ABSTRACT

The thesis deals with the self-consistent electronic band structure calculations performed on a number of binary inter-metallic materials. The objective of the present work is the study of the structural, electronic, magnetic, thermal, and superconducting properties of some of the transition metal based compounds. The systems studied are $V_3X$ ($X = \text{Ga, Sb, Au}$) and $V_6\text{GaSb}$ compounds, $\text{HfX}_2$ ($X = \text{Tc, Re, Os}$) compounds, and $\text{ZrX}_2$ ($X = \text{V, Re, Os}$) compounds. In this work, the electronic band structure calculations are performed on a number of inter-metallic compounds at their equilibrium and compressed volumes. The tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic sphere approximation (ASA) was used for this purpose.

The $V_3X$ ($X = \text{Ga, Sb and Au}$) and $V_6\text{GaSb}$ compounds crystallize in $A_3B$-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. At higher energies there is a hybridization of the $d$-bands of the vanadium with the $p$-bands of other elements. The density of states (DOS) at the Fermi energy is found to be strongly influenced by the Sb-concentration, and decreases (increase) with the increase of the Sb (Ga) content. As a consequence, the electron-phonon interaction parameter, electronic specific heat and the superconducting transition temperature have all been found to
decrease (increase) with the increase of Sb (Ga) content. Computation of the Gruneisen constant ($\gamma_G$), electronic specific heat coefficient ($\gamma$), electron-phonon coupling constant ($\lambda$) and superconducting transition temperature ($T_C$) has also been carried out for these compounds.

Both spin-polarized and non-spin-polarized calculations are carried out for $V_3$Ga and $V_3$Au compounds. The magnetic phase stability is determined from the total energy calculations for both the non-magnetic and magnetic phases. The $V_3$Ga and $V_3$Au compounds are found to have a magnetic moment of 1.08 $\mu_B$ and 1.64 $\mu_B$ per formula unit. The magnetic property of these compounds persists until the volume compression by 17% and 8%, respectively, and then, for further volume compression, the magnetism is lost. The magnetic moment is seen to decrease linearly with the lattice parameter of $V_3$Ga, and non-linearly, for $V_3$Au. The magnetic property of the compound is found to be mainly due to the $d$-electrons of V-atoms.

The hafnium superconducting alloys, namely, HfX$_2$ (X = Tc, Re and Os) are found to crystallize in hexagonal C14 Laves structure (MgZn$_2$-type structure). All the electronic properties, such as the DOS and energy bands were calculated for the equilibrium lattice parameters. The value of the density of states at the Fermi energy is found to increase from HfTc$_2$ to HfOs$_2$, and this may be attributed to the increase in the interatomic separation, which causes a reduction in the overlapping of the Hf $d$-orbitals with the $p$-orbitals of X. This reduction in the $p$-$d$ hybridization results in the narrowing down of the $d$-bands, causing a higher density of states at $E_F$. The high DOS around $E_F$ is, evidently, due to the strong pile up of $p$- and $d$-bands.
in all the three alloys, and account for the structural stability. The calculated band structure of HfX$_2$ ($X = Tc$, Re and Os) is almost flat in the Γ'-A direction just above $E_F$, and cuts $E_F$ along the K-Γ' direction. This flat band feature is responsible for the superconductivity in this system. It should be mentioned that from the results of the band energy properties of the alloys, the Debye temperature ($\Theta_D$) and electronic specific heat coefficient ($\gamma$) have also been calculated for HfX$_2$. The calculated values of $\lambda$ and $T_C$ for these compounds are observed to be in good agreement with the available experimental results existing in the literature.

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 carried out and their ground state lattice parameters and primitive cell volumes have been obtained by fitting the electronic total energy with the Murnaghan equation of state. The band structure and related properties at the Fermi energy are found to be dominated by the $d$-bands in general. The density of states at Fermi energy is found to be strongly influenced by the $d$-bands, due to the X- atoms in all these three compounds. The values of $\gamma$ and $T_C$ for the hexagonal phase for ZrX$_2$ ($X = V$, Re and Os) compounds have also been calculated. The high DOS around $E_F$ is, evidently, due to the strong pile up of $p$- and $d$-bands in all the three alloys, and account for their structural stability. The electron-phonon coupling constant ($\lambda$), superconducting transition temperature ($T_C$) have been estimated using the electronic band structure results.
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’s 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.