

THEORETICAL STUDIES OF LANTHANIDE TRANSITION METAL INTERMETALLICS IN CsCl-STRUCTURE



by

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AUTHORIZATION TO SUBMIT THESIS

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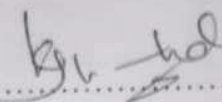
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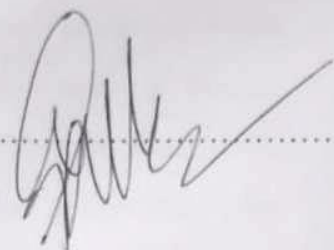
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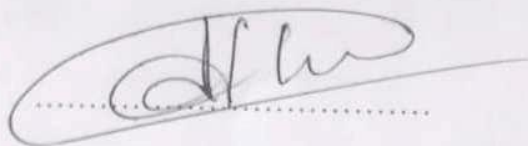


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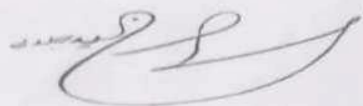


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Abstract

The objectives of this work was to explore the structural, electronic, elastic, magnetic and thermoelectric properties of the strongly correlated electron system, LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) and ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu). The procedure used in this work was the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) calculations based on density functional theory. The structural, electronic and magnetic properties of these compounds are calculated by LDA, GGA, LDA+U, LDA+SOC and LDA+U+SOC schemes. The calculated lattice parameters are found to be in close agreement with the available experimental results. The localized behavior as well as relativistic effects of electrons in the d-states of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds are also revealed. These compounds have 3d, 4d and 5d orbitals and, hence strong electron-electron correlation and spin orbit coupling (SOC) effects were expected therefore the structural and electronic properties are also determined by using the Hubbard potential U to incorporate correlation effects, while to consider relativistic effects, SOC is used. The spin-orbit coupling effect splits the d/f-state of the elements within the compounds. The SOC effect increases from 3d to 5d transition elements in the ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds, which shows fascinating response of SOC effect as electronic structure changes from element to element. The elastic constants of these compounds are also calculated. Our calculated elastic constants values of the compounds are consistent with the available experimental as well theoretical results. From the elastic constants, different mechanical properties such as bulk modulus (B), Young's modulus (Y), shear modulus (G), Poisson's ratio (ν), Kleinman parameters (ζ) and anisotropic ratio (A) for the compounds

under study are also evaluated. Furthermore, the mechanical parameters i.e; Paugh ratio (B/G) and Cauchy pressure (C'') are calculated to determine the ductility and brittleness of the materials under study. The obtained mechanical properties are then applied to find the sound velocities and Debye temperature. Furthermore, post-DFT calculations are carried out to investigate the Seebeck coefficient and electrical conductivity of the ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) at constant temperature, 300K. High values of Seebeck coefficient and electrical conductivity are observed for these materials. The considerable values of the calculated Power Factor for these materials at room temperature shows that these materials maybe useful for high temperature thermoelectric devices.

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List of Publications

This thesis consist on the following published papers .

1. **Rashid Iqbal**, Zahid Ali, S. Jalali-Asadabad, H. A. R. Aliabad, Iftikhar Ahmad “Electron correlation and spin-orbit coupling effects in scandium intermetallic compounds ScTM (TM = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au)” *Int. J. Mod. Phys. B*, Vol. 31, 1750263-16 (2017)
2. **Rashid Iqbal**, Muhammad Bilal, S. Jalali-Asadabad, H. A. R. Aliabad, Iftikhar Ahmad “Theoretical investigation of thermoelectric and elastic properties of intermetallic compounds ScTM (TM=Cu, Ag, Au and Pd)” *Int. J. Mod. Phys. B*, Vol. 31, 1850004-12 (2017)

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Chapter 1

Introduction

The importance of the various physical and chemical properties of compounds have always attracted materials scientists for their possible scientific and technological applications. Materials like superconductors, metals, semiconductors, insulators and half metals are designed and investigated by both experimentalists and theoreticians due to their extensive applications in science, technology, medical sciences, agriculture and high-tech devices. Researchers are looking for micro size and nano size materials with better performance in modern computers and solar cells as well as communication devices. They are working around the globe to make strong but lighter materials for the manufacturing of airplanes and automobiles and are also trying to investigate materials of remarkable properties for scientific and technological applications along with large financial impact [1].

Density functional theory (DFT) is extensively used during the last three decades due to its tremendous applications in the field of materials science [2]. Computational method is cheaper and less time consuming as compared to experimental techniques. This field provides large number of opportunities for researchers to get new ideas about materials. Computational calcula-

tions need fundamental knowledge about materials such as lattice constants, space groups and atomic positions to investigate different physical properties of solids [3]. Despite the unavailability of experimental parameters, DFT provides the opportunity to predict physical properties of the modelled materials. This means that before synthesis through experimental techniques, materials engineers can design new compounds and predict their properties through DFT. It also helps the experimentalists in defining a proper direction for their research. In this approach, researchers can evaluate various ground state parameters of modeled compounds like lattice parameter, bulk modulus, first order pressure derivative of bulk modulus and volume as well as other properties.

DFT is based on quantum mechanical methodology with the help of which many body system of atoms can be treated properly. It was first introduced by Hohenberg and Kohn [4], whereas later on Kohn and Pople [5] were granted Nobel Prize in 1998, because of acknowledgment of its applications in chemistry. It plays important role in investigating various physical properties like electronic, structural, thermoelectric, optical and elastic properties of solids. It has proved its worth in comparison to experimental results.

In this work structural, elastic, magnetic and thermoelectric properties of LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) and ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds are calculated within the scheme of FP-LAPW approach [6, 7] implemented in the WIEN2k package [8], while post DFT approach is used to investigate the thermoelectric properties based on Boltzmann's theory [9]. The density of the electronic states of the materials are investigated to understand the electronic arrangement and magnetic properties of the materials. The compounds under study are strongly correlated electrons systems.

The strongly correlated electron systems are considered valuable materials due to their interesting physical properties and applications. Strong electron-electron correlation effect exhibits very important role in magnetic, electronic and mechanical properties of materials [10, 11]. Negative thermal expansion [12], high temperature superconductivity [13], magnetocaloric effect [14], colossal magneto-resistance effect [15], multiferroicity and [16], metal-insulator-transitions [17] like exotic properties are observed in strongly correlated electron systems. Composition, pressure, temperature and stress are known as external parameters and strongly correlated electron systems show extremely sensitive to small changes in these parameters [18]. The understanding and description of strongly correlated electron systems is very difficult.

Strongly correlated transition and rare earth intermetallic materials are attractive due to their d and f-electrons. A strong effect of one electron in the system on the other electron in the case of the transition metal or the lanthanide based compounds is observed [19]. The reason for the different physical properties of these compounds is due to the d/f electron occupancy in the orbitals as well as their hybridization with other orbitals of atoms [20, 21]. The various physical properties of these intermetallics are caused by the itinerant as well as localized behavior of d/f electrons. Related physical properties are mainly due to the localized and itinerant nature of these electron states of these compounds, while dissimilar properties are because of the presence of different types of such electrons. Low symmetry stable crystal structure, complex anisotropic property and high bulk modulus are observed in case of itinerant electrons while local magnetic moments, low bulk modulus and high symmetry stable crystal structure are due to the localized electrons [22, 23]. The mechanical properties of strongly correlated

materials are also important for their technological applications. Elasticity is the basic criterion to understand the mechanical properties of a material. The elastic constants are parameters, which describe the elastic nature of a material. The suitable doping of transition and rare earth elements can severely change the mechanical properties of a material [24, 25].

Limited work in literature has been reported about the crystal structure, elastic, electronic and magnetic properties of intermetallic materials LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) and ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu). Due to the strong electron correlation effects in these compounds, strong interaction in the different states of the elements in these compounds is obvious [26, 27]. Hence it is quite challenging to obtain the accurate physical properties of these compounds both theoretically and experimentally. However, to get the rational and logical information about the physical properties of these materials through electronic structures, it is essential to take into account the strong electron-electron correlation effects in these materials.

The purpose of the present work is to provide a detail study on the structural, electronic, magnetic and elastic properties of LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) and ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds using local density approximation (LDA) and Generalized Gradient approximation (GGA). For the thermoelectric properties, we have done post DFT calculations by using the Boltztrap package. Spin orbit coupling plays significant role in these materials, therefore it has also been taken into account for all the compounds under study. In strongly correlated electron systems, the Coulomb repulsion between electrons of the f-state metals (rare earth) and d-state metals (transition) are too strong to overcome kinetic energy. Therefore, DFT+U method [28, 29]

is used with LDA and GGA to boost the study related to the d/f state electrons of these strongly correlated systems. There are several methods to optimize the U value and according to the literature [30, 31], various methods are used to optimize U but they are not always very efficient, but a recently published work [32], describes an efficient scheme. Therefore, we optimized the U value using the method discussed by Yazdani et al [32]. As Sc-TM based compounds are strongly correlated materials, therefore we have studied the degree of localization for this class of materials and their correlation effects are calculated. It is well known that the correlation effect is the main cause of the superconductivity in the cuprates. It is also known that correlations have significant role in the Mott insulating antiferromagnetic state in the compounds. The mechanism of high temperature superconductivity is completely different from the Bardeen Cooper Schrieffer (BCS) theory which is useful for conventional superconductivity and not unconventional superconductivity, as indicated in Ref. [33].

In strongly correlated systems, including d/f electrons compounds, spin-orbit coupling can change the value of the density of states at the Fermi level and as a result substantially affects the physical properties of a compound. This depends on the degree of localization and sometimes the degree of 4f-electrons can be even much smaller than the effects of d-electrons. In the strongly correlated materials, the localization can vary from system to system and drastically depends on the crystalline environment [34, 35]. Thus, the spin orbit coupling (SOC) is required for each compound under investigations and hence is evaluated for each system individually and is one of the main tasks of this work.

This thesis consist of 5 chapters. Chapter 1 includes a detailed introduction of the work. Chapter 2, comprises review of literature. Detail infor-

mation about DFT, Cubic-elastic package along with mathematical relations and thermoelectric studies with Boltztrape code are summarized in chapter 3. The calculated results are presented in chapter 4 and then conclusion about this work is finalized in the chapter 5.

Chapter 2

Literature Review

2.1 Strongly Correlated Electron Systems

The electron electron repulsion effect in the strongly correlated electron systems was theoretically initiated in 1930s. These theoretical considerations were emerged before the intensive experimental work. The idea introduced by Wigner [36] used the notion of an electron crystal lattice. In strongly correlated electronic system motion and position of an electron is affected by moment and position of all other electrons due to the coulomb repulsive interaction. The inclusion of the phenomenon of strongly correlated electron systems in the solid state physics is the most exciting and base of diverse aspect of materials properties. Strong electron-electron correlation effects and large electronic repulsion are observed respectively in (3d, 4d) electrons (Transition metals) and f-electrons (Lanthanides) based compounds. In these compounds Columbic interaction between electron-electron increases as much as the kinetic energy because of hopping in the crystal of partially localized electrons such as d/f. The existence of partially localized nature of d/f states electrons make the system more complicated. Therefore, simple approxima-

tions fail to investigate real nature of these compounds. Hence, most reliable theoretical tools are required to deal properly the strongly correlated compounds. The establishment of computational and analytical techniques are challenging task in material science for strongly correlated electron systems.

2.2 Intermetallic Compounds

Two or more metals, by definitive stoichiometric ratio are combined and organize a specific crystallographic unit cell is called intermetallic compounds. The physical properties of the intermetallic compounds are quite different from the physical properties of the constituent elements from which the system is alloyed. There are two types of intermetallic available in literature such as semiconductor and magnetic intermetallic. Semiconductor intermetallic come into existence by the combination of metal while magnetic intermetallic is due to the non-magnetic materials [37]. The intermetallic compounds exist mostly in metallic nature. Presently above 30,000 intermetallic compounds are identified in binary, ternary, and multi-components form and their characterization, physical, chemical and structure properties are also described [38]. While it is more interesting that the first rare-earth CsCl-type binary compounds were reported in 1933 [39].

2.3 Lanthanide Transition Intermetallics

A series of binary intermetallic compounds can be formed by the reaction of rare-earth with the other elements and results into different compositions and types of crystal structures. For example LnTM , LnTM_2 , LnTM_3 , Ln_3TM and Ln_5TM_3 (Ln = Lanthanide, TM = Transition elements) are dif-

ferent compositions of rare earth intermetallics with other transition metals. The majority of the lanthanides intermetallic compounds are found to exist in LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) cubic type CsCl-structure, having interesting physical properties such as high values of specific strength, high melting points, ductility and related properties as compared to other compositions. These materials are extensively used in the automobile and aerospace technologies. Another important application of these compounds is seen in making commercial aircraft turbines because of their high ductility and high fracture toughness nature at room temperature.

Researchers are now interested to investigate physical and chemical properties of binary LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds because of having incomplete 4f shells and the single crystals structure.

Lanthanide based intermetallic compounds have already been characterized in B2-phase with CsCl type structure and having space group Pm-3m (number. 221) [40]. CsCl Crystal type structure is presented in Fig 2.1.

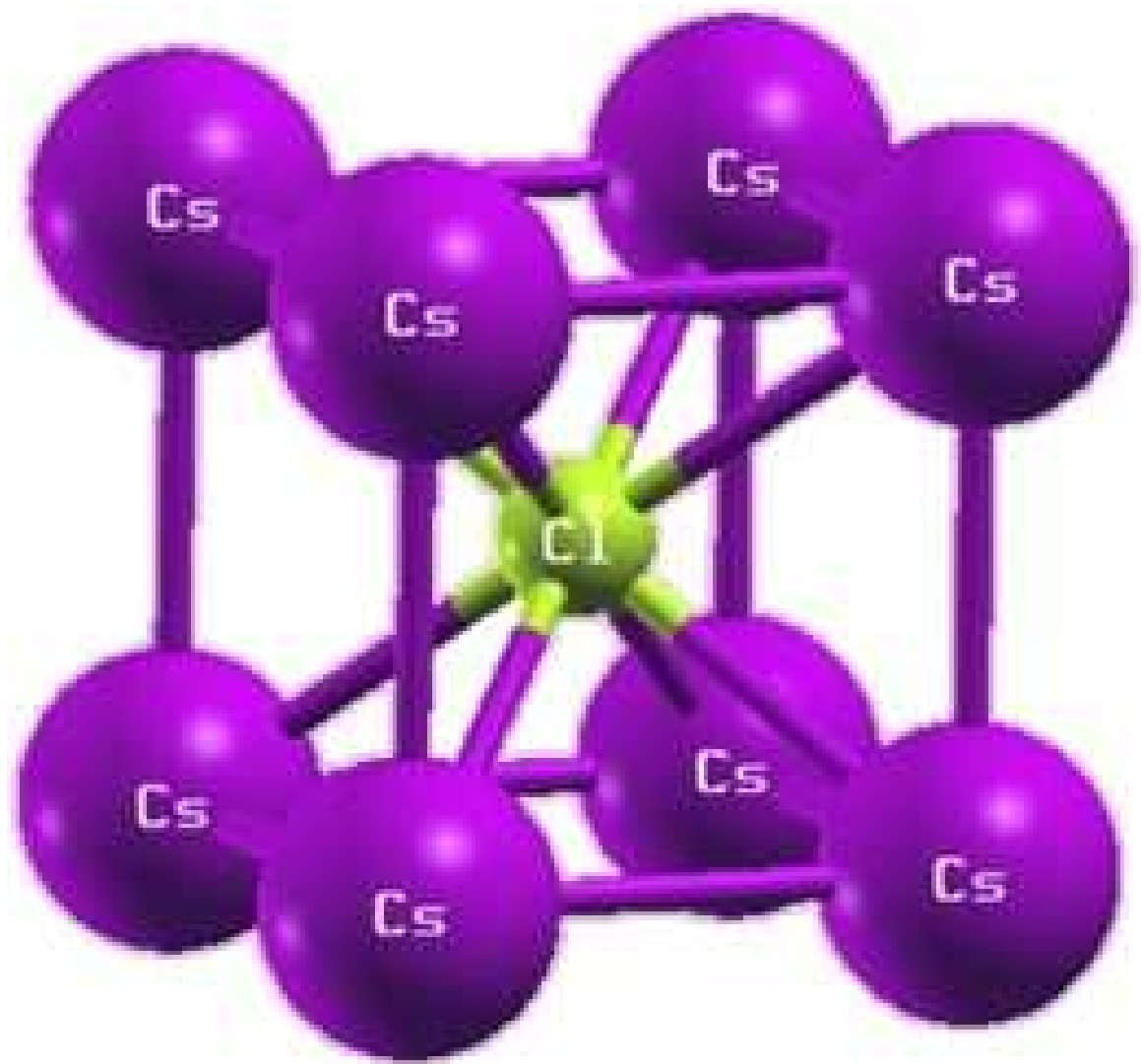


Figure 2.1: CsCl-structure

Here Cs atoms hold (0, 0, 0) positions at the eight corners of the cubic cell and Cl atoms are located at center (0.5, 0.5, 0.5) of the cubic cell [41].

Researcher are interested to investigate various physical properties of intermetallic compounds. Chandrabhan et al. [42] studied the structural, electronic and mechanical properties of REAg (RE= Pr, Er, La and Y) compounds using DFT calculation within the generalized gradient approximation (GGA). They determined different ground state parameters like lattice constant (a_0), bulk modulus (B) and its pressure derivative (B'). They show that all these compounds are metallic in nature and their dense Fermi energy level is due to hybridization of RE-d,f and Ag-s,p bands. They also found that except for ErAg, in all the REAg compounds the lowest lying band is due to RE 'p', 'd' 'f' , Ag 'p' and Ag 's' states. However in ErAg metallicity is due to crossing of Er 'p' 'f' and Ag 'p' states at Fermi level. They also investigated ductile and brittle characteristic of these compounds among all these compounds ErAg is most ductile due to the presence of strong metallic bonding [42].

First-principle calculations were performed by Shi et al. [43] to investigate the structural, electronic mechanical and thermal properties of CeAg compound. They used GGA and LDA approximation to treat exchange correlation functional and found that GGA is more accurate than LDA. They also confirm Thermodynamically stable phase of this compound through formation energy. While the author also found angular covalent bonding nature of this compound using electronic properties such that the greater separation between the d bands of Ce and Ag resulted into the weaker bond hybridization, which prevents formation of directional covalent bond. Mechanical properties such as Poisson ratio, elastic modulus, bulk modulus, anisotropy factor and shear modulus of this compound was also investigated using three

independent elastic moduli (C_{11} , C_{12} and C_{44}). This compound was found mechanically stable and ductile in nature. The authors also studied different thermodynamical quantities including heat capacity and thermal expansion coefficient with respect to temperature and pressure.

Mechanical, electronic and magnetic behavior of TmX ($\text{X} = \text{Ag, Cu}$) compounds were investigated using the FP-APW + l0 method within the generalized gradient approximation (GGA) [44]. They used optimized k-mesh of $14 \times 4 \times 14$ k-points in the irreducible part of Brillouin zone and calculate the ground state parameters lattice constant (a_0), bulk modulus (B_0) and its pressure derivative (B'). Band structure and density of state are studied in both channel, spin up and spin down, to investigate electronic properties of these compounds. They identified ferromagnetic metallic nature these compounds. They also determined that metallic nature of these compounds is due to Tm-f state electrons. Mechanical properties such as Young's modulus (Y), shear modulus (G) and Poisson's ratio (ν) are also studied in terms of elastic constants (C_{ij}) at ambient temperature and pressure.

Vaitheeswaran et al. [45] investigated electronic structure, elastic constants and lattice dynamics of LaAg compound using GGA for exchange correlation energy within DFT calculations. They found that GGA approach is more favorable because the calculated elastic constants were in close agreement with the available experimental data. From elastic calculation, they confirmed the ductile nature which is unusual for B2-type intermetallics. After careful investigation of electronic state, they concluded that La 5d-state crossed the Fermi level causes metallic nature.

Density functional perturbation theory calculation are carried out to study phonon dispersion relations. Author also confirmed orthorhombic structure at high pressure.

Calculations were carried out using full potential LAPW method within LSDA approximation to study the electronic structure of REX (RE = Er, Y; X = Ag, Zn, Rh, Cu and Mg) compounds. Charge density of the whole crystal play a very important role in splitting of the crystal field and also shows contribution to crystal field (CF) from the different regions of REX crystals e.g; spherical components of the self-consistent potential caused of the crystal field splitting of trivalent (RE^{3+}) energy levels [46].

First principle calculations are carried out using FP-LAPW method within the GGA and LDA plus Hubbard potential (LDA+U). They studied the electronic structure and elastic properties of YAg, YCu and DyCu. They reported the density of states at the Fermi level are 1.08, 1.09, and 1.04 states/(eV unit cell) for YAg, YCu and DyCu, respectively. Mechanical properties of these compounds are investigated using elastic constants and found the ductile nature of these compounds. The author also showed highly isotropic behavior of these compounds [41].

Gitanjali and co-workers [47] investigated various properties of the compounds EuCd and GdCd using first-principles(FP-LAPW) method within DFT. For the treatment of exchange-correlation potentials, the author used GGA and LSDA. They determined the ground state lattice constant (a_0) and bulk modulus (B) and its derivative (B_0) with respect to pressure of these compounds . The author reports that GGA is more favorable as compare to LSDA for this calculation. To explore the electronic structure of these materials the electronic structure are also investigated for the purpose. Bonding nature of these compounds are investigated through calculating the electronic charge density plots along (110) plane. It is observed that EuCd has ionic bonding while GdCd has covalent bonding along with some ionic characteristic. The author also calculated three independent elastic constants

(C_{11} , C_{12} and C_{44}) at ambient pressure for these compounds to investigate the mechanical properties like Poisson's ratio, shear modulus, elastic anisotropy and Young's modulus. They have also investigated Debye temperature for these materials.

2.4 Scandium Transition Intermetallics

The element Scandium is one of the first transition metal element which belong to rare earths family, however the unpaired 4f electrons state doesn't exit in this family. The thermal properties indicates that it has high melting temperature of the value 1814 k and have small density ($2.989g/cm^3$). When interact chemically with other transition (TM) elements, the Scandium material combine chemically with other to have a series of intermetallic compounds and compounds formed crystallizes in the cubic CsCl (B2) structure.

The Scandium based transition metal compounds Sc-TM are considered interesting materials for applications in the production of materials for spacecraft and electronics as due to low density and other interesting physical properties. Furthermore, it is found that some of the compounds based on Scandium have high ductility and high fracture toughness at normal temperature.

In the last decade, investigations about physical properties of Scandium based transition compounds was carried to explore the hide feature of the Sc-TM materials. However till now a limited progress has been done in this area as mentioned below.

First principle calculations are performed to investigate structural, electronic, bonding, elastic and mechanical properties of scandium based compounds, ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) within GGA

for exchange and correlation energy. Ground state properties are determined from structural optimization. The electronic and bonding nature of ScX compounds are investigated using the concept of Fermi surfaces, band structures, contour plots and DOS. The author also reported mechanical properties and ductile nature of these compounds using independent elastic moduli. Metallic natures of these compounds are confirmed from DOS and band structure. While the elastic constants also show that these compounds are mechanically stable in cubic CsCl structure. The author also investigated the ductile nature of these compounds using different criteria including Pugh's rule, Cauchy's pressure and Frantsevich's rule. It was found that among all these compounds the most ductile material is ScNi. Average sound velocities and Debye temperature are also calculated [62].

Density functional calculation are performed within the GGA for exchange and correlation potentials to investigate electronic, structural and mechanical properties of ScPt, ScNi and ScPd compounds. The electronic and bonding nature of these compounds are investigated with the aid of band structure and Fermi surfaces. The metallic characters of these compounds were confirmed from band structures. Different parameters such as Pugh's criteria, Frantsevich rule and Cauchy pressure ($C_{12} - C_{44}$) concept were used to determine the ductile nature of these compounds. It was found that amongst all these, ScNi is most ductile, because of its strong metallic bonding nature. It was also observed that metallic behavior of these compounds are due to d state of Sc or X. The author also reported the shear modulus (G_H), Young's modulus (E), Poisson's ratio (ν) and anisotropic ratio (A) using elastic constants [63].

Rajagopalan et al. [64] studied the lattice parameters and elastic constants of ScX (X= Ag, Cu, Pd, Ru, Rh) compounds as well as electronic

structure calculations using the FP-LAPW method. The author also calculates independent elastic moduli for the purpose to investigate their ductile nature of these compounds.

Self-consistent local density functional calculations are performed using LMTO method to investigate electronic structure of ScRh, ScRu, ScPd and ScAg compounds [65]. The author investigated the electronic structure using bands structure, local partial and total densities of states of these compounds. The electronic structure shows metallic behavior of these compounds. Different parameters including lattice constants, heats of formation and the bulk modulus are also estimated. They also measured nuclear magnetic resonance or NMR relaxation times represented by T_1 and T_2 at the Sc and La sites in ScB (B = Pd, Rh, Cu, Ag, Ir, Ru) and LaAg compounds. In temperature range (30K and 300K), the product ($T \times T$) is constant. The author also observed the affect of magnetic impurities on the susceptibility and spin-lattice relaxation time below 30K. The electronic structure is also analyzed in terms of local susceptibilities. Using two-band model the compounds are categorized in the following three groups. Group I: ScAg, ScPd, ScCu and LaAg. In this group large d spin and orbital is due to A site only. Group II: This group consist upon only ScRu. In this group large d spin and orbital are due B site only. Group II: YRh, ScRh and ScIr belong to this group. Where the d spin and orbital originate from both A and B sites. While it is also observed that the contributions of d spin are less than those of groups I or II [66].

Self-consistent Korringa Kohn Rostoker or KKR method was used to investigate the electronic structures of TiFe, ScCu, VMn and ScCo compounds to determine the stability of these materials in CsCl structure. It is found that bonding and antibonding orbitals are well parted because of the deep

valley of density-of-states in the middle region of these compounds. The author noted that d-bands of Cu are located well below as compared to the d-bands of Sc, while the s and p-electrons are polarized at the Cu-cell by about 0.6/atom. The author also observed that ionic bonding nature caused of stable ordered lattice of ScCu [67].

Band structure calculations are performed for TiFe, VMn, ScCo, FeCo, and MnNi to understand theoretical theory of neutron scattering due to magnetic moments using a linearized APW method. The author used atomic high field side or HFS densities of $3dn/4S^2$ configuration with the exchange potential to determine potentials for transition-metal alloys in CsCl structure [68].

X- band Electron Spin Resonance or ESR spectrometer is used to study X-band ESR spectra of ScNi, ScPd, YNi, and YPd compounds. Molecules in argon matrices were observed at 4K. Interaction with nuclei is caused of hyperfine splittings.

2.5 Elastic and Mechanical Properties

The mechanical behavior of crystalline material is called elasticity. It displays great significance in many fields such as chemistry, solid state physics, geological and materials sciences etc. Elasticity of a material reveals the retaliation to the external agency and is associated to the spreading of sound waves in a material as well as to the strength and hardness of the materials [69]. Material elasticity basically depends on cohesive forces (attraction among molecules) of a solid and its thermodynamical parameters including Debye temperature, melting point and phonon spectra. Therefore, significant information related to interatomic potentials and bonding forces can

be obtained by elasticity of materials [70]. Elastic constants of a material play central role in describing the elasticity. The mechanical stability criteria and the mechanical properties of materials can be investigated by using these constants. Therefore, understanding of these constants is needed for the practical applications of the materials [71]. DFT provides the opportunity as compared to the experimental techniques to calculate accurate and effective elastic constants so that mechanical properties of new materials are described. Elastic constants can be calculated under the action of stress that yields deformation (strain) in a material. Here the relation between stress and strain can be considered identical. Materials may also exhibit homogeneous response to the applied stress. The elastic constants are actually the fourth-rank tensor. In case of the crystalline materials, in connection with the generalized Hooks law, these constants can be expressed as:

$$\sigma_{ij}=C_{ijkl}\varepsilon_{kl},$$

where σ_{ij} represents the external force (stress tensor), C_{ijkl} is for the elastic stiffness tensor and comprise on 81 elastic constants while strain tensor is expressed by ε_{kl} . Independent elastic constants reduces due to different crystal structure symmetries such that $C_{ijkl} = C_{klij}$, the elastic tensor C_{ijkl} is minimized to 6×6 matrix C_{ij} where i, j = 1, 2, 3, 4, 5, 6.

Chapter 3

Theoretical Background and Computational Methods

In the present work DFT studies are carried out to investigate the structure, electronic, elastic, magnetic and thermoelectric properties of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) and LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds in the frame work of DFT implemented in the WIEN2k package [73, 74]. This theory uses electronic density, to solve the problems associated to many body system. The main reason of complexity of many body system is due to dependency of the wave function $\psi(r)$ on position of a partical [75]. There are also large number of particles where single wave function is associated with each particle in a system. Therefore, it is very difficult to deal such systems. As compared to wave function, if we take into account electronic density of a system, this will be very easy to treat the many body system because the electronic density functional depends only on a single parameter position. In this way the calculations becomes very easy, as compared to many-body wave functions approach, therefore DFT is considered a more reliable approach.

Hence by DFT, the problem can be dealt very easily for a system which leads to investigate many physical as well as chemical properties. The theoretical technique DFT helps us to have a clear of the electronic structure in periodic systems and can also provide the opportunity to study the bulk properties of the materials. This chapter deals with the study of basic description of DFT as well as providing information that how to calculate basic ground state properties. Boltzmann's transport theory is post DFT approach providing information about calculation of TE properties of materials.

3.1 Quantum Mechanical Many Body Problem

Unit cells are distributed periodically all over the space in solid crystals. Each unit cell containing atoms is the basic identity and play important role in investigating the properties of a solid material. Except amorphous, this theory is applicable to all kinds of solids [76]. If the unit cell is dealt quantum mechanically, then the crystal unit cell can be considered as a quantum mechanical many body system. Each unit cell consists of n_0 nuclei and n electrons and these n_0 and n in mutual interaction mode [77]. At quantum level, Schrodinger equation can be used to find properties of a many body system that includes both the nuclei and the electrons and wave function of such a many body system is written as

$$\psi(R_i, r_j)$$

where R represents the location of nuclei and r are the localization of electrons, respectively. By solving the following Schrodinger equation, one can get the many-body Hamiltonian represented by the following wave function:

$$\hat{H}\psi_i(r, R) = E\psi_i(r, R) \quad (3.1)$$

In the above equation ψ is the eigenfunction. And the $\hat{H}$ represents the hamiltonian for the individual particle. Hamiltonian operator is the sum of electrons and nuclei, interaction energy and kinetic energy, and can be written as:

$$\hat{H} = \hat{T}_c + \hat{T}_e + \hat{U}_{cc} + \hat{U}_{ce} + \hat{U}_{ee} \quad (3.2)$$

where T_c , T_e , U_{cc} , U_{ce} and U_{ee} are different operators and represent respectively, the nuclei kinetic energy, the electrons kinetic energy, the nuclei-nuclei interaction energy, the nuclei and electrons interaction energy and the electron-electron interaction energy. The indices (0), i and j represent the nuclei and electrons respectively whereas (r_i) and (i, R) represents the location of the electron and nucleus respectively while Z shows the nucleus charge.

In order to find the solution of these equations, few approximations are required. For example, the mass of nucleus is greater than the mass of electron by ten thousands times. Therefore, we ignore the term T_c because of its small value and consider as a perturbation. This type of hypothesis is introduced in 1927 and is known as the Born-Oppenheimer approximation [78]. According to this approximation electrons are more mobile as compared to cores such that inertia of the electrons is dragged by the ions. The electron motion is considered as adiabatically ionic motion. Now the Born-Oppenheimer hamiltonian is considered as an unperturbed hamiltonian and can be written as:

$$\hat{H}_{B.O} = \hat{U}_{c.c} + \hat{T}_e + \hat{U}_{e.e} + \hat{U}_{c.e}. \quad (3.8)$$

By solving the following Born-Oppenheimer Schrodinger equation, one can get the Born-Oppenheimer energy (E_{BO}):

$$\hat{H}_{B.O} | \psi \rangle = E_{B.O} | \psi \rangle \quad (3.9)$$

Born-Oppenheimer operator can also be written as:

$$\hat{H}_{B.O} = \hat{H}_{e.l} + \hat{U}_{c.c} \quad (3.10)$$

where

$$\hat{H}_{e.l} = \hat{T}_e + \hat{U}_{e.e} + \hat{U}_{c.e} \quad (3.11)$$

One can get the electronic ground state energy by solving the following equation:

$$\hat{H}_{e.l} | \psi(r, R) \rangle = E_{e.l} | \psi(r, R) \rangle \quad (3.12)$$

It is difficult to solve the above equation analytically because hundreds of atoms with large number of electron are involved in the system where the wave function associated to each electron is the function of the electron position in the system. Several alternate methods are available to resolve such a difficult problem but the most favorable approach is the DFT. The main source of information about the many body problem is its mathematical formulism which can play important role in describing the exact ground state energy of the system. The ground state functional can be expressed by combining the Hohenberg-Kohn formulism with the Kohn-Sham formulism given as:

$$E[n(r)] = [\sum(\psi)] - \frac{1}{2} \times \nabla^2(\psi) + \frac{1}{2} \int d^3r d^3r' \frac{n(r) \times n(r')}{|r - r'|}$$

+

$$\int d^3r V_{ext}(r) \times n(r) + E_{x,c}[n] \quad (3.13)$$

Here in above expression, on the right side, first term is the energy related to the motion of electron, the second term reveals Hartree energy and is known as the repulsion electronic density and the third term is related to the electron-nuclei interaction. The above described terms can be calculated with high accuracy. Apart from all these easily calculated terms, there is also a fourth term expressed by (xc) is called exchange-correlation. The exact calculation of this term is very difficult but still it is considered as one of the essential part of this equation because with out this term exact ground state energy of the required system with high accuracy cannot be calculated. This term is actually the combination of two effects such that exchange and correlation and is due to the electron kinetic and potential energies. Presently, exact mathematical expression for this term is not available. However, few approximations are used to estimate exchange-correlation energy to determine different ground-state properties of a system with accuracy. Different approximations are available to treat properly the exchange correlation functional of a system. Few most common of them are described as under.

3.2 Local Density Approximation

LDA is considered as a building block for the density functional theory. One can get functional as a result of this approximation which is used abundantly in the applied density functional theory [7]. Homogeneous electron gas concept is used in this approximation. One can treat the exchange part analytically in this ideal situation. Other physical properties of the system

are also found density dependent. As we know that the density parameter is position dependent as $n(r)$ and also exhibits identical behavior for all position $n(r) = n_0$. Therefore, exchange-correlation energy is functional dependent and can be expressed as.

$$E_{x,c} = E_{x,c}[n(r)] = E_{x,c}[n_0] \quad (3.14)$$

Exchange-correlation part can be easily demonstrated using the knowledge of the system energy. Exchange-correlation energy density $xc(r)$ of homogeneous gas is considered as function of density at specific region r . The defined energy is known as the individual particle density n_0 . The exchange-correlation energy is considered as Local functional of the density and in mathematical form can be written as under:

$$E_{x,c}^{LDA}[n] = \int n(r) \varepsilon_{x,c}^{hom}(n(r)) dr \quad (3.15)$$

The term given in the above equation, exchange-correlation energy is the combined effect of the exchange E_x^{hom} and the correlation E_c^{hom} energy and in equation form can be expressed as:

$$E_{x,c}^{hom}[n] = E_x^{hom}[n] + E_c^{hom}[n] \quad (3.16)$$

Using Hartree-Fock method to solve analytically the exchange part, we will get

$$E_x[n] = -\frac{3}{4} \times \left(\frac{3}{\pi}\right)^{\frac{5}{3}} \int n^{\frac{4}{3}}(r) dr \quad (3.17)$$

The unknown correlation energy $E_c[n]$ of the system can be obtained by subtracting two types of known energies such as exchange and kinetic energy.

There are some drawbacks in LDA [7] approximation which are discussed as under. This approximation one can get underestimate value of lattice parameters and it can not treat properly strong correlations system. Instead the above mentioned limitation, this approximation has gained tremendous attraction because of its accurate and precise calculation in some cases. Magnetic calculation of the system is also possible by using the extended form of this approximation while considering the spin of each electron. The intrinsic characteristic of electron such that its moment play a key role in the magnetic property of the system, therefore we deal with two types of electron densities, the spin-up and the spin-down electron densities. Due to this reason we will solve two times more equation in this case. The spin-dependent exchange-correlation energy can be expressed as:

$$E_{x,c}[n] = E_{x,c}[n^\uparrow, n^\downarrow] \quad (3.18)$$

Two types of exchange-correlation potentials are used to deal a system properly including specific phenomenon such that collinear magnetism. Exchange functional and Local spin density approximation(LSDA) are known as accumulative approximation and can be written as:

$$E_x^{LSDA} = (-2)^{\frac{2}{3}} \times \frac{3}{4} \times \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int (n^{\uparrow\frac{4}{3}} + n^{\downarrow\frac{4}{3}}) dr \quad (3.21)$$

3.3 Generalized Gradient Approximation

LDA approach gained great attention among the researchers due to its true performance in many cases while providing good and more coherent results with the available experimental data during the calculations of different physical properties of materials. Although there were no reasons about the consid-

eration that electronic density $n(r)$ should be uniform at certain region r . It will be more than reasonable to consider that in specific region r , electronic density depends on density of position and will not be uniform spatially. The GGA [79] is similar to LDA and is known as semi-local approximations. In this approximation energy related to the exchange and correlation term is considered as a functional of the electronic density and its higher order derivatives. This is because of the variable electronic density.

$$E_x c^{GGA}[n] = \int n(r) \varepsilon_{xc}[n, \nabla n, \nabla^2 n, \dots] dr \quad (3.23)$$

GGA-PBE [79] and GGA-sol [80] are the modified form of GGA.

3.4 GGA+U

Both approximation LDA and GGA exhibits very good performance for most of the solids while show very poor performance in the electron-electron correlation effects. Because the Coulomb repulsion between electrons are too strong to overcome kinetic energy in strongly correlated electron systems consisting of the transition and the rare earth metal with d and f-state respectively. XC-functional of both LDA and GGA approaches can not treat properly the localized valence electrons. For example, Mott insulators are predicted as metals because of poor performance of the XC-functionals of LDA and GGA method in the localization of valance electrons. DFT+U method is introduced [28, 29] for the purpose to properly treat the strongly correlated systems. The DFT+U method is one of the simple approach and is based on Hubbard model Hamiltonian. Therefore, standard DFT functional LDA and GGA are modified by adding a Hubbard (U) parameter.

The mathematical expression of is given as [81]:

$$E_{(LSDA+U)} = E_{(LSDA)} + [\frac{(U - J)}{2} \times \sum_{\sigma} (n_{m,\sigma} - n_{m,\sigma}^2)] \quad (3.1)$$

where U and J are two interaction terms known as on-site Coulomb interaction and the exchange interaction respectively while s and m represent spin projection and occupation number of orbital momentum. The difference between U and J is called effective parameter and is written as $U_{eff} = U - J$.

3.5 Spin-orbit Coupling

Band theory describes the motion of electrons in energy bands of the solid materials. Energy bands of some solids are affected due to relativistic correction, including spin-orbit coupling (SOC) phenomenon, to the Schrodinger wave equation. This unique phenomenon produces the splitting in the electronic bands and also produce non-degeneracy effect in the band structures. SOC effect can be explained by using the second variational method [82]. This method uses scalar-relativistic basis. Therefore, reduced number of original basis are required for this method. In order to reduce basis, Hamiltonian scalar-relativistic part in the scalar-relativistic basis is diagonalized. After adding the SOC effects, the Hamiltonian for the case becomes as:

$$H\tilde{\psi} = \varepsilon\tilde{\psi} + H_{so}\tilde{\psi} \quad (3.2)$$

3.6 Augmented Plane Wave Plus Local Orbital Method(Full Potential Method)

The most accurate approach known as full-potential linearized-augmented plane-wave (FP-LAPW) method [6] is used to solve Kohn-Sham equations to obtain the electronic state density plus total energy of crystal solids. This method is working in the frame of augmented plane wave (APW) method [84]. The space divided into two portion in APW approach called the Mufntin (MT) sphere and the interstitial region. The electrons which are far away from the nucleus are considered as free electrons and are expressed by plane waves in interstitial region. In the Mufntin (MT) spheres, it is described by spherical harmonic radial functions. In whole space the potential can be expressed as:

$$V(r) = \begin{cases} V(r) & \text{if } r \in MT \\ constant & \text{if } r \in I \end{cases}$$

APW method is found insufficient in solving density functional equations. It is because of poor treatment of eigen states of the system. Andersen [6] introduced a modified form of APW method known as linearized augmented plane wave method (LAPW) to solve this sort of problem. This method treated properly eigen states and yields the eigen energies with single diagonalization. Specific electrons of an atom which are bound to the nucleus and does not participate in chemical bonding are called core electrons. These electrons are only localized in specific region known as Mufntin (MT) spheres. Those electrons which leaks out from Mufntin (MT) sphere and take participation in chemical bonding process are called valance electrons. In atom there are also some states which are neither core nor valance and are known

as semi-core states. These states have specific characteristic such that angular momentum number is the same while principle quantum number is lower as compared to valance states. Such states exist in the transition and rare-earth metal atoms. The main issue in the LAPW approach is, it can not treat semi-core states properly. This issue was solved by Singh [53] by modification in the LAPW method while adding local orbital concept and it became as LAPW+lo. In this method inside the MT spheres all the extra basis function are localized such that at the Mufntin radius its values fall to zero. The performance of LAPW+lo method is enhanced with the help of full potential(PF-LAPW) method. In this approach, charge density and potential are expanded by spherical harmonics inside the MT sphere and are expanded by plane waves inside the interstitial region.

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\tilde{r}) & \text{if } r \in MT \\ \sum_G V_G e^{iG \cdot r} & \text{if } r \in I \end{cases}$$

In our this work, spin polarized density functional calculations are performed within the frame work of the full-potential linearized augmented plane waves plus local orbitals (FP-LAPW +lo) technique [6] to investigate the structural, electronic, magnetic, elastic and thermoelectric properties of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) and LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds. These theoretical investigations are carried out by LDA [7], LDA + U and LDA+SOC [85] functionals. The muffin-tin radii are considered in such a manner that no charge leakage can occur. The basis set is expanded in terms of plane waves up to RMT $R_{MT} K_{max} = 7$ where R_{MT} is the smallest atomic radius and K_{max} is the maximum value of k-vector. Furthermore, the maximum angular momentum, l_{max} is set to 10. However, in the interstitial

region, maximum value of charge density is considered as $G_{max}=12$. A k-mesh of 3000 k-points is considered in the Brillouin zone having the grid size of $14 \times 14 \times 14$ using the Monkhorst and Pack mesh [86]. The orientation of spins in the spin-orbit coupling calculations are considered to be along the [100] direction.

3.7 Cubic-elastic Package

Cubic independent elastic constants of materials are calculated using different methods available in the literature [87, 88, 89, 90]. In the present work we investigated different elastic properties of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) and LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds using our home cubic-elastic package [91]. These constants are theoretically determined by using the total energy equation of system. To simplify Eq.(3.5), we neglect $O[\varepsilon_i^3]$. Taylor's series of cubic elastic constants can be expressed in matrix form as:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (3.3)$$

The Bulk modulus B_0 of the system is expressed in terms of the elastic constants C_{11} and C_{12} as [91]:

$$B_0 = \frac{C_{11} + 2C_{12}}{3} \quad (3.4)$$

With the help of deformation matrix D, the cubic system can be distorted.

The second order derivative of energy for all the three types (Dortho, Dcubic and Dmonoc) of distortion deformations are:

$$\frac{d^2 E}{d\epsilon^2} = 2V_0(C_{11} - C_{12}), \quad (3.5)$$

$$\frac{d^2 E}{d\epsilon^2} = 3V_0(C_{11} + 2C_{12}), \quad (3.6)$$

and

$$\frac{d^2 E}{d\epsilon^2} = 4V_0(C_{44}). \quad (3.7)$$

Mechanical properties of the understudy compounds can be explained by calculating Hill shear modulus, Voigt shear modulus, Youngs modulus, Reuss shear modulus, shear constant, Cauchy pressure, Lames coefficients, Poisson ratio, Kleinman parameter and anisotropy.

3.8 WIEN2k code and Technical Details

Low cost and less time consuming tool WIEN2k can be used to determine the ground state properties of materials within the frame work of DFT [92]. WIEN2k works on plane wave plus local orbitals method(FP-LAPW+lo) concept. Among the available techniques, DFT is one of the reliable approach to investigate the structure, electronic, optical, magnetic, elastic and thermoelectric properties of materials. This theoretical approach also explains all electron related phenomena including relativistic effects. In this method calculations are performed at 0 K temperature and the optimized structure are used to study the ground characteristic of materials.

3.9 Boltzmann's Transport Theory

The Boltzmann's transport theory is that in which we study about the flow of charges as well as heat under the external field. The external field can be either an electric field or the difference of temperature between the two ends of the material. Electrons and phonons are treated as thermoelectric carriers while the internal scattering processes is caused to restrict their motion. During the collision of interacting particles, exchange of energy and momentum is occurred. Equilibrium of carriers is also changed due to interaction. In this context there are two available theories that can be applied to such a non equilibrium transport phenomenon. These are the Semi-classical Boltzmann transport theory and the Green-Kubo theory [93, 94]. Kubo theory plays very important role in connection between transport parameters and correlation function of the heat flow or electric current. However, Boltzmann considered effects of scattering on thermoelectric parameteres and also its relation to the relaxation time involved in the scattering. The Boltzmann's transport theory has shown good performance in a number of applications as it provides good results consistent with data obtained from experiments. Here stress is given to unify electronic structure into Boltzmann's transport theory to obtain the transport coefficients. For the case, let we have a system of particles having wave vector k while positioned in a small region. Distribution function for such arrangement is $v = v(r, k, t)$. This function can be changed like external fields, diffusion or scattering centers due to some reason. As diffusion take place due to transport, therefore, change in distribution function with time can be express as:

$$\dot{v} = \dot{v}_{(diff)} + \dot{v}_{(field)} + \dot{v}_{(coll)} \quad (3.27)$$

where time derivative is expressed by dots on the function. The term $\dot{v} = 0$ shows the equilibrium state. Because in this situation, the number of entering particles must be equal to the number of leaving particles. At equilibrium state the Boltzmann's equation can be written as:

$$\dot{v}_{(diff)} + \dot{v}_{(field)} = - d/dt v_{(coll)} \quad (3.28)$$

When relaxation time $\tau(k)$ is introduced for the description of scattering phenomenon and the particles come to equilibrium in time then $v(r, k, t)$ approaches $v^0(k)$.

$$\frac{d}{dt}v = -\frac{v(k) - v^0(k)}{\tau(k)} \quad (3.29)$$

The rate of change of diffusion and external field distribution can be written as:

$$-\dot{v}_{(diff)+(field)} = \frac{\partial v}{\partial r} \times \frac{r}{dt} + \frac{\partial v}{\partial k} \times \frac{e\varepsilon}{\hbar} \quad (3.30)$$

Here the function is based on (r, k, t) while

$$\frac{r}{dt} = v(k) \frac{1}{\hbar} \times \frac{\partial E}{\partial k} \quad (3.31)$$

In above equation v is changed by v^0 because v slightly deviates from v^0 , and from the definition of v^0 one can obtain the relation for $\frac{\partial v}{\partial r}$.

$$\frac{\partial v}{\partial r} = -\frac{\partial v^0}{\partial E} \left(\nabla \mu + \frac{(E - \mu)}{T} \right) \nabla T \quad (3.32)$$

The distribution function can be obtained by putting the above equations (3.32), (3.30), (3.29) and (3.30) in Eq.(3.28). The final equation becomes:

$$v(k) = v^0(k) + (-\frac{\partial v^0}{\partial E})v(k) \times \tau(k) \{e\varepsilon - (\frac{\partial \mu}{\partial T} + \frac{(E - \mu)}{T})\nabla T\} \quad (3.33)$$

3.10 BoltzTraP Code and Technical Details

BoltzTraP program is based on post DFT and is used to predict semi-classical transport coefficients [9] as well as other thermoelectric parameters of the system. Here a dense k-mesh is needed for the calculation of self-consistent band energies. This code uses WIEN2k [95] as well as other computer based programs for calculations. Smoothed Fourier interpolation of the energy bands is used by this code obtained during SCF calculations. The introduction of group velocities is very important and one can get by taking derivatives of the energies to resolve the band energy. Preliminary WIEN2K [95] code can be used to get information about the energies. The derivatives are calculated by using the analytical approach required for the transport distributions.

Chapter 4

Results and Discussions

4.1 Electronic Correlation Effect and Spin-Orbit Coupling Effect in Scandium Inter-metallic Compounds ScTM (TM = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au)

4.1.1 Introduction

The electron-electron correlation effects (EECE) and spin-orbit coupling (SOC) have attracted great attention in materials physics due to their important roles in defining many fascinating properties like superconductivity [96, 97] conductor-insulator transitions in Mott-insulators [98], transport properties [99], half-metallicity and spin-charge separation etc. [100]. The prominent roles of EECE and SOC are generally observed in the transition metals (TM) with d-states. Although, they are interesting and play crucial roles in understanding the physics and chemistry of materials. They are complex to be completely realized for various materials.

SOC effect is usually considered in the condensed matter phenomenon as a weak relativistic correction to the Schrödinger equation (SE), however, in nowadays it is attracting enormous attention due to its capability to justify the observed phenomenon [101, 102, 103, 104] as some TM confirms that this effect is more than just a minor correction to the SE. This effect causes non-trivial topological order in TM based compounds due to the large SOC effect, especially in the 4d and 5d TM compounds [105, 106, 108, 109]. Unlike earlier believes, it is a well-established fact of the modern condensed matter physics that this effect plays a key role and hence modifies and/or controls some significant properties of the 4d and 5d TM compounds.

Like SOC, the EECE is another unique effect in TM compounds and on the basis of this effect, materials are categorized; strongly correlated electron systems, intermediate and weakly correlated systems. The parameter that categorizes materials is U/W values, where U is the Hubbard potential and W is the band width. We represent this ratio by 'Ce'. The Ce value is larger than one for the strongly correlated electron systems, and it is approximately equal to one for intermediately correlated systems and it is less than one for weakly correlated electron systems [85]. It is generally observed that the EECE decreases and the SOC effect increases as one moves from top to bottom in a TM column in the periodic table. As mentioned above, these two effects are critical in TM compounds for understanding their physics and chemistry. Therefore, the understanding of these effects is quite necessary for the applications of these compounds in various emerging technologies.

In this section, we systematically investigate the EECE as well as SOC effects for TM compounds from left to right or from top to bottom in the periodic table in intermetallic ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds.

4.1.2 Structural properties

The structural optimizations are performed using experimental lattice constants [40] by LDA, LDA+U, and LDA+SOC for ScTM (TM= Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) compounds. Furthermore, the Hubbard U parameter is also optimized for each compound by comparing the calculated lattice constants with the experimental lattice constants. The obtained optimized U values are found to be 3, 2, 4, 1, 3, 9, 6, 8 and 1eV for the TM atoms in ScCo, ScRh, ScIr, ScNi, ScPd, ScPt, ScCu, ScAg and ScAu compounds, respectively. In addition to the optimization of the suitable U values for the TM atoms in the materials under study, the U value is also optimized to be 2 eV for the d-state of Sc atom in all of these compounds. The calculated values of the lattice constants for these compound along with their ground state properties like volume (V_o), bulk modulus (B) and energy (E_o) by LDA, LDA+U and LDA+SOC are presented in Table 4.1.

Table 4.1 Calculated and experimental structural properties like lattice constant (a_0) in unit ($\text{\AA}$) volume (V_0) (a.u.^3), Bulk modulus B (GPa), ground state energy (E_0) (Ry) of ScTM (TM= Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) by LDA, LDA+U and LDA+SOC

Materials		LDA	LDA+U	LDA+SOC	Exp.	Others
ScCo	a_0	3.014	3.150	3.0349	3.160 ^a	3.13 ^c
	V_0	184.722	210.9	188.6350		
	B	106.182	94.33	147.6379		122.5 ^c
	E_0	-4307.370	-4306.976	-4307.383		
ScRh	a_0	3.163	3.201	3.152	3.205 ^a	3.22 ^c , 3.254 ^d
	V_0	213.527	221.3	211.41		
	B	106.755	144.52	77.76		161 ^c , 169 ^d
	E_0	-11086.563	-11092.390	-11086.597		
ScIr	a_0	3.168	3.209	3.162	3.206 ^a	3.23 ^c
	V_0	214.559	223.00	213.45		
	B	230.906	192.88	195.98		168.5 ^c
	E_0	-37221.335	-37232.601	-37221.775		
ScNi	a_0	3.080	3.149	3.091	3.165 ^a	3.169 ^b
	V_0	197.194	210.701	199.38		
	B	107.854	128.857	140.502		109 ^b
	E_0	-4561.887	-4565.724	-4561.893		
ScPd	a_0	3.239	3.282	3.237	3.283 ^a	3.206 ^b , 3.329 ^d
	V_0	229.251	238.595	228.869		
	B	136.139	155.899	135.480	128 ^c	112.6 ^b , 137 ^d
	E_0	-11609.813	-11615.771	-11609.852		
ScPt	a_0	3.235	3.269	3.228	3.270 ^a	3.307 ^b
	V_0	228.523	235.4870	227.035		
	B	172.463	159.518	153.667	162.8 ^c	139.62 ^b
	E_0	-38398.064	-38409.315	-38398.563		
ScCu	a_0	3.173	3.239	3.169	3.256 ^a	
	V_0	215.492	229.329	214.782		
	B	107.359	95.747	109.9818		
	E_0	-4830.018	-4833.878	-4830.030		
ScAg	a_0	3.346	3.422	3.3137	3.416 ^a	3.439 ^d
	V_0	252.717	270.4591	245.5576		
	B	66.282	85.3627	56.502		99 ^d
	E_0	-12149.930	-12155.949	-12149.983		
ScAu	a_0	3.324	3.378	3.3136	3.373 ^a	
	V_0	247.935	260.1168	245.5269		
	B	102.297	131.6965	121.8447		
	E_0	-39599.945	-39611.977	-39600.479		

^a[40], ^b[65], ^c[63], ^d[62]

The results show that the computed lattice constants of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds by LDA+U are closer to the experimental values reported in Ref. [40]. This shows that the LDA+U is a suitable theoretical tool for the cases under study. Generally DFT underestimates or overestimates the physical properties due to the approximations used for the exchange-correlation term. As these intermetallic systems are correlated compounds, therefore the LDA+U is more effective in these materials as compared to the other exchange-correlation potentials, i.e., LDA and LDA+SOC, which underestimate the lattice constants of the present compounds with a higher difference from experimental results.

The results presented in Table 4.1 show an increasing trend in bulk moduli of the materials, i.e., 94.33, 144.52, 192.88, 128.857, 155.899, 159.518 GPa for ScCo, ScRh, ScIr, ScNi, ScPd, ScPt, respectively, while this trend is broken down for ScCu, ScAg and ScAu. The value decreases for ScCu (95.747 GPa) and then increases in a sequence of ScAg (85.362 GPa) and ScAu (131.696 GPa), respectively. This shows that ScAg is a soft material as compared to ScCu and ScAu due to the greater melting point of Cu ($1085C^{\circ}$) and Au ($1064C^{\circ}$) as compared to Ag ($962C^{\circ}$).

To study the stable magnetic phase of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) intermetallics, double cell optimizations are performed for each compound in different magnetic phases. It is obvious from the Table 4.2 and Figs. 4.1, 4.2 and 4.3 that ScCo, ScPd, ScPt and ScCu have lowest energies in their ferromagnetic phase; ScIr, ScNi and ScAu have lowest energies in the anti-ferromagnetic state, whereas ScAg has the lowest energy in its non-magnetic phase. Hence, ScCo, ScPd, ScPt, and ScCu compounds are stable in the ferromagnetic state and ScIr, ScNi and ScAu are stable in anti-ferromagnetic whereas ScAg is stable in the non-magnetic phase.

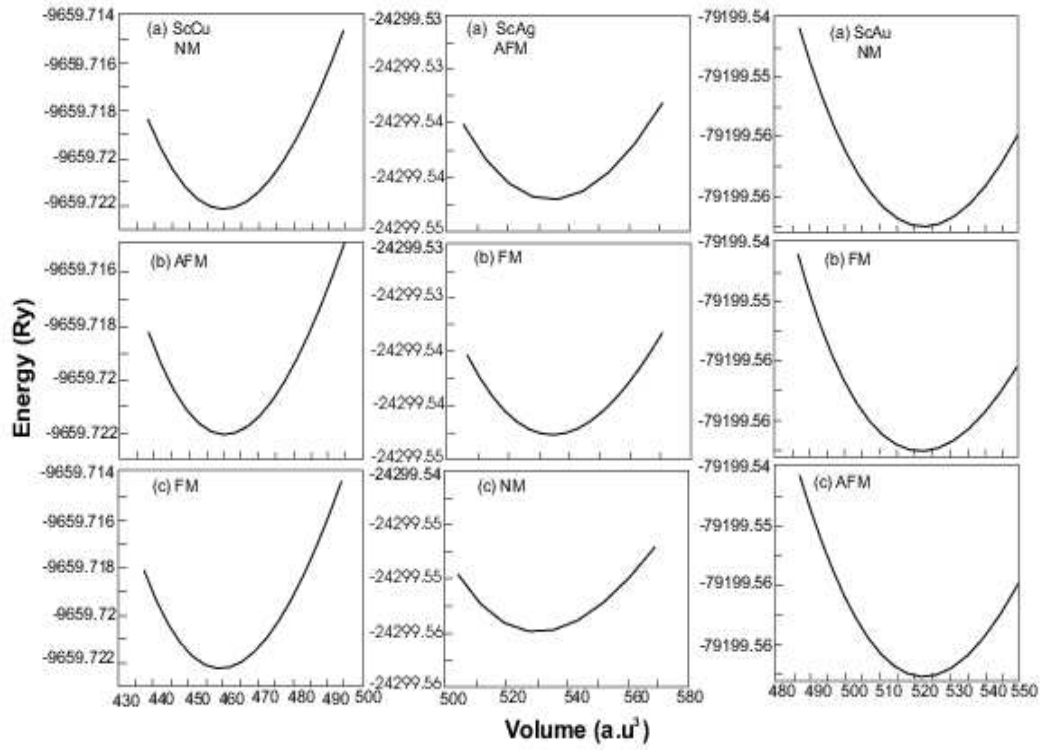


Figure 4.1: Optimization plots of ScTM (TM= Cu, Ag and Au) for the stability of the magnetic states.

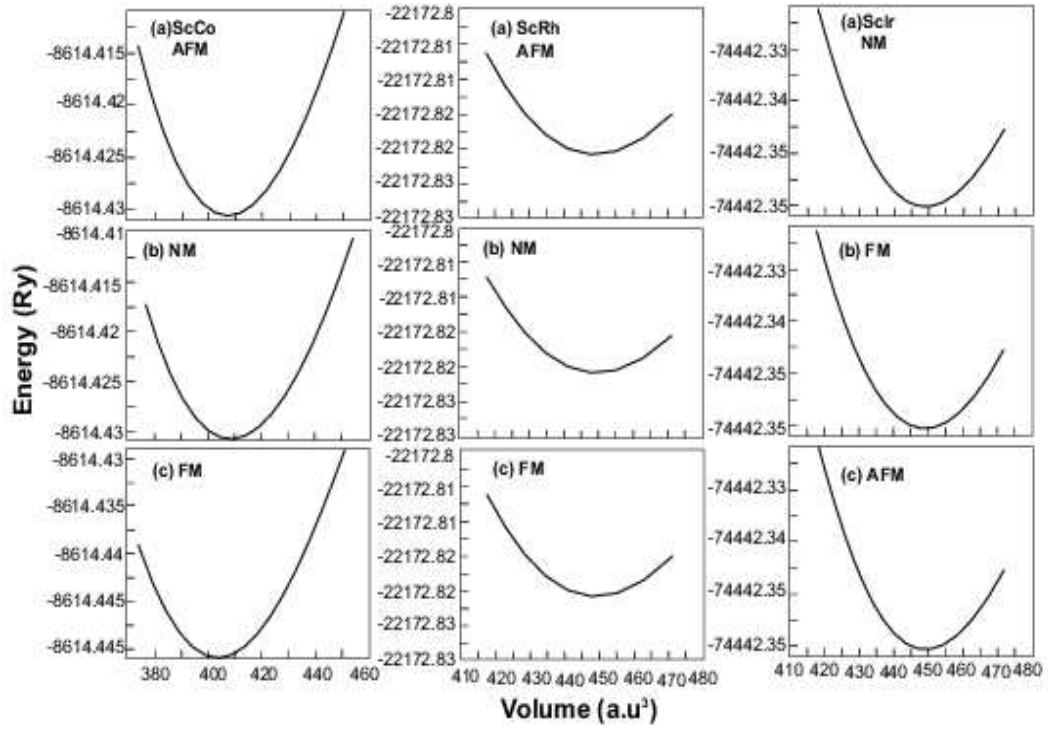


Figure 4.2: Optimization plots of ScTM (TM= Co, Rh and Ir) for the stability of the magnetic states.

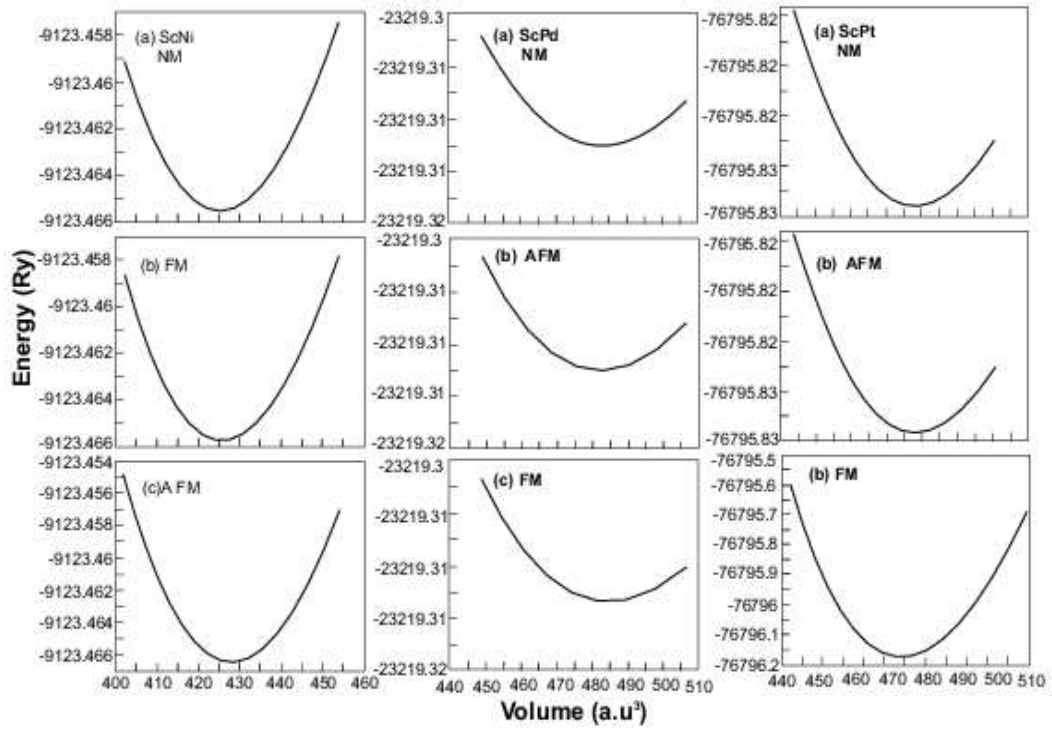


Figure 4.3: Optimization plots of ScTM (TM= Ni, Pd and Pt) for the stability of the magnetic states.

Table 4.2 Calculated magnetic energies of nonmagnetic (NM), ferromagnetic (FM) and anti-ferromagnetic (AFM) phases of the doubled cell and U/W ratios of the unit cell of ScTM (TM = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) compounds.

Compounds	$E_{\text{NM}}(\text{Ry})$	$E_{\text{FM}}(\text{Ry})$	$E_{\text{AFM}}(\text{Ry})$	U/W (eV)
ScCo	-8614.430856	-8614.450993	-8614.430552	1.8571
ScRh	-22172.820724	-22172.820812	-22172.82043	0.8253
ScIr	-74442.350246	-74442.350267	-74442.350358	1.4950
ScNi	-9123.4656000	-9123.465750	-9123.466460	0.7177
ScPd	-23219.312562	-23219.313555	-23219.312577	1.5975
ScPt	-76795.834028	-76795.834552	-76795.834110	4.0153
ScCu	-9659.722139	-9659.722394	-9659.722163	6.2558
ScAg	-24299.554958	-24299.547728	-24299.547414	6.6033
ScAu	-79199.562584	-79199.562629	-79199.562711	0.5212

The calculated optimizations curves of these compounds are shown in Figs. 4.1, 4.2 and 4.3 and the corresponding ground state energies for all the three magnetic phases non-magnetic, ferromagnetic and anti-ferromagnetic phase are shown in Table 4.2.

4.1.3 Electronic Properties

Electronic structure is very important to explain numerous physical properties of a material. The total and partial densities of states calculated by LDA, LDA+U and LDA+SOC for all ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds are plotted in Figs. 4.4 and 4.5.

Fig. 4.4 explains total density of states (TDOS) of these intermetallic systems by LDA, LDA+U and LDA+SOC. In all these plots, the Fermi levels are crossed by the densities of states. Hence, all these compounds are predicted to be metals.

Fig. 4.5 shows the partial DOSs of Sc and TM d-states. The plots reveal the origin of the metallic nature of these compounds. From the figure it can be seen that in ScCo, ScRh, ScIr, ScNi, ScPd and ScPt compounds, the Fermi levels are crossed by the d-states of both Sc and TM elements with dominant contributions of Co, Rh, Ir, Ni, Pd and Pt d-state, whereas in ScCu, ScAg and ScAu compounds, the Fermi level is also crossed by the density of both Sc and TM d-states. In the latter statement, the dominant participant is Sc d-state which is due to the fact that in the Cu, Ag and Au cases the d-states are completely filled. The same phenomenon is also reported by Fatima et al. [62] for such type of compounds.

Fig. 4.6, 4.7 and 4.8 explain the effects of SOC in these intermetallics. Without SOC the Sc and TM (Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) d-states split into two sub-states e_g and t_{2g} , where e_g state is high in energy as compared to the t_{2g} state. After applying SOC the d-states (e_g and t_{2g}) further split into sub-energy states such that e_g split into d_{z^2} and $d_{x^2-y^2}$, and t_{2g} state split into $d_{zx} + d_{yz}$ and d_{xy} energy bands. Fig. 4.6 also provides micro level information about these states participated across the Fermi level. In ScCo compound without SOC the Fermi level is crossed by the t_{2g} d-state

of Sc and e_g d-state of Co. After applying SOC the dominant participating states at the Fermi level are Sc $d_{zx} + d_{yz}$ and Co $d_{x^2y^2}$ energy bands. In ScRh, without SOC the Fermi level is crossed by both energy states e_g and t_{2g} of Sc, having maximum contribution in the conduction region, whereas the e_g -state of Rh is localized in the valence region, while e_g crosses the Fermi level. After applying SOC, Sc d-state splits into five further sub energy bands such as d_{z^2} , d_{xy} , $d_{x^2y^2}$, $d_{xz} + d_{yz}$, whereas Rh d-state is also splitted in the same number of energy states. In the case of Rh, the most dominant energy state is $d_{x^2y^2}$ which crosses the Fermi level, as shown in figure 4.6. A similar trend is observed for ScIr. Figures 4.7 and 4.8 explain similar phenomenon for ScNi, ScPd, ScPt, ScCu, ScAg and ScAu compounds without SOC and with SOC effect. U optimization plays an important role in the determination of strength of the electronic correlations effect in these compounds [85].

Fig. 4.9 shows the band width of TM versus valence electron number. It can be seen from the figure that the width of the d-state of the TM increases from 3d to 5d, which shows that the correlation effect decreases in these compounds in the sequence of $3d \rightarrow 4d \rightarrow 5d$, which is in agreement with the same trend reported for TM by Sasioglu et al. [85]. This shows that our results are logical and consistent to the reported work of the elemental behavior of TM.

In ScTM compounds the ratio of Hubbard U-parameter to the width of TM d-state (U/W) shows different correlation behavior as compared to the elemental response, see Fig. 4.10. This is due to the fact that in compounds different types of bonding and quantum interactions are involved. The calculated values of U/W are 1.8571, 0.8253, 1.4950, 0.7177, 1.5975, 4.0153, 6.2558, 6.6033 and 0.5212 for ScCo, ScRh, ScIr, ScNi, ScPd, ScPt, ScCu, ScAg and ScAu, respectively (Table 4.2). It is clear from the table

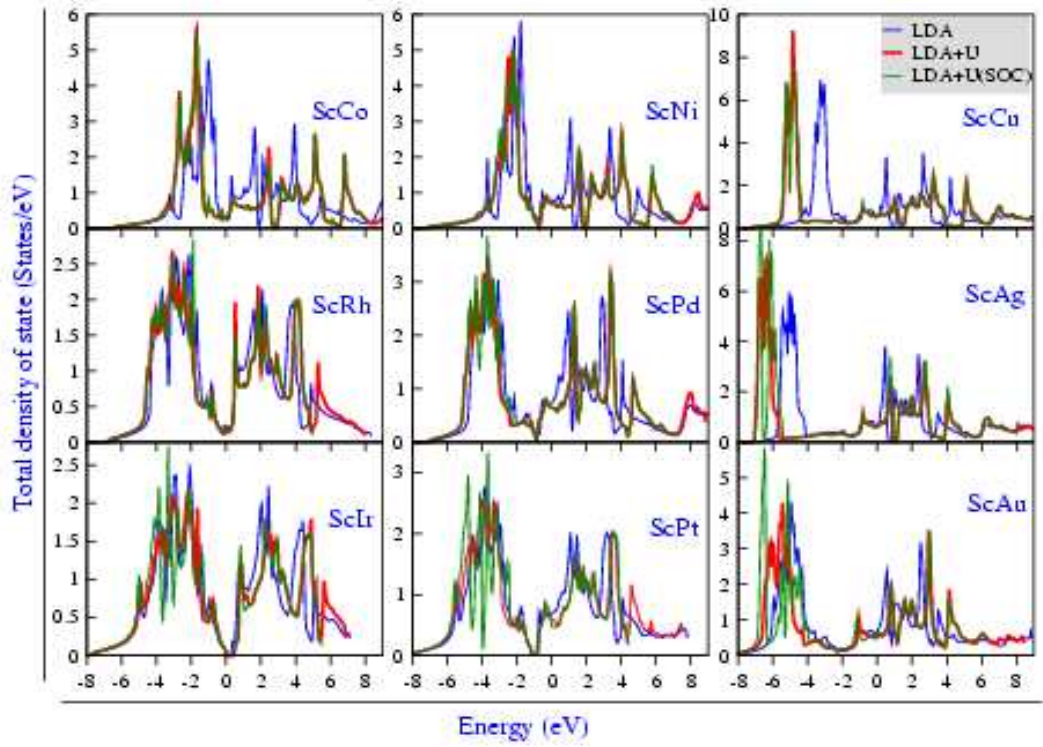


Figure 4.4: Total DOSs for ScTM (TM= Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) compounds.

that ScCo, ScIr, ScPd, ScPt, ScCu and ScAg are strongly correlated compounds, because their U/W ratio is greater than 1, while ScRh, ScNi, ScAu are weakly correlated compounds, because their U/W values are less than 1. The same phenomenon is also observed by Sasioglu et al. [85] in particular TM elements Cu and Ag such that their U/W ratios are greater than one.

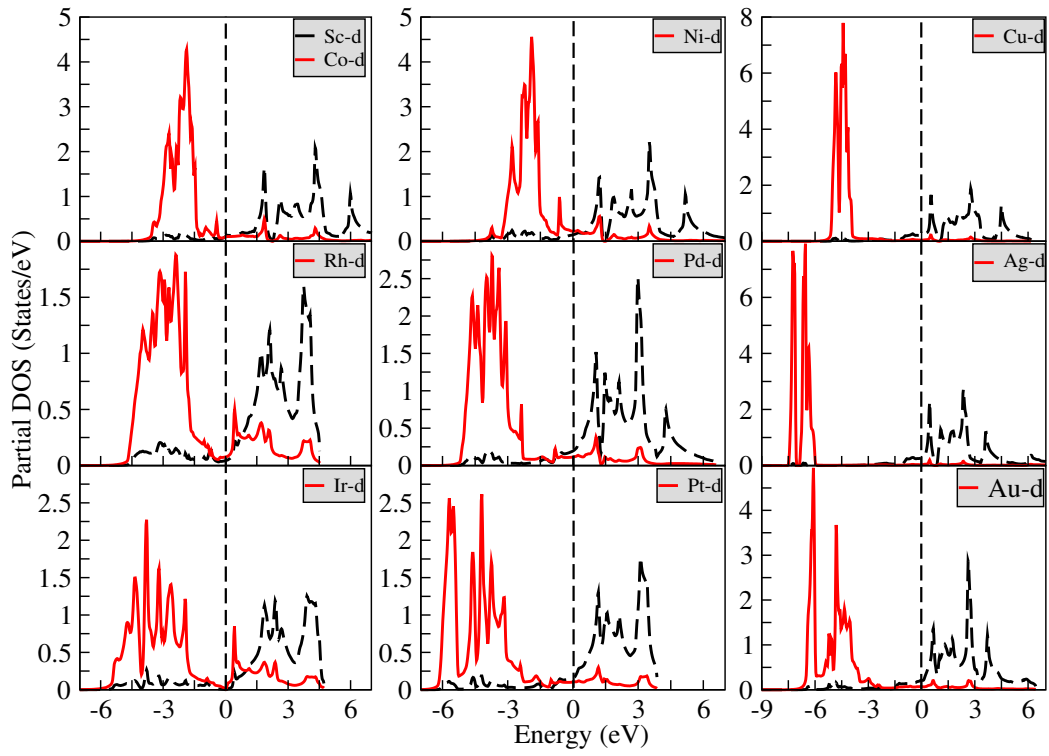


Figure 4.5: TM d-states DOS of ScTM (TM= Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au) compounds.

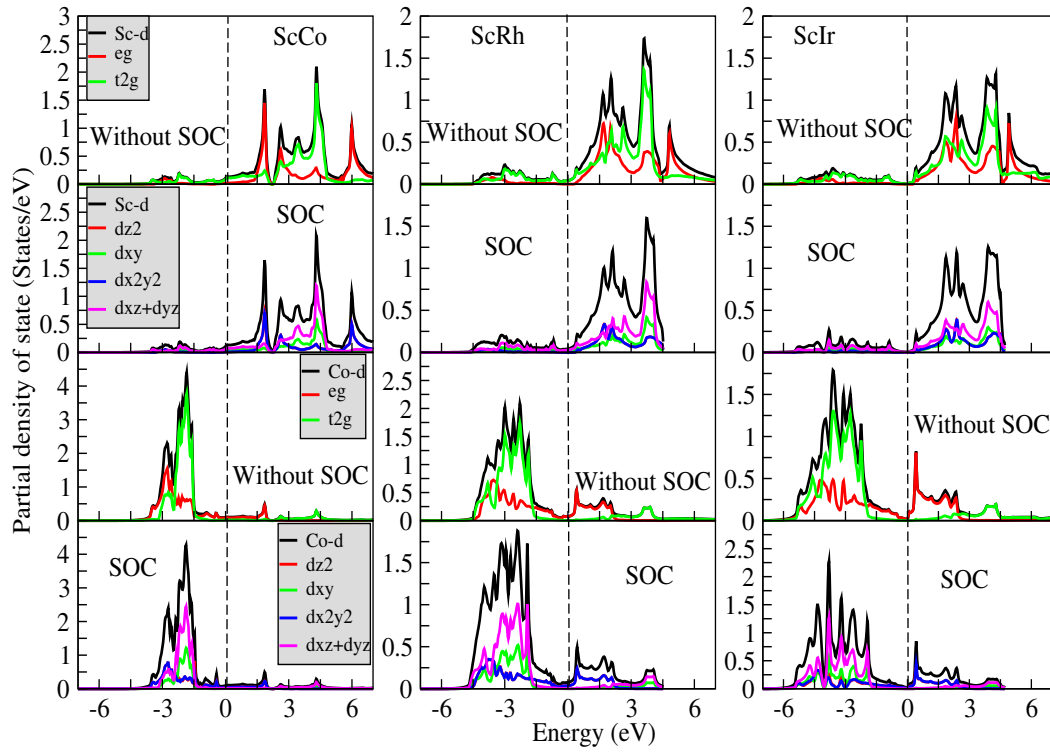


Figure 4.6: Partial DOS of ScCo, ScRh and ScIr compound with SOC and without SOC

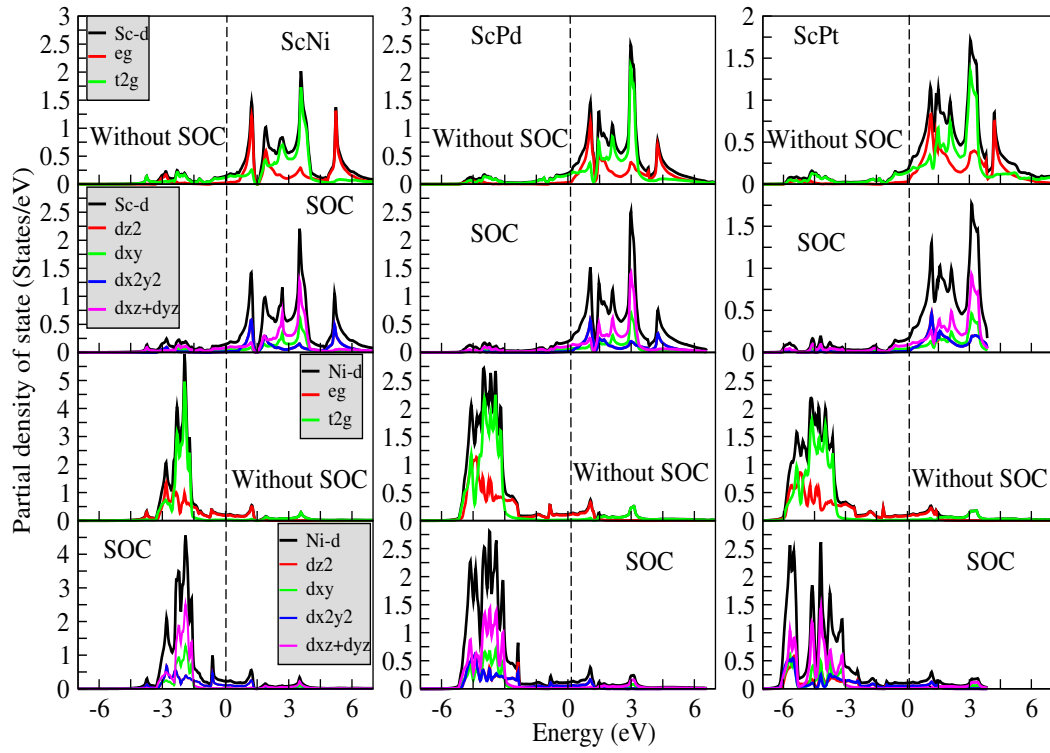


Figure 4.7: Partial DOS of ScNi, ScPd and ScPt compound with SOC and without SOC

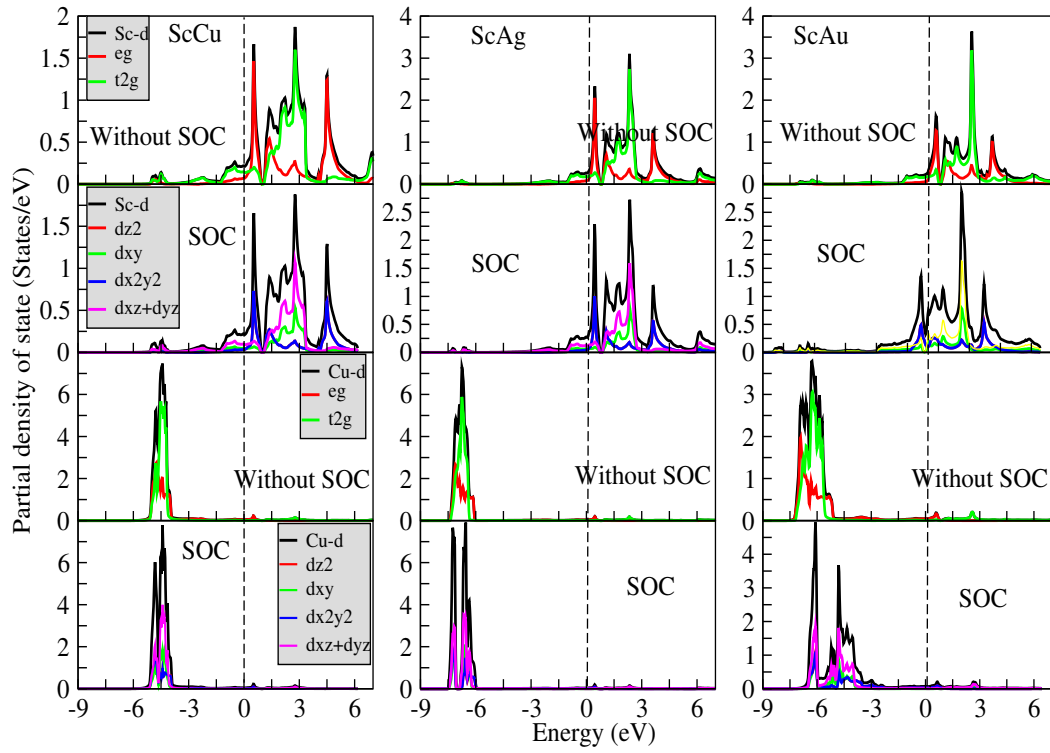


Figure 4.8: Partial DOS of ScCu, ScAg and ScAu compound with SOC and without SOC

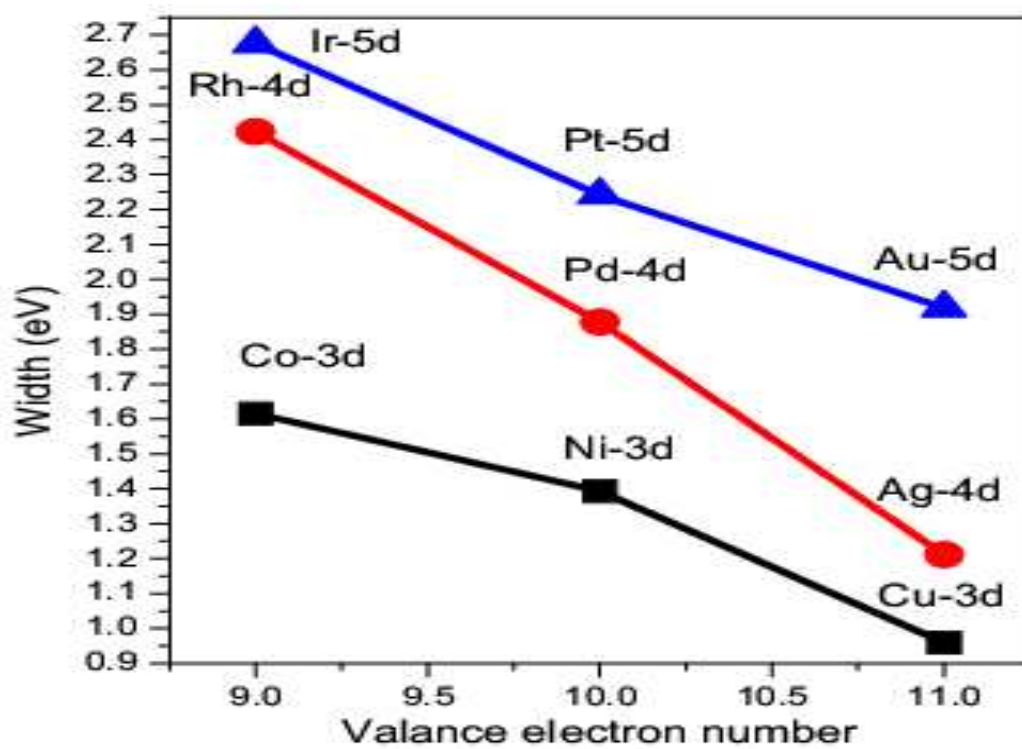


Figure 4.9: Plot between bandwidth (W) and valance electrons of TM = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au.

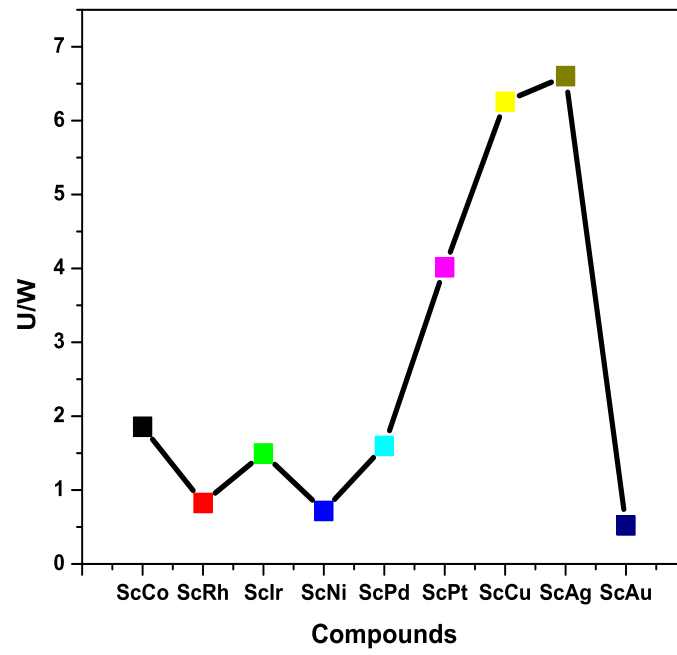


Figure 4.10: The ratio U/W of the effective Coulomb interaction (U) and the d-state band width (W) for the TM (Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au).

4.1.4 Magnetic Properties

From section (4.1) it is confirmed that ScCo, ScRh, ScPd, ScPt and ScCu are ferromagnetic, and ScIr, ScNi and ScAu are anti-ferromagnetic, whereas ScAg is a non-magnetic materials. To study the origin of magnetism in these compounds, LDA, LDA+U and LDA+U+SOC spin-polarized calculations are performed. At the Fermi energy (E_F), electron spin-polarization for a material can be calculated by the equation [110, 111]:

$$P = \frac{D \uparrow (E_F) - D \downarrow (E_F)}{D \uparrow (E_F) + D \downarrow (E_F)} \quad (4.1)$$

where in equation (4.1) $D \uparrow (EF)$ ($D \downarrow (EF)$) represents the DOS in spin up (down) channel at the Fermi level. The type of materials can be identified using the value of P such that zero value of P shows non-magnetic behavior of materials. Spin polarization of electrons at Fermi level is 100%, when the value of $D \uparrow (EF)$ is zero (non zero) and the value of $D \downarrow (EF)$ is non zero (zero). These types of calculations are very important to understand the magnetic nature of materials. The calculated spin and orbital contributions of the magnetic moments are listed in Table 4.3 for ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) compounds.

Table 4.3 Calculated spin magnetic moments in the interstitial region ($M_{\text{int.}}$), spin magnetic moments per atom inside the muffin-tin sphere ($M_{\text{Sc}}/M_{\text{TM}}$), total spin magnetic moment inside muffin-tin spheres per cell (M_{Total}), orbital magnetic moment per atom inside the muffin-tin sphere ($M_{\text{Sc}}/M_{\text{TM}}$), orbital total magnetic moments per cell (M_{Total}) and total magnetic moments per cell ($M_{\text{Total}}(\text{Spin})+M_{\text{Total}}(\text{orbital}) = \text{Total}$) of ScTM(TM= Co, Rh, Ir, Ni, Pt, Pd, Cu, Ag and Au) compounds by LDA, LDA+U and LDA+U+SOC.

Compounds	Sites	LDA	LDA+U	LDA+U(SOC)		Total
		MTMT	Spin	Orb.		
ScCo	M ^{int}	0.0049	-0.3425	-0.3374	-----	0.2363
	M ^{Sc}	0.0011	-0.3317	-0.3241	0.0076	
	M ^{Co}	-0.0316	0.8611	0.08265	0.0637	
	M ^{Total}	-0.0256	0.1868	0.1649	0.0714	
ScNi	M ^{int}	-0.0025	0.0019	-0.0018	-----	-0.0039
	M ^{Sc}	-0.0017	-0.0001	-0.0017	0.0001	
	M ^{Ni}	0.0168	-0.0172	-0.0013	0.0008	
	M ^{Total}	0.0125	-0.0154	-0.0049	0.0009	
ScCu	M ^{int}	0.0001	0.0039	0.0044	-----	0.0114
	M ^{Sc}	0.0003	0.0059	0.0057	0.0000	
	M ^{Cu}	-0.0004	0.0016	0.0011	0.0000	
	M ^{Total}	-0.0000	0.0114	0.0113	0.0000	
ScRh	M ^{int}	-0.0031	-0.0054	-0.0081	-----	-0.0047
	M ^{Sc}	-0.0024	-0.0027	-0.0071	0.0003	
	M ^{Rh}	0.0012	-0.0012	0.0091	0.0009	
	M ^{Total}	-0.0042	-0.0095	-0.0060	0.0013	
ScPd	M ^{int}	-0.0001	0.0002	0.0006	-----	0.0018
	M ^{Sc}	0.0007	0.0035	0.0011	0.00009	
	M ^{Pd}	-0.0015	-0.0053	0.0000	0.00002	
	M ^{Total}	-0.0008	-0.0016	0.0017	0.00011	
ScAg	M ^{int}	0.0003	0.0002	0.0009	-----	0.0026
	M ^{Sc}	0.0007	0.0025	0.0016	0.0000	
	M ^{Ag}	-0.0007	-0.0004	0.0001	-0.0000	
	M ^{Total}	0.0003	0.0022	0.0026	0.0000	
ScIr	M ^{int}	-0.0018	-0.0025	-0.0012	-----	0.0003
	M ^{Sc}	-0.0012	-0.0021	-0.0012	0.0001	
	M ^{Ir}	0.0029	0.0048	0.0023	0.0002	
	M ^{Total}	-0.0000	0.0000	-0.0001	0.0003	
ScPt	M ^{int}	0.0004	-0.0008	0.0002	-----	0.0007
	M ^{Sc}	0.0027	0.00013	0.0004	0.0000	
	M ^{Pt}	0.0018	-0.0002	0.0001	0.0000	
	M ^{Total}	0.0051	0.0002	0.0007	0.0000	
ScAu	M ^{int}	0.0007	0.0007	0.0005	-----	0.0011
	M ^{Sc}	0.0027	0.0040	0.0009	-0.0001	
	M ^{Au}	-0.0015	-0.0013	-0.0002	-0.0000	
	M ^{Total}	0.0020	0.0034	0.0012	-0.0001	

It can be seen from the table that for ScCo the interstitial magnetic moment inside the muffin-tin sphere as calculated by LDA is $0.0049\mu_B$, by LDA+U is $-0.3425\mu_B$ and by LDA+U+SOC is $-0.3374\mu_B$. The spin magnetic moments in the series of ScTM (TM= Co, Ni, Pd, Rh, Ir, Pt, Au, Ag and Cu) are $0.0011\mu_B$, $-0.3317\mu_B$ and $-0.3241\mu_B$ for Sc and $-0.0316\mu_B$, $0.8611\mu_B$ and $0.08265\mu_B$ for Co, whereas the orbital magnetic moments calculated by LDA+U + SOC for Sc is $0.0076\mu_B$ and for Co is $0.0637\mu_B$. The total magnetic moment per ScCo cell, i.e., $M_{\text{Total}}(\text{Spin}) + M_{\text{Total}}(\text{orbital}) = M_{\text{Total}}$, is $0.2363\mu_B$. It can be observed that in ScCo compound, Sc atom and the interstitial region are found with negligible negative magnetic moments. Hence, the effective magnetic moment due to spin is because of the 3d-state electrons of the transition atom (Co) as shown Fig.4.11 and for ScRh, ScPd, ScPt, ScCu are also shown in Figs. 4.12, 4.13, 4.14 and 4.15.

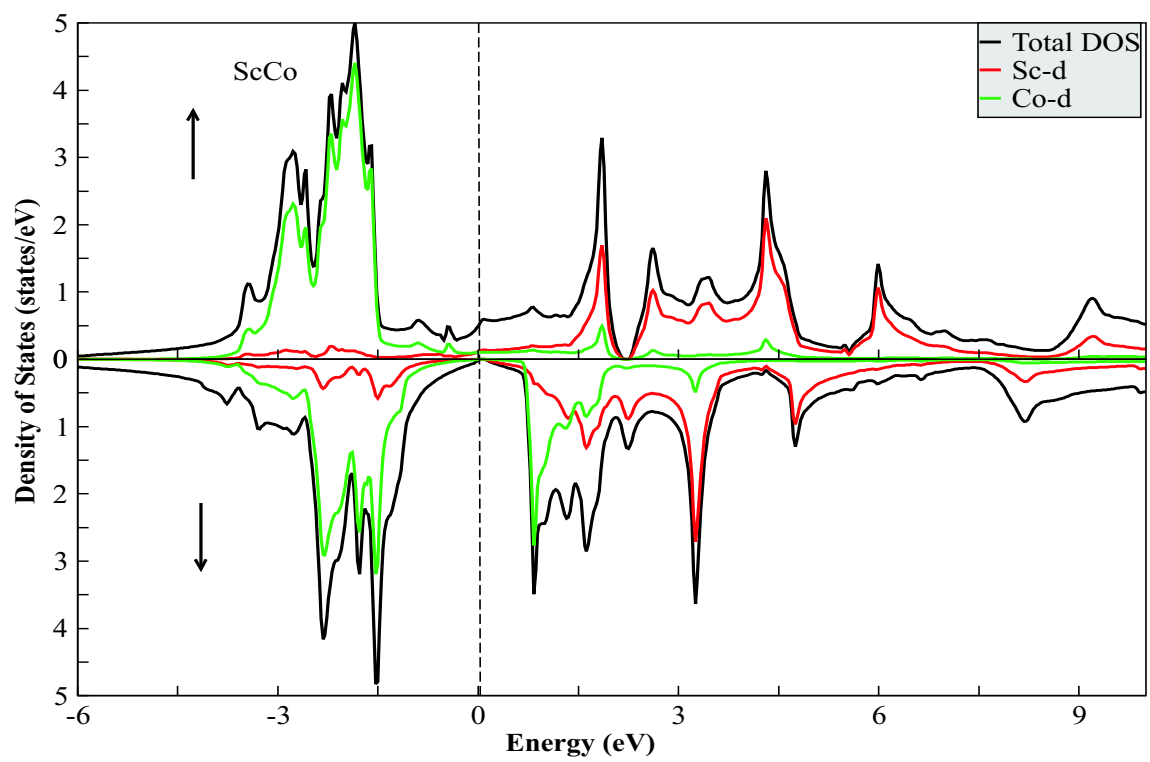


Figure 4.11: Doubled cell FMTDOS for spin up and spin down of ScCo compound.

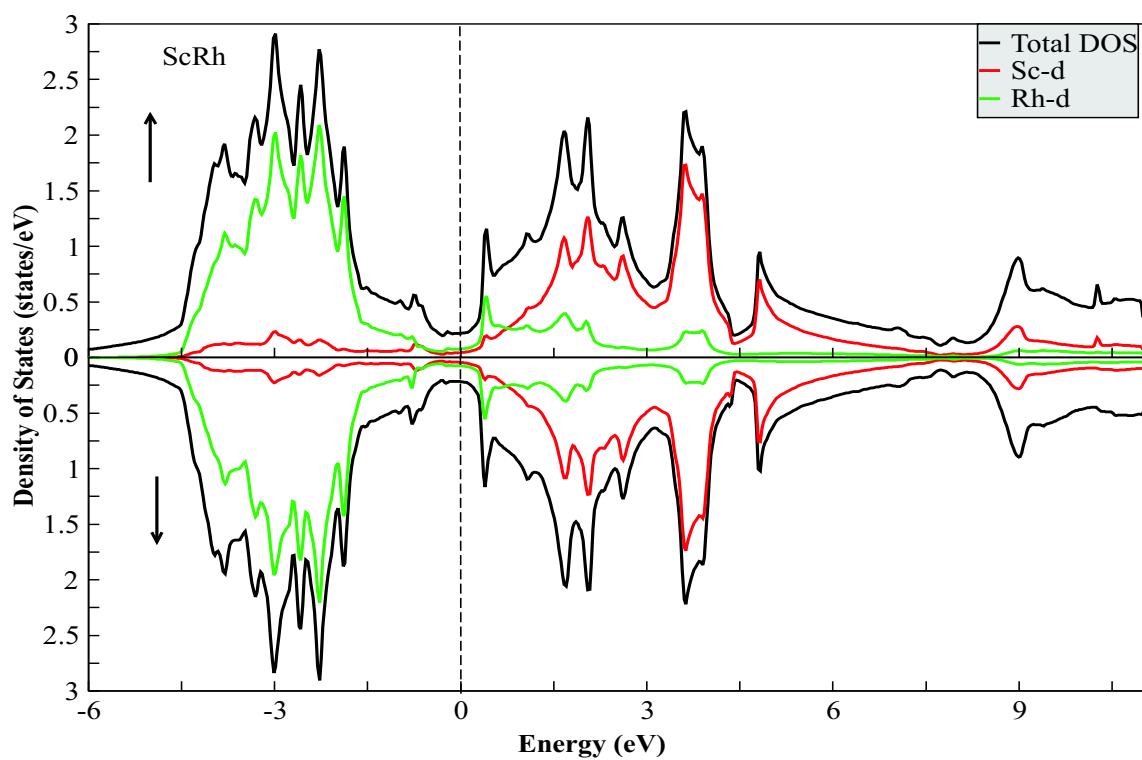


Figure 4.12: Doubled cell FMTDOS for spin up and spin down of ScRh compound

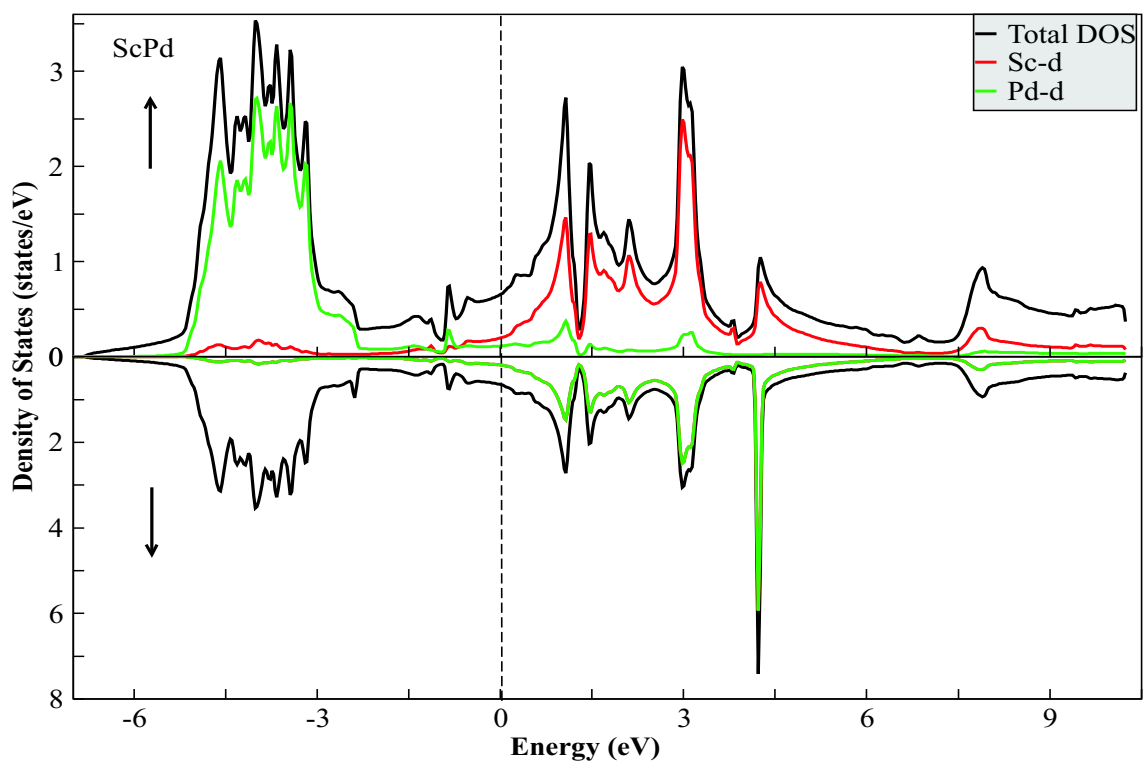


Figure 4.13: Doubled cell FMTDOS for spin up and spin down of ScPd compound

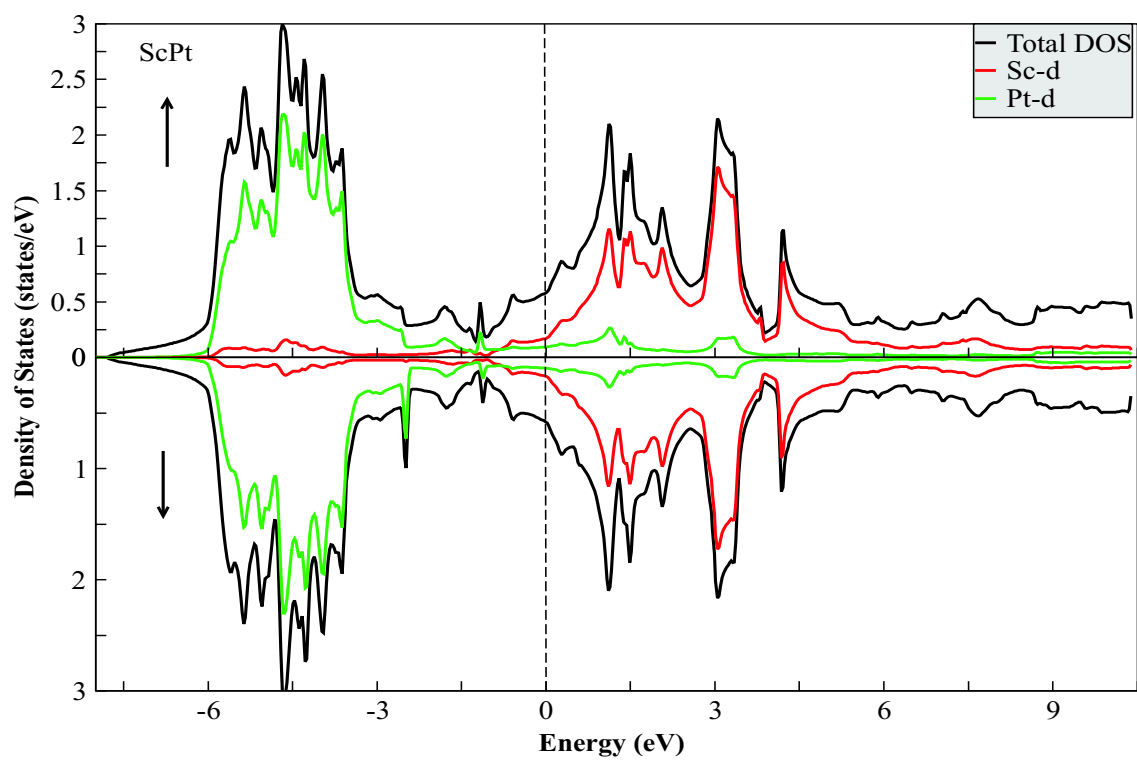


Figure 4.14: Doubled cell FMTDOS for spin up and spin down of ScPt compound

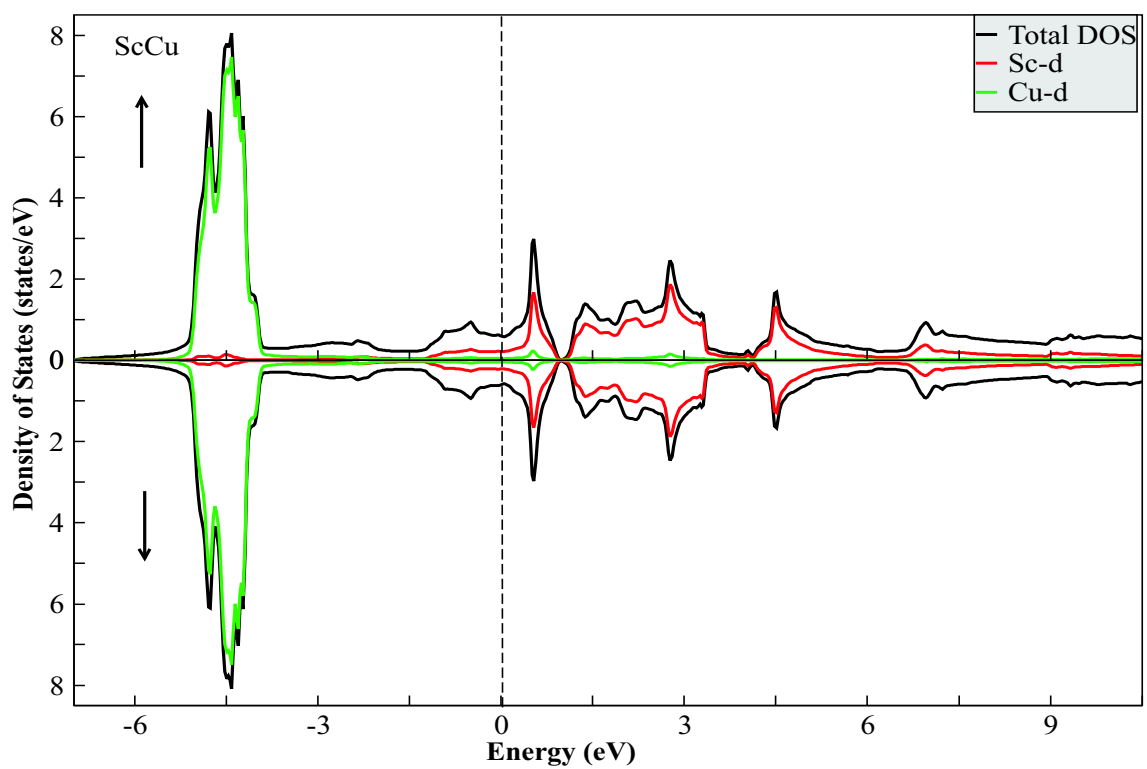


Figure 4.15: Doubled cell FMTDOS for spin up and spin down of ScCu compound

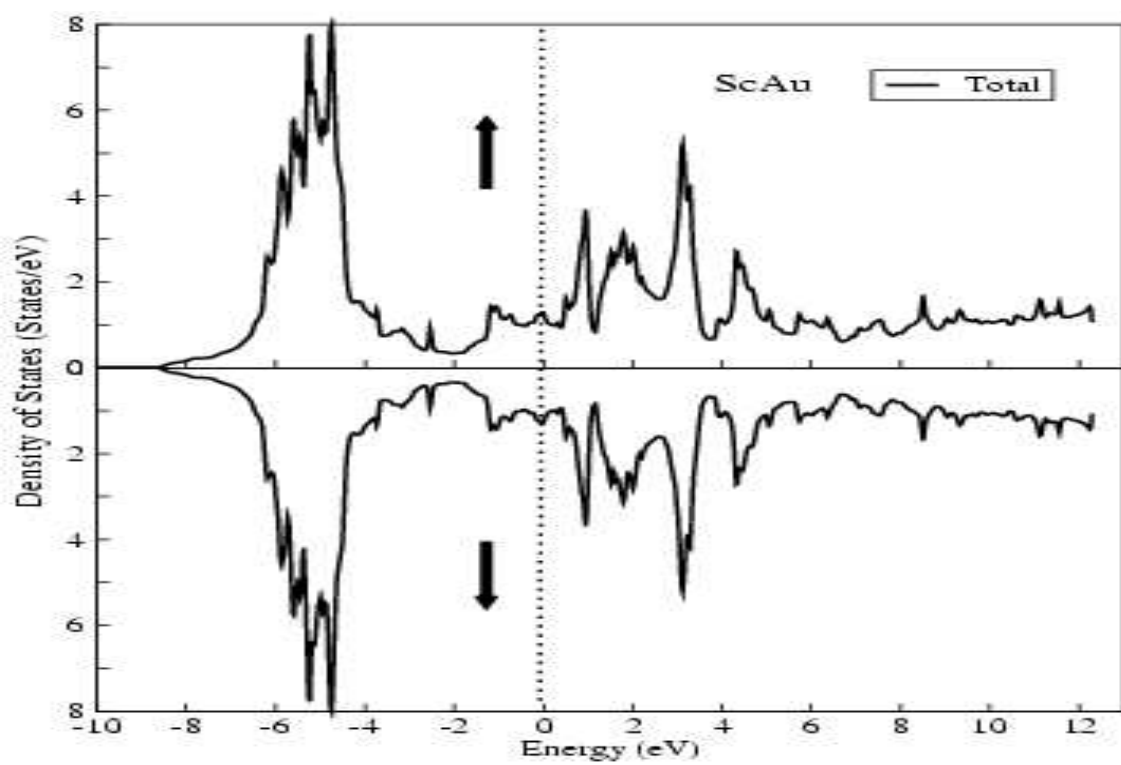


Figure 4.16: Doubled cell AFMTDOS for spin up and spin down of ScAu compound.

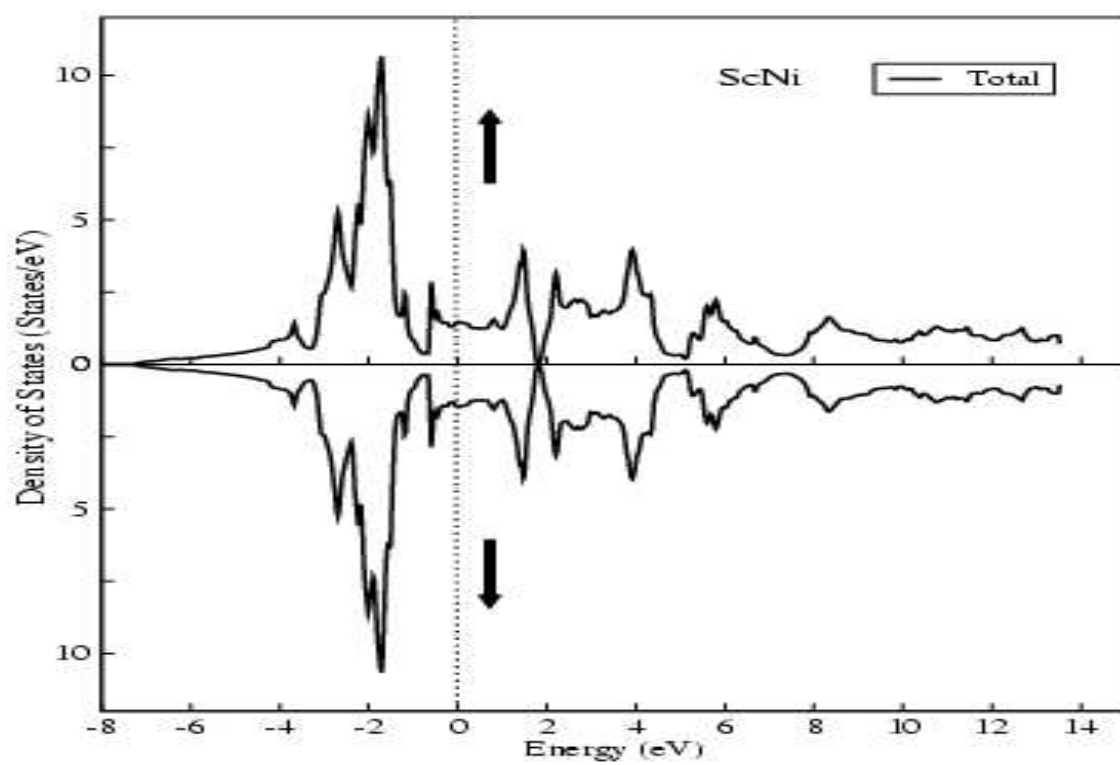


Figure 4.17: Doubled cell AFMTDOS for spin up and spin down of ScNi compound.

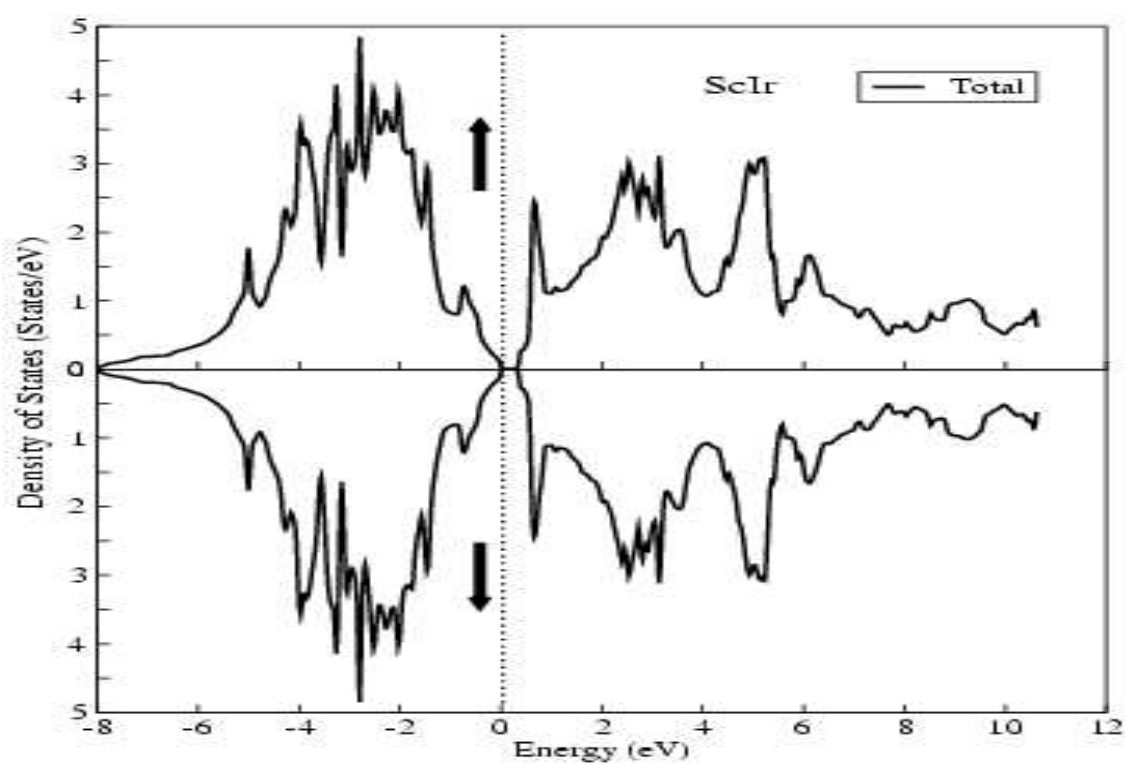


Figure 4.18: Doubled cell AFMTDOS for spin up and spin down of ScIr compound

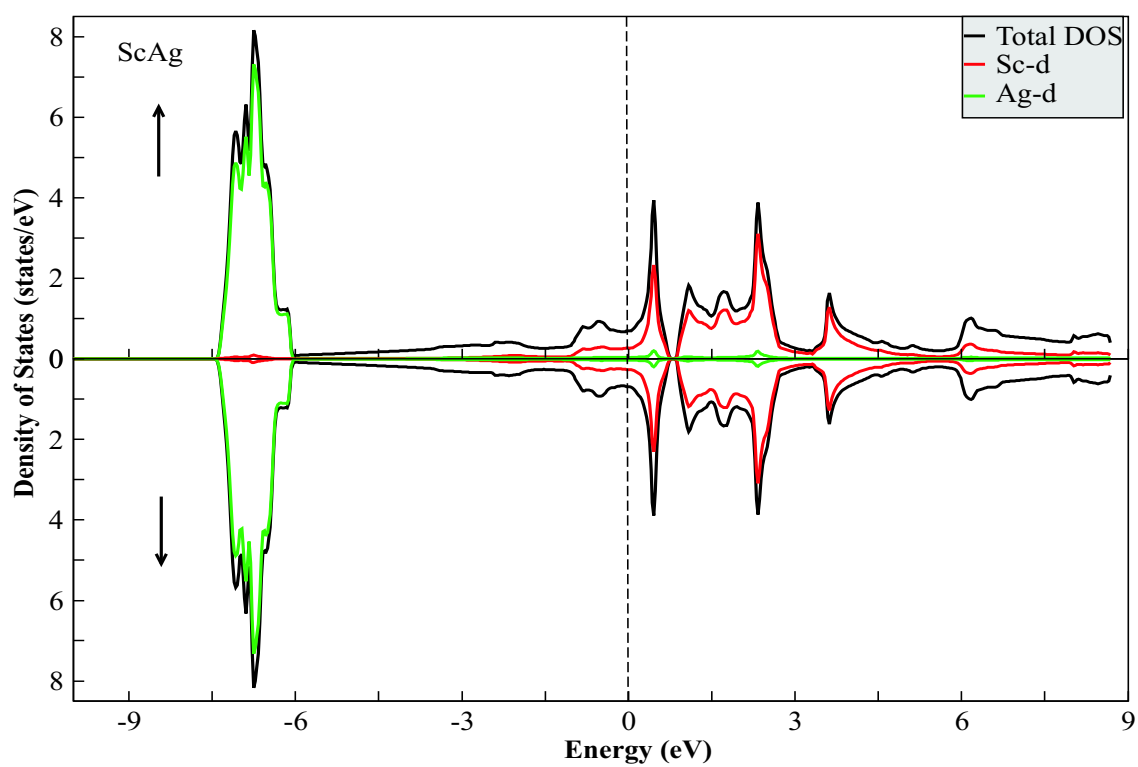


Figure 4.19: Doubled cell NMTDOS for spin up and spin down of ScAg compound

In the case of ScNi, the interstitial magnetic moment inside muffin-tin sphere calculated by LDA is $-0.0025\mu_B$, by LDA+U is $0.0019\mu_B$ and by LDA+U+SOC is $-0.0018\mu_B$. The spin magnetic moments of Sc is $-0.0017\mu_B$, $-0.0001\mu_B$, $-0.0017\mu_B$ and for Ni is $0.0168\mu_B$, $-0.0172\mu_B$, $-0.0013\mu_B$, whereas the orbital magnetic moments by LDA + U + SOC for Sc is $0.0001\mu_B$ and for Ni is $0.0008\mu_B$. The total magnetic moments per ScNi cell is $-0.0039\mu_B$.

In ScCu compound the interstitial magnetic moment inside the muffin-tin sphere by LDA is $0.0001\mu_B$, by LDA+U is $0.0039\mu_B$ and by LDA+U+SOC is $0.0044\mu_B$. The spin magnetic moment is $0.0003\mu_B$, $0.0059\mu_B$, $0.0057\mu_B$ for Co and $-0.0004\mu_B$, $0.0016\mu_B$, $0.0011\mu_B$ for Cu. The orbital magnetic moment by LDA + U + SOC for Sc is $0.0000\mu_B$ and for Cu is $0.0000\mu_B$. The total magnetic moments per ScNi cell $M_{\text{Total}}(\text{Spin}) + M_{\text{Total}}(\text{orbital}) = 0.0114\mu_B$. The interstitial magnetic moment and Sc magnetic moment is negligible which means that in the total magnetic moment the dominant contribution is due to the TM d-state. In the ScCu the dominant contribution is observed due to d-state of Sc element, because Cu d-state is completely filled, while the Sc d-state is partially filled. A similar trend is also seen in ScRh, ScPd, ScAg, ScIr and ScPt compounds.

To confirm the anti-ferromagnetic behavior of these compounds, we performed the double cell self-consistent field calculations. The spin dependent total densities of states of these compounds are presented in Figs. 4.16, 4.17 and 4.18. It is clear from the Figs. 4.16, 4.17 and 4.18 that DOSs of ScNi, ScIr and ScAu compounds in both channels are mirror reflection, which confirm the metallic anti-ferromagnetic nature of these compounds and for ScAg is given in Fig.4.19.

4.2 Theoretical investigation of thermoelectric and elastic properties of intermetallic compounds ScTM (TM= Cu, Ag, Au and Pd)

4.2.1 Introduction

The availability of energy is the main requirement for the everyday life. However in most processes of utilization of energy especially in heat related phenomenon, the maximum part of energy is wasted to the environment. Thermoelectric power generation is presently taking the increasing interest, as during this waste heat is used for useful purposes to overcome the energy deficiency for useful purpose. For the case to achieve the power generation from the waste heat, high temperature with higher values of Seebeck coefficient thermoelectric (TE) materials are essential. The high Seebeck coefficient values are commonly obtained in the materials with having narrow band gap semiconductors as well as with the low values of carrier's concentration [112].

Similar to thermoelectric power generation, the thermoelectric cooling is also important. Thermoelectric cooling requires low temperature materials, however the literature lacks the study of low temperature as compared to TE materials of high temperature, resultantly the studies of the metallic TE materials are scanty [113, 114]. Lin et al. [115] worked on antiperovskites compound $SnCxCo_3$ and investigate the TE properties around 250 K and found maximum value of ZT (0.035). Recently, Bilal et al. [116] also worked upon theoretically on antiperovskites $SnNCa_3$ compound to study the TE properties and also showed the relation between Seebeck coefficients and

spin orbit coupling at room temperature and found that Seebeck coefficient increases significantly with the result of described phenomenon. The focus of this section is to look for low temperature TE materials in intermetallic, therefore we examine the TE properties of metallic compounds ScTM (TM= Cu, Ag, Au and Pd). The other aspect of this section is to systematically study the effect of SOC on the electronic and thermoelectric properties of these compounds with 3d, 4d and 5d electron states.

Thermoelectrics gained attention because it produces electricity from waste heat [117, 118, 119, 120, 121]. As TE generators directly convert thermal energy to electrical energy, therefore they do not adversely affect the environment [122]. On the other hand there are no moving parts in TE generators which avoid noise pollution. Scandium (Sc) form intermetallic compounds with transition metals TM, (TM= Cu, Ag, Au and Pd). These intermetallic crystallize with the cubic CsCl (B2) structure with space group Pm-3m (Number: 221) [40]. These compounds are also well known for interesting features of strong electron-electron correlation and spin orbit coupling effects [123, 105, 106, 107, 124].

Interesting work is available in the literature on the different physical properties of these materials. Different researchers worked experimentally and theoretically on the structural, electronic, elastic, specific heat and magnetic susceptibilities of ScTM (TM = Ag, Cu, Pd, Rh and Ru) compounds [125, 66, 126, 127, 65, 128, 62, 63]. A comprehensive theoretical investigations of the electronic structure and phonon properties of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) materials is done by Arikan et al. [129] using a density functional theory with (GGA) flavor and investigated the different ground state properties. From the investigation about the materials it is found, all these compounds are metallic in nature. Literature clearly indicates dense

electronic states in these materials at the Fermi levels which is one of the basic physical properties that predict the effectiveness of a material in thermoelectricity. Keeping in view of this important aspect, here in this section we investigate TE properties of ScTM (TM = Cu, Ag, Au and Pd) at room temperature. To the best of our knowledge, study wise this is the first ever attempt made on the TE properties of these materials.

As these compounds have d states, hence the correlation and SOC effects play key role in the physical properties of these compounds. Sasloglu et al. [130] reported that correlation effects decreases and spin-orbit coupling (SOC) effect increases as one moves from 3d to 5d period of the periodic table. SOC effect is considered as a weak relativistic correction in Schrödinger's equation in condensed matter outside high energy physics [101, 102, 103, 104]. Hubsch et al. [131] reported that 3d transition metal based compounds are strongly correlated electron systems due to their high localization nature. Spin-orbit coupling caused non-trivial topological order in transition metal based compounds [123, 105, 106, 107, 124] due to large SOC effect, especially in 4d and 5d. SOC and electron correlation strongly affect the electronic structures of these compounds [131]. The elastic constants of these materials are also calculated, which are further used to calculate mechanical properties such as Young's modulus, Hill shear modulus, anisotropy, Poisson's ratio and Kleinman parameter of these materials.

4.2.2 Structural properties

The structural optimizations are performed using experimental [40] lattice constants of the Scandium transition metal (TM) ScTM (TM = Cu, Ag, Au and Pd) compounds. The physical properties of the transition metal compounds depend on the proper localization of the d-orbital. In 3d-orbitals,

strong Coulomb repulsion exists because of the highly localized nature while there are small repulsion in 4d and 5d because of their slightly delocalized nature [130]. In order to treat such systems, where d-orbitals are participating, the Coulomb repulsion is optimized by optimizing U-value for each compound. The optimization of U for each compound is carried out by adjusting the calculated lattice constants with the experimental values. The optimized U values for each element Cu, Ag, Au and Pd are 0.44, 0.59, 0.07 and 0.22 Ry, respectively, while this U value is kept constant for scandium, i.e., $U=0.15$ Ry. The calculated values of the lattice constants for all the compounds along with other ground state parameters like volume and energy are listed in Table 4.2.1. It is obvious from the table that the estimated lattice constants for ScTM (TM=Cu, Ag, Au and Pd) compounds using the LDA+U method are in accordance with the experimental values, whereas other approximations LDA and LDA+SOC underestimate the lattice constants.

Table 4.2.1 Experimental and calculated structural properties like lattice constant (a_0) in unit ($\text{\AA}$) volume (V_0) in unit (a.u.^3), ground state energy (E_0) in unit (Ry) of ScTM (TM = Cu, Ag, Au and Pd) by LDA, LDA+U and LDA+SOC

Materials	Parameters	LDA	LDA+U	LDA+SOC	Exp.	Others
ScCu	a_0	3.172	3.239	3.169	3.256 ^a	
	V_0	215.491	229.329	214.782		
	E_0	-4830.018	-4833.878	-4830.030		
ScAg	a_0	3.345	3.422	3.3137	3.416 ^a	3.439 ^c
	V_0	252.716	270.459	245.557		
	E_0	-12149.930	-12155.949	-12149.983		
ScAu	a_0	3.324	3.378	3.3136	3.373 ^a	
	V_0	247.934	260.116	245.526		
	E_0	-39599.944	-39611.977	-39600.479		
ScPd	a_0	3.238	3.282	3.237	3.283 ^a	3.206 ^b , 3.329 ^c
	V_0	229.250	238.595	228.869		
	E_0	-11609.813	-11615.770	-11609.852		

^a[40], ^b[63], ^c[65]

4.2.3 Density of states(DOS)

Electronic structure plays key role in defining thermoelectric properties of a material. A dense DOS is required at Fermi level for good TE performance. Total and partial DOS for ScCu in spin-up state, without the effect of SOC and with SOC is depicted in Fig. 4.20. The DOS of other materials are approximately similar to DOS of ScCu. Partial DOS shows that d-states of the material play important role in the electronic structure and consequently other properties of the material. It is clear from Fig. 4.20 that the SOC effect splits the d-state of Sc and Cu into d_{z^2} , d_{xy} , $d_{x^2-y^2}$ and $d_{xz} + d_{yz}$ states. After splitting, the combined effect of density of d-states of Sc increases at the Fermi level. Therefore, it can be seen that DOS at the Fermi level boosts due to the effect of SOC. This means that SOC effects will consequently enhance the thermoelectric properties of these materials. Other materials also show same behavior. The figure also shows that the major participation of the DOS at the Fermi level are due to the d-state of the both elements; crosses the Fermi level, which indicates the material metallic. The same phenomenon is also observed for the rest of the ScTM (TM = Ag, Au and Pd) compounds and similar nature for these compounds are reported in Ref. [129]. Apart from this, Fig.20 also provides information about the dominant contributions of the d-state to the density of states at the Fermi level in ScCu compound that originates from Sc site due to large contribution of d sub-states (d_{xy} , $d_{x^2-y^2}$, $d_{zx} + d_{yz}$) and Cu($d_{x^2-y^2}$).

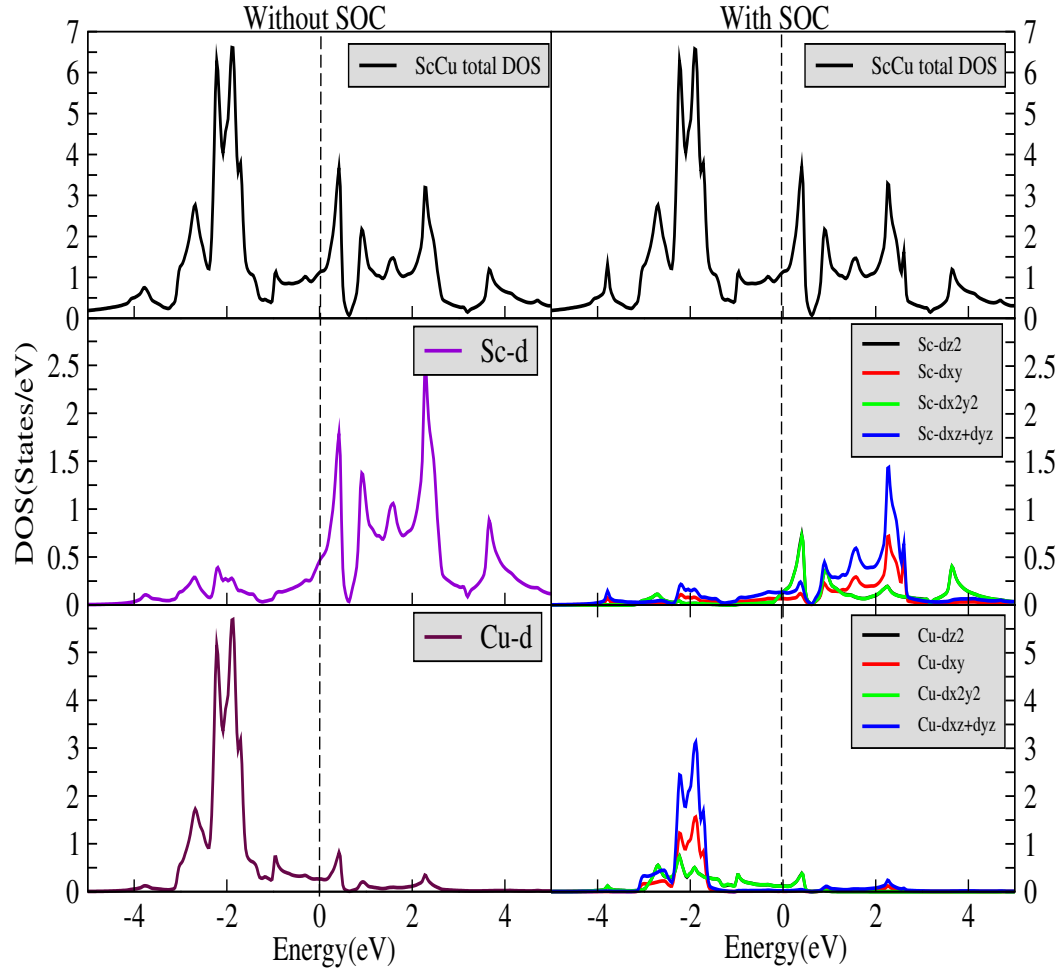


Figure 4.20: The total as well as the partial (DOS) for ScCu without SOC effects and with SOC

4.2.4 Seebeck coefficient

Seebeck effect is referred as the potential difference created between two ends of a material as a result of the temperature gradient. Free charge carriers move from hot to cold environment due to temperature gradient between the ends of a material. For an efficient TE material, we need large values of Seebeck coefficient.

Fig. 4.21 presents curves of Seebeck coefficients for ScCu, ScAg, ScAu and ScPd at 300 K with and without considering SOC effects. ScAg shows the highest value of Seebeck coefficient among these materials. All materials exhibit approximately similar responses with little differences in detail. It is clear from the figure that SOC has large effect on Seebeck coefficient of these materials. SOC effect increases Seebeck coefficients for these materials in both n-type and p-type regions. This is because of the increase in density of states at Fermi level on applying SOC effects. For p-type ScAg, Seebeck coefficient reaches the maximum value of $230\mu V/K$ at -0.05 eV chemical potential. Overall pattern of Seebeck coefficients of these materials show good response in both n-type and p-type regions. The peak values are obtained in the small value of the chemical potential which means these materials will show good thermoelectric properties in this region.

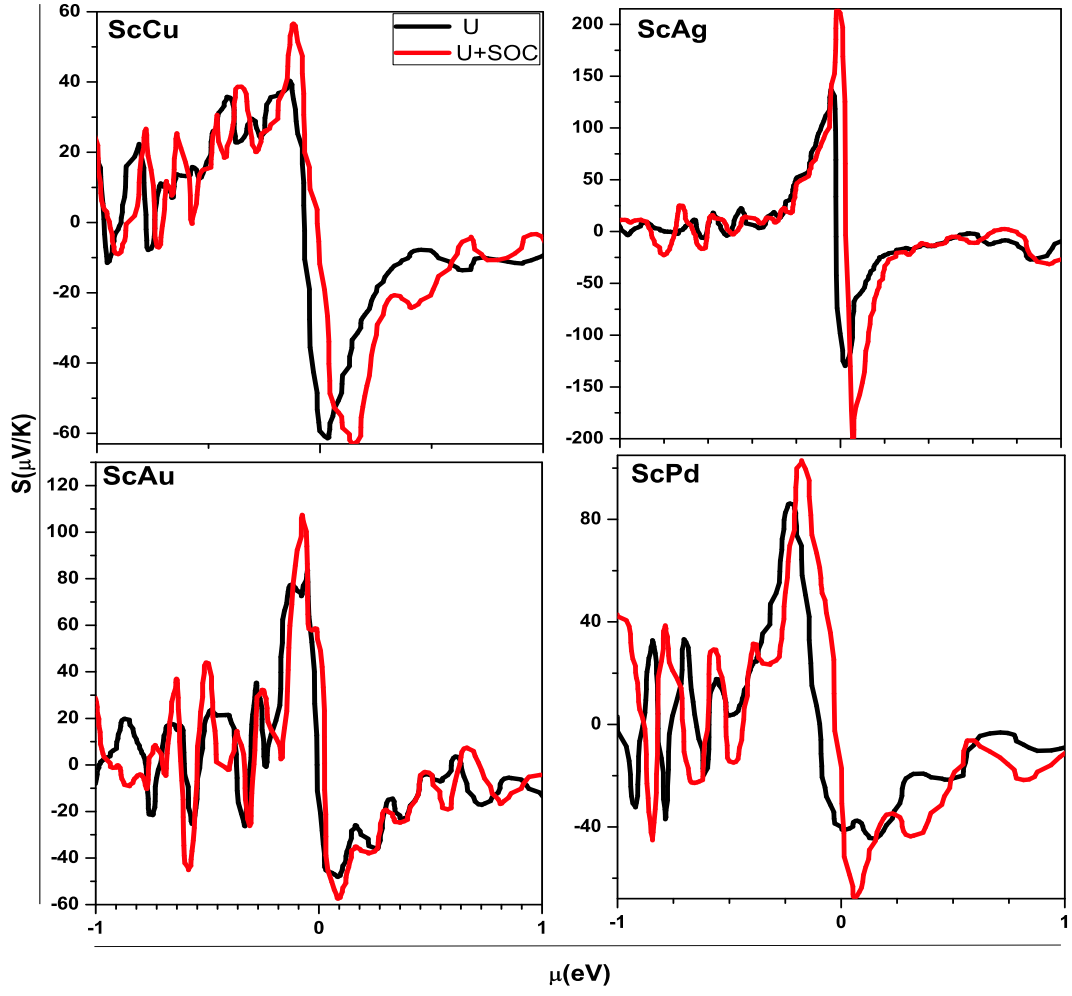


Figure 4.21: Seebeck coefficients for ScTM(TM=Cu, Ag, Au and Pd) at 300K temperature with U and U+SOC.

4.2.5 Electrical conductivity

High values of electrical conductivity materials are required for TE applications. Fig.4.22 presents electrical conductivities, with and without the effects of SOC for ScTM (TM=Cu, Ag, Au and Pd) compounds against chemical potential at 300K temperature. The figure shows that electrical conductivities have smallest values near the zero value of the chemical potential, however the value of electrical conductivity as chemical potential is increased. For good performance of TE device, we need large values of electrical conductance therefore, our calculated results show that ScAu and ScPd have good TE behavior in the limit from -0.25 and 0.25eV as these compounds have non zero values in this region. In case of ScAg and ScCu, electrical conductivity stay at zero in the vicinity of -0.25 and 0.25 eV chemical potential. Highest value of electrical conductivity is achieved for ScPd which reaches to approximately $13 \times 10^{20}/\Omega s$ in p-type region. Furthermore, we can see that all these materials show better response in p-type region as compared to n-type region.

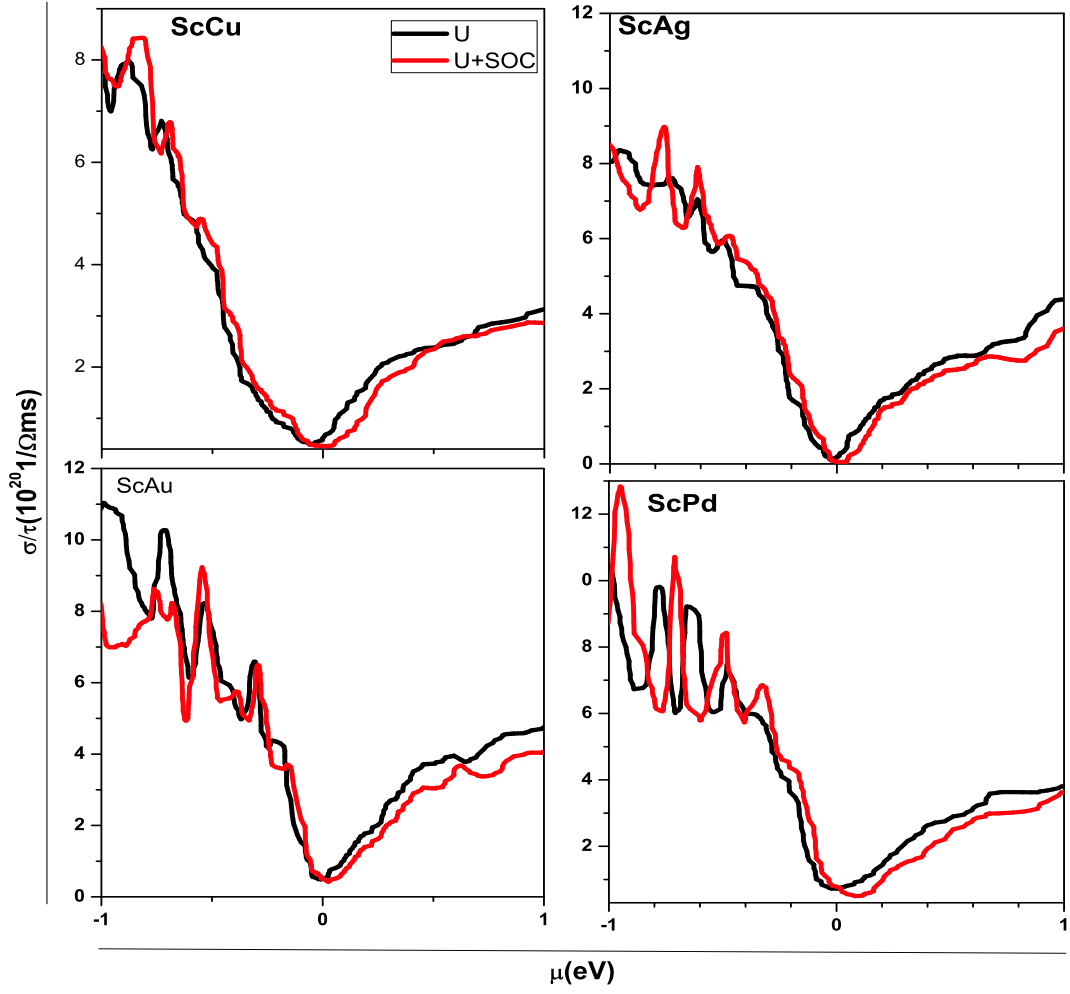


Figure 4.22: Electrical conductivities for ScTM(TM=Cu, Ag, Au and Pd) compounds at 300K temperature as a function of chemical potential with U and U+SOC.

4.2.6 Power factor

The power factor ($PF = S^2\sigma$) shows the efficiency of a thermoelectric material, where S is the Seebeck coefficient and σ is the electrical conductivity of a material. It is clear from Power factor that we need good results of Seebeck coefficient and electrical conductivity for better TE performance. Fig.4.23 presents power factor, with and without the effects of SOC, for ScTM (TM=Cu, Ag, Au and Pd) compounds against chemical potential at 300K temperature. The figure shows that power factor increases with the effects of spin orbit coupling.

ScAu has the large values of power factor. While comparing to other materials under consideration and at room temperature it reaches to $200 \times 10^2 W/cmK^2s$ at 0.2eV chemical potential, considering the effects of SOC. This is because this material has high values of both Seebeck coefficient and electrical conductivity in this region. As the Seebeck coefficient shows good performance in the small value of chemical potential from -0.25 to 0.25 eV, for the reason the peak values of power factor in this region for all materials. Furthermore, we can see that all these materials show good TE response in n-type as well as in p-type regions.

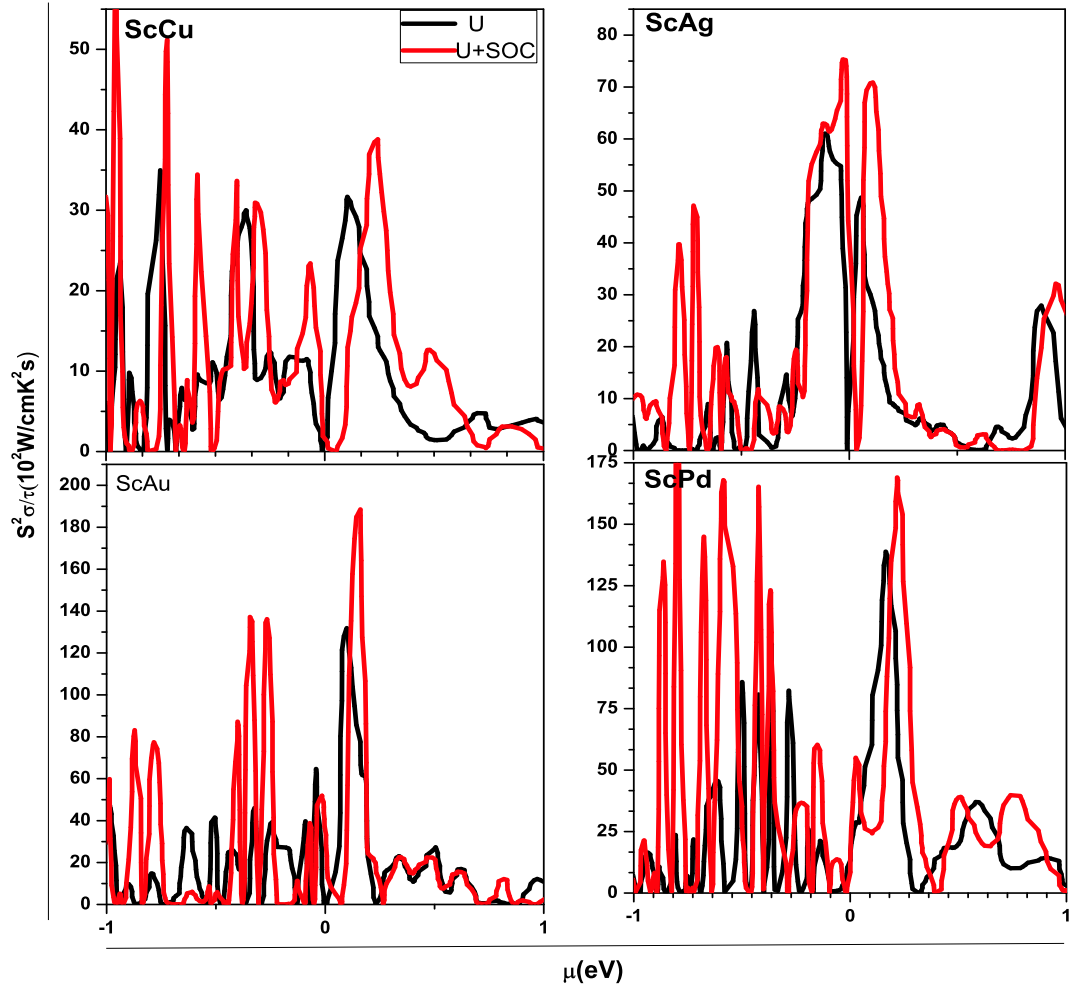


Figure 4.23: Power Factor for ScTM(TM=Cu, Ag, Au and Pd) compounds at 300K temperature as a function of chemical potential with U and U+SOC.

4.2.7 Mechanical Properties

The elastic constants (C_{11} , C_{12} and C_{44}) for ScTM (TM = Cu, Ag, Au and Pd) compounds are calculated and compared with the available results. Table 4.2.2 shows that all these compounds are mechanically stable under the stability criteria, i.e., $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{44} > 0$ [132, 133]. Our results for ScPd are in close agreement with the experimental results [40].

The mechanical properties of these compounds like bulk modulus (B), Young's Modulus (Y), shear modulus (G_H), anisotropy (A) and Poisson's ratio (ν) are evaluated from the calculated elastic constants for each compound. The calculated values of modulus for the compounds under study are listed in Table 4.2.3.

It is clear from the table that ScAu has the largest value of shear modulus (52.77 GPa) among all these compounds which shows that this compound is the most hard material in these compounds. The smallest value of shear modulus is for ScAg (40.78 GPa) show that this material has small resistance to deformation.

Young's modulus shows the stiffness of a material [134]. The calculated values of Young's modulus are presented in Table 4.2.3. From the results in the table that ScAu has the largest Young's modulus (138.75 GPa) than other compounds hence ScAu has highest stiffness among these compounds. The higher values of Young's modulus as compared to shear modulus further elaborates the stiffness of these materials.

The ductile nature of a material is very important from engineering point of view and can be determined by B/G ratio. For ductile materials, B/G is greater than 1.75 and for brittle behavior of the materials, B/G ratio is less than 1.75 [135]. Table 4.2.3 presents calculated B/G values for ScTM (TM=Cu, Ag, Au and Pd) compounds. The table shows that all compounds

under investigation are ductile. It can be noted from the table that among all ductile compounds ScPd has the largest value of the B/G ratio (2.48 GPa) and hence reveals the highest value of ductility.

Cauchy's pressure C'' is another parameter to describe the ductile/brittle behavior of a material. The positive value of Cauchy's pressure shows ductile nature and the negative value indicates the brittle behavior of a material [132]. It is clear from Table 4.2.3 that the values of Cauchy's pressure are positive for all these materials which further confirm the ductile nature of all these compounds. The Cauchy's pressure gives us bonding nature of a material [133]. The values of Cauchy's pressure presented in Table 4.2.3 indicate that metallic bond nature is dominant in these materials.

Poisson's ratio is another important parameter that maybe used to explain various mechanical properties specifically the incompressibility of a material. The typical value of Poisson's ratio lies between 0 and 0.5. Incompressibility increases as one moves from 0 to 0.5 [136]. The Poisson's ratio values are tabulated in Table 4.2.3. It is clear from the table that Poisson's ratios for all these materials fall within the above limit, hence these compounds are less compressible against deformation. Furthermore, this ratio is also used to determine the nature of inter-atomic forces. The typical range of Poisson's ratio for central forces is 0.25 to 0.5 [137]. The calculated values of the Poisson's ratio indicate that the dominant inter-atomic forces for these compounds are central forces.

The anisotropy (A) is a parameter, which shows whether the structural properties of a material remain same in all directions, or not. For isotropic medium $A = 1$ and if $A \neq 1$ then the medium will be anisotropic. The calculated anisotropic ratios for all these compounds are listed in Table 4.2.3. The table shows that for all these materials the anisotropic ratio deviates from

Table 4.2.2 Calculated values of elastic constants in unit GPa of ScTM (TM=Cu, Ag, Au and Pd)

Compounds		C_{11}	C_{12}	C_{44}
ScCu	Present	184.370	114.050	64.090
	Other ^b	130.869	70.215	52.425
ScAg	Present	116.900	73.370	62.040
	Other ^b	105.469	68.091	51.307
ScAu	Present	172.630	100.920	68.380
ScPd	Present	169.640	80.650	44.340
	Exp ^a	173.100	106.600	45.500
	Other ^b	151.070	90.850	49.130

^a[62], ^b[64]

unity which means their properties vary in different directions; hence these compounds are anisotropic except ScPd, which has the value approximately equal to one. This shows that this material is nearly isotropic material.

The internal strain of a material is estimated from the Kleinman parameter (ζ). This parameter describes the bond bending and bond stretching. The lower limit ($\zeta = 0$) and upper limit ($\zeta = 1$) corresponds to bond bending and bond stretching, respectively. The calculated values of this parameter for the compounds are listed in Table 4.2.3. The table shows that in all these compounds the bond stretching is dominant than bond bending.

The ratio of bulk modulus to C_{44} (B/C_{44}) may be used to estimate the plasticity of a material [138]. Table 4.2.3 presents B/C_{44} values for these materials. It is clear from the table that B/C_{44} ratio is highest for ScPd (2.48GPa) and lowest for ScAg (1.41 GPa). The largest value of B/C_{44} for ScPd (2.48 GPa) indicates the highest degree of plasticity.

Table 4.2.3 The calculated values of Voigt's bulk modulus B , Young's modulus Y , Shear modulus G , B/G ratio, Cauchy Pressure (C''), Poisson's ratio (ν), Anisotropy constant (A), Kleinman Parameter (ζ) and B/C_{44} .

Comp.	B	Y	G	B/G	C''	V	A	ζ	B/C_{44}
ScCu	137.48	134.66	50.37	2.73	49.95	0.34	1.8	0.99	2.14
ScAg	87.88	105.97	40.78	2.15	11.33	0.29	2.85	0.99	1.41
ScAu	124.82	138.75	52.77	2.36	32.54	0.31	1.90	0.97	1.82
ScPd	110.3	117.5	44.4	2.48	36.31	0.32	0.99	0.79	2.48

4.3 Elastic and Mechanical Properties of Binary Intermetallic LnTM in CsCl-Structure

4.3.1 Introduction

Intermetallic compounds, especially combination of transition metal and lanthanide, have attracted great attention in modern condensed matter physics, for their rich physics and chemistry, as well as extensive high-tech applications in advanced technologies [139, 140, 141]. The f-state electrons in these compounds have unique features and interestingly their properties vary from element to element as we move from left to right in the lanthanide series in periodic table. The f-state is weakly localized in Ce, Pr, Nd and Sm, while strongly localized in the rest of lanthanides [142].

Like lanthanides, transition metal (TM) compounds have also interesting features of strong electron-electron correlation effects and spin orbit coupling. TM compounds with 3d are well known for their strong electron-electron correlation effects; whereas the spin-orbit coupling (SOC) effect increases if one proceeds from compounds with 3d to 4d to 5d. Though, SOC effect

is negligible in 3d TM compounds but has attracted serious attention of researchers in the modern condensed matter physics and solid state chemistry in 4d and 5d compounds, although it was considered a weak relativistic correction to Schrodinger equation outside high energy physics [101, 102, 103, 104]. Lanthanide-transition metal compounds are strongly correlated, which have high correlation effects and due to this the electronic states interaction with each other is very strong. [26, 27]. This affects the characterization of the accurate physical properties of these compounds and become challenging for scientists.

One of the families of these challenging compounds is LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir). The valence state of lanthanide elements play key role in the phase stability of these compounds, where the size of LnTM decreases gradually from left to right (Ce to Lu) except Eu and Yb where this unusual behavior of these two compounds is due to their divalent (R^{+2}) nature and the other have trivalent nature [143].

CsCl-type LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds have been investigated experimentally using different experimental techniques. The lattice parameters of EuCd and GdCd are measured by Indelli and Palenzona [144] using X-ray powder diffraction method. They also measured the electrical resistivity (ρ), temperature derivative of electrical resistivity ($d\rho/dT$), thermoelectric power and temperature derivative of thermoelectric power (dq/dT) of these compounds. They confirmed the ferromagnetic nature of GdCd below room temperature. The geometric structures, type of magnetic order, electrical resistivity and temperature-dependent thermoelectric power of TbZn and TbCu are reported in earlier works [145, 146]. Meenakshi et al. [48] reported that the stable crystal structure of ErCu upto 23.6 GPa is CsCl-structure, whereas Gefen et al. [51]

studied the temperature dependent elastic moduli of this compound in the temperature range 77 K to 300 K. Yoshiuchi et al. [147] revealed the strong localization of 4f-electrons in CeCd and PrCd compounds. They also confirmed the anti-ferromagnetic (AFM) behavior of these compounds at low temperatures. The ductile nature of LnTM compounds (Ln = Ce, Nd, Dy, Ho, Er, and TM = Cu, Ag) at low temperatures is reported by Gschneidner et al. [141] and Takasugi et al. [148]. Single crystal diffraction technique confirms the CsCl-structure of GdRh compound [149]. The thermal expansion measurements for HoCu and DyCu are reported by Ibarra et al. [149] and Amara et al. [150]. They found antiferromagnetic order in these compounds. The electronic properties of YCu and GdCu are investigated by Chaboy and Ibarra [151] using x-ray absorption spectroscopy and they found metallic nature of these compounds.

The detailed literature review on these LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds reveals that just like experimental studies, limited theoretical works are available on these compounds, and hence they need extensive theoretical investigations. Makode et al also carried out first principle studies about the properties of binary compounds LnAg [152]. Yaojun et al. [153] investigated the structural, mechanical, electronic and thermal properties of CeAg compound using density functional theory. The mechanical properties and bonding features of YAg, CeAg, HoCu, LaAg, LaZn, LaMg compounds are investigated by Sekkal et al. [154] using density functional theory. Spin polarized mechanical and magnetic properties of TmX (X = Cu, Ag) compounds are carried out by Chand et al. [44] using first principle calculations. Devi et al. [155] studied Cd and Hg base rare-earth compounds LnCd and LnHg (Ln = Sc, La and Yb) using full-potential linearized augmented plane-waves (FP-LAPW) method. The

structural, electronic and elastic properties of TbCu and TbZn compounds are carried out by Singh et al. [53] and LnHg (Ln = Ce, Pr, Eu, and Gd) compounds by Devi et al. [156] using density functional theory approach.

Intermetallic LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds have interesting physical and chemical properties as well as extensive applications in the high-tech devices and hence need extensive theoretical studies. In this section various physical properties such as structural, elastic and mechanical properties of these compounds are theoretically investigated using density functional theory.

4.3.2 Structural Properties and Mechanical properties

The calculations of the lattice constants of the compounds under study are essential for the determination of their elastic constants and other mechanical properties. The structural optimizations of LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) compounds are performed using experimental lattice constants [40] by GGA and GGA+U. Hubbard parameter U is optimized for each compound by comparing the calculated lattice constants with the experimental lattice constants. A list of calculated lattice constants for all the compounds under study is depicted in Table 4.3.1.

Table 4.3.1

Calculated lattice constants (in Å) of LnTM compounds (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and TM = Cu, Zn, Rh, Pd, Ag, Cd, Ir, Hg) with GGA and GGA+U.

Comp.	R→	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RCu	GGA	3.473	3.404	3.403	3.401		3.375		3.329
	GGA+U	3.503	3.480	3.488	3.470		3.422		3.360
	Exp.	3.503	3.479	3.461	3.447		3.415		3.390
RZn	Present	3.525	3.498		3.506				
	GGA+U	3.619	3.610		3.587				
	Exp.	3.601	3.576		3.546				
RRh	Present					3.334		3.322	3.302
	GGA+U					3.377		3.335	3.319
	Exp.					3.372		3.347	3.332
RPd	Present			3.446		3.425	3.422	3.409	3.385
	GGA+U			3.492		3.485	3.442	3.482	3.470
	Exp.			3.486		3.458	3.440	3.447	3.417
RAg	Present	3.601	3.583	3.573	3.578		3.510		3.492
	GGA+U	3.659	3.635	3.620	3.601		3.580		3.560
	Exp.	3.650	3.625	3.608	3.593		3.562		3.541
RIr	Present				3.340	3.335		3.319	3.305
	GGA+U				3.391	3.360		3.341	3.323
	Exp.				3.383	3.352		3.346	3.332

The comparison of the calculated values to the experiments shows close resemblance [40]. These calculated structural parameters are then used as input parameters for the calculation of the elastic constants. The structural stability, hardness, bonding nature, elastic anisotropy, compressibility and internal strain properties of a material can be determined through the three independent elastic constants i.e., C_{11} , C_{12} and C_{44} .

The independent elastic constants, C_{11} , C_{12} and C_{44} , for the compounds under study are calculated and presented in Table 4.3.2. However, to check the reliability and effectiveness of our theoretical model, we have also calculated the elastic constants of the theoretically and experimentally known compounds GdCu, TbCu, DyCu, HoCu, TmCu, GdZn, TbZn, HoZn and TmAg. The comparison of our calculated lattice constants with the other available theoretical results in literature and with the experimental results confirms the accuracy/effectiveness of our theoretical approach used for the calculations of the lattice constants in the present work. From these results we infer that our results for LnTM (Ln= Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), (TM= Rh, Pd, Ag, Ir) compounds will be also consistent with the experimental values, which are to the best of our knowledge missing in the literature. Hence, this data will fill the gap in literature for the elastic constants of these compounds and their other mechanical properties. So, this data will fill the gap as well as provide platform for future studies of these compounds. The table also indicates that all the compounds under study qualify the stability criteria, $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{44} > 0$ [71, 158], and hence are mechanically stable.

The mechanical properties of these compounds like bulk modulus (B_0), Young's Modulus (Y), shear modulus (G_H), anisotropic ratio (A) and poisson's ratio (ν) are evaluated from these three independent elastic constants

for each compound for their technological applications. The calculated values of shear modulus for the compounds under study are listed in Table 4.3.2. It is clear from the table that among all these compounds, YbPd has the largest values of shear modulus (49.12 GPa), indicates that this compound is the hardest of all of these compounds. The smallest value of shear modulus is observed for DyPd, shows small resistance to deformation.

The Young's modulus tells about the stiffness of a material. The high value of Young's modulus reveals stiffer material [134]. The calculated values for this key mechanical parameter for compounds are depicted in Table 4.3.3. The data presented in the table shows that LuIr has the largest Young's modulus among all these compounds and hence it is the stiffest of all.

The ductile nature of a material is very important from the engineering point of view and can be determined by using the B_0/G ratio suggested by Pugh [135]. The critical value for the B_0/G ratio is 1.75, i.e. for ductile materials, this ratio is greater than 1.75 and for brittle materials it is lesser than 1.75. The values of this ratio for all the materials under study are presented in Table 4.3.3, which confirm that the compounds under investigations are all ductile in nature. It can be noted from the table that among all these compounds DyPd has the largest value of the B_0/G ratio (6.44 GPa) and hence has the highest value of ductility.

The Cauchy's pressure (C'') is another parameter to describe the ductile/brittle behavior of a material. It is clear from Table 4.3.2, that Cauchy's pressure values are positive for all these materials, which further confirm the ductile nature of the compounds under study. The Cauchy's pressure is also used to describe the bonding character in a material [133]. The positive value of Cauchy's pressure corresponds to metallic bonding while the negative Cauchy pressure attributes to directional bonding or covalent bonding.

The positive values indicate that the bonding nature in these compounds is metallic.

Poisson's ratio is a very important parameter and maybe used to explain various mechanical properties specifically the incompressible nature of a material. The typical value of Poisson's ratio lies between -1 and 0.5. The results for the Poisson's ratio are tabulated in the Table 4.3.3. It is clear from the table that Poisson's ratio for all these materials fall within the above range, hence these compounds are stable and incompressible against deformation. Furthermore, this ratio is also used to determine the nature of inter-atomic forces. It is well known that the typical range for Poisson's ratio is dealing with central forces is in the range from 0.25 to 0.5 [137]. The calculated values of the Poisson's ratio indicate that the dominant inter-atomic forces in these compounds are central forces.

The anisotropic ratio (A) gives us the information about measure of elastic anisotropy in a material. For isotropic medium $A = 1$ and if $A \neq 1$ then the medium will be anisotropic. The calculated anisotropic ratio for the compounds are listed in Table 4.3.3. The table shows that for all these materials response anisotropic ratio deviate from unity, hence these compounds are elastically anisotropic and the properties are different in different directions.

The internal strain of a material is estimated from the Kleinman's parameter (ζ). This parameter describes the bond bending and bond stretching. The lower limit ($\zeta = 0$) and upper limit ($\zeta = 1$) corresponds to bond bending and bond stretching respectively. The calculated values of this parameter for the compounds are listed in Table 4.3.3. The calculated values in the table predict that in these compounds the bond stretching is dominant than bond bending.

The ratio (B_0/C_{44}) is used to measure the plasticity of a given substance

[138]. This ratio for all the materials under study are listed in Table 4.3.3. The largest value of B_0/C_{44} for DyPd (7.94 GPa) among all the compounds indicates the highest degree of plasticity. However, the smallest value for ErIr (0.56) indicates the lowest value of plasticity. The rest of materials lie in the range of 0.56 to 7.94. This means that DyPd contains delocalized bonds and ErIr has localized bonds.

Longitudinal (v_l), transverse (v_t) and average (v_m) sound velocities as well as Debye temperature (θ_D) for these intermetallic compounds LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) are also evaluated from the calculated elastic constant using standard relations [132]. The calculated values for these parameters are listed in Table 4.3.4. Debye temperature is important thermodynamic parameter and different related physical properties can be estimated from this parameter. No experimental and theoretical data is available for the comparison of these quantities. It is evident from the table that LuRh has the largest value of Debye temperature among all the compounds under study and exhibits highest thermal conductivity.

Table 4.3.2 Present (Pre), Other (Oth) and experimental (Exp) values of elastic constants C_{11} , C_{12} , C_{44} in GPa for LnTM compounds.

Comp.	R→	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RCu	C_{11}	115.17	110.26	98.27	111.01		128.36		
	Exp.						98.00 ^{c*} (125.40) ^{d*}		
	Oth.	108.29 ^a	122.81 ^c	122.61 ^b	124.19 ^b		107.2 ^c (131.27) ^d		
	C_{12}	53.71	55.99	50.32	56.08		56.81		
	Exp						69.50 ^{c*} (51.00) ^{d*}		
	Oth	35.17 ^a	51.34 ^c	52.08 ^b	55.36 ^b		61.80 ^c (55.01) ^d		
	C_{44}	35.95	40.45	35.86	44.78		44.69		
	Exp	26.50 ^{a*}		38.00 ^b (44.00) ^b			43.80 ^{c*} (39.40) ^{d*}		
RZn	Oth	30.85 ^a	32.37 ^c	33.91 ^b	36.58 ^b		35.95 ^c (42.80) ^d		
	C_{11}	87.14	51.44		112.49				
	Exp								
	Oth	113.23 ^a	82.39 ^g		87.97 ^b				
	C_{12}	47.49	32.58		52.57				
	Exp								
	Oth	37.32 ^a	30.75 ^g		43.73 ^b				
	C_{44}	47.31	21.88		52.42				
RRh	Exp	37.60			47.30				
	Oth	38.83 ^a	26.37 ^g		39.58 ^b				
	C_{11}					127.94		113.94	184.76
	C_{12}					53.69		48.95	54.85
RPd	C_{44}					32.73		26.15	44.38
	C_{11}			99.70	97.59	108.92	84.53	109.45	146.51
	C_{12}			45.20	35.89	41.86	45.47	36.66	48.78
	C_{44}			15.65	34.54	28.46	28.15	35.49	36.61
RAg	C_{11}	83.12	83.36	65.23	63.68		118.39		76.20
	Exp						110.63 ^d		
	Oth						123.23 ^d		
	C_{12}	36.13	21.99	43.05	32.58		72.29		32.07
	Exp						60.63 ^d		
	Oth						69.34 ^d		
	C_{44}	30.66	14.39	34.26	28.55		40.38		31.38
	Exp						39.00 ^d		
RIr	Oth						40.24 ^d		
	C_{11}				133.84	143.01	109.66	111.96	182.98
	C_{12}				71.62	85.09	89.61	77.55	85.99
	C_{44}				42.29	84.08	25.78	48.07	63.69

^a[159], ^b[49], ^c[53], ^d[44], ^f[156]

Table 4.3.3

The calculated values of bulk modulus (B_0), Young's modulus, Shear modulus (G), B_0/G ratio, Cauchy's pressure (C''), Poisson's ratio (ν), Anisotropy constant (A), Kleinman's parameter (ζ) and B_0/C_{44} .

Comp.	B_0	Y	G	B_0/G	C''	ν	A	ζ	B_0/C_{44}
ErRh	122.25	90.23	24.23	5.04	20.96	0.30	0.88	0.70	3.74
YbRh	141.36	75.79	30.04	4.70	22.80	0.32	0.80	0.72	5.41
LuRh	124.88	131.95	29.34	4.25	10.47	0.27	0.68	0.52	2.81
DyPd	124.29	53.24	19.28	6.44	29.55	0.35	0.57	0.76	7.94
HoPd	119.13	82.99	26.03	4.57	1.35	0.25	1.11	0.63	3.44
ErPd	121.19	78.96	31.05	3.90	13.40	0.29	0.84	0.65	4.26
TmPd	126.17	64.96	35.58	3.54	17.32	0.31	1.44	0.89	4.48
YbPd	142.51	89.91	49.12	2.90	1.17	0.25	0.97	0.58	4.02
LuPd	94.22	106.43	30.13	3.12	12.17	0.28	0.74	0.57	2.57
GdAg	89.82	70.72	38.36	2.34	5.47	0.27	1.30	0.73	2.93
TbAg	87.14	50.93	33.01	2.63	7.60	0.30	0.46	0.48	6.06
DyAg	89.11	57.22	37.80	2.35	8.79	0.31	3.08	1.10	2.60
HoAg	84.26	57.17	32.81	2.56	4.03	0.27	1.83	0.85	2.95
LuAg	126.73	68.45	36.65	3.45	0.69	0.25	1.42	0.70	4.04
Holr	90.66	98.85	38.97	2.32	29.33	0.32	1.35	0.89	2.64
ErIr	111.77	140.10	33.40	3.35	1.01	0.28	2.90	0.99	0.56
TmIr	46.79	49.91	23.46	1.99	63.83	0.41	2.57	1.40	2.36
YbIr	60.80	85.38	24.26	2.50	29.48	0.34	2.79	1.16	0.87
LuIr	41.70	147.57	23.74	1.76	22.30	0.29	1.31	0.78	1.75

Table 4.3.4

The calculated values of density ρ (g/cm³), sound velocity of transverse wave v_t (m/s), sound velocity of longitudinal waves v_l (m/s), average velocity v_m (m/s) and Debye temperature $\theta(D)$ (K) of compounds.

Comp.	ρ	v_t	v_l	v_m	$\theta(D)$
ErRh	12.10	1686.37	3204.92	1885.69	212.15
YbRh	12.49	1510.81	2948.41	1692.32	191.08
LuRh	12.81	2008.66	3610.84	2236.92	254.11
DyPd	10.91	1339.12	2862.96	1507.62	164.12
HoPd	11.01	1723.82	3007.3	1914.96	209.06
ErPd	11.31	1639.2	3043.08	1829.94	200.41
TmPd	11.41	1459.69	2822.65	1634.1	179.12
YbPd	11.71	1749.7	3047.09	1943.42	213.82
LuPd	12.04	1847.23	3362.04	2059.13	228.17
GdAg	9.42	1709.64	3064.41	1903.48	198.27
TbAg	9.62	1426.28	1593.13	1593.13	166.77
DyAg	9.84	1488.73	2842.01	1665.2	174.84
HoAg	9.88	1503.96	2712.6	1675.3	175.63
LuAg	11.02	1571.37	2744.35	1745.77	187.55
HoIr	15.91	1532.76	2989.01	1716.82	192.81
ErIr	16.08	1846.95	3322.18	2056.93	231.33
TmIr	16.40	1037.46	2702.95	1176.61	132.97
YbIr	16.58	1385.8	2815.02	1556.02	175.85
LuIr	16.90	1838.14	3392.01	2051.12	232.84

Chapter 5

Conclusions

In this thesis first principle calculations are carried out to understand the correlation and spin orbit coupling effects in lanthanide transition metal intermetallic compounds. Different theoretical schemes are used for calculations like LDA, LDA+U and LDA+SOC, where LDA+U produced the best results as compared to the available experimental results. The Hubbard potential U was optimized for each compound and U/W ratio was evaluated to determine correlation strength for each compound. Based on our results, it is concluded that ScTM (TM= Co, Ir, Pd, Pt, Cu, Ag) compounds are highly correlated systems, whereas ScTM (TM = Rh, Ni, Au) are intermediate correlated compounds. SOC effects are also evaluated and discussed in all materials. The calculated density of state shows metallic behavior of these compounds. Metallic behavior is attributed to either d-state of scandium or TM elements. The stable magnetic phase of these compounds is also determined. It is concluded that ScCo, ScRh, ScPd, ScPt and ScCu are ferromagnetic and ScIr, ScNi, ScAu are anti-ferromagnetic, whereas ScAg is a non-magnetic material. We have also investigated the structural, electronic, thermoelectric and mechanical properties of ScTM (TM=Cu, Ag, Au

and Pd) intermetallic compounds. Our calculated results for structural and elastic properties are consistent with the available experimental results. Seebeck coefficient for ScAg gives the highest value of $230 \mu\text{V/K}$ among these materials. Power factor of $200 \times 10^2 \text{W/cmK}^2$ is achieved for ScAu material. The obtained results for elastic constants fulfil the mechanical stability criteria these compounds and hence they are mechanically stable. The B/G ratio concludes that these compounds are ductile. The positive Cauchy's pressure and Poisson's ratio ($\nu < 0.35$) further confirm the ductility of these compounds. The deviation of anisotropy constant from unity concludes the anisotropic nature of these compounds except ScPd whose value is approximately equal to one. The greater value of B/C_{44} concludes the highest degree of plasticity in ScPd as compared to other materials ScTM. The calculated structural, mechanical and thermal properties of the LnTM (Ln= Dy, Ho, Gd, Yb, Lu, Tb, Er, Tm and TM= Pd, Ag, Rh, Ir) intermetallic compounds confirm consistency with the available experimental data. The calculated elastic constants obey the necessary mechanical stability criteria suggesting that all these compounds are mechanically stable. The calculated mechanical properties for these compounds using elastic constants i.e; B_0/G ratio concludes that these compounds are ductile in nature. The positive Cauchy's pressure C'' and Poisson's ratio ($\nu < 0.35$) further confirm the ductility of these compounds. The deviation of anisotropy constant from unity reveals the anisotropic nature of these compounds. The greater value of B_0/C_{44} confirm the highest degree of plasticity in DyPd as compared to other materials LnTM.

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