E_F$ . McMillan's (1968) and the Allen Dyne's (1975) formulae have been used for the investigation of superconducting transition temperature ( $T_C$ ).

The structure and summary of the thesis are comprised in seven chapters as briefed below:



**Chapter 1** is the introductory chapter, which gives a brief survey of the electronic band structure and associated properties of the compounds and their applications.

**Chapter 2** presents the theoretical concepts and methods for understanding the electronic structure of solids. It provides briefly the various methods of electronic band structure studies.

**Chapter 3** The tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic sphere approximation (ASA) is adopted for computing the electronic structure of the above-mentioned compounds in the present work. The description of this method is given in this chapter. The U von Barth and L Hedin exchange correlation parameterization scheme (von Barth and Hedin 1972) is used, to generate the self-consistent potential parameters. The method of tetrahedron (Jepsen & Andersen 1971) is used to calculate the density of states. This method requires a minimal basis set and is computationally fast.

**Chapter 4** deals with the estimation of thermal properties, such as Debye temperature, electronic specific heat co-efficient and superconducting transition temperature and these studies have been carried out by using the results of electronic band structure and related characteristics, for the  $\text{CuS}_2$  ( $\text{FeS}_2$ -type structure) compound in two different phases, (cubic phase and orthorhombic phase) under pressure. Apart from the electronic band structure and structural stability, the density of states (DOS) and Fermi energies ( $E_F$ ) are also calculated for various unit cell volumes. The equilibrium ground-state properties were calculated for the lattice parameters that correspond to the minimum of the electronic total energy. From the total energy it has been observed that the cubic phase is the stable phase under normal pressure and the calculated lattice parameter values are in good agreement with the experimental report (Folmer et al 1988) available in the literature.



Computations have been carried out to understand, from a fundamental point of view, the above mentioned structural phase transition of  $\text{CuS}_2$ . The result indicates that, in both the phases of the material, the p-bands dominate in their conduction band. The DOS around  $E_F$  is found to be high and it is due to the strong pile up of mainly the p-states and a little of d-states, in both the phases of  $\text{CuS}_2$ , and accounts for the structural stability. Thus, the DOS at the Fermi level is almost exclusive of p-character. The Debye temperature ( $\theta_D$ ) and electronic specific co-efficient ( $\gamma$ ) are important parameters that are closely related to the thermal properties of materials. Hence, the estimation of these quantities has also been made for both the cubic and orthorhombic phases. To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Gruneisen model. The calculated values of  $\lambda$  and  $T_C$  are observed to be in good agreement with the available experimental results (Bither et al 1966) in the literature. Thus, the present studies have provided a better understanding of the fundamental electronic, structural, thermal and superconducting properties of the  $\text{CuS}_2$  pyrite structure compound.

**Chapter 5** discusses the studies on the A15-structure, inter-metallic compounds of  $\text{Ti}_3\text{Au}$ ,  $\text{Ti}_3\text{Pt}$ , and  $\text{Ti}_3\text{Ir}$ . The basic electronic properties of these materials have been computed and, the results have been used for the studies of electronic ground-state, thermal and superconducting properties of the compounds. The total energies are calculated as a function of primitive cell volume for all the above-mentioned compounds, and are fitted to the Birch equation of state (EOS) to obtain the ground-state properties, such as equilibrium lattice constants, bulk modulus, cohesive energy and heat of formation. The obtained results are compared with the available experimental and other theoretical results. The domination of d- and p-bands is clearly evident in all the three materials. They are also found to be very strongly hybridized. A highly dense accumulation of the p- and d-bands occurs around the Fermi energy for all the three compounds. The band structures show that



the Fermi energy decreases with the decrease in the atomic number of M (M=Au, Pt, Ir) element. The DOS at the Fermi level is observed to be almost exclusively of d-character with little contribution from p-bands. The cohesive energy, heat of formation,  $\theta_D$  and  $\gamma_G$  of  $Ti_3Au$ ,  $Ti_3Pt$ , and  $Ti_3Ir$  compounds has been computed. The electron-phonon coupling parameter  $\lambda$  has been estimated using the electronic band structure results and the superconducting transition temperature  $T_C$  is calculated using McMillan's formula (McMillan 1968). It is found that, among the three compounds,  $Ti_3Ir$  has the highest  $T_C$  value. The  $T_C$  values estimated by the present work for all the three compounds,  $Ti_3Au$ ,  $Ti_3Pt$ , and  $Ti_3Ir$ , are found to agree reasonably with the available experimental values reported earlier (Blaugher et al 1969). Thus, the present studies have provided comprehensive understanding of the fundamental electronic, thermal and superconducting properties of these three materials.

**Chapter 6** the details of studies and results of  $Sb_2Te_xSe_{3-x}$  ( $x=3, 2, 1, 0$ ) compounds regarding their electronic structure, Fermi energy and density of states, etc., are presented. The thermal properties of the compounds, namely Debye temperature, electronic and lattice specific heat, electronic and lattice thermal conductivities, etc., have been computed for all these antimony compounds and the results are corroborated well with the earlier experimental reports. The bulk modulus  $B_0$  is used to obtain the Debye temperature ( $\theta_D$ ) (Moruzzi et al 1988) for the three trigonal systems ( $Sb_2Te_3$ ,  $Sb_2Te_2Se$ ,  $Sb_2TeSe_2$ ) and one orthorhombic structure ( $Sb_2Se_3$ ). The Debye temperature  $\theta_D$  values obtained here are found to be in close agreement with the available experimental results (Dyck et al 2010) in the literature. It has been observed that  $\theta_D$  values show increasing trend with the increase of Se content. The studies further reveal that the electronic properties are highly dominated by the p-orbitals originating mainly from Sb. Semi-metallic nature of all the four compounds is clearly displayed in their band structure and



density of states results. The energy gap and density of states at  $E_F$  increase as Se content increases for all the compounds; however, the Fermi energy and bulk modulus values increases with the increases of Se content from  $Sb_2Te_3$  to  $Sb_2TeSe_2$ , and then they decreases considerably for  $Sb_2Se_3$ . Such a drastic change of these properties for  $Sb_2Se_3$  is attributed to the structural phase change from trigonal to orthorhombic structure.

**Chapter 7** summarizes the results of the work done and presents the scope for future study.

