FIRST PRINCIPLES STUDY OF ELECTRONIC STRUCTURE, MAGNETIC AND OPTICAL PROPERTIES OF SOME HEUSLER ALLOYS

Synopsis submitted to Madurai Kamaraj University

in partial fulfillment of the requirements for the award of the degree of

Doctor of Philosophy in Physics

By

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DECEMBER 2019

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SYNOPSIS

1.1 INTRODUCTION

Recently, Heusler alloys have attracted much attention due to their applications in spintronics and spin filtering devices. In general, outstanding Heusler compounds should possess a number of desirable magnetic performances, such as, large magnetization; spin polarized magneto resistive devices, spin-transfer torque magnetic memory element, transportation and processing. The history of Heusler alloys began in 1903, when German Physicist Friedrich Heusler discovered the presence of ferromagnetic property in the fusion of nonmagnetic Mn, Cu, and Sn. That is the addition of sp elements (Al, In, Sn, Sb or Bi) in Cu-Mn alloy turns it into a ferromagnetic material, even though no ferromagnetic element was not present initially in the alloy. Basically, Heusler alloys are classified into four general categories based on their electronic structure. They are full- Heusler alloys, half- Heusler alloys, inverse-Heusler alloys and quaternary- Heusler alloys. The Heusler materials are widely used in spintronics, magnetic tunnel junction, shape memory effect, and opto- electronic devices, such as, sensors, magneto resistors, photo voltaic detectors and light emitting diodes. Aside from the potential technological applications, the fundamental Physics of half metallic ferromagnetic materials is also profuse and fascinating. The occurrence of half metallic nature in several Heusler alloys bears promise for applications of these materials in spin polarized magneto resistive devices. Amongst the entire search for novel materials of improved optical and electronic properties, Heusler alloys play a key role due to their wide band gap, large magnetization and high Curie temperature (T_c).

Due to the technological importance of these Heusler compounds, it appears necessary to comprehend the behavior of their structural, electronic, elastic, optical, vibrational and thermodynamical properties at both normal and high pressures.

1.2 MOTIVATION FOR THE PRESENT INVESTIGATION

To improve the performance of spintronic devices like the spin filter and the spin valve, one has to search for new magnetic materials with high spin polarization. Among them, half-metallic Heusler compounds are the ideal choice of high-spin-polarization materials due to their 100% spin polarized charge carriers at the Fermi level. Today, more than a century after their discovery by Heusler, they are still a field of active research. New properties and potential fields of applications emerge constantly. The prediction of half metallic ferromagnetism is the most recent example. Surprisingly, the properties of many Heusler compounds can easily be predicted by the valence electron count. Magnetic materials underpin modern technologies, ranging from data storage to energy conversion to contactless sensing. However, the development of a new high-performance magnet is a long and often unpredictable process, and only about two dozen magnets are featured in main stream applications.

The investigation of Heusler alloys has drawn attention due to both from a fundamental as well as an application point of view. Also, only a limited theoretical works were carried out on Heusler alloys under the pressure effect and substitution approach. This field is still in its infancy and it has stimulated to study the structural stability and structural phase transition under compression, change in electronic properties, mechanical, magnetic and optical properties of Heusler alloys with different atomic configurations by the first principles calculations for the development of new half metallic ferromagnetic materials, by understanding the properties and practical uses under normal and high pressures. This motivated us to investigate the elaborate theoretical research on the Heusler alloys. In this thesis, an ab initio interpretation of

the structural stability, structural phase transition, electronic structure, mechanical, magnetic and optical properties of some Heusler alloys in different phases of cubic crystal structure have been carried out under normal and high pressures, besides to simply propose a new half metallic ferromagnetic materials.

1.3 SCOPE OF THE STUDY

The scope of the present work is to study the ground state properties, electronic structure, mechanical, magnetic and optical properties of some Heusler alloys under normal and high pressures. More specifically, the aim of the present work is to determine the half metallic ferromagnetism and spin polarization of the Heusler alloys under normal and high pressures.

1.4 OBJECTIVES OF THE STUDY

The objectives of the present study are:

- To obtain the ground state properties like lattice parameter, cell volume, cohesive energy, formation energy, bond length, bulk modulus and its pressure derivative of some Heusler alloys.
- To investigate the structural stability and phase transition in Heusler alloys under normal and high pressure by computing the total energy.
- To investigate their electronic structures by computing total and partial density of states at normal and high pressure.
- To estimate the elastic constants, bulk modulus, Young's modulus, shear modulus, Poisson's ratio, Pugh ratio (B/G) and hardness of some Heusler alloys.

- ❖ To analyze their magnetic order, such as, ferromagnetic state and non magnetic state by computing the total energy and their spin magnetic moment.

- ❖ To estimate the Curie temperature T_C for some Heusler alloys.

- ❖ To investigate the optical properties such as dielectric function $\varepsilon(\omega)$, refractive index $n(\omega)$, reflectivity $R(\omega)$ and energy loss function $L(\omega)$.

1.5 MATERIALS INVOLVED

The materials used in the framework of the present thesis are only the elements which belong to 3d transition metals, some group I- II elements and few group IV- V elements (sp- elements). The chosen Heusler alloys are IrMnSn, IrMnSb, PtMnSn, PtMnSb, AuMnSn, AuMnSb, NiCrSi, NiCrGe, NiCrGa, NiCrAl, NiCrIn, NiCrSn, LiBeAs, LiBeSb, LiBeBi, LiScGe, LiScSi, CoMnSb, NiMnSb, CoMnBi, CoCrBi, CoFeTiSi, CoFeTiGe, CoFeTiAs, NiFeTiSi, NiFeTiGe, NiFeTiAs, Co_2TiAl, Co_2TiGa, Co_2TiIn, $Fe_{2-x}Co_xTiSi$, $Fe_{2-x}Co_xTiGe$, $Fe_{2-x}Co_xTiSn$, Fe_2TiAl, Fe_2VAl and Fe_2CrAl.

1.6 METHODOLOGY

The present work is theoretical and computational type based on modern density functional theory. The first principles calculations are performed based on density functional theory as implemented in VASP software. It uses a plane wave basis set and periodic boundary conditions. The interaction between ions and electrons can be described by projector augmented-wave method with different approximations (LDA, GGA, GGA-PBE, GGA-PW91 and so on) for exchange-correlation functional. VASP uses efficient matrix diagonalization schemes and an efficient Pulay/Broyden charge density mixing. Traditional self-consistency cycle is used to calculate the electronic ground state with the combination of efficient numerical methods which

leads to robust and fast scheme for evaluating the self-consistent solution of the Kohn-Sham functional.

1.7 ORGANIZATION OF THE THESIS

In the present work, the structural stability, electronic structure, mechanical, magnetic and optical properties of some Heusler alloys are computed. The entire work is divided into ten chapters.

In chapter I, the formation and various types of Heusler alloys, structural and magnetic properties of Heusler alloys and their applications are discussed. The concept of half-metallic ferromagnetism and Slater Pauling rule are outlined.

In chapter II, the quantum mechanical description of many body systems, the density functional theory, the local density approximation, generalized gradient approximation and the theory of VASP (*Vienna Ab initio Simulation Package*) are discussed. The ab initio calculations are performed using density functional theory as implemented in VASP.

In chapter III, the structural stability, structural phase transition, electronic structure, mechanical and magnetic properties of Mn based half Heusler alloys such as IrMnSn, IrMnSb, PtMnSn, PtMnSb, AuMnSn and AuMnSb are investigated in C_{1b} structure. The three possible atomic arrangements in C_{1b} structure are α, β and γ phases. The structural stability is analysed among these three phases. It is found that all the half Heusler alloys IrMnSn, IrMnSb, PtMnSn, PtMnSb, AuMnSn and AuMnSb are stable in α- phase. A pressure-induced structural phase transition from α phase to β phase is observed in IrMnSn, IrMnSb, PtMnSn, PtMnSb, AuMnSn and AuMnSb. The electronic structure reveals that these alloys are metals at normal pressure and exhibits half metallic behavior at high pressure. The bulk modulus obtained using Birch-Murnaughan equation of states agree well with the values computed using the elastic

constant values. The elastic constants obey the stability criteria suggesting that all the half Heusler alloys are mechanically stable at ambient condition. It is found that all these half Heusler alloys are magnetic at normal pressure. The Hubbard U correction to the GGA- PBE calculations greatly improves the lattice constant values, electronic structure and the magnetic properties.

Chapter IV describes the structural stability, electronic, mechanical and magnetic properties of Ni based half Heusler alloys NiCrSi, NiCrGe, NiCrGa, NiCrAl, NiCrIn and NiCrAs C_{1b} structure. It is found that all the above half Heusler alloys are most stable in α- phase. When the pressure varies the compounds NiCrSi, NiCrGe, NiCrGa, NiCrAl, NiCrIn and NiCrAs undergo phase transition. The structural phase transition from most stable α phase to γ phase is observed for NiCrSi, NiCrGe, NiCrGa, NiCrAl and NiCrIn and α phase to β phase is observed for NiCrAs under atomic compression. The observed transition pressure (P_T) values for NiCrSi, NiCrGe, NiCrGa, NiCrAl, NiCrIn and NiCrAs are 88.8 GPa, 76.9 GPa, 77.6 GPa, 107.5 GPa, 78.1 GPa and 43.2 GPa respectively. The cohesive energy and formation enthalpy values reveal that they are thermodynamically stable. The density of states predicted the half metallic nature of these compounds at normal pressure. The electronic half metallic to metallic phase transition is observed in NiCrSi, NiCrGe, NiCrGa, NiCrAl, NiCrIn and NiCrAs at the pressures of 88.8 GPa, 76.9 GPa, 77.6 GPa, 107.5 GPa, 78.1 GPa and 43.2 GPa respectively. The computed elastic constants obey the necessary mechanical stability condition suggesting that all the half Heusler alloys are mechanically stable at ambient condition. The Debye temperature for NiCrZ alloys is computed. It is noted that all these NiCrZ Heusler alloys are ferromagnetic at normal pressure. A ferromagnetic to non-magnetic phase transition is observed at high pressure.

In chapter V, the ground state properties and the structural stability of Ni based half Heusler alloys, such as, LiBeAs, LiBeSb, LiBeBi, LiScGe and LiScSi are investigated and electronic structures are also analysed. It is found that the α- phase is the most stable phase for LiBeAs, LiBeSb and LiBeBi compounds and β- phase for LiScGe and LiScSi. These Li based alloys has been observed as semiconducting Heusler alloys. The half Heusler compounds LiBeAs, LiBeSb, LiBeBi, LiScGe and LiScSi exhibit semiconducting behaviour with the energy gap values of 1.079 eV, 1.187 eV, 1.019 eV, 0.919 eV and 0.782 eV respectively. The optical parameters, such as, dielectric function ε(ω), refractive index n(ω) and energy-loss function L(ω) are calculated for these compounds. The refractive index of all the compounds shows the isotropic and anisotropic behavior at low and high energies respectively.

In chapter VI, the ground state properties and structural stability of CoMnSb, NiMnSb, CoMnBi and CoCrBi are analyzed among the three phases (α, β, γ) of considered cubic $C1_b$ structure. It is found that γ- phase is the most stable phase for CoMnSb, CoMnBi and CoCrBi and α- phase is the stable phase for NiMnSb half Heusler alloys. The structural phase transition from most stable γ phase to α phase is observed for CoMnSb, α phase to β phase for NiMnSb and γ phase to α phase is observed for CoMnBi and CoCrBi at the pressures of 79.23 GPa, 71.47 GPa, 14.58 GPa and 16.91 GPa in CoMnSb, NiMnSb, CoMnBi and CoCrBi respectively.The high bulk modulus indicates that these half Heusler alloys are incompressible materials. The electronic structure confirms that these Mn and Cr based half Heusler alloys are half-metallic in nature. A half metallic to metallic transition is observed in CoMnSb, NiMnSb, CoMnBi and CoCrBi at the pressures of 79.23 GPa, 71.47 GPa, 14.58 GPa and 16.91 GPa respectively. The computed Young's modulus value indicates that CoMnSb is the stiffest material. The calculated values of A indicate that these half Heusler alloys have complete elastic anisotropy. It is found that these alloys are stable in ferromagnetic (FM) state. The ferromagnetic to non magnetic phase transition occurs

at the pressures of 686.2 GPa and 617.9 GPa, 613.8 GPa and 573.7 GPa in CoMnSb, NiMnSb, CoMnBi and CoCrBi respectively.

In chapter VII, the ground state properties, structural, electronic and elastic properties of different phases of Fe based quaternary Heusler alloys are analysed. It is found that all the quaternary Heusler alloys CoFeTiSi, CoFeTiGe, CoFeTiAs, NiFeTiSi, NiFeTiGe and NiFeTiAs are stable in α- phase. A pressure-induced structural phase transition is observed in CoFeTiSi, CoFeTiGe, CoFeTiAs, NiFeTiSi, NiFeTiGe and NiFeTiAs. The electronic structure reveals that these materials are half metals at normal pressure whereas metals at high pressures. The electronic half metallic to metallic phase transition is observed in CoFeTiSi, CoFeTiGe, CoFeTiAs, NiFeTiSi, NiFeTiGe and NiFeTiAs at the pressures of 151.6 GPa, 33.7 GPa, 76.4 GPa, 85.3 GPa, 87.7 GPa and 96.5 GPa respectively. The computed elastic constants obey the necessary mechanical stability condition suggesting that all the quaternary Heusler alloys are mechanically stable at ambient condition. The Debye temperature values for CoFeTiSi, CoFeTiGe, CoFeTiAs, NiFeTiSi, NiFeTiGe and NiFeTiAs are reported. It is found that all these quaternary Heusler alloys are magnetic at normal pressure and at high pressure, these alloys are found to be non-magnetic. The Hubbard U corrections to the GGA- PBE calculations greatly improves the lattice constant values, structural phase transition, electronic structure and the magnetic properties of Fe based ferromagnetic quaternary Heusler alloys.

In chapter VIII, ground state properties, structural, electronic and elastic properties at ambient and high pressure are studied for Co_2TiAl, Co_2TiGa and Co_2TiIn. The site preference in Co_2TiAl, Co_2TiGa and Co_2TiIn are analyzed among the two different crystal structures, namely, $L2_1$(Cu_2MnAl structure) and XA (Hg_2CuTi structure) phases. It is found that Cu_2MnAl ($L2_1$) structure is more stable than Hg_2CuTi (XA) structure for these alloys. These full Heusler compounds Co_2TiZ exhibit an

energy gap in the spin down direction. The spin flip gap (E_g) observed in Co_2TiAl, Co_2TiGa and Co_2TiIn are 0.366 eV, 0.460 eV and 0.517 eV respectively. Hence, these alloys are half mertallic at normal pressure. At the pressures of 76.5 GPa, 73.1 GPa and 63.9 GPa, half-metallic to metallic phase transition is observed in Co_2TiAl, Co_2TiGa and Co_2TiIn. These Heusler alloys are found to be ferromagnetic at normal pressure. It is seen that ferromagnetism is quenched at the pressures of 380.9 GPa, 363.0 GPa and 317.8 GPa in Co_2TiAl, Co_2TiGa and Co_2TiIn respectively. The dielectric function, energy loss function and refractive index of Co_2TiAl, Co_2TiGa and Co_2TiIn are computed. The phonon calculations for Co_2TiAl, Co_2TiGa and Co_2TiIn compounds in cubic $L2_1$ structure are carried out and it is found that these compounds are stable.

In chapter IX, Cobalt atom is substituted in the place of Fe atom in the stoichiometry $Fe_{2-x}Co_xTiZ$ (Z= Si, Ge, Sn), (x= 0, 0.5, 1, 1.5, 2) to improve the electronic and magnetic properties of Fe_2TiZ (Z= Si, Ge, Sn) Heusler alloys. The site preference is analyzed among the two different crystal structures, namely, $L2_1$(Cu_2MnAl structure) and XA (Hg_2CuTi structure) phases and it is found Cu_2MnAl structure is found to be more stable compared to Hg_2CuTi structure. In the density of states plot, an energy gap is observed for both spin up and spin down states of Fe_2TiSi, Fe_2TiGe and Fe_2TiSn, which predicts the semiconducting nature of Fe_2TiSi, Fe_2TiGe and Fe_2TiSn. The substitution of Co atom in Fe_2TiSi, Fe_2TiGe and Fe_2TiSn for Fe, changes the semiconducting behavior to half metallic behavior in $Fe_{2-x}Co_xTiZ$ (Z= Si, Ge, Sn) alloys. The magnetic properties of $Fe_{2-x}Co_xTiX$ (X= Si, Ge, Sn) full Heusler alloys are computed. It is found that ferromagnetic state is more stable for these alloys (except Fe_2TiSi, Fe_2TiGe and Fe_2TiSn). All the studied full Heusler alloys (except Fe_2TiSi, Fe_2TiGe and Fe_2TiSn) shows 100% spin polarization. Thus ,the substitution of Co atom in Fe_2TiSi, Fe_2TiGe and Fe_2TiSn for Fe, changes the non-magnetic state to ferromagnetic state in $Fe_{2-x}Co_xTiZ$ (Z= Si, Ge, Sn) alloys.

Chapter X deals with the site preference, electronic structure, magnetic phase transition and mechanical stability of Fe_2YAL (Y= Ti, V, Cr). The structural stability between $L2_1$ phase and XA phase is analyzed. $L2_1$ phase is predicted as the stable phase for these alloys. The density of states predicts metallic behavior for Fe_2TiAl, Fe_2VAl whereas, half metallic behavior for Fe_2CrAl at normal pressure. At the pressures of 28.9 GPa and 33.0 GPa, metallic to half-metallic phase transition is observed in Fe_2TiAl whereas half-metallic to metallic phase transition is observed in Fe_2CrAl respectively. These alloys satisfy Born Huang stability criteria $C_{11}+2C_{12}>0,\ C_{11}>|C_{12}|,\ \ C_{44}>0$ and hence these alloys are mechanically stable. Spin polarized calculation shows that Fe_2VAl is non-magnetic while Fe_2TiAl and Fe_2VAl are ferromagnetic with small magnetic moment values. It is seen that ferromagnetism is not existed at the pressures of 417.8 GPa and 392.8 GPa in Fe_2TiAl and Fe_2CrAl respectively.

The results of the research work and the conclusion are summarized in "Summary and Conclusion".