CHAPTER 1

A BRIEF SURVEY OF THE PROPERTIES AND APPLICATIONS OF INTERMETALLIC COMPOUNDS

1.1   INTRODUCTION

Intermetallic compounds have played a significant role in the advancement of many branches of science and engineering. Intermetallic compounds are generally brittle and have a high melting point. They often offer a compromise between ceramic and metallic properties, when hardness and / or resistance to high temperatures are important enough to sacrifice some toughness and ease of processing. They can also display desirable magnetic, superconducting and chemical properties, due to their strong internal order and mixed (metallic and covalent / ionic) bonding, respectively. Intermetallic compounds have given rise to various novel materials' developments. High strength-low density, larger electrical resistivity-high melting point etc., are some of the specific properties that enhance the importance of intermetallic compounds. The search for new materials with improved properties continues, and hence, the study of intermetallic compounds assumes considerable importance. This chapter presents a brief survey of the various properties of these intermetallic compounds and their importance.

1.2   PROPERTIES AND SOME OF THE APPLICATIONS OF INTERMETALLICS

The range of physical properties possessed by the variety of intermetallic compounds finds its use as (a) high strength materials (b) oxidation resistant materials (c) good insulators (d) good thermal conductors and so on. A few of the most desired properties of intermetallic compounds are discussed below.

1.2.1   Mechanical Properties

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: Ni_3Al, $NiAl$, Ti_3Al, $TiAl$, Fe_3Al and $FeAl$, 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. Intermetallic compounds for high temperature applications must be oxidation - resistant, and in most cases, the aluminides satisfying all these conditions are the strongly favored candidates for high-temperature applications.

1.2.2 Thermoelectric Properties

The importance of intermetallic compounds for thermoelectric conversion is a result of their particularly favorable transport properties - Seebeck coefficient (thermoelectric power), electrical conductivity, and thermal conductivity as compared with metals and elemental semiconductors. The principal thermo element currently in use is PbTe and other compounds like hexaborides LaB_6 (Korsukova et al 1984), which have very high melting temperatures. Improving the performance of thermoelectric materials is necessary, if future refrigeration and power generation applications are to be realized. Since the discovery of Bi_2Te_3, (Gordiakova & Sinani 1958, Wright 1958) thermoelectric materials have attracted attention because of their high Seebeck coefficients, very low electrical resistivity, and high atomic weights (Bulusu & Walker 2008). Several interesting thermoelectric materials have been discovered more recently, such as skutterudites (Sales et al 1996), complex chalcogenides (Chung et al 2000), germanium based clathrates (Nolas et al 1998), half-Heusler alloys (Young et al 2000), a phonon glass-electron crystal system with exceptionally low thermal conductivity (Schmitt et al 2012), zintl phases (Brown et al 2006), and strongly correlated intermetallic semiconductors (Basov et al 1994, Amagai et al 2004, Haussermann et al 2002, Hadano et al 2009). This last 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). It is essential to have high thermoelectric efficiency.

1.2.3   Electronic Properties

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. It is well known that particularly favorable 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 favorable 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).

The valence and conduction bands overlap considerably for intermetallics 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, see also Mattheiss1975). 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 (Matthesis 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. 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.

1.2.4   Thermal Properties

Ordered intermetallic compounds have attracted much interest for high temperature structural applications (Stoloff 1984, Sauthoff & Metallkde 1986). Thermal conductivity is the one of the important physical properties necessary at elevated temperature structural applications of metallic materials

(Ashby 1989). The rapid heat transfer afforded by high thermal conductivity enables efficient cooling, which suppresses the appearance of life limiting heat-attacked spots, resulting in higher operating temperatures. High thermal conductivity assures the uniform distribution of temperature, which reduces the thermally induced stresses and, thereby, improves the fatigue properties (Miracle & Darolia 1995). 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 intermetallic compounds (Terada et al 1997).

The Debye temperature is an important parameter of a solid (Blackman 1955, Alers 1965). From the calorimetric measurements it is well known, that it varies with the temperature. Thermal conductivity is the property of a material that indicates its ability to conduct heat. However, in order to know if the material is a potential candidate for thermal barrier coating application, its thermal conductivity needs to be investigated. 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).

1.2.5   Magnetic Properties

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 $SmCo_5$ (Brooks et al 1991), were found to be useful as permanent magnets. Another important milestone in the magnetic behavior 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.

1.3   SUPERCONDUCTING PROPERTIES OF INTERMETALLIC COMPOUNDS

The superconducting properties of several hundreds of intermetallic compounds 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). More about the superconducting properties is discussed in the following section; all the compounds studied in the present thesis are superconductors.

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 $Nb_3Al_{0.75}Ge_{0.75}$ ($T_C = 20$ 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 & Goldberg 1973). 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 & Goldberg 1973). Although in the past decade, interest has been mainly focused on ceramic oxides, there are many unresolved questions related to the above mentioned anomalies.

Table 1.1 **Structural phases and superconducting transition temperatures of different binary intermetallic substances**

Structure Type	Substance	T_C (K)
C18	$CuTe_2$	<1.25-1.3
Cubic	$AuZn_3$	1.21
B4	InSb	2.1
Hexagonal	Bi_4Rh	2.7
Cubic	BHf	3.1
Orthorhombic	BiPd	3.7
C14	$ZrRe_2$	6.8
C15	HfV_2	9.4
C16	$RhZr_2$	11.3
A15	Nb_3Sn	18.0
A12	$NbTc_3$	10.5

1.3.1 Applications of Different Types of Superconducting Intermetallic Compounds

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 $2*10^6$ A/m^2 (Dew-Hughes 1973). There is great interest in

the superconducting A15 materials, particularly in those members which have high transition temperatures and high critical current values. 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). Here, the superconductivity in AB type compounds and in particular the (1) A_3B A15 type compounds and (2) AB_2 Laves phase compounds, is briefly explained.

1.3.1.1 A_3B type

Among the intermetallic superconductors, the most favorable group is the one based on the A_3B compound. In the cubic A15 structure, six binary compounds have T_C over 17 K. The highest known T_C prior to 1986, close to 23 K is obtained in Nb_3Ge, 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 Hc_2 (T) values for A 15 superconducting compounds are very high. The typical A15 compounds (Flukiger et al 1974) as V_3Au show the strongest variation in T_C. VanReuth & Poulis (1967) found for V_3Au an increase of T_C from $T_C < 0.012$ 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_3Ge ($T_C = 1.5$ K) (Gurvitch 1980) varies as T^5 dependence at low temperatures.

1.3.1.2 AB_2 type

Recently, the binary transition metal carbides or silicides compounds with hexagonal crystal class (space group P63/mmc) have been extensively investigated both by theoretical calculations and experimental methods (Wang et al 2007), because many of them exhibit outstanding

mechanical properties and chemical stability; for instance, they are very hard compounds and have high melting point, low density, high thermal conductivity, etc. (Zhou et al 2009). Among the AB_2, C15 type, it is interesting to observe $HfMo_2$ alloy in three different crystal structures, b.c.c., C15 and C36. T_C is the highest for the b.c.c. modification, about 1K, is about 0.07K for the C15 structure and below 0.05K for the C36 structure in general agreement with the idea (Rapp 1970) that T_C decreases when the symmetry of the lattice decreases. The Laves phase superconductor ZrV_2 ($T_C \sim 8K$) in twinned crystalline form, undergoes a cubic to rhombohedra structural transformation around 100K (Roy et al 1994). The Laves-phase (C15) compounds V_2Zr, V_2Hf exhibit relatively high superconducting transition temperature (Roberts, 1976) (8-10K) and high critical magnetic fields (Inoue & Tachikawa 1975) (~23T). Besides these good superconducting properties, these materials can be fabricated in the form of ductile multifilamentary superconducting wires of high critical current density, which could be particularly useful for generating high magnetic fields .These materials are insensitive to neutron radiation (Brown et al 1977) compared to other superconducting materials. Another characteristic feature of these compounds is their ability to absorb large amounts of hydrogen, making them suitable materials for storing hydrogen (Shaltiel 1980).

Since the present thesis concentrates on the A_3B and AB_2 type structured compounds, more details about the superconducting property of the specific compounds and the theoretical method of evaluating them are discussed in the following chapters.

1.4   PRESENT WORK

The computational materials science is one of the important disciplines of research and renders very significant support towards the development of science and technology. The computational methods, such as

the density functional theory calculations, the molecular dynamic simulations, the Monte Carlo methods, etc., provide the foundation for the important technological advances (Suter et al 2009, William & Martin 1991). In many cases, the electronic structure calculations and the simulation studies of a given material can be done by computational methods which can save money, work force and time, instead of testing in a laboratory.

The present work is to study of the structural, electronic, magnetic, thermal, and superconducting properties of some of the transition metal based compounds. In this work, the electronic band structure calculations are performed on a selected few inter-metallic compounds at their equilibrium, compressed primitive cell volumes. The systems studied are V_3X (X = Ga, Sb, Au) and V_6GaSb compounds, HfX_2 (X = Tc, Re, Os) compounds, and ZrX_2 (X = V, Re, Os) compounds.

The aim of this work is to study the electronic, magnetic, thermal and superconducting properties, with the help of the band structure and density of states results. The bandstructure of the solids has been studied using the self-consistent field approximation (Slater 1953), and has been proved to be immensely successful, especially in the physics of materials and superconductors. The electronic band structure computations have been carried out using the tight-binding linear muffin-tin (TB-LMTO) technique within the atomic sphere approximation (ASA) (Andersen & Jepsen 1984, Andersen 1975). Within this method, the atom and orbital decomposition of the electron density of states is well defined. The band structure calculations are performed for the above mentioned compounds, in the compressed and expanded volume range, by varying the V/V_0 in the unit cell. The computed values of the Fermi energy (E_F), density of states at E_F, etc., have been used to calculate the Debye temperature (Θ_D), electronic and lattice specific heats, super conducting properties, etc.

This thesis is organized into seven chapters. The structure of the thesis is as follows:

Chapter 2 presents the method adopted for calculating the electronic structure of solids. It describes briefly the various methods of band structure calculations.

Chapter 3 describes the tight-binding linear muffin-tin orbital method within the atomic sphere approximation adopted for calculating the electronic structure of the compounds. The detailed description of this method is given in this Chapter. The Hedin & Lundqvist (1971), exchange correlation parameterization scheme 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 V_3X (X = Ga, Sb and Au) and V_6GaSb compounds, which crystallize in the A_3B-type structure. The electronic, ground state, thermal and superconducting properties of A_3B based intermetallic compounds in cubic structures are presented. The structural stability of these compounds is also studied. The scope of this Chapter is to study the inter-metallic A15 based on *3d* elements. For each material, the equilibrium lattice parameters were obtained, by minimizing the electronic total energy with respect to the cell volume. The variations of the lattice constants are in compliance with the variation of the size of the atoms in their compounds. A comparison of the calculated and experimental lattice parameters of these compounds shows very good agreement between them. The electronic band structures of these four compounds along the high symmetry directions of the Brillouin zone are clearly evident in all the four materials that these *d*-states dominate in their conduction. The calculated results are observed to be in good agreement with the available results

existing in the literature. An estimation of the Gruneisen constant (γ_G), electronic specific heat coefficient (γ), electron-phonon coupling constant (λ) and superconducting transition temperature (T_C) were deduced for these compounds. Both spin-polarized and non-spin-polarized calculations are carried out for the V_3Ga and V_3Au of these compounds.

Chapter 5 describes the prediction of hafnium superconducting alloys, namely, HfX_2 (X = Tc, Re and Os). They are found to crystallize in hexagonal C14 Laves structure alloys ($MgZn_2$-type structure). This chapter gives a systematic examination of the DOS and energy band structure calculations for the above-mentioned compounds. All the electronic properties such as the DOS and energy bands were calculated for the equilibrium lattice parameters. For each case, the equilibrium lattice parameters were obtained, by minimizing the electronic total energy (E_T) with respect to the cell volume. The cell volumes are varied by varying the a-parameter and maintaining the c/a ratio constant. Thus, the present studies have provided a better understanding of the fundamental electronic and superconducting properties of hexagonal C14 Laves structure alloys. The electronic specific heat coefficient (γ), electron-phonon coupling constant (λ) and superconducting transition temperature (T_C) of HfX_2 (X = Tc, Re and Os) are calculated theoretically and compared with the experimental values.

In Chapter 6, the results of the *ab initio* electronic band structure calculations of hexagonal C14 Laves structure type ($MgZn_2$-type structure) ZrX_2 (X = V, Re and Os) compounds are given. The values of the superconducting transition temperature for $ZrRe_2$ and $ZrOs_2$ are experimentally determined in hexagonal C14 Laves structure type except ZrV_2 (Giorgi & Szklarz 1970, Kuentzler & Waterstrat 1986). The ground state lattice parameters and primitive cell volume have been obtained by fitting the electronic total energy with the Murnaghan equation of state (1944), and are

found to be in good agreement with the experimental results. The band structure and related properties at the Fermi energy are dominated by the d-bands in general. The values of γ and T_C for the hexagonal phase for ZrX_2 (X = V, Re and Os) compounds were calculated. To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Gruneisen model. The electron-phonon coupling constant (λ) can be estimated using the electronic band structure results. The superconducting state parameters have been computed using the McMillan's (1968) and the Allen-Dyne's (1975) formulae. The values of λ and T_C are calculated and compared with the available experimental results existing in the literature.

Thus the present studies comprise the computation of electronic band structure properties and the electronic total energy calculations as a function of volume for all the above-mentioned compounds. The electronic total energy as a function of primitive cell volume are fitted to the Murnaghan equation of state (EOS) to obtain the ground-state properties such as equilibrium lattice constants and bulk modulus. The electronic band structure and density of states are presented both in the equilibrium volume and at the compressed volumes, and the results obtained are discussed in comparison with the experiment results available in the literature.

The last Chapter (Chapter 7) summarizes the conclusions drawn on the electronic structure calculations performed on different systems. From the observations of the band structure studies on V_3X, HfX_2, and ZrX_2, it is found that the main contribution to the conduction state is due to the d-electrons in all systems. In the A_3B system, the d-electrons of the A atom dominate in their conduction. In the AB_2 system d-electrons of the B atom dominate in their conduction. For these compounds, using the density of states and band structure results, the electronic, thermal, magnetic and superconducting properties are calculated, and compared with the available results.