

Theoretical studies of strongly correlated lanthanide intermetallics LnX_3 ($\text{X}=\text{In}, \text{Sn}$)



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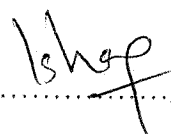
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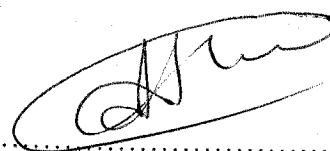
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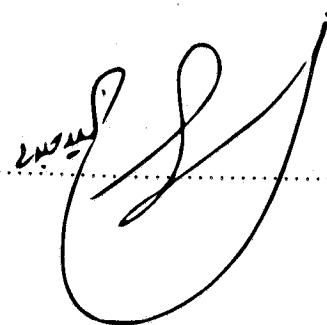
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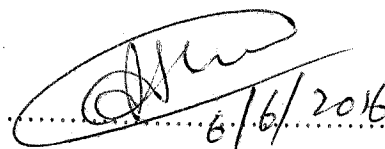
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Abstract

In this thesis the structural, elastic and electronic properties as well as electric field gradient of the strongly correlated intermetallics LnX_3 ($\text{Ln} = \text{La-Gd}$, $\text{X} = \text{In, Sn}$) have been investigated by using the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method within the framework of density functional theory. The structural properties of these compounds are calculated by LDA, GGA, meta-GGA, WC, B3PW91, LDA+U and GGA+U schemes. The calculated lattice parameters are found consistent with the available experimental results. Our results show contraction of lattice constant along the series and the divalent state of Eu is also verified. The itinerant and localized behavior of electrons in f -states of these compounds is also discussed.

These compounds have $4f$ orbitals and hence strong electron-electron correlation effect is expected, therefore, the electronic properties are also calculated with the Hubbard potential U (GGA + U and LDA + U) and the effect of Hubbard potential on the density of states is discussed in details. The relativistic effects are also considered by including the spin-orbit coupling (SOC). The spin-orbit coupling predict the correct electronic properties and also reveals the splitting of $4f$ states of the rare-earth elements. It affects the band structures of the compounds and induces non-degeneracies in some degenerate states in the vicinity of the Fermi level. Furthermore, the SOC effect increases from left to right in the lanthanide series in the LnIn_3 and LnSn_3 , which shows interesting nature of SOC effect in the periodic table.

The elastic constants of these compounds are also calculated. Our calculated values for the elastic constants of the compounds are closer with the available experimental values as compared to the other theoretical results. The mechanical properties for the compounds under studies such as shear

modulus, bulk modulus, Young's modulus, Kleinman parameters, anisotropic ratio, Poisson's ratio, Lamé's coefficients are also determined . The Cauchy pressure and B/G ratio are also investigated to evaluate the ductile and brittle nature of LnIn_3 and LnSn_3 compounds. The Sound velocities for shear and longitudinal waves, and Debye temperature also explored on the basis of mechanical properties.

The Electric field gradients (EFG) are also calculated for the rare-earth intermetallics LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr and Nd}$) using the GGA, GGA + U, as well as GGA + SOC. Our results show that the EFGs calculated by GGA+U approach are in better agreement with the available experimental values of the Mössbauer spectroscopy as compared to the other theoretical schemes. Our results show nonzero EFGs at rare-earth sites in the AFM phase. The present research will add some theoretical understanding of these materials and will also fill the gap about some of the physical properties of these compounds in literature.

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MUHAMMAD SHAFIQ

Dedicated
To
My Family

List of publications

This thesis consists the following published and under-review articles

1. M. Shafiq, Iftikhar Ahmad, and S. Jalali Asadabadi, “Theoretical studies of strongly correlated rare-earth intermetallics RIn_3 and RSn_3 ($R = Sm, Eu, \text{ and } Gd$)” *Journal of Applied Physics*, 116, 103905 (**2014**).
2. M. Shafiq, Iftikhar Ahmad and S. Jalali-Asadabadi, “Mechanical properties and variation in SOC going from La to Nd in intermetallic RIn_3 and RSn_3 ($R = La, Ce, Pr, Nd$)” *Royal Society of Chemistry Advances*, 5, 39416-39423 (**2015**).
3. M. Shafiq, Iftikhar Ahmad and S. Jalali-Asadabadi, “EFG analysis of $LnIn_3$ and $LnSn_3$ ($Ln = La, Ce, Pr, Nd$) compounds” (Submitted).
4. M. Shafiq, Iftikhar Ahmad and S. Jalali-Asadabadi, “Rare-earth intermetallics $LnIn_3$ and $LnSn_3$ ” (Review Article, Submitted).

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Chapter 1

Introduction

Strongly correlated electron systems are attractive materials in condensed matter physics for their extensive applications in various technologies and interesting physics. The strong electron-electron correlation effect in some materials is very important and it play a basic role in the striking feature of the magnetic, electronic, optical and mechanical properties of these materials [1, 2]. Some of the exotic properties of the strongly correlated electron systems are high temperature superconductivity [3], colossal magnetoresistance effect (CMR) [4], magnetocaloric effect [5], metal-insulator-transitions [6], multiferroicity [7] and negative thermal expansion [8].

The strongly correlated electron systems are extremely sensitive to small changes in external parameters, i.e. composition, pressure, temperature and stress [9]. It is very difficult to understand and explain strongly correlated electron systems and the phenomena associated with strong correlations completely. This is due to the fact that various strongly correlated materials offer challenging degree of freedom for technologically importance and practical applications.

Among the various intermetallic materials under the title of strongly cor-

related systems, the f -block elements ($4f$ -lanthanides also refers as rare-earth elements) and compounds are more attractive and interesting due to the f -electrons. In lanthanides and lanthanides based compounds the effect of one electron on the other is very strong [10]. The different occupancy of f -electrons in the orbitals is responsible for the remarkable physical properties of these compounds [11, 12]. The physical properties of f -electron based intermetallics also depend on the hybridization of f -state with other orbitals.

The role of f -electrons on f -based lanthanide intermetallics may be revealed by knowing the localized and itinerant behavior of f -electrons. The physical properties of these materials are mainly dependent on the localized and itinerant nature of f -electron state. The compounds with itinerant f -electrons show high bulk modulus, complex anisotropic properties and low symmetry stable crystal structure, however materials with localized f -electrons exhibit low bulk modulus, local magnetic moments and high symmetry stable crystal structure [13, 14].

The lanthanides (Ln) or rare-earth elements with group IIIA and IVA have been found in different compositions like LnX , LnX_2 and LnX_3 , where LnX and LnX_2 type compounds exhibit a series of phase transition with pressure [15]. LnX_3 compounds crystallize in different crystal structures with different atomic coordination and bond-length values and due to these reasons the rare-earth intermetallics LnX_3 show exceptional physical properties in various practical applications [16]. The LnX_3 compounds show a large range of structural stability at high pressures and temperatures [11].

Rare-earth tri-indium LnIn_3 and rare-earth tristannide LnSn_3 series belong to LnX_3 type rare-earth compounds. LnIn_3 and LnSn_3 compounds crystallize in the most stable AuCu_3 -type crystal structure and the lattice parameters across the whole series are consistent and display lanthanide con-

traction [17, 18]. The large number of LnX_3 intermetallic compounds can be obtained by replacing X by other element of group IIIA, IVA and transition metals, however due to their proper coherent melting, it is easy for LnX_3 compounds to grow in a single crystal [19]. Furthermore, for many of the LnX_3 compounds listed in this family, the cubic structure is the more favorable structure for superconductivity as compared to the lower symmetry structures [18].

The mechanical properties of a solid material are essential for its technical and scientific applications. The mechanical properties of a compound are characterized by its elasticity. The parameters that describe the elasticity of a solid material are called elastic constants. The mechanical properties also predict the effectiveness of different elements and compounds for their expected practical applications. The rare-earth elements are used to change the mechanical behavior of materials [20, 21]. In the past lead based solders (Pb-Sn) were commonly used but as lead is toxic and hence it was essential to remove lead from the electronic and soldering devices. Therefore, after considerable efforts the LnSn_3 ($\text{Ln} = \text{La, Ce, Er and Eu}$) based solders were identified as suitable replacement of Pb-Sn solders. The addition of rare-earth elements also increases the performance and ductility of solders [22, 23]. Furthermore, the cubic structure of LnX_3 compounds, leads to more ductility in the aerospace industries [24].

In the past the technical importance of the intermetallic compounds LnIn_3 and LnSn_3 have been established in terms of structural, electrical and magnetic applications. If we consider the interesting properties of these materials, their use is still not as much as it could be and hence it is necessary to investigate other properties such as elastic and mechanical properties of LnIn_3 and LnSn_3 materials with high level of accuracy that may increase the

practical applications of these materials and also provide fundamental information about these materials under strain. To obtain the rational and logical electronic structures and other physical properties of these compounds, it is necessary to treat the strong electron-electron correlation effects in these materials. Therefore, the present study also includes the revisit of the structural and electronic properties (calculated by LDA and GGA) of LnSn_3 and LnSn_3 compounds by using an additional local Hubbard repulsion potential of magnitude U , i.e., DFT + U techniques. The relativistic effects are also considered by introducing the spin-orbit coupling (SOC) effects to increase the accuracy of the calculations.

The interaction of the atomic nucleus with the extra nuclear field i.e., electric field gradient (EFG), is very useful in condensed matter physics. EFG is one of the most powerful tools that describes this interaction [91]. Theoretically the EFG calculations were extremely complicated, but in the recent years the ab-initio calculations based on DFT [26] are very successful in the calculations of EFG. In this work we also concentrate on the EFG analyses of the LnSn_3 and LnSn_3 compounds.

In the present thesis all the calculations are performed by using the FP-LAPW + lo method under the framework of density functional theory. We have carried out the calculations by using different exchange and correlation potentials. The elastic constants of LnX_3 are calculated with the *Cubic-elastic* software [27] using the energy approach implemented in the WIEN2k code [28].

The present thesis is organized as, chapter 1 provides the introduction and motivation of the work. In chapter 2, the review of literature along with the theories of elastic constants and EFG are presented. The information about DFT and *Cubic-elastic* package with their numerical relations is summarized

in chapter 3. Chapter 4 focuses on our contributions which includes results of our DFT calculations of the structural, elastic, mechanical and thermal properties as well as EFG calculations of the LnSn_3 and LnSn_3 compounds. Furthermore, the results are also discussed in the same chapter. The overall work is summarized in the last section under the title of conclusions.

Chapter 2

Literature Review

2.1 Strongly Correlated Electron Systems

The history of the strongly correlated electron systems was started in the thirties of the last century (1930s). The theoretical concepts emerged first in this field before the intensive experimental work. The main ideas were introduced by Wigner using the notion of an electron crystal lattice [29]. In the strongly correlated electronic materials the movement of one electron depends on the movements and positions of all other electrons due to Coulomb interaction. The strongly correlated electron systems are the most exciting and diverse materials in condensed matter physics. A variety of $3d$ and $4d$ electron compounds, rare-earth compounds, some actinide compounds and some organic molecular systems display strong electron-electron correlation effects. In the strongly correlated materials the d and f electrons of the materials dominate low energy properties.

In these materials the partially localized d and f electrons hop in the crystal and the Coulomb repulsive force between electron-electron are as large as kinetic energy. The diverse physical properties of these materials

are due to the partially localized nature of d and f electrons. The duality because of the itinerant and localized nature of d and f electrons makes these systems quite complex and simple approximations fail to explain their true nature. Therefore, these compounds are treated by more sophisticated theoretical tools and the development of analytical and computational tools for the strongly correlated electron systems is one of the key challenges of the modern condensed matter physics.

2.2 Intermetallic Compounds

Intermetallics are those compounds in which two or more than two metals are alloyed by well defined stoichiometric ratio and have arranged crystallographic unit cell. The physical properties of the intermetallic compounds have nothing common with the physical properties of the composing elements. For example the metal conductors may form intermetallic semiconductor and non-magnetic starting elements may make a magnetic intermetallic compound. The same is also true for a variety of other physical properties such as superconductivity, anisotropy and mechanical properties [30]. The majority of the intermetallic compounds are metallic. More than 30,000 binary, ternary, and multi-component intermetallic compounds have been identified and characterized and their crystal structures and some chemical and physical properties are also reported [31].

2.3 Rare-earth Intermetallics

Different compositions and structure types of the lanthanides based binary intermetallic compounds are formed with the other elements of the periodic

table. The rare-earth intermetallic compounds with other metals occur in different compositions LnX , LnX_2 , LnX_3 , Ln_3X and Ln_5X_3 (Ln = rare-earth, X = magnetic or non-magnetic elements). It is necessary to mentioned here that La, Ce, Pr, Sm, Gd, Er, Y and Yb, are the most studied systems and due to cost and availability reasons Eu, Tm and Lu are comparatively less studied. The group VIIB elements and Fe forms LnX_2 composition, however intermetallic compounds with IB and IIB except Au, the LnX and Ln_3X compositions are available. The majority of the lanthanides intermetallic compounds also exist in LnX_3 composition.

2.4 Rare-earth Tri-Indium (LnIn_3) and Tris-tannide (LnSn_3) Compounds

The rare-earth elements form many compounds with group IIIA and IVA of Periodic table. The intermetallic compounds LnIn_3 and LnSn_3 or LnX_3 (Ln = lanthanide) involving in this series crystallize in the cubic AuCu_3 -type crystal structure with space group $Pm - \bar{3}m$ (no. 221) [32]. The crystal structure of LnX_3 is shown in figure 2.1. The point groups of the Ln and X atoms are cubic $m - 3m$ and non-cubic $4/mmm$, respectively. In the AuCu_3 structure, the lanthanide atoms (Ln) are located in 1a (0, 0, 0) position, whereas the non-magnetic elements In or Sn (or X) occupy 3c (0, 1/2, 1/2) position [17].

LnIn_3 and LnSn_3 compounds demonstrate the characteristic lanthanide contraction along the period caused by additional electron added to $4f$ orbital, with the exception of $\text{Ln} = \text{Eu}$ and Yb. The increase of the nuclear charge provides more attractive force for the electron cloud and the atom contracts in comparison with its earlier atom. The increase in the lattice

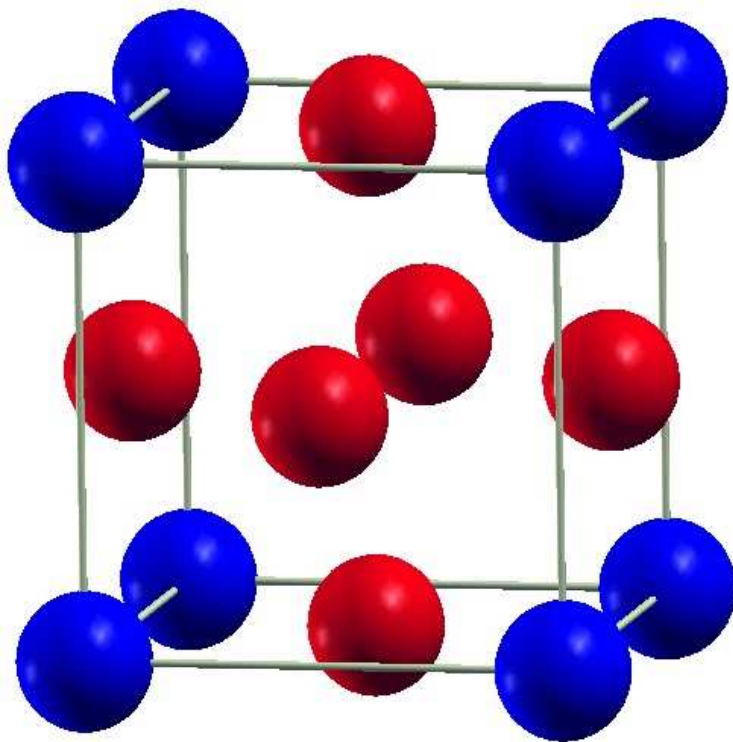


Figure 2.1: The LnX_3 crystal structure (Blue = Ln, Red = X)

parameter of LnIn_3 and LnIn_3 ($\text{Ln} = \text{Eu}$ and Yb) is due to the fact that europium and ytterbium atoms exist in divalent (2^+) ionic state and the rest of lanthanides have trivalent (3^+) ionic state. As the number of f electrons increases, there is an increase in the effective nuclear charge by +1 in each element of lanthanide series brings the valence shell near to the nucleus leading to a progressive reduction in the atomic radii of Ln^{+3} , while in case of Ln^{+2} ions (Eu and Yb) an appreciable increase in the atomic radii might be expected to give only two valence electrons because of the stability of half-filled (Eu) and filled f orbitals (Yb) [33]. The lattice constant of LnIn_3 and LnSn_3 compounds in divalent state is larger by almost 2 % than trivalent state [17, 34].

In the LnIn_3 series the first compounds synthesized were LaIn_3 , PrIn_3 , SmIn_3 and NdIn_3 in 1947. The lattice constants and the cubic structure (AuCu_3 -type) of PrIn_3 , SmIn_3 , NdIn_3 and LaIn_3 are reported by Iandelli [35]. CeIn_3 was reported by Vogel and Klose in 1954 [36] while GdIn_3 and DyIn_3 were introduced by Baenziger and Moriarty [37]. The rest of LnIn_3 ($\text{Ln} = \text{Tb}$, Ho , Er , Tm , Yb and Lu) intermetallic compounds were investigated by Kuzma and Markiv in 1963 [38]. They also discussed the non existence of the EuIn_3 . Later on Gorlich et al. [39] reported EuIn_3 by investigating the Mössbauer effect in EuIn_3 . In the LnIn_3 family, the only compound PmIn_3 has not yet been experimentally confirmed. The reason is that, the promethium is the most stable isotope having half life of 17 years. Some hypothetical phase diagrams show the existence of PmIn_3 [40, 41].

The LnIn_3 intermetallic compounds display a variety of interesting magnetic properties and have received extensive attention of both experimental and theoretical studies [42, 43, 44]. The Curie-Weiss behavior is observed in almost all LnIn_3 compounds at high temperature, except with $\text{Ln} = \text{La}$,

Sm and Yb [42, 45]. LaIn_3 and LuIn_3 are non-magnetic materials because of their empty and full $4f$ shell, respectively [46]. PrIn_3 and YbIn_3 show paramagnetic ordering at low temperature [47]. The rest of LnIn_3 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ and Tm) compounds attribute to antiferromagnetic (AFM) ordering at low temperature [48, 49]. EuIn_3 also shows antiferromagnetic phase at low temperature but exists in Eu-In binary phase diagram [39].

Sato et al. [50] carried out the electronic specific heat study of LnIn_3 compounds. The smaller value of electronic specific heat coefficient is obtained for LaIn_3 ($\gamma = 5.3 \text{ mJ}/(\text{K}^2 \cdot \text{mol})$) and the larger value of gamma is observed for CeIn_3 ($\gamma = 120 \text{ mJ}/(\text{K}^2 \cdot \text{mol})$) in comparison with the remaining LnIn_3 compounds. This increase in the electronic specific heat coefficient throughout the series is due to electron-magnon correlation and the larger value of gamma in CeIn_3 is due to Kondo effect.

The Fermi surface properties and the de Haas-van Alphen (dHvA) effect in LnIn_3 compounds are reported in literature [51, 52, 53, 54, 55, 56, 57]. It is observed that the Fermi surfaces of all LnIn_3 compounds are almost same as those of LaIn_3 , except CeIn_3 and YbIn_3 , which have very different Fermi surfaces. It is due to the fact that CeIn_3 is Kondo lattice compound, show heavy fermions system and in YbIn_3 , the rare earth Yb is divalent in contrast to trivalent rare-earth elements in other LnIn_3 compounds. The specific heat measurement of some LnIn_3 ($\text{Ln} = \text{La}, \text{Ce}$ and Pr) compounds in the temperature range 1.5-300 K show that specific heat of these compounds varies linearly with temperature [58, 59]. Some of LnIn_3 compounds exhibit superconductivity. The superconducting transition temperatures (T_c) for LaIn_3 , LaSn_3 and CeIn_3 are 0.71 K, 6.5 K, and 0.2 K, respectively [60, 61].

The lanthanides-tristannide intermetallic compounds LnSn_3 series, are

under study since 1933. The previous experimental studies confirm the existing of LnSn_3 compounds with $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$ and Yb [62, 63], while LnSn_3 compounds containing heavier rare-earth elements ($\text{Tb, Dy, Ho, Er, Tm}$ and Lu) fail to form LnSn_3 composition [18]. The earlier researchers claimed that apart of YbIn_3 , the rare-earth elements do not form LnSn_3 composition at room temperature. They were of the opinion that the composition LnSn_x ($x > 3$) exists for these compound but not in the crystal structure AuCu_3 . Miller and Hall [64] in 1972 prepared LnSn_3 composition in the cubic AuCu_3 -type crystal structure with heavier rare-earth elements i.e., $\text{Ln} = \text{Tb, Dy, Ho}$ and Er under unusual conditions of high pressure and temperature. They also tried prepare TmSn_3 and LuSn_3 , but these two compounds were not synthesized.

The magnetic properties of LnSn_3 compounds have been a focus of interest due to their relatively simple structure AuCu_3 [65, 66]. The magnetic ordering in most of the LnSn_3 compounds is antiferromagnetic. The magnetic properties of PrSn_3 and NdSn_3 have been determined by neutron diffraction while the magnetic structure of $(\text{Sm, Eu and Gd})\text{Sn}_3$ have been investigated by Mössbauer spectroscopy [67].

Some of the LnSn_3 intermetallic compounds indicate superconductivity with relatively high temperature. Gambino et al. [19] investigated the superconducting behavior of LaSn_3 with superconducting transition temperature $T_c = 3.6\text{K}$. Kawashima et al. [68] reported that YbSn_3 also exhibit superconductivity with critical temperature $T_c = 6.5\text{K}$.

The Fermi surfaces, dHvA effects and magnetoresistance of LaSn_3 and CeSn_3 compounds are reported in the literature [46, 69]. It is observed that analogy exists between the Fermi surfaces of LaSn_3 and CeSn_3 . Hasegawa et al. [70] investigated the electronic structure and the relativistic effects

on the band structure of CeSn_3 using the itinerant-electron model for $4f$ electrons. The effect of spin-orbit interaction on Fermi surfaces and band structure of LaSn_3 compound in the vicinity of the Fermi level has been studied by Hasegawa et al. [71] using APW method. The effective moments $\mu_{eff}(\mu_B)$, Néel temperature $T_N(\text{K})$ and paramagnetic Curie temperature $\theta_P(\text{K})$ of LnIn_3 and LnSn_3 compounds are presented in Table 2.1.

Table 2.1: Effective moments $\mu_{eff}(\mu_B)$, Néel temperature $T_N(\text{K})$ and paramagnetic Curie temperature $\theta_P(\text{K})$ of LnIn_3 and LnSn_3 compounds.

Compound	$\mu_{eff}(\mu_B)$	$T_N(\text{K})$	$\theta_P(\text{K})$	Ref.
LaIn_3	Puli Para	—	—	[42]
CeIn_3	Para	11	-46	[42]
PrIn_3	3.67	—	-10	[42]
NdIn_3	2.54	7	-17	[42]
SmIn_3	—	16	—	[42]
EuIn_3	—	10	10	[42]
GdIn_3	8.20	45	-85	[42]
TbIn_3	8.90	36	-62	[42]
DyIn_3	10.78	23	-35	[42]
HoIn_3	10.65	11	-18	[42]
ErIn_3	9.75	6	-10	[42]
YbIn_3	Puli Para	—	—	[42]
LuIn_3	Puli Para	—	—	[42]
LaSn_3	Para	—	—	[18]
CeSn_3	Para	—	—	[65]
PrSn_3	3.55	8.6	-10	[65]
NdSn_3	3.6	4.7	-34	[65]
SmSn_3	12.0	12	—	[65]
EuSn_3	7.65	38	-75	[18]
GdSn_3	8.0	35	-73	[65]

Endoh et al. [72] experimentally calculated the elastic constants and crystalline electric field effects on the elastic constants of the compounds SmX_3 ($X = \text{Pd, In, Sn, Tl, Pb}$) by means of the ultrasonic measurements. Kasaya et al. [73] investigated temperature dependent elastic constants of SmSn_3 compound using X-ray diffraction method.

The experimental measurements of EFG using Mössbauer spectroscopy of PrSn_3 , NdSn_3 and SmSn_3 compounds are performed by Borsa et al. [78]. They used the summation method of de Wette [79] in order to calculate EFG at axial symmetry at tin (Sn) site. Shenoy et al. [66] determined the EFG of LnSn_3 compounds with the variation of the rare-earth atom (Ce, Pr and Nd), whereas Sanchez et al. [67] experimentally determined the EFG of LnSn_3 compounds ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$ and Yb). From the nearly constant quadrupole interaction, they concluded that the charge distributions around Sn nucleus are symmetric. The EFGs studies of LnIn_3 and LnSn_3 series have been done by Schwartz and Shirley using the time differential perturbed angular correlations (TDPAC) method [80]. Kohori et al. [81] reported the EFG measurement by evaluating electric quadrupole interaction of CeIn_3 by nuclear quadrupole resonance (NQR) in AFM phase.

Some theoretical studies on the pressure dependent structural, electronic and elastic properties of the intermetallic compounds LaIn_3 , LaSn_3 , CeIn_3 and CeSn_3 are available in literature [74, 75, 76, 77], but their theoretical results are not consistent with the experiments because of the improper treatment of the exchange correlation potential in those calculations.

Lalic et al. [82] calculated EFG at In nucleus of CeIn_3 compound using density functional theory with FP-LAPW method, showing that $5p$ shell is responsible for EFG in CeIn_3 . The measurement of the EFG at In and Sn sites for LnIn_3 ($\text{Ln} = \text{Sm, Eu}$ and Gd) and LnSn_3 ($\text{Ln} = \text{Tm, Yb}$ and Lu)

have been performed by Jalali-Asadabdi and Akbarzadeh [34]. They also calculated the EFGs at Cd impurity site in LnIn_3 and LnSn_3 compounds. Betsuyaku et al. [83] performed the EFG calculations of LaIn_3 and CeIn_3 compounds by using local density approximation (LDA). Jalali-Asadabadi [84] investigated the EFGs of CeIn_3 compound at both Ce and In sites in nonmagnetic, ferromagnetic and AFM phases using GGA and GGA+U by means of DFT. Ilkhani et al. [85] have performed pressure dependent EFG studies of CeIn_3 in AFM phase. They observed that, increase in pressure causes increase in EFG.

2.5 Elastic and Mechanical Properties

The elasticity of a crystalline material shows great importance in solid state physics, materials science, chemistry and geological sciences. Elasticity describes the response of a material to the external force and is related to the strength and hardness of a material, and the propagation of sound waves in a material [86]. The elasticity of a material has basic relation with the cohesive forces of the solid and its thermodynamical properties, such as melting point, Debye temperature and phonon spectra. Therefore, the elasticity provides important information about the bonding forces and interatomic potentials [87]. The elasticity of material can be described by the elastic constants of a material and therefore, the understanding of the elastic constants is necessary for the practical applications of the compound as they provide the mechanical properties and mechanical stability of the material [88]. The accurate and efficient calculations of the elastic constants based on DFT provides an alternative to experiments, especially for searching and predicting the mechanical properties of new materials.

In order to describe the elastic constants of a material, the external force (stress tensors) is applied on the material, which produces deformation expressed by strain tensor. The applied stress and the resultant strain are considered to be uniform. The material under stress is also assumed to be homogeneous. The elastic constants of a crystalline material are specified by fourth-rank tensor and are defined in terms of the generalized Hooke's law as:

$$\sigma_{i,j} = C_{ijkl}\varepsilon_{kl} \quad (2.1)$$

where $\sigma_{i,j}$ is the stress tensor, C_{ijkl} is the elastic stiffness tensor contains 81 elastic constants and ε_{kl} is the strain tensor. The number of independent elastic constants depends on the symmetry of the crystal structure. The different symmetries of the crystal structure reduce the number of elastic constants. The use of Voigt's notation by replacing $xx = 1$, $yy = 2$, $zz = 3$, $yz = 4$, $xz = 5$, and $xy = 6$, the elastic tensor C_{ijkl} is reduced to 6×6 matrix C_{ij} as a result of symmetry (and $C_{ijkl} = C_{klij}$) with $i, j = 1, 2, 3, 4, 5, 6$. In matrix notation the elastic constants of a single crystal is written as [89]:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} \quad (2.2)$$

The number of elastic constants is further reduced with the material symmetries. The triclinic structure has the highest number of elastic constants, while the cubic structure has the least number of elastic constants. For cubic symmetry the x, y and z axes are identical, therefore the corresponding longitudinal elastic constants are equal i.e, $C_{11} = C_{22} = C_{33}$. In shear

elastic constants ($i \geq 4$) the diagonal elastic constants for cubic crystal are equal i.e, $C_{44} = C_{55} = C_{66}$ and the remaining are equal to zero, for example $C_{45} = C_{54} = 0$. The off-diagonal and mixed elastic constants for cubic crystal are also equal to zero, for example $C_{14} = C_{41} = 0$. Hence, for cubic crystals the matrix is defined as:

$$C_{cubic} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (2.3)$$

Thus for cubic systems we have only three independent elastic constants C_{11} , C_{12} and C_{44} .

2.6 Electric Field Gradient

The interaction between atomic nucleus and extra nuclear field are quite useful in many circumstances. The nuclei having nuclear spin quantum number $I \geq 1$ exhibits quadrupole interaction (QI), which takes place from the interaction between electric field gradient and nuclear quadrupole moment (NQM) at the nuclear position [90].

Electric field gradient (EFG) serves as a powerful tool that provides the interaction between nucleus and the electric field in the vicinity of a nucleus. The value of EFG vary from site to site, and can be calculated for non-equivalent atoms in the solid material under investigation. EFG also provides the structural information of solid materials on atomic scale [91]. At nuclear center the origin of EFG is the surrounding charge distribution of atoms,

electrons, bonds and molecular structure, therefore EFG is very sensitive to extremely small changes in the dynamics and crystal structure.

The EFG is second rank traceless tensor and is defined as the second derivative of classical electrostatic potential at the nuclear site. Thus after the diagonalization:

$$V_{ij} = \partial^2 V / (\partial x_i \partial x_j) = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} \quad (2.4)$$

In Cartesian reference, EFG has three components V_{xx} , V_{yy} and V_{zz} . The standard conventions $|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$ are chosen for these components. The main principal components are V_{zz} and asymmetry η parameter, related by:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (2.5)$$

The asymmetry parameter describes the symmetry of the EFG and takes value from 0 to 1. For $\eta = 0$, the axis about which the axial symmetry is specified has the largest magnitude of EFG and in case when $\eta = 1$, the axis about which the axial symmetry is described has a zero EFG. The Principal component V_{zz} and asymmetry parameter are needed for the total characterization of EFG.

The quadrupole coupling constant (C_Q) and the asymmetry parameter (η) are the experimental observable quantities. To calculate the experimental EFG, different conversion relations are used to examine the experimental results of the nuclear quadrupole interaction. The quadrupole coupling constant (C_Q) which describes the magnitude of EFG is related by:

$$C_Q = \frac{eQV_{yy}}{h} \quad (2.6)$$

The magnitude of EFG can also be expressed in terms of quadrupole frequency as:

$$\nu_Q = \frac{eQV_{yy}}{4I(2I-1)\hbar} \quad (2.7)$$

The asymmetry parameter is a dimensionless quantity, whereas quadrupole coupling constant is typically measured in the units of kHz or MHz. Experimentally EFG can be measured with perturbed angular correlations (PAC), Mössbauer spectroscopy (MS), nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) [92].

Chapter 3

Theory and Computational Techniques

In this chapter the theoretical foundations of the calculations performed in this work are discussed. The ab-initio techniques and different approximations, that are used to calculate reliable results and that better describe the structural, electronic and other physical properties, are explained. The details of the *Cubic-elastic* package are also illustrated in this chapter.

The theoretical knowledge of the various physical properties of solids is a challenging task in materials science. Crystals are composed of atoms and molecules make many body problems, are often studied at their ground states for simplicity. To study such a complex many body problems ie., metals, semiconductors, insulators etc., one way is to perform computer simulations of the modeled crystal by using different approaches such as classical force field and quantum mechanical schemes. The former classical schemes require experimental data in order to produce theoretical results like ground state structural parameter or vibrational frequencies (phonons). However, if the experimental parameters are not available, one can carry out the calculations

of a solid materials using ab-initio or first principle method.

The solution of many body problem quantum mechanically or ab-initio method requires the accurate solution of the Schrödinger equation. However with the modification of the Born-Oppenheimer, it is still difficult to solve Schrödinger equation for many body crystalline solids. The former theoretical methods such as free electron model, Hartree theory, Hartree-Fock theory and Thomas-Fermi model are inadequate to produce any quantitatively remarkable results in solid state physics. However, these models provide basic ideas for the development of the density functional theory. For instance, in Thomas-Fermi model, the density of electrons is used as a basic variable as an alternative to the wave function that turned out to be very fruitful. The evolved form methods is DFT [26], which is commonly used for the correct treatment of complex systems by using exact exchange-correlation functional. DFT is used to describe different properties of solids such as, structural stability, chemical bonding, phase transition, electronic, magnetic, optical, elastic and mechanical behavior.

3.1 Density Functional Theory

The basic idea of the density functional theory comes from the two foundation theorems formulated by Hohenberg and Kohn (HK) [93]. These theorems explain that the ground-state energy of N-electron system can be determined from the electron density. The theorem states that external potential is a functional of the electron density. The ground-state energy and density in a given external potential can be calculated by the minimization of the three-dimensional density functional. For a given external potential the energy

functional is given as:

$$E_v[n] = \int V_{ext}(r)n(r)dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n] \quad (3.1)$$

where $n(r)$ is electron density, $G[n]$ is the universal functional independent of external potential V_{ext} and applicable for any number of electrons in the system. The above equation shows that electron density $n(r)$ uniquely defines the total energy of the system. Thus for the treatment of the many body system it is not necessary to know the many-body wave function. The complexities with Hohenberg-Kohn theorem of many-body system is the determination of the universal functional $G[n]$.

3.2 Kohn-Sham Equations

The basic concept of Kohn and Sham (KS) [26] is to introduce non-interacting electron moves in an effective external potential V_{eff} of all other electrons of the system. It is assumed that the ground state density of the non-interacting electrons system is equal to that of the interacting system. Kohn and Sham defined the unknown universal functional $G[n]$ of HK as:

$$G[n] = T_s[n] + E_{XC}[n] \quad (3.2)$$

where T_s is the kinetic energy of a non-interacting electron or Kohn-Sham electron and E_{xc} is the exchange and correlation part, accounts for all correlation energies. The kinetic energy of the KS non-interacting system in term of one electron orbital ϕ_i is:

$$T_s[n] = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \quad (3.3)$$

The electron density of the non-interacting KS system is given by:

$$n(r) = \sum |\phi_i(r)|^2 \quad (3.4)$$

The ground-state energy of HK in KS formulism is:

$$E_{KS}[n] = T_s[n] + \int V_{ext}(r)n(r)dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|}drdr' + E_{xc}[n] \quad (3.5)$$

The minimization of density $n(r)$ is obtained by solving the single-particle Schrödinger equation:

$$[-\frac{1}{2}\nabla^2 + V_{eff}(r)]\phi_i(r) = \varepsilon_i(r)\phi_i(r) \quad (3.6)$$

where ε_i is the i th Kohn-Sham eigenvalue and

$$V_{eff}(r) = V_{ext}(r) + V_{ee} + v_{xc}(r), \quad (3.7)$$

$$v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} \quad (3.8)$$

In Eq. (3.8) the potential due to exchange correlation energy v_{xc} is the functional derivative of E_{xc} . The KS equation (Eq. (3.6)) is solved self-consistently. For this purpose one starts with the guess density $n(r)$ and using this density builds the total density-functional Hamiltonian including columbic, ionic and exchange-correlation potentials and solves the KS equation self-consistently in order to compute the new charge density. At this stage new density is checked for self-consistency. The process is repeated iteratively until the convergence is achieved i.e, the computed charge density is numerically equal to the guess density. Now all the desired quantities such as ground state energy, forces, band structure etc. are computed.

The Kohn-Sham equations permit DFT to be used in practical calculations for real systems. KS introduced E_{xc} term which plays a vital role in the failure or success of DFT, however the exact exchange-correlation functional is not known and need approximation.

3.3 Exchange-Correlation Functional

The exchange-correlation term E_{xc} , accounts for all sort of interactions such as spin dependent interactions (Pauli Exclusion Principle) and spin independent interactions like Coulomb interaction. It also includes the difference between the kinetic energy of non-interacting and interacting systems. The development of density functional approximations increase the importance of DFT for a wide range of problems in physics and chemistry [94, 95, 96]. Despite the success of DFT it is still a challenge to construct a functional that could be universally applicable. The exchange-correlation approximations used in this work are discussed in the following sections.

3.3.1 Local Density Approximation

In the local density approximation (LDA), the exchange-correlation is evaluated by using the uniform electron gas corresponding to the local density $n(r)$:

$$E_{xc}^{LDA}[n(r)] = \int \varepsilon_{xc}^{LDA}(n(r))n(r)d^3r \quad (3.9)$$

Here $\varepsilon_{xc}^{LDA}(n)$ is the exchange correlation energy per particle for a system of uniform density. LDA is simple and significantly practical approximation to calculate different properties of solids. The LDA gives the accuracy of about 10-20 % in cohesive energies and ionization energy of atoms. The LDA shows impressive results in bond lengths and equilibrium lattice constants with accuracy of about 1 %, however band gaps and surface energies calculated within LDA are severely underestimated. The failure of LDA is due to the consideration of uniform density at each point.

3.3.2 Generalized Gradient Approximation

One of the first extensions to LDA was GGA. In GGA the gradient of density is used in order to describe the deviation of exchange-correlation energy from the homogenous electron gas. The general form of GGA functional is [97]:

$$E_{xc}^{GGA}[n(r)] = \int \varepsilon_{xc}^{GGA}(n, \nabla n) n(r) d^3r \quad (3.10)$$

GGA shows improvement over LDA for slowly varying density systems. The GGA improves the calculated chemical bonds and cohesive energies in comparison to the LDA. The GGA increases the lattice constants and equilibrium volumes and decreases the bulk moduli as compared to the LDA results. The GGA is also not very successful to fix the band gap problem of semiconductors especially with *d* state like ZnS . Several forms of GGA functionals are available in the literature for the treatment of the exchange-correlation energy [95, 96, 98, 99, 100, 101]. The most commonly used and reliable GGAs are LYP [95] and PBE [96].

3.3.3 GGA+U

The LDA and GGA functionals provide good results for most of the solids but are not efficient to describe materials with electron-electron correlation effects. For the strongly correlated electron systems, transition metals with *d*-state and rare-earth metals with *f*-state, the Coulomb repulsion between electrons are too strong to overcome kinetic energy. The LDA and GGA xc-functionals do not properly treat the localization of the valence electrons. For example in Mott insulators the electron's localization is missed and hence are predicted metallic by LDA and GGAs xc-functionals. For this purpose DFT+U method is introduced [102, 103] to improve the study of the strongly correlated systems. The DFT+U method is the simplest approach with low

computational cost, based on Hubbard model Hamiltonian. Therefore, a Hubbard (U) correction is added to standard DFT functional, e.g, LDA+U, GGA+U etc. The basic expression for LDA+U functional is given as [104]:

$$E_{LSDA+U} = E_{LSDA} + \frac{U - J}{2} \sum_{\sigma} (n_{m,\sigma} - n_{m,\sigma}^2) \quad (3.11)$$

The two interaction terms U and J are the on-site Coulomb interaction and the exchange interaction, respectively, n is the occupation number of orbital momentum m and σ is spin projection. The U - J is replaced by effective parameter $U_{eff} = U - J$.

3.4 Spin-orbit Coupling

In solids materials the motion of electrons is described by energy bands. A relativistic correction to the Schrödinger wave equation as spin-orbit coupling (SOC) effects the energy bands of some solids. The SOC effect splits energy bands and produces non-degeneracies in the band structures. The SOC effect is included by a second variational method [105]. The second variational method, uses the scalar-relativistic basis, based on the reduction of the original basis. For this purpose, the scalar-relativistic part of the Hamiltonian is diagonalized in the scalar-relativistic basis. Then the full Hamiltonian matrix including SOC is constructed using the eigen functions of the the scalar-relativistic Hamiltonian. Once the effects of spin-orbit coupling is included, the full Hamiltonian is given as:

$$H\tilde{\psi} = \varepsilon\tilde{\psi} + H_{so}\tilde{\psi} \quad (3.12)$$

where H_{so} is spin-orbit Hamiltonian and is defined as [106]:

$$H_{so} = \frac{\hbar}{2Mc^2} \frac{1}{r} \frac{dV}{dr} \begin{pmatrix} \vec{\sigma} \cdot \vec{l} & 0 \\ 0 & 0 \end{pmatrix} \quad (3.13)$$

where $\vec{\sigma}$ is the Pauli spin matrices.

3.5 Full Potential Linearized Augmented Plane Wave Plus Local Orbital Method

The full-potential linearized-augmented plane-wave (FP-LAPW) method [107] is one of the most accurate method to solve Kohn-Sham equations for the electronic structure and total energy calculations of crystalline solids. This method is based on the augmented plane wave (APW) method [108]. In APW method the space is divided into Muffin-tin (MT) spheres and interstitial region. The electrons far away from the nucleus behave as free electrons and are described by plane waves (interstitial region) and the spherical harmonic radial functions are used in the nonoverlapping spheres (MT region). The potential of the whole space is written in the form:

$$V(r) = \begin{cases} V(r) & (r \in MT) \\ \text{constant} & (r \in I) \end{cases} \quad (3.14)$$

APW method cannot describe the eigenstates accurately, which makes APW method insufficient for solving density functional equations. To overcome this problem, Andersen [107] modified APW method and introduced the linearized augmented plane wave method (LAPW). Due to the flexible basis the LAPW method properly explains the eigenstates and produces the eigenenergies with single diagonalization.

The electrons in an atom, which are bound to the nucleus may not contribute to the chemical bonding and hence are known as core electrons with the corresponding core states. The core electrons are localized in the MT spheres. The electrons leaking out of the MT sphere are valence electrons and participate in the bonding process of the material. For many atoms some

states, that neither lie in the valence states, nor in the core states are termed as semicore states. The semicore states have the same angular momentum number but lower principle quantum number as that of valence states. The semicore states exist in the rare-earth and transition metal atoms.

The most serious shortcoming of LAPW method is the treatment of the semicore states. This dilemma is solved by Singh [109] by introducing local orbitals implemented in the LAPW (LAPW+lo) method. In the LAPW+lo method the extra basis function is localized in the MT spheres i.e., its value falls to zero at the MT radius. The accuracy of the LAPW+lo can be further increased by full potential LAPW (PF-LAPW) method. In PF-LAPW method, the potential and charge density inside MT sphere are expanded by spherical harmonics and in the interstitial region described by plane waves:

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & (r \in MT) \\ \sum_G V_G e^{iG \cdot r} & (r \in I) \end{cases} \quad (3.15)$$

In our calculations the radii of the muffin-tin spheres have been chosen as 2.50 a.u. for the lanthanide elements as well as for Sn and In. To attain better convergence, the plane waves is set to $R_{MT}K_{max} = 7$, where R_{MT} is the atomic radius in a unit cell and K_{max} is the maximum value of k-vector in the plane waves expansion. For the valence wave function inside a muffin-tin spheres the maximum value of angular momentum $l_{max} = 10$ is considered. In the interstitial region the charge density in Fourier expansion is selected up to $G_{max} = 12$. High accuracy is required to calculate elastic properties, therefore by increasing the number of k-points, we tested the convergence of the total energy and hence the total energy is converged for 6000 k-points with a dense k mesh of 165 k-points in the irreducible wedge of the Brillouin zone with a grid size of $18 \times 18 \times 18$ using the Monkhorst and Pack mesh [110].

3.6 *Cubic-elastic* Package

There are several methods available in the literature to calculate the elastic constants of cubic materials [111, 112, 113, 114]. In this work we used *Cubic-elastic* package [27] for the calculation of the elastic properties of LnIn_3 and LnSn_3 compounds. To obtain reliable results the energy approach [115] is used by means of WIEN2k [28]. The elastic constants are calculated by applying small strain (σ) to the solid. The change in the internal energy of the system can be expanded in the form of Taylor series and is given by:

$$E(V, \varepsilon_i) = E(V_0, 0) - P(V_0) \Delta V + \frac{1}{2} V_0 \sum_{i,j}^6 C_{i,j} \varepsilon_i \varepsilon_j + O[\varepsilon_i^3] \quad (3.16)$$

Here V_0 is the volume and $P(V_0)$ is the pressure of the undistorted lattice at volume V_0 and C_{ij} are the elastic constants. In order to simplify Eq. (3.16) it is necessary to neglect the higher power term $O[\varepsilon_i^3]$. Using Voigt notations by substituting $xx \rightarrow 1$, $yy \rightarrow 2$, $zz \rightarrow 3$, $yz \rightarrow 4$, $zx \rightarrow 5$ and $xy \rightarrow 6$ and considering additional symmetries imposed by the cubic crystal symmetry; the number of elastic constants are decreased. In fact, only three independent elastic constants C_{11} , C_{12} and C_{44} are left for a cubic crystal. In matrix representation the Taylor expansion of the cubic elastic constants can be written as:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (3.17)$$

The Bulk modulus B_0 is related to elastic constants C_{11} and C_{12} by equation [116]:

$$B_0 = \frac{C_{11} + 2C_{12}}{3} \quad (3.18)$$

The original cubic system can be distorted by applying the deformation matrix D . The following deformation matrices are used to determine C_{11} , C_{12} and C_{44} [27].

$$(D_{ortho}) = \begin{pmatrix} 1 + \varepsilon & 0 & 0 \\ 0 & 1 - \varepsilon & 0 \\ 0 & 0 & \frac{1}{1 - \varepsilon^2} \end{pmatrix} \quad (3.19)$$

$$(D_{cubic}) = \begin{pmatrix} 1 + \varepsilon & 0 & 0 \\ 0 & 1 + \varepsilon & 0 \\ 0 & 0 & 1 + \varepsilon \end{pmatrix} \quad (3.20)$$

$$(D_{monoc}) = \begin{pmatrix} 1 & \varepsilon & 0 \\ \varepsilon & 1 & 0 \\ 0 & 0 & \frac{1}{1 - \varepsilon^2} \end{pmatrix} \quad (3.21)$$

By taking the second order derivative of the energy of the orthorhombic distortional deformation (D_{ortho}), volumetric cubic deformation (D_{cubic}) and monoclinic distortional deformations (D_{monoc}), the values of C_{11} , C_{12} and C_{44} can be determined. The second order derivative of energy for D_{ortho} is:

$$\frac{d^2 E}{d\varepsilon^2} = 2V_0(C_{11} - C_{12}) \quad (3.22)$$

The second order derivative of energy for D_{cubic} is:

$$\frac{d^2 E}{d\varepsilon^2} = 3V_0(C_{11} + 2C_{12}) \quad (3.23)$$

and the second order derivative of energy for D_{monoc} is:

$$\frac{d^2 E}{d\varepsilon^2} = 4V_0C_{44} \quad (3.24)$$

In addition to elastic constants, Voigt shear modulus, Reuss shear modulus, Hill shear modulus, Young's modulus, shear constant, Cauchy pressure, Poisson ratio, Lamé's coefficients, Kleinman parameter and anisotropy constant are also calculated to explain the mechanical properties and elastic stabilities of the compounds under study.

3.7 WIEN2k code

In the present thesis WIEN2k code based on FP-(L)APW+lo method is used to perform the calculations. This code is mainly used for crystalline materials with periodic boundary conditions. The WIEN2k is written in FORTRAN90 and developed by P. Blaha and co-workers [117]. Different versions of the code with modification are available (WIEN93, WIEN95, WIEN97, WIEN2k). WIEN2k has two main parts, where in the first part initialization is performed, that is used to check Muffin-tin spheres overlapping, generate structure, detect symmetry operations, generate k-mesh in the Brillouin Zone (BZ) and obtain the guess density. In the second part the self-consistency cycle is performed iteratively in which KS equations are used to achieve convergency and calculate the output parameter (new density, energies, stresses, forces etc). WIEN2k is used to predict a verity of properties of solids such as geometry optimization, plotting band structures and density of states, X-ray spectra, electron density, electric field gradient etc.

Chapter 4

Results and Discussions

4.1 LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) Compounds

4.1.1 Introduction

The rare-earth elements and, in particular lanthanide series are well known for their incomplete $4f$ shell. The unpaired electrons in the $4f$ shell determines the physical properties of the rare-earth elements and compounds [65, 49]. The rare-earth intermetallic compounds are attractive materials for researchers due to their unique interesting properties such as high melting points, high temperature ductility, high temperature mechanical properties and good electrical as well as magnetic properties. The unusual physical properties make them potential candidates for automobile, aviation and aerospace applications. In addition, high strength and stiffness, and low specific weight corrosion resistance make rare-earth intermetallics better materials than other metals for the development of commercial aircraft turbines [118]. Due to the absence of d electrons near the Fermi level almost 90 % of

intermetallic compounds show ductile nature [119].

Intermetallic compounds LnIn_3 and LnSn_3 (Ln = rare earth) show many interesting properties due to their incomplete $4f$ shell such as the presence of various magnetic structures, magnetic to non magnetic transition, valence fluctuations and magnetic moment formation [120, 121]. LnSn_3 intermetallic compounds are used as best alternative of lead based solders and improve the performance of lead-free solders [22]. Rare-earth (RE) intermetallic compounds LnIn_3 and LnSn_3 (Ln = Sm, Eu, Gd) have cubic AuCu_3 - type crystal structure, space group $Pm - \bar{3}m$ (No. 221), and exhibit a verity of phenomena [17, 32]. In the AuCu_3 structure the rare earth atoms (Ln) are located at 1a (0, 0, 0) position. The non-magnetic elements In or Sn occupy 3c (0, 1/2, 1/2) positions [32]. Most of LnIn_3 and LnSn_3 compounds order antiferromagnetically at low temperature below 45 K [42, 43, 44]. The stability of the LnIn_3 and LnSn_3 phase decreases along the light rare earths from La to Gd [122]. The magnetic measurement and lattice constant values of the rare-earth based compounds show the characteristic lanthanide contraction, with the exceptional case of the compounds contain Eu and Yb atoms, in which the rare earth ions are divalent [18].

In LnIn_3 series, SmIn_3 , EuIn_3 and GdIn_3 compounds indicate antiferromagnetic (AFM) transition with Néel temperature $T_N = 16\text{K}$, 10K and 42K respectively [39, 48, 49]. For LnSn_3 series the compounds SmSn_3 , EuSn_3 and GdSn_3 exhibit AFM transition at temperatures $T_N = 12\text{K}$, 36.5K and 16.5K , respectively [67]. The magnetic properties and lattice parameters of the lanthanide LnIn_3 series are reported by Buschow et al. [42] from magnetic susceptibilities measurements where they observed that at low temperature most of the lanthanides LnIn_3 compounds are AFM. Sanchez et al. [67] calculated the electronic and magnetic properties of LnSn_3 , compounds (Ln = La,

Ce, Pr, Nd, Sm, Eu, Gd, Yb) using Mössbauer resonance. They found that Eu and Gd compounds point to complex magnetic structures. The Fermi surface properties of LnIn_3 and LnSn_3 were determined by Ōnuki and Settai [47]. The structural properties such as lattice parameter and bulk modulus of LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}$ and Gd) have been calculated by Jalali-Asadabadi et al. [34] using LDA, GGA and GGA + spin polarized approximations under the framework of DFT. Endoh et al. [72] experimentally calculated the elastic constants and the crystalline electric field effect on the elastic constants of the series of compounds SmX_3 ($\text{X} = \text{Pd}, \text{In}, \text{Sn}, \text{Tl}, \text{Pb}$) by means of the ultrasonic measurements. the valency of rare earth in LnIn_3 and LnSn_3 and the influence of valency on the electric field gradients (EFG) have been interpreted by Jalali-Asadabadi et al. [17] using density functional theory (DFT).

The elastic constants show the response of a compound to the external forces. The elastic constants determine the strength, brittleness/ductility, and hardness of materials. It also provides information about bonding character, anisotropy and structural stability [123]. In this section we discuss the structural, electronic, elastic and mechanical properties of rare earth LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) compounds. This study is important in the sense that present study is important because it reports for the first time elastic, mechanical and thermal properties of these compounds by ab-initio calculation.

4.1.2 Structural Properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) Compounds

The structural properties of LnIn_3 and LnSn_3 (Sm, Eu and Gd) are calculated by finding the total energy of the unit cell for each compound with respect to

volume using Birch-Murnaghan equation of state [125]. Lattice constants and bulk moduli are obtained by LDA, GGA, LDA+U and GGA+U potentials. The theoretically calculated results along with the available experimental data are tabulated in Table 4.1. The table shows that GGA lattice constants of SmSn_3 and GdSn_3 are in closer agreement to experiment than GGA+U lattice constants of SmSn_3 and GdSn_3 , whereas GGA+U lattice constant of EuSn_3 is closer to experiment than GGA lattice constants of EuSn_3 . This confirms that SmSn_3 and GdSn_3 behave as itinerant compounds, whereas EuSn_3 behaves as localized compound. This in turn verifies that EuSn_3 is a divalent system, while SmSn_3 and GdSn_3 are trivalent. The same is true for the LnIn_3 cases where $\text{Ln} = \text{Sm}, \text{Eu}$ and Gd .

Table 4.1 also shows that as we move from Sm to Gd, the lattice constants are contracted which is attributed to the lanthanide contraction i.e., the decrease in the atomic radius along the lanthanide series from left to right due to poor shielding effect of the $4f$ electrons with exception for Eu and Yb which display divalency in $4f$ series (EuIn_3 and EuSn_3) and hence our results nicely confirms this fact in both LnIn_3 and LnSn_3 cases. It is also clear from the table that LDA and LDA+U underestimate the lattice parameters which is consistent with the general trend of these approximations. Furthermore, the bulk moduli (Table 4.1) are also calculated for the compounds under investigation. So far we know, no experimental data are available for the bulk moduli and their pressure derivatives, so our result are considered as a prediction for these properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}$ and Gd).

Table 4.1: The calculated values of lattice parameters (a in $\text{\AA}$) and bulk moduli (B_0 in GPa) of LnIn_3 and LnSn_3 compounds.

Comp.		E_{xc}	a	B_0
SmIn_3	This work	LSDA	4.5645	60.4711
		GGA	4.6246	53.6537
		LDA+U	4.5595	56.2006
		GGA+U	4.7198	52.0019
		Expt ^a .	4.626	
EuIn_3	This work	LSDA	4.5707	63.7229
		GGA	4.6269	53.2488
		LDA+U	4.5639	63.2119
		GGA+U	4.7592	54.2521
GdIn_3	This work	LSDA	4.5167	62.3367
		GGA	4.5743	66.5797
		LDA+U	4.5075	66.2844
		GGA+U	4.6557	68.5292
		Expt ^a .	4.607	
SmSn_3	This work	LSDA	4.6052	68.8160
		GGA	4.6545	56.4352
		LDA+U	4.6135	65.4388
		GGA+U	4.7523	54.2082
		Expt ^b .	4.687	
EuSn_3	This work	LSDA	4.6313	73.2400
		GGA	4.6727	52.9966
		LDA+U	4.6316	58.2304
		GGA+U	4.7742	44.4547
		Expt ^b .	4.744	

Continuation of Table 4.1					
GdSn ₃	This work	LSDA	4.6412	61.0454	
		GGA	4.6412	61.0453	
		LDA+U	4.5947	72.2621	
		GGA+U	4.7227	67.5417	
		Expt ^b .	4.678		
a [67], b [80]					

4.1.3 Electronic Properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm, Eu, Gd}$) Compounds

In order to understand the electronic properties of the compounds under investigation, we first determine the total density of states (DOSs) and $4f$ DOSs with LDA and GGA. As in $4f$ orbital electron system, such as lanthanides the electron-electron correlation effects are strong, so for the better understanding of the $4f$ state, we adopt LDA+U, GGA+U and spin orbit coupling. The total and $4f$ DOSs calculated with different exchange and correlation potentials for LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm, Eu and Gd}$) are shown in Figs. 4.1, 4.2 and 4.3, respectively. The Fermi level is set at 0 eV. It is clear from Figs. 4.1, 4.2 and 4.3 that no band gaps are available at Fermi level for all these intermetallic compounds; hence all these compounds are metallic in nature.

Fig. 4.1 presents the total DOS (blue lines) and $4f$ DOS (red lines) using GGA for these compounds. The dominating character around the Fermi level is from rare earth elements. The tail of $4f$ states also crosses the Fermi level except GdIn_3 and GdSn_3 . For both GdIn_3 and GdSn_3 the $4f$ states lie below the Fermi level. From Fig. 4.1 we can see that the strong peaks which is due to $4f$ states located at -0.1 eV, -0.38 eV, -4.5 eV, -0.45 eV, -0.90 eV, and -4.5 eV for SmIn_3 , EuIn_3 , GdIn_3 , SmSn_3 , EuSn_3 and GdSn_3 respectively.

In Fig. 4.2 we have reported the total and $4f$ DOSs within LDA+U (black lines) and GGA+U (red lines) schemes. It is clear from the figure that the maximum peaks which is due to $4f$ states are shifted towards lower energies as compared with GGA (Fig. 4.1), this is in agreement with the previous DFT calculations that Hubbard U open the gap between occupied and unoccupied states [126].

Fig. 4.3 shows the total and $4f$ DOSs with GGA+SO. One can see that

the SOC does not change the energy position of $4f$ states. SOC causes to remove the spin degeneracy and so $4f$ DOSs calculated by GGA, LDA+U and GGA+U are split into two peaks. The two peaks corresponding to $j = 5/2$ and $j = 7/2$. The peaks corresponding to $j = 5/2$ are filled in all compounds and the peaks corresponding to $j = 7/2$ are filled in GdIn_3 and GdSn_3 and partially filled in the remaining compounds. In LnIn_3 and LnSn_3 compounds the magnetic moment arises from the f -electrons of lanthanides atom.

The total DOSs for LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) compounds in anti-ferromagnetic (AFM) phase are presented in Fig. 4.4. For AFM the calculations we construct $1 \times 1 \times 2$ cubic super-cell. It is clear from the figure that DOSs is symmetric in both spin up and spin down channels. Their magnetic moments are in opposite directions, and the corresponding total magnetic moment is equal to zero. At zero temperature all these compounds under study are in AFM phase. The calculated results are in good agreement with the experimentally [39, 48, 49, 67] observed AFM-like behavior in LnIn_3 and LnSn_3 compounds at low temperature.

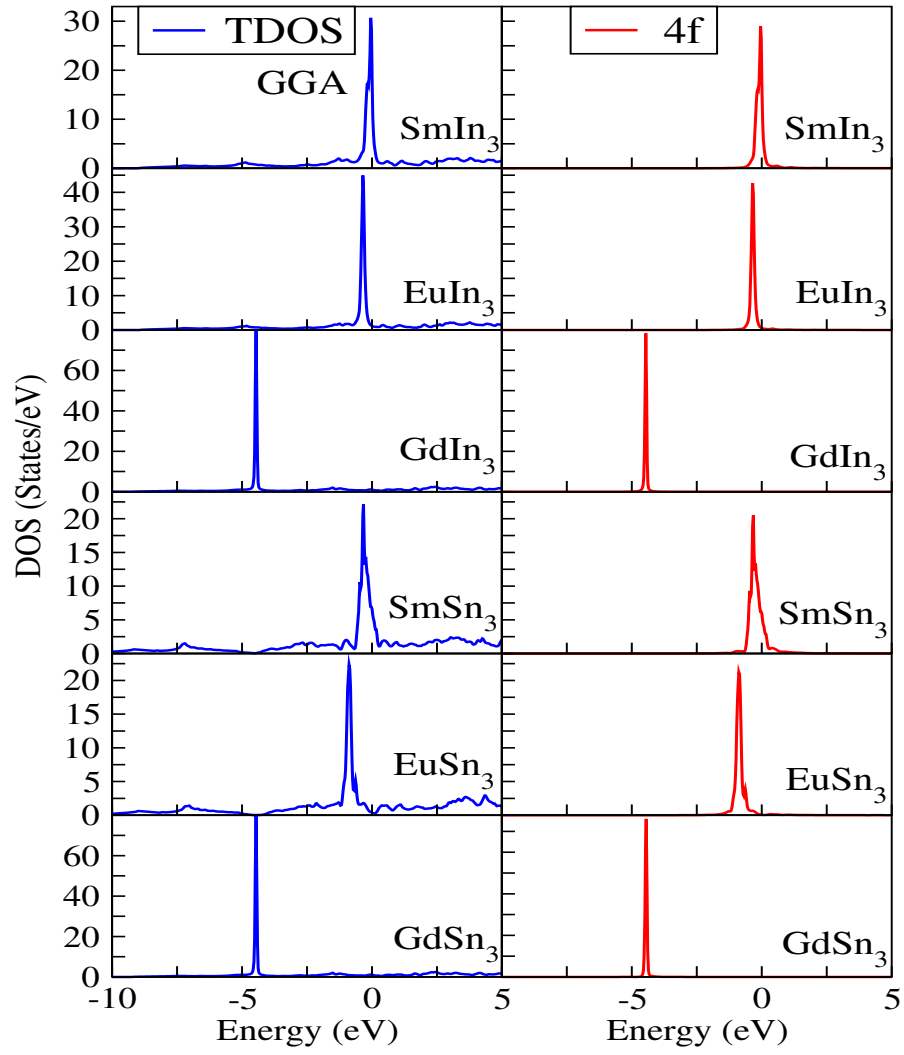


Figure 4.1: Total density of states TDOS (blue lines) and partial 4f DOS (red lines) of LnIn_3 and LnSn_3 for $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ calculated with GGA

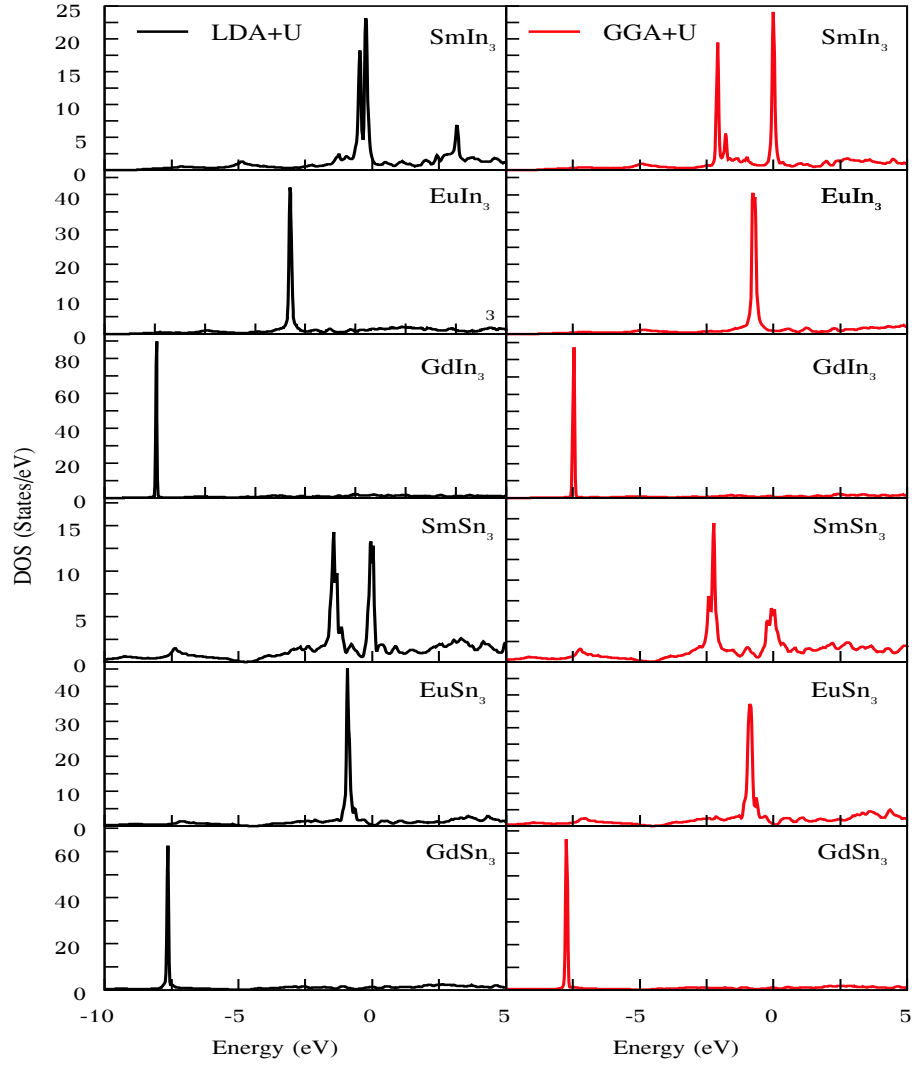


Figure 4.2: Total density of states TDOS with LDA+U (black lines) and GGA+U (red lines) of LnIn_3 and LnSn_3 for $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$

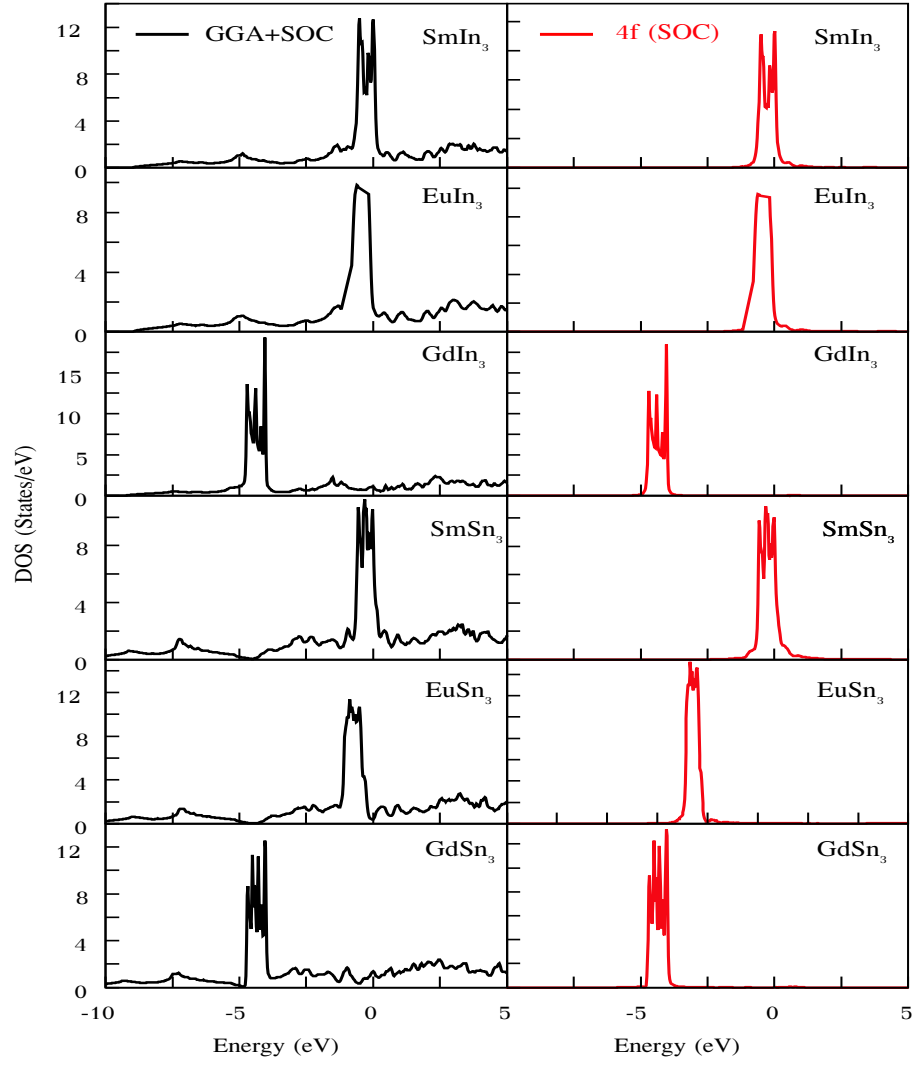


Figure 4.3: Total density of states TDOS (black lines) of LnIn₃ and LnSn₃ and partial 4f DOS (red lines) for Ln = Sm, Eu, and Gd calculated with GGA+SOC

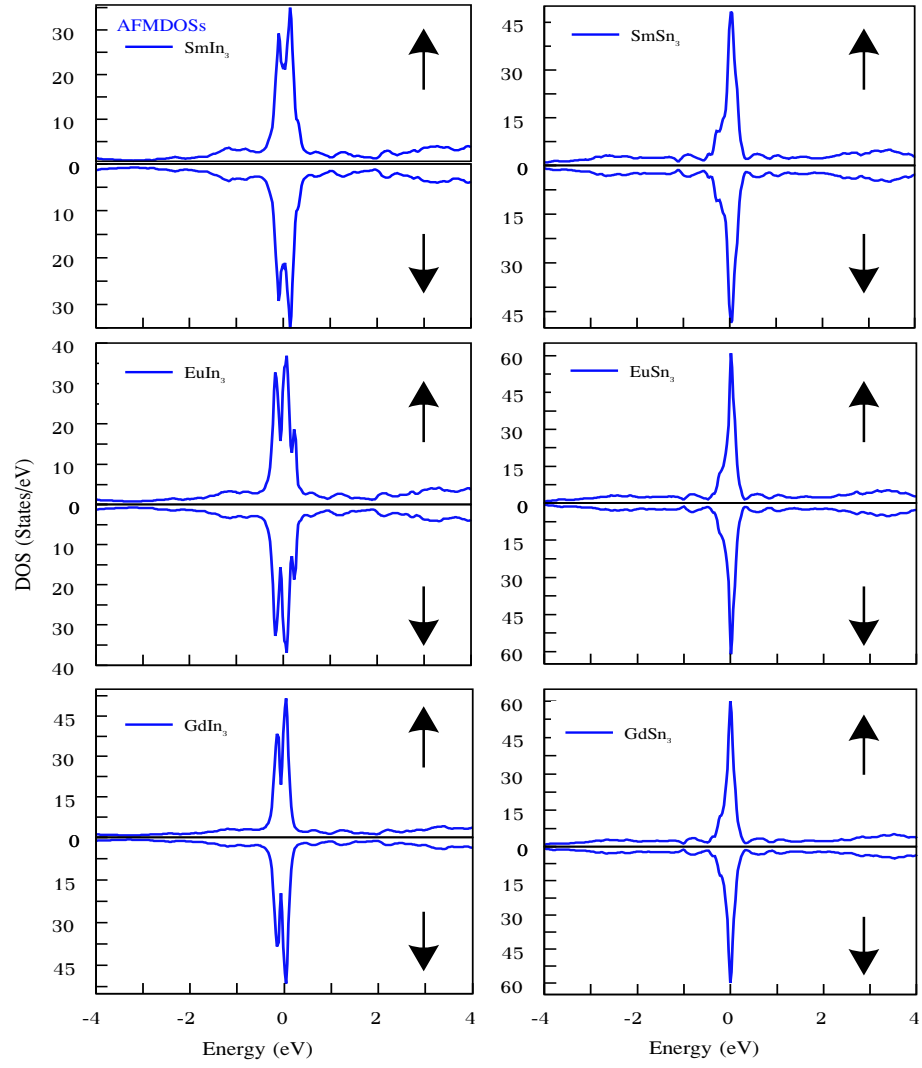


Figure 4.4: AFM DOSs for the double cell of LnIn_3 and LnSn_3 for $\text{Ln} = \text{Sm}$, Eu , and Gd

4.1.4 Elastic and Mechanical Properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) Compounds

Elastic constants of a solid are very important that describe the response to the applied stress and they are related to different fundamental solid-state phenomena such as intra-atomic bonding, equations of state, phonon spectra and structure stability. Elastic properties are also connected to the thermodynamical properties such as specific heat, thermal expansion, Debye temperature, and Gruneisen parameter. The elastic properties of solids are the indicators of mechanical strength which is a matter of great practical significance.

The three elastic constants C_{11} , C_{12} and C_{44} for LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) compounds are calculated with GGA approximation with and without spin polarization and are listed in Table 4.2. The only experimental available values of C_{11} and C_{44} for SmIn_3 and SmSn_3 Ref. [72] are used for comparison. The experimental values of C_{11} and C_{44} are at 100K and we have calculated the elastic constants at 0K. Thus the difference in temperature causes a small disagreement between our calculated and experimental values. The stability of a given crystal structure follows certain criteria. Furthermore, our calculated elastic constants fulfills the required stability conditions for the cubic structures of the compounds under study i.e., $C_{11} - C_{12} > 0$; $C_{44} > 0$ and $C_{11} + 2C_{12} > 0$ [88, 127]. The fulfillment of the above criteria justifies that these intermetallic compounds are elastically stable. Table 4.2 shows that the nonmagnetic phase largely influences the elastic properties of LnIn_3 and LnSn_3 compounds. The nonmagnetic ordering decreases the elastic constants values.

Table 4.2: The calculated values of elastic constants C_{11} , C_{12} , C_{44} (GPa) with spin polarization (GGA+SP) and without spin polarization (GGA).

Comp.	E_{xc}	SmIn ₃	EuIn ₃	GdIn ₃	SmSn ₃	EuSn ₃	GdIn ₃
C_{11}	GGA+SP	139.068	113.716	119.369	93.191	118.316	128.143
	GGA	100.476	100.413	118.385	99.429	94.142	114.310
	Exp.	125.3 ^c		95.4 ^c			
C_{12}	GGA+SP	60.276	56.308	63.034	42.836	61.175	59.806
	GGA	59.290	67.402	75.417	39.203	65.844	63.171
C_{44}	GGA+SP	28.171	28.450	27.862	43.003	51.377	52.275
	GGA	30.426	22.588	31.348	32.211	28.788	44.195
	Exp.	32.9 ^c		34.3 ^c			

^c [72]

The mechanical parameters such as bulk modulus B_0 , shear modulus G , Young's modulus Y , Poisson's ratio ν , anisotropic ratio A , which are the important mechanical parameters for industrial applications, are calculated from the elastic constants of the compounds under investigation and presented in Table 4.3. These are important parameters to characterize the mechanical behavior of a material. We explain the mechanical properties on the basis of results obtained by GGA spin polarized calculations. The average shear modulus, $G = G_H$, is a measure of resistance to plastic deformations upon stress [128]. As per Hill [129] average shear modulus, G is defined as arithmetic mean of Voigt shear modulus G_V and Reuss shear modulus G_R , which can be expressed as:

$$G_H = \frac{G_V + G_R}{2} \quad (4.1)$$

where

$$G_V = \frac{1}{5}(3C_{44} + C_{11} - C_{12}) \quad (4.2)$$

and

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (4.3)$$

The calculated value of $G = G_H$ is given in Table 4.3, which indicates that GdSn_3 exhibits the largest value of $G = G_H$, 44.082 GPa and GdIn_3 is with the lowest value of shear modulus that is 27.962 GPa. The other compounds lie in the range between these two values. The Young's modulus Y , the resistance of solid material to the linear strain along edges, is defined as the ratio between stress and strain. The compound is stiffer for the larger value of Y . It can be evaluated out from the computed values of Voigt shear modulus G_V and bulk modulus B_0 by the following equation:

$$Y = \frac{9B_0G_V}{3B_0 + G_V} \quad (4.4)$$

The presented value of Young's modulus Y in Table 4.3 shows that GdSn_3 compound is the stiffest of all. The higher values of young modulus as compared to Bulk modulus indicates the stiffness of these compounds. The ductile/brittle behavior of the materials can be calculated by the ratio of bulk modulus to shear modulus (B/G) proposed by Pugh [130]. The critical value for the ductile and brittle character was found to be 1.75. A high B/G ratio corresponds to ductility, whereas a low value is associated to a brittle nature of materials. It is clear from Table 4.3 that all compounds show ductile behavior, whereas SmSn_3 is brittle.

Cauchy's pressure is the difference between two particular elastic constant ($C'' = C_{12} - C_{44}$). Pittifor [131] suggests that Cauchy's pressure can be used to describe the bonding character of a compound. The positive value of Cauchy's pressure corresponds to metallic bonding while the materials with negative Cauchy's pressure attribute to the angular or directional bonding (covalent bonding). The increase in the negative value of Cauchy pressure leads to the more directional bonding, lower mobility characteristic of the material. Our calculated Cauchy's pressure for LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) are given in the table show that all these compounds have positive Cauchy's pressure and hence the metallic character in their bonds is dominant except SmSn_3 with negative value of Cauchy's pressure. The negative value of Cauchy's pressure for SmSn_3 indicates the directional or covalent bonding in this compound (brittleness). Furthermore, the positive and negative values of Cauchy's pressure are the indicator of the ductile and brittle nature which confirms that SmIn_3 , EuIn_3 , GdIn_3 , EuSn_3 and GdSn_3 are ductile whereas SmSn_3 is brittle.

The Poisson's ratio, ν is calculated using the relation:

$$\nu = \frac{3B_0 - Y}{6B_0} = \frac{1}{2} - \frac{Y}{6B_0} \quad (4.5)$$

Poisson's ratio is the measure of compressibility of a material. As Poisson's ratio approaches to 0.5, the material has a tendency to become incompressible [132] and at $\nu=0.5$ the material is near to incompressible. Our calculated values for ν lie between 0.347 and 0.230, which indicate that these materials are less compressible and stable against elastic deformation. The ν provides more information about the characteristics of the bonding forces. The lower and upper value of Poisson's ratio for the central forces in the material is 0.25 and 0.5, respectively [133]. The calculated values of ν for the compounds under investigation show that the interatomic forces are central forces except SmSn_3 in which the interatomic central force is not predominant.

A parameter ζ introduced by Kleinman is known as internal strain parameter [111]. It describes the relative tendency of bond bending versus the bond stretching. The lower limit corresponds to the minimizing bond bending and upper limit leads to bond stretching. Harrison [134] linked the Kleinman parameter in an approximated way to the elastic constants by following equation:

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} - 2C_{12}} \quad (4.6)$$

Our calculated results of ζ ranges from 0.879 to 0.728 indicate that bond bending is dominant in our materials. However, the larger value of the predicted values show that the contribution of bond stretching is also involved in these compounds.

The elastic anisotropic ratio A is another important parameter that determines whether the elastic properties remain constant in different direction or not? Anisotropic ratio A is also closely related with the possibility of inducing micro-cracks into the materials and can be calculated from the following equation [129]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (4.7)$$

“ A ” is unity for completely isotropic materials and the deviation from unity measures the amount of elastic anisotropy. The calculated values of anisotropic ratio A are given in Table 4.3 clearly indicate that these compounds are anisotropic.

Lame’s constants (λ, μ) can be calculated from Young’s modulus and Poisson’s ratio by using the following equations:

$$\lambda = \frac{Y\nu}{(1+\nu)(1-2\nu)} \quad (4.8)$$

and

$$\mu = \frac{Y}{2(1+\nu)} \quad (4.9)$$

Greater the value of Young modulus greater will be the values of Lame’s co-efficient. The two parameters together constitute a parameterization of the elastic moduli for homogeneous isotropic media. λ is known as Lame’s first constant and μ is Lame’s second constant. Their values for LnIn_3 and LnSn_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) are given in Table 4.3. Our results show that Lame’s second modulus is equal to Voigt’s shear modulus ($\mu = G_V$). For isotropic materials $\lambda = C_{12}$ and $\mu = C'$. As our compounds are strongly anisotropic compounds and do not satisfy the condition for isotropic compounds i.e., $\lambda = C_{12}$ and $\mu = C'$.

Another important mechanical parameter is the shear constant which is calculated by using the following relation:

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad (4.10)$$

Its values for the compounds under considerations are given in Table 4.3. It is also known as tetragonal shear modulus. The dynamical stability of a material requires that $C' > 0$. The positive values of our calculated materials indicate that they are mechanically stable materials. The higher values

of shear modulus corresponding the larger rigidity of the material to the tetragonal distortions.

Table 4.3: The calculated value of Voigt's shear modulus (G_V), Reuss's shear modulus (G_R), Hill's shear modulus (G_H), B/G ratio, Cauchy Pressure (C''), Poisson's ratio (ν), Kleinman Parameter (ζ), Anisotropy constant (A) Lames Coefficient (λ and μ), and and Shear Constant (C').

Comp.	SmIn ₃	EuIn ₃	GdIn ₃	SmSn ₃	EuSn ₃	GdIn ₃
G_V	32.661	28.552	27.963	35.873	42.254	45.032
G_R	31.795	28.551	27.962	33.512	38.943	43.132
G_H	32.228	28.551	27.962	34.693	40.598	44.082
Y	87.034	76.060	75.308	89.640	107.831	114.318
B/G	2.685	2.642	2.926	1.719	1.976	1.873
C''	32.105	27.858	35.208	-0.167	9.798	7.531
ν	0.332	0.332	0.347	0.249	0.276	0.269
ζ	0.728	0.826	0.879	0.769	0.861	0.780
A	0.715	0.991	0.988	1.708	1.798	1.530
λ	64.766	56.410	63.171	35.706	52.052	52.563
μ	32.661	28.552	27.963	35.873	42.254	45.032
C'	39.396	28.704	28.168	25.178	28.571	34.169

The thermo-physical properties like longitudinal v_l , transverse v_s , average v_m , sound velocities and Debye temperature $\theta(D)$ of these compounds are also calculated. The Debye temperature can be calculated using the following classical relation [135]:

$$\theta(D) = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (4.11)$$

where h is the Plank's constant and k_B is the Boltzmann's constant, N_A is the avagadro number, ρ is the density, M is the molecular weight, v_m is the average sound velocity and n is the number of atoms per formula unit. The average sound velocity in a polycrystalline material is approximately given by [136]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{2}{v_l^3} \right) \right]^{\frac{-1}{3}} \quad (4.12)$$

where v_l and v_s are the longitudinal and transverse sound velocities which can be obtained using the shear modulus G and the bulk modulus B_0 from Navier's equation, respectively [137]:

$$v_l = \left[\frac{B + \frac{4G}{3}}{\rho} \right]^{\frac{1}{2}} \quad (4.13)$$

and

$$v_s = \left[\frac{G}{\rho} \right]^{\frac{1}{2}} \quad (4.14)$$

The calculated values of the sound velocities, Debye temperatures as well as theoretical densities which can be obtained from the elastic constants are presented in Table 4.4. It is clear from the Tables 4.3 and 4.4 that the Debye temperature is directly related to the elastic moduli. Thus greater the elastic moduli, higher will be the Debye temperature. For the comparison no experimental data is available in the literature.

Table 4.4: The calculated values of density $\rho(g/cm^3)$, sound velocity of transverse wave $v_s(m/s)$, 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_l	v_s	v_m	$\theta(D)$
SmIn ₃	7.813	4071.39	2030.98	2278.69	143.75
EuIn ₃	7.652	3851.53	1931.63	2166.54	135.58
GdIn ₃	8.254	3800.59	1841.57	2069.55	132.35
SmSn ₃	7.835	3676.06	2104.25	2337.86	146.48
EuSn ₃	7.553	4162.83	2288.30	2550.71	157.71
GdIn ₃	8.092	4179.62	2334.02	2598.46	163.82

4.2 LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) compounds

4.2.1 Introduction

The rare-earth (Ln) intermetallic compounds are strongly correlated electron systems, where in this family of compounds LnX_3 ($\text{Ln} = \text{rare-earth}$ and $\text{X} = \text{In, Sn}$) are most exciting for their interesting physics. The LnX_3 compounds have attracted both experimental and theoretical attentions because of their diverse bulk properties such as low superconducting transition temperature, magnetic susceptibility and thermoelectric power as a function of their electron concentration [74, 75]. These compounds offer many possibilities by replacing X atom ($\text{X} = \text{In, Sn, Tl, Pb, etc}$), and their single crystals can be easily grown due to their congruently melting [19]. Many of the LnX_3 compounds crystallize in the cubic symmetries which is more favorable structure for superconductivity than lower symmetry [18]. Furthermore, these compounds are stable in the cubic structure at standard temperature and pressure (STP) and remain stable over a wide range of pressures [11]. In LnSn_3 solders (Sn-solder) the rare-earth element La, Ce, Er and Eu are used which is a suitable replacement of the Pb-Sn solder [22]. The amount of RE element in Sn-solder improves both the physical and mechanical properties and particularly enhances the ductility of the solder [23].

Due to the incomplete $4f$ shell, the spin-orbit interactions strongly effect the unoccupied $4f$ states of rare-earth atom in the vicinity of Fermi level, therefore the calculations of the accurate properties and the development of analytical and computational method for the lanthanides compounds is a challenging task for both, theoretical and experimentalists researchers [138].

LnX_3 ($\text{Ln} = \text{La, Ce, Pr and Nd}$, $\text{X} = \text{In and Sn}$) intermetallic compounds crystallize in the cubic AuCu_3 -type crystal structure with space group $Pm - \bar{3}m$ (No. 221). The point groups of Ln and X atoms are the cubic $m-3m$ and non-cubic $4/mmm$, respectively [17].

In the LnX_3 compounds, the valency of lanthanide can be inferred through lattice constant measurement technique. The lattice constant of Ln^{2+} is larger than Ln^{3+} by almost 10 % for pure lanthanides [139]. For diluted lanthanides LnX_3 ($\text{Ln} = \text{Eu, Yb}$) (addition of other elements with lanthanides), the lattice constant increases less than 2 % as compared to other LnX_3 compounds. This shows unusual nature of Eu and Yb, which display divalency in these $4f$ series of compounds [17, 34]. Most of LnIn_3 and LnSn_3 compounds are antiferromagnetic (AFM) [43, 42] except Pauli paramagnetic LaIn_3 , and paramagnetic LaSn_3 , CeSn_3 and PrIn_3 [46, 47, 140]. The AFM transition, Néel temperature (T_N), for CeIn_3 , NdIn_3 , PrSn_3 and NdSn_3 are 10 K, 5.9 K, 8.6 K, and 4.7 K respectively [68, 141, 142]. Some of the LnIn_3 and LnSn_3 exhibit superconductivity. The superconducting transition temperatures (T_c) for LaIn_3 , LaSn_3 and CeIn_3 are 0.71 K, 6.5 K, and 0.2 K, respectively [60, 61]. Moreover CeIn_3 and PrSn_3 are heavy fermions compounds [143, 144]. Due to both localized and itinerant characters of f electrons CeIn_3 is also called mixed valence or intermediate valence [145] and CeSn_3 is categorized as Kondo compound with valence fluctuation [146]. The Fermi surface properties and de Haas-van Alphen (dHvA) effect in LnX_3 compounds are reported by Ōnuki and Settai [47], whereas the pressure dependent electronic structure and optical conductivity of CeIn_3 compound in AFM phase are experimentally investigated by Iizuka et al. [120].

Some theoretical studies on the pressure dependent structural, electronic and elastic properties of the intermetallic compounds LaIn_3 , LaSn_3 , CeIn_3

and CeSn_3 are available [74, 75, 76, 77] in literature but their theoretical results are not consistent with the experiments because of the improper treatment of the exchange correlation potential in those calculations. In those studies, they have used LDA and GGA; whereas it is evident that LnIn_3 and LnSn_3 compounds are strongly correlated electron systems with $4f$ electrons. Therefore, to obtain the rational and logical electronic structure and other physical properties of these compounds, it is necessary to treat the strong correlation effects by an additional local Hubbard repulsion of magnitude U , i.e., DFT+ U techniques as well as spin-orbit coupling (SOC) effect to increase the accuracy of the calculated results.

These deliberations are considered in carrying out the calculations of the structural, electronic, elastic and mechanical properties of the intermetallic compounds, LnX_3 ($\text{Ln} = \text{La, Ce, Pr and Nd}$, $\text{X} = \text{In and Sn}$). The calculations are carried out by using the FP-LAPW+lo method under the framework of DFT. We have carried out these studies with the motivation that the elastic and mechanical properties of CeIn_3 , CeSn_3 , PrIn_3 , PrSn_3 , NdIn_3 and NdSn_3 have never been explored, neither theoretically nor experimentally, which may be have promising materials with good mechanical properties for practical applications. This section will cover the missing information in literature about these materials and will also provide basis for future experiments.

4.2.2 Ground State Structural Properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) compounds

The ground state structural properties of LnX_3 ($\text{Ln} = \text{La, Ce, Pr and Nd}$, $\text{X} = \text{In and Sn}$) are calculated by finding the total energy of the unit cell for each compound with respect to volume using Birch-Murnaghan equation of

state [125]. Lattice constants (a) and zero pressure bulk moduli (B_0) are determined by a variety of schemes including, LDA, GGA, GGAsol, WC-GGA, LDA+U, GGA+U, m-GGA and B3PW91 hybrid functional.

The theoretically calculated results of lattice constants and bulk moduli along with the available experimental data are listed in Table 4.5 and Table 4.6 respectively.

The calculated GGA, GGA+U and m-GGA lattice constants are slightly larger than those of GGAsol, WC-GGA, LDA+U and B3PW91, while the calculated values for the bulk moduli by GGA, GGA+U and m-GGA for these compounds are smaller than those of the GGAsol and WC-GGA and B3PW91. This confirms that the general trend of these approximations, GGA overestimates and LDA underestimates lattice constants [101]. Table 4.5 indicates that the computed lattice constants with B3PW91 hybrid functional are in better agreement with the experimental values than the other theoretical approaches. It is further clear from the table that B3PW91 is the best performing functional for strongly correlated systems as compared to other schemes. Table 4.5 also shows that as we move from La to Nd, the lattice constants are contracted, which can be attributed to the lanthanide contraction, i.e., the decrease in the atomic radius along the lanthanide series from left to right due to the poor shielding effect of the $4f$ electrons. Table 4.6 shows that the calculated bulk moduli by B3PW91 for all the compounds are very close to each other and lie in the range of 52.950 and 70.686 GPa. This trend of the bulk moduli is also evident from the calculated results by GGA-sol, GGA, m-GGA WC-GGA and LDA+U. No experimental data to the best of our knowledge is available for the bulk moduli, so our results are considered as a prediction for these properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd) compounds.

Table 4.5: The calculated value of lattice parameters (a in Å) of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr}$ and Nd) compounds.

	LDA	LDA	GGAsol	GGA	WC	LDA+U	GGA+U	B3PW91	m-GGA	Exp.
LaIn ₃	4.645	4.697	4.787	4.704	4.698	4.835	4.738	4.789	4.732 ^a	
CeIn ₃	4.554	4.601	4.718	4.609	4.612	4.761	4.676	4.708	4.687 ^a	
PrIn ₃	4.546	4.605	4.705	4.617	4.647	4.795	4.669	4.701	4.670 ^a	
NdIn ₃	4.540	4.603	4.689	4.609	4.626	4.765	4.647	4.696	4.653 ^a	
LaSn ₃	4.686	4.728	4.816	4.736	4.738	4.864	4.773	4.815	4.769 ^b	
CeSn ₃	4.589	4.626	4.755	4.637	4.636	4.785	4.710	4.749	4.721 ^b	
PrIn ₃	4.582	4.632	4.729	4.647	4.661	4.839	4.709	4.734	4.716 ^b	
NdIn ₃	4.581	4.624	4.713	4.637	4.644	4.776	4.701	4.713	4.705 ^b	

a [42], b [67]

Table 4.6: The calculated value of bulk moduli (B_0 in GPa) of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr}$ and Nd) compounds.

	LDA	LDA	GGA _{sol}	GGA	WC	LDA+U	GGA+U	B3PW91	m-GGA
LaIn_3		60.816	58.184	52.293	58.653	60.188	53.720	56.213	52.157
CeIn_3		74.382	63.580	52.703	63.166	61.029	51.628	61.100	50.536
PrIn_3		63.110	61.015	53.319	61.106	54.015	59.587	53.044	54.791
NdIn_3		63.493	61.943	52.527	59.278	69.926	49.240	64.591	49.120
LaSn_3		65.837	60.339	53.861	59.064	61.507	56.910	55.646	50.004
CeSn_3		79.210	71.621	67.212	71.920	71.445	55.026	70.686	60.948
PrIn_3		70.565	66.817	52.580	64.541	67.438	52.322	55.720	49.704
NdIn_3		72.514	62.381	56.295	66.712	69.969	51.222	52.950	51.046

4.2.3 Electronic Structure and Density of States of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) compounds

In order to reveal the electronic band structure, spin polarized total density of states (TDOS) and $4f$ density of states are calculated by employing GGA and LDA for the exchange and correlation functional. The DOSs calculated by GGA and LDA approximations are quite similar and only GGA density of states and $4f$ -DOS for LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr}$ and Nd , $\text{X} = \text{In}$ and Sn) are presented in Fig. 4.5, where the Fermi level is set at 0 eV. It is clear from the figure that no band gap is available at Fermi level for any of the intermetallic compounds under consideration; hence all these compounds are metallic in nature. The figure also reveals the dominating character of the f -state in all these compounds. It is also evident from the figure that no prominent peak occurs at the Fermi level for any of these compounds under study; therefore all these compounds are ductile in nature. The maximum peak of LaIn_3 and LaSn_3 are above the Fermi level in the unoccupied states around 2.74 eV and 2.95 eV, respectively. Therefore, LaIn_3 and LaSn_3 compounds show more ductility than the remaining LnIn_3 and LnSn_3 compounds, which is due to the large separation between the Fermi level and the f -state according to previous study [119].

The strongly correlated systems such as lanthanides (actinides) [84, 149] which involve $4f$ ($5f$) orbitals have interesting physical and chemical properties, because these electrons can be localized or itinerant depending on the crystal symmetry. Therefore, to understand the effects of the $4f$ orbitals in the lanthanides based compounds, the calculations are also carried out with the Hubbard potential U (GGA+ U and LDA+ U). The total density of

states (TDOS) with GGA+U and partial density of states (DOS) of f -states, as well as, the TDOS with- GGA are plotted in Fig. 4.6. It is clear from the figure that both GGA and GGA+U provides different DOS. The differences in the DOSs for all the compounds can be clearly seen from the figure. The figure clearly indicates that the strong peaks which are due to the $4f$ states are significantly shifted up and down by the application of the Hubbard potential (U) as compared to the GGA scheme. This is in agreement with the previous DFT calculations that Hubbard potential opens the gap between the occupied and unoccupied sates [126].

Spin-orbit coupling (SOC), which was evidently a weak relativistic correction to the Schrödinger equation in condensed matter physics has recently attracted enormous attention in the condensed-matter physics because of its vital role in $5d$, $4f$ and $5f$ orbitals. The spin and orbital degrees of freedom are implicated at a neighboring level by the SOC, where the total angular momentum gives a good interpretation of the ordered phases and different properties of a material and can also demonstrate the possible uses of a material in diverse devices with prominent functionalities [150]. To see the effect of the spin-orbit coupling (SOC) in the compounds under study their band structures along high symmetry directions with GGA and GGA+SO are presented in Fig. 4.7. It is evident from the figure that the effect on the band structures of LaIn_3 and LaSn_3 is very small, which is in agreement with the earlier work [74, 151]. The comparison of the band structures of these compounds reveals that, as one moves from La to Nd, the effect of SOC increases. This might be due to the fact that as the Coulomb attraction on an electron in a particular orbit increases, from La to Nd in the Periodic Table, the orbit shrinks and hence the electron speeds up to conserve the momentum of the system; where with this increase in the speed the relativistic

effects of SOC increases. The differences between the GGA and GGA+SOC band structures at the vicinity of the Fermi level are shown in the inset of each compound in Fig. 4.7 lifting some degeneracies in the band structures. The figure also shows that the band along symmetry line between X and M in CeIn_3 compound, dips below the Fermi level in the GGA scheme but stays above the Fermi level when the SOC is introduced. The degeneracy in PrIn_3 is observed at R symmetry line, whereas in CeSn_3 and PrSn_3 the degeneracies occur at M symmetry line. The SOC effects can be clearly seen for different symmetry lines in NdIn_3 and NdSn_3 .

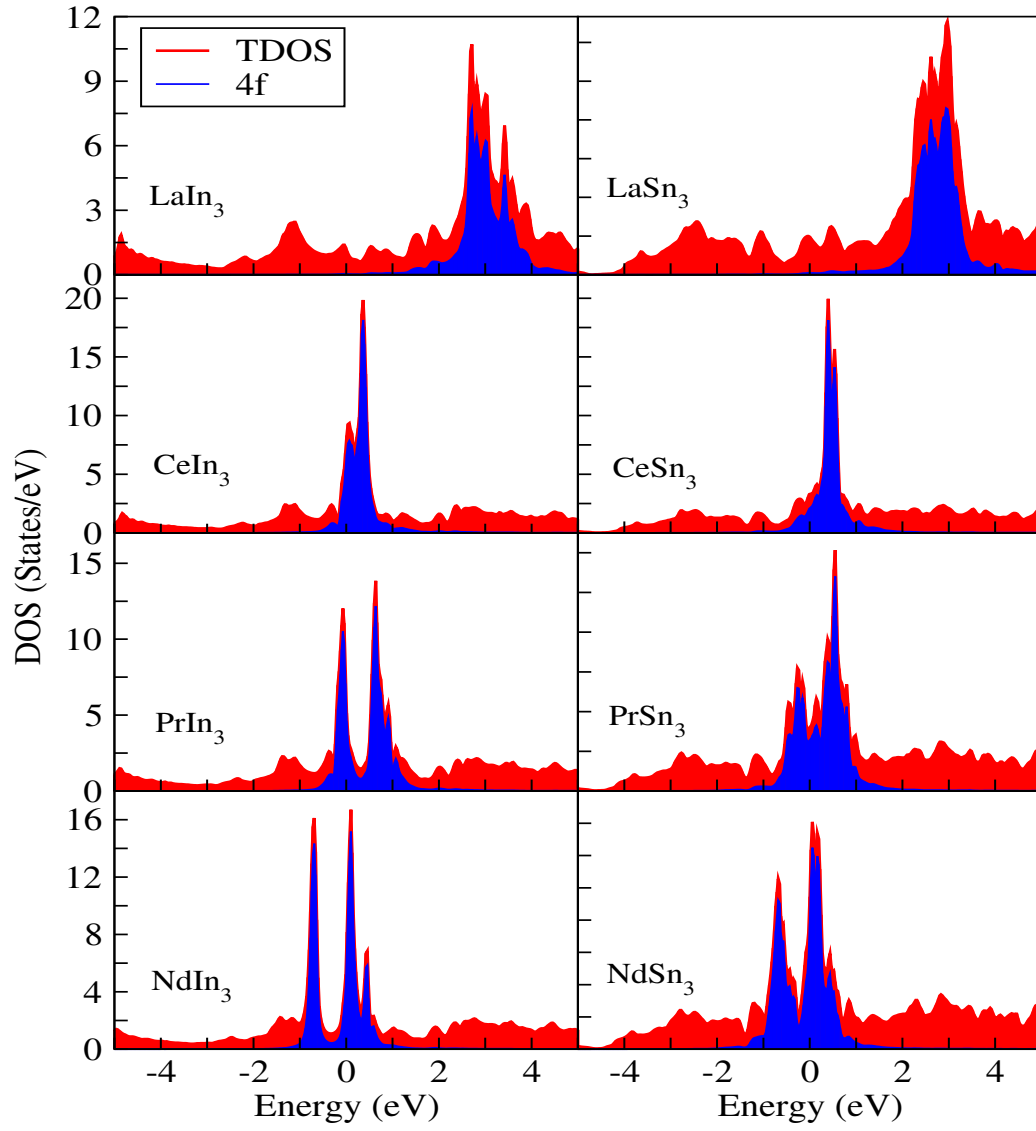


Figure 4.5: Total density of states TDOS (red shading) and partial 4f DOS (Blue Shading) of LnIn_3 and LnSn_3 for $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd calculated with GGA

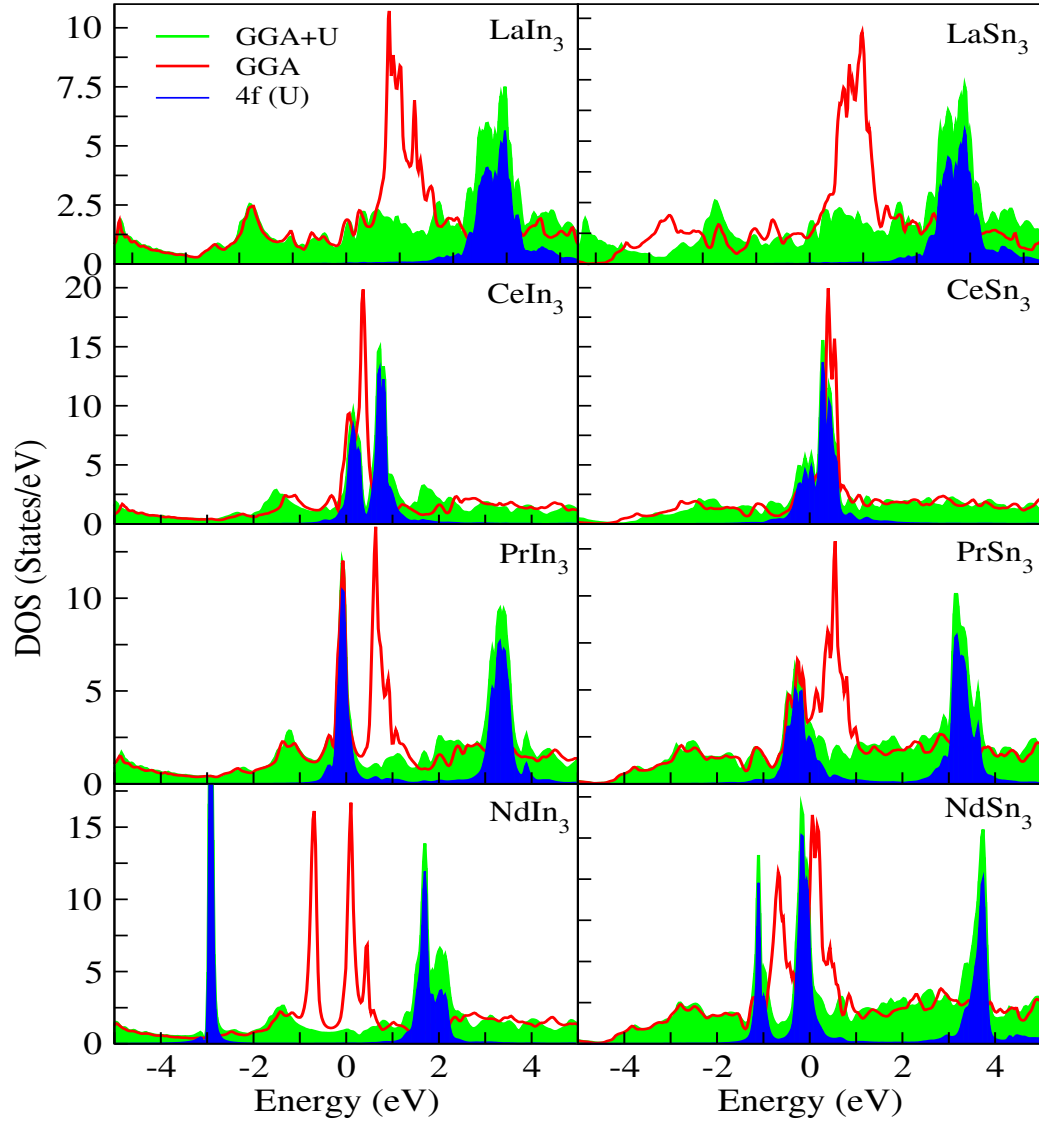


Figure 4.6: Total density of states (TDOS) with GGA (red lines), GGA+U (green shading) and PDOS GGA+U-4f (blue shading) of LnIn_3 and LnSn_3 for $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd

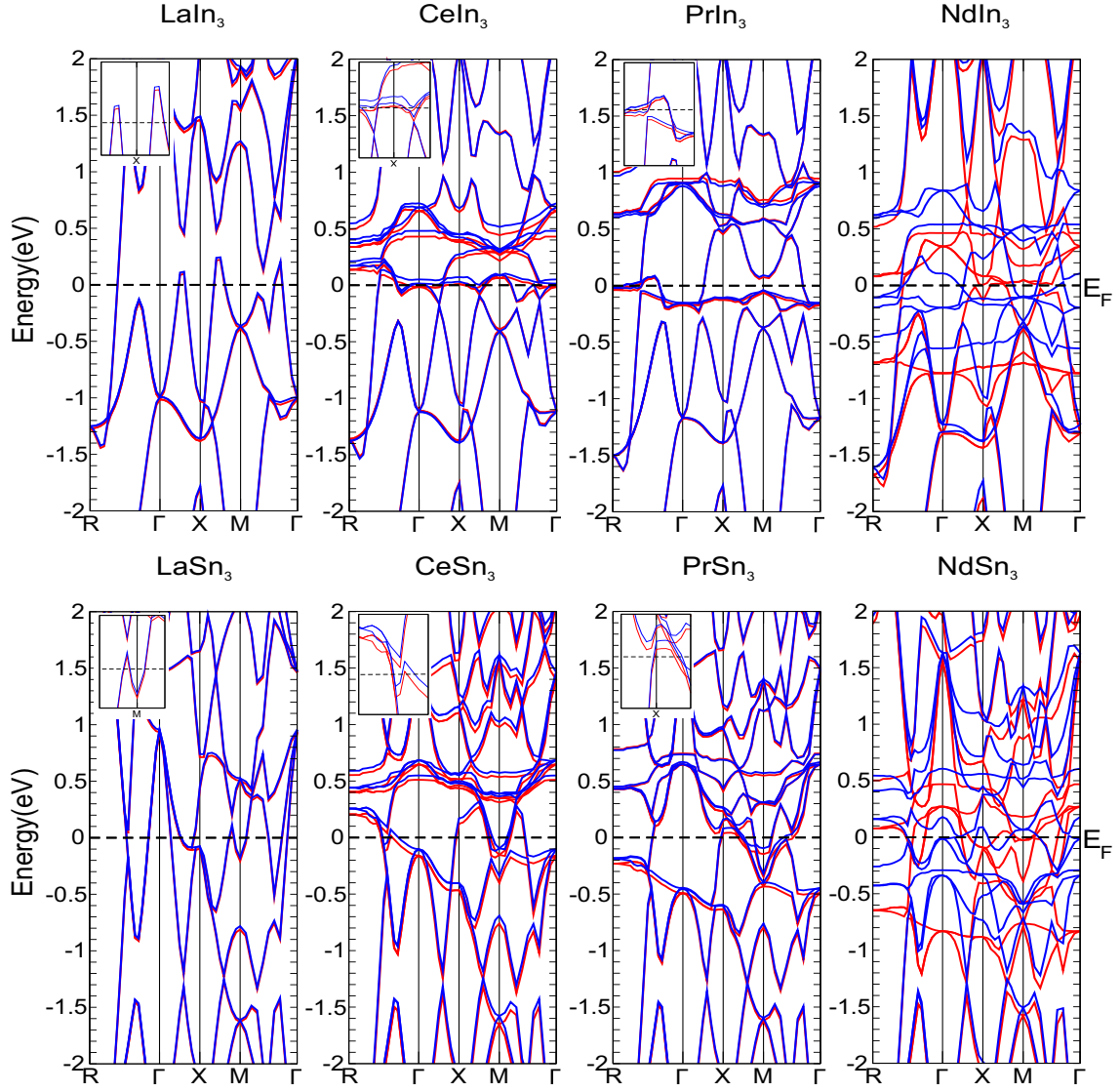


Figure 4.7: Comparison of electronic band structures calculated with GGA and SOC for LnIn_3 and LnSn_3 . The red lines show band structure with GGA without SOC, while the blue lines show the band structure with SOC

4.2.4 Elastic and Mechanical Properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) compounds

The elastic constants of solids give significant information regarding the nature of the forces operating in solids. Elastic constants are very important for understanding the relation between the crystal structure and bonding nature. These constants also reveal the structural stability and various other important physical properties of materials. The elastic constants C_{11} , C_{12} , and C_{44} for LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr}$ and Nd) are calculated within GGA and GGA_{sol} with spin polarization and are given in Table 4.7. The available experimental elastic constants (for LaSn_3) along with other theoretical results are also listed in the Table 4.7. The experimental data is unavailable for these compounds except LaSn_3 . It is evident from the table that our calculated values for the elastic constants of LaSn_3 compound with GGA_{sol} are in excellent agreement with the experimental values of Stassis et al. [152], extracted from the phonon dispersion curves, as compared to other theoretical results reported in Refs. [74, 76]. Hence, from the consistency of our calculated values with the experimental results for this compound, we infer that our calculated values for the remaining compounds under investigation will be also consistent with the corresponding experimental values. Moreover, the stability criteria initiated by Born [88] for cubic systems in term of elastic constants, i.e., $C_{11} - C_{12} > 0$; $C_{44} > 0$; $C_{11} + 2C_{12} > 0$ are well satisfied by these compounds. The fulfillment of these criteria justifies that these intermetallic compounds are elastically stable.

Table 4.7: The calculated values of elastic constants C_{11} , C_{12} , C_{44} (GPa) with GGA-sol and (GGA).

Comp.	E_{xc}	LaIn ₃	CeIn ₃	PrIn ₃	NdIn ₃	LaSn ₃	CeSn ₃	PrSn ₃	NdSn ₃
C_{11}	GGA _{sol}	89.265	95.500	83.878	82.569	69.273	99.084	80.343	87.167
	GGA	97.525	100.909	80.152	85.405	86.732	85.005	80.247	96.191
	Exp.					70.50 ^a			
	Others					97.30 ^b			
						83.17 ^c			
C_{12}	GGA _{sol}	42.555	45.609	37.137	41.498	42.328	53.678	38.842	34.211
	GGA	50.885	49.383	29.183	60.287	57.967	44.094	25.357	
	Exp.					42.00 ^a			
	Others					53.6 ^b			
						45.51 ^c			
C_{44}	GGA _{sol}	27.280	29.879	32.365	35.340	27.584	48.904	28.575	30.375
	GGA	28.125	37.543	34.767	33.997	35.463	45.431	28.370	27.367
	Exp.					33.50 ^a			
	Others					44.20 ^b			
						31.22 ^c			

a [152], b [74], c [76]

The trend of the mechanical properties of a material could be predicted from its elastic constants. As the elastic constants C_{11} , C_{12} , and C_{44} , calculated by both, GGA and GGAsol, exchange and correlation effects are very close to each other; therefore in present study the mechanical properties of the compounds are evaluated by the GGAsol results. The main mechanical parameters, i.e. shear modulus (G), Young's modulus (Y), Pugh's ratio (B/G), Cauchy's pressure (C''), Poisson's ratio (ν) and anisotropic ratio (A), which are important for industrial applications are calculated and presented in Tables 4.8. These important parameters are used to differentiate the mechanical behavior of a material.

The average Hill's [129] shear modulus, $G_H = G$, determines resistance to plastic deformations upon shear stress is the arithmetic mean of Reuss and Voigt shear modulus [128, 153]. The value of G_H given in Table 4.8 indicates that CeSn_3 offers more resistance to plastic deformation than the remaining compounds. The Young's modulus (Y) defines the ratio between the longitudinal stress and strain. The larger the value of Y , the stiffer will be the material. From Table 4.8 one can see that CeSn_3 has greater value of Young's modulus (stiffer). The higher values for the Young's moduli as compared to their Bulk moduli confirm the stiffness of these compounds. Hill's and shear moduli are further used to explain the ductile and brittle nature of a compound.

Pugh [130] suggested index of ductility and brittleness of a material. The Pugh's ratio (B/G) reflects the competition between the shear and cohesive strength of a material and describes its ductile/brittle character. If B/G is greater than the critical value 1.75, the material will be ductile; otherwise the material will be brittle in nature. It is evident from Table 4.8, that B/G ratio for all LnIn_3 and LnSn_3 compounds show ductile behavior ($B/G > 1.75$). The

larger value of B/G for LaSn_3 (2.412) and for LaIn_3 (2.267) reveals higher value of ductility. The same nature has also been observed in the DOS plot (Fig. 4.5) for LaSn_3 and LaIn_3 , showing more ductile nature than the other compounds. Ductile and brittle behavior of a compound can be also discussed in terms of elastic constants C_{12} and C_{44} . The Cauchy's pressure (C'') is used for this purpose and its positive/negative value shows the ductile/brittle behavior of a compound. The positive value of Cauchy's pressure (from Table 4.8) indicates that all the compounds under investigation are ductile in nature, which confirms the results of Pugh's B/G ratio. The Cauchy's pressure is also used to indicate the bonding character of the compounds. The positive value of Cauchy pressure is responsible for ionic bonding, while a material with Cauchy pressure is responsible for angular or directional bonding (covalent bonding). It is clear from Table 4.8, that all the compounds possess positive value of Cauchy's pressure having metallic bond and hence high mobility characteristics.

Poisson's ratio ν usually compute the stability of a crystal against shear (compressibility). Its typical lower and upper bound limits are -1 and 0.5 respectively. The lower limit bound is where the material does not change its shape and the upper limit bound is where the volume of the material remains unchanged [154]. Our calculated values for Poisson's ratio lie between 0.313 and 0.265, which show that these materials are less compressible and stable against external deformation. Poisson's ratio also demonstrates the ductile/brittle nature of a material. For ductile compounds $\nu \approx 0.3$ and for brittle compounds $\nu > 0.35$. The Poisson's ratio for all of these compounds is less than 0.35 ($\nu < 0.35$), which further confirms the ductile nature of these compounds. Furthermore, the Poisson's ratio also gives the details about bonding forces. For central forces in solids, the lower limit of ν is 0.25

and upper limit of ν is 0.5 [133]. The table shows that the calculated values of Poisson's ratio fall in this limit and the dominant interatomic forces are central forces.

The Kleinman internal strain parameter (ζ) describes the relative tendency of bond bending versus bond stretching [111]. Minimizing bond bending leads to $\zeta = 0$, while, minimizing bond stretching leads to $\zeta = 1$. The calculated Kleinman parameters in Table 4.8 predict that in LnIn_3 and LnSn_3 compounds bond stretching is dominant (upper limit of ζ).

Anisotropic ratio (A) which measures the elastic anisotropy of a material is very important property and is closely related to the induced microcracks in a material [155]. For an ideal isotropic material, anisotropic ratio is unity and deviation from unity measures the amount of anisotropy. From Table 4.8 one can see that the value of anisotropic ratio is found to be much greater than 1. The deviations from unity specify that these compounds are not elastically isotropic and their properties strongly vary in different directions.

The important parameter, which defines the dynamical stability of a material, is shear constant C' . It is also one of the criteria of mechanical stability and shows stability to the tetragonal distortion. Its values for the compounds under consideration are given in the Table 4.8. The positive values of shear constant ($C' > 0$) fulfills the required criteria of dynamical stability. From the calculated value of C' it is predicted that these compounds are dynamically stable materials.

Table 4.8: The calculated value of Voigt's shear modulus (G_V), Reuss's shear modulus (G_R), Hill's shear modulus (G_H), B/G ratio, Cauchy Pressure (C''), Poisson's ratio (ν), Kleinman Parameter (ζ), Anisotropy constant (A), and Shear Constant (C').

Comp.	LaIn ₃	CeIn ₃	PrIn ₃	NdIn ₃	LaSn ₃	CeSn ₃	PrSn ₃	NdSn ₃
G_V	25.710	27.906	28.767	29.418	22.139	38.424	25.445	28.816
G_R	25.562	27.689	28.047	27.430	19.849	33.459	24.830	28.686
G_H	25.636	27.797	28.407	28.424	20.994	35.941	25.138	28.916
Y	67.219	72.832	73.020	74.939	57.971	97.183	65.749	72.940
B/G	2.267	2.239	1.856	1.942	2.412	1.915	2.095	1.794
C''	15.275	15.730	4.772	6.158	13.744	4.774	10.267	3.836
ν	0.307	0.305	0.269	0.274	0.309	0.265	0.292	0.266
ζ	0.796	0.797	0.743	0.838	0.994	0.902	0.807	0.666
A	1.168	1.198	1.385	1.721	1.974	2.154	1.377	1.147
C'	23.355	24.946	23.371	20.536	13.973	22.703	20.751	26.478

4.2.5 Sound Velocities and Debye Temperature of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) compounds

The thermo-physical properties like longitudinal v_l , transverse v_s , average sound velocities v_m , and Debye temperature of the compounds under study are also investigated. The Debye temperature $\theta(D)$ of a compound can be calculated by using the following relation [135]:

$$\theta(D) = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (4.15)$$

Similarly, the average sound velocity v_m for any compound can be calculated by the following equation:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{2}{v_l^3} \right) \right]^{\frac{-1}{3}} \quad (4.16)$$

where v_l and v_s are the longitudinal and transverse sound velocities which can be determined in terms of the shear modulus G and the bulk modulus B_0 as:

$$v_l = \left[\frac{B + \frac{4G}{3}}{\rho} \right]^{\frac{1}{2}} \quad (4.17)$$

and

$$v_s = \left[\frac{G}{\rho} \right]^{\frac{1}{2}} \quad (4.18)$$

The calculated theoretical densities, sound velocities and Debye temperatures are reported in Table 4.9. The calculated densities are in excellent agreement with available experimental values in parentheses. A material with greater Debye temperature will be stiffer and exhibits high thermal conductivity. Table 4.9 shows that CeSn_3 is stiffer than the other compounds ($\theta(D) = 151.05$), which confirms the result of Young's modulus for CeSn_3 ($Y = 97.183$). The lower Debye temperature of LaSn_3 is the consequences of the lower elastic constants as compared to the rest of the compounds.

Table 4.9: The calculated values of density $\rho(g/cm^3)$, sound velocity of transverse wave $v_s(m/s)$, 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_l	v_s	v_m	$\theta(D)$
LaIn ₃	7.316(7.45 ^a)	3551.97	1871.88	2092.91	130.18
CeIn ₃	7.661	3600.34	1904.86	2166.58	136.73
PrIn ₃	7.737	3421.79	1916.10	2132.72	134.78
NdIn ₃	7.871	3439.08	1900.38	2117.45	134.46
LaSn ₃	7.358(7.46 ^a)	3269.06	1689.14	1891.06	116.92
CeSn ₃	7.664	3902.84	2165.59	2412.16	151.05
PrSn ₃	7.804	3323.42	1794.79	2003.25	126.14
NdSn ₃	7.936	3375.35	1908.81	2122.88	134.12
<i>a</i> [19]					

4.3 EFG analysis of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr, Nd}$) Compounds

4.3.1 Introduction

Analyzing nucleus-electron interactions beyond the nuclear point charge approximation can provide very useful information in condensed matter physics. Electric field gradient (EFG) is one of the physical quantities which can be resulted from this analysis. The EFG serves as a powerful tool to measure the interaction between atomic nucleus and electronic charge density around the nucleus [156]. The EFG takes place due to the rate of Coulomb potential change at the nucleus and the nature of EFG is very sensitive to a slight change in bonding, structure and dynamics of an atom [157, 158]. These properties are highly dependent upon the symmetry of the electronic charge density of core electrons [159] and valence electrons [160]. EFG can be used as a measure of the degree of electron's localization in the solids [17]. Experimentally EFG cannot be measured directly, but it can be obtained by different techniques such as Mössbauer spectroscopy (MS), perturbed angular correlation (PAC) spectroscopy, nuclear magnetic resonance (NMR), and nuclear quadrupole resonance (NQR) [92]. However, theoretically EFG can be accurately predicted by ab-initio method using density functional theory (DFT) [161]. Various theoretical studies are reported in the literature on the EFG in a variety of materials, for example, intermetallics, [162] metal complexes [163] magnetic [84] or multiferroic compounds [164].

In this section we calculate the EFG for the LnX_3 ($\text{Ln} = \text{La, Ce, Pr}$ and Nd , $\text{X} = \text{In}$ and Sn) series.

The structural and magnetic properties of LnIn_3 ($\text{Ln} = \text{Ce, Pr, Nd, Gd}$,

Tb, Dy, Ho, Er, and Tm) compounds have been reported by Buschow et al. [48] and the magnetic behavior of LnSn_3 , ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Gd}$) have been investigated by Tsuchida and Wallace [65]. From the magnetic measurement it was observed that most of LnIn_3 and LnSn_3 compounds have antiferromagnetic (AFM) ordering with the exceptional Pauli paramagnetic LaIn_3 , and paramagnetic LaSn_3 , CeSn_3 and PrIn_3 [47, 51, 140]. The structural, electronic and magnetic properties of LnSn_3 , compounds ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Yb}$) have been investigated using the 23.8 keV Mössbauer resonance of ^{119}Sn [67]. The Fermi surface properties and the de Haas-van Alphen (dHvA) effect in LnX_3 compounds were reported by Ōnuki and Settai [47].

The purpose of this work is to perform ab-initio calculations to undertake the EFG's of these LnIn_3 and LnSn_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) compounds, in order to fill the gap about the physical properties of these compounds in literature. The calculations are carried out with the FP-LAPW+lo method within the framework of density functional theory (DFT).

4.3.2 Electric Field Gradient of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) Compounds

A nucleus with nuclear spin quantum number $I \geq 1$ have nuclear quadrupole moment Q , which can interact with the electric field gradient (EFG). The EFG is a second rank traceless symmetric tensor with five independent components and originates to the deviation of the electron charge distribution from the spherical distribution in the vicinity of nucleus ($\leq 0.2\text{\AA}$) [17]. In particular, EFG is defined as the second derivative of a classical electrostatic potential with respect to Cartesian coordinates $V_{ij} = \partial^2 V / (\partial x_i \partial x_j)$ at nuclear position. The two main independent components are principal component V_{zz}

and asymmetry parameter $\eta = V_{xx} - V_{yy}/V_{zz}$, where the standard convention $|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$ is chosen for the principal axes. This also guarantees that η varies between 0 (axially symmetric) and 1 ($V_{xx} = 0$) [156, 167]. These two components are used in the analysis of the EFG measurements. In the principal axes system where EFG tensor is diagonal, the main component V_{zz} of EFG has been obtained by using the following relation [168]:

$$V_{zz} = \lim_{r \rightarrow 0} \sqrt{\frac{5}{4\pi}} \frac{V_{20}}{r^2} \quad (4.19)$$

where V_{20} is the radial potential and is given by [168]:

$$V_{20}(r=0) = \frac{4\pi}{5} \int_0^{R_{MT}} \frac{\rho_{20}}{r^3} \left(\frac{r}{R_{MT}}\right)^5 r^2 dr + 4\pi \sum_K V(\hat{K}) J_2(K R_{MT}) Y_{20}(\hat{K}) \quad (4.20)$$

where J_2 is spherical Bessel function, Y_{20} is the spherical harmonic for $l=2$, $m=0$. ρ_{20} is the component of charge density, ρ_{LM} for $L=2$, $M=0$ when it is expressed by lattice harmonics, i.e., LM form.

The first term in Eq. 4.20 is known as valence contribution of EFG (V_{zz}^{val}). V_{zz}^{val} comes from the non-spherical electron density of the valence and semicore electrons in Muffin-tin spheres. The sum of the second and third terms represents the lattice contribution of EFG (V_{zz}^{latt}) and arises from the outside of the Muffin-tin spheres and interstitial region.

The calculated values of the largest component of the EFG's (V_{zz}^{tot}) and their valence (V_{zz}^{val}) and lattice (V_{zz}^{latt}) contributions for LaIn_3 , PrIn_3 , LaSn_3 and CeSn_3 compounds using GGA and GGA+SOC are presented in Table 4.10. The calculated values of EFG's are also compared with the experimental values obtained from Mössbauer spectroscopy [67]. As LaIn_3 , PrIn_3 , LaSn_3 and CeSn_3 compounds exist in paramagnetic phase [47, 51, 140], therefore as a first approximation the calculations for these compounds are performed in nonmagnetic phase. It is clear from Table 4.10 that in non-

magnetic phase, the GGA functional provides good results in comparison with the experimental values for these compounds. In these compounds only the In and Sn nuclei which have a non-cubic symmetry, exhibit the electric quadrupole interaction, and have nonzero EFG. At rare-earth elements La, Ce and Pr sites (Table 4.10) the EFGs are zero due to the cubic symmetry for all the nonmagnetic phase with and without SOC effects. The results show that, the magnitude of EFGs for LaIn_3 and PrIn_3 are closer to each other, hence the electron density distributions near the In nuclei are similar. The same also holds for Sn nuclei in LaSn_3 and CeSn_3 .

Table 4.10: Calculated main component of the EFG, V_{zz}^{tot} , valence part V_{zz}^{val} and lattice part V_{zz}^{latt} (in $10^{21}\text{V}/\text{m}^2$), at In and Sn sites for nonmagnetic phase compared with the available experimental EFG values.

		GGA			GGA+SOC			
Comp.	site	V_{zz}^{tot}	V_{zz}^{val}	V_{zz}^{latt}	V_{zz}^{tot}	V_{zz}^{val}	V_{zz}^{latt}	Exp.
LaIn_3	In	11.914	11.945	-0.031	11.833	12.084	-0.251	
PrIn_3	In	12.832	12.853	-0.021	12.115	13.096	-0.981	
LaSn_3	Sn	16.719	16.761	-0.042	16.945	17.247	-0.302	16.89^a
CeSn_3	Sn	18.487	18.518	-0.031	18.546	18.863	-0.317	17.97^a

a [67]

Table 4.11: Calculated main component of the EFG, V_{zz}^{tot} , valence part V_{zz}^{val} and lattice part V_{zz}^{latt} (in $10^{21}V/m^2$), at In and Sn sites for AFM phase compared with the available experimental EFG values.

		GGA			GGA+SOC			GGA+SOC			
Comp.	site	V_{zz}^{tot}	V_{zz}^{val}	V_{zz}^{latt}	V_{zz}^{tot}	V_{zz}^{val}	V_{zz}^{latt}	V_{zz}^{tot}	V_{zz}^{val}	V_{zz}^{latt}	Exp.
CeIn ₃	Ce	0.023	0.025	-0.002	-2.739	-2.732	-0.007	-0.042	0.244	-0.286	11.60 ^a
	In	12.691	12.716	-0.025	11.693	11.683	0.010	12.455	12.945	-0.490	
NdIn ₃	Nd	-0.134	-0.135	0.001	-1.339	-1.335	-0.004	0.124	0.777	-0.653	
	In	12.362	12.386	-0.030	11.759	11.784	-0.025	12.423	12.482	-0.059	
PrSn ₃	Pr	-0.284	-0.285	0.001	-2.629	-2.627	-0.002	-0.248	-0.162	-0.086	15.65 ^a
	Sn	17.174	17.206	-0.032	16.466	16.499	-0.033	17.214	17.402	-0.188	
NdSn ₃	Nd	-0.207	-0.208	0.001	-1.616	-1.614	-0.002	-0.316	0.251	-0.567	
	Sn	17.217	17.247	-0.030	16.981	17.014	-0.033	17.305	17.723	-0.418	

^a [67]

Table 4.11 presents the calculated values of the EFG's (V_{zz}^{tot}) and their related valence (V_{zz}^{val}) and lattice (V_{zz}^{latt}) contributions for CeIn_3 , NdIn_3 , PrSn_3 and NdSn_3 compounds. LnIn_3 and LnSn_3 compounds with $\text{Ln} = \text{Ce}, \text{Pr}$ and Nd , exist in AFM phase [68, 141, 142]. The calculations for these compounds are performed in the magnetically split AFM phase by using GGA, GGA+U and GGA+SOC.

The results listed in Table 4.11 are compared with the available experimental results. It is evident from Table 4.11 that our calculated results by GGA and GGA + SOC approach overestimate the EFGs with respect to the experimental values. Our theoretical calculations for EFG values performed with GGA+U agree well with the experimental results. As lanthanides can form strongly correlated systems due to their $4f$ electrons, hence the better agreement confirms that we have properly treated correlations among the $4f$ electrons within GGA+U calculations. Table 4.11 also indicates nonzero EFG values at rare-earth (Ce, Pr and Nd) site. The nonzero EFG values are due to the fact that AFM ordering can cause a slight deviation from the cubic symmetry around the rare-earth atom.

The main contribution of the EFG is due to the anisotropy of charge distribution in the vicinity of nuclei. In order to further analyze these contributions, we evaluate the orbital contributions V_{zz}^{p-p} , V_{zz}^{s-d} , V_{zz}^{d-d} , V_{zz}^{p-f} , V_{zz}^{f-f} . Fig. 4.8 shows the orbital contributions of nonmagnetic phase and AMF phase of the compounds under consideration using GGA, GGA+U and GGA+SOC.

It is clear from the Fig. 4.8, that the $p-p$ contribution is dominant at In and Sn sites in case of all approximations for both nonmagnetic and AFM phases. The dominant value of $p-p$ contribution indicates that, the electron density of $5p$ electrons around the indium (in LnIn_3) and tin (in LnSn_3)

atom is identical across the series and independent of rare-earth atom. It is also seen from Fig. 4.8, that $s-d$, $d-d$, $p-f$ and $f-f$ contributions are very small to the valence EFGs and comparable in magnitude. Fig. 4.9 presents the orbital contribution of Ce atom in CeIn_3 . It is evident from the figure that at Ce site the $f-f$ contributions dominates as compared to the p -states. This demonstrates that at rare-earth nuclei (Ce, Pr, and Nd) , the main contribution to valence EFGs are originated by $4f$ states.

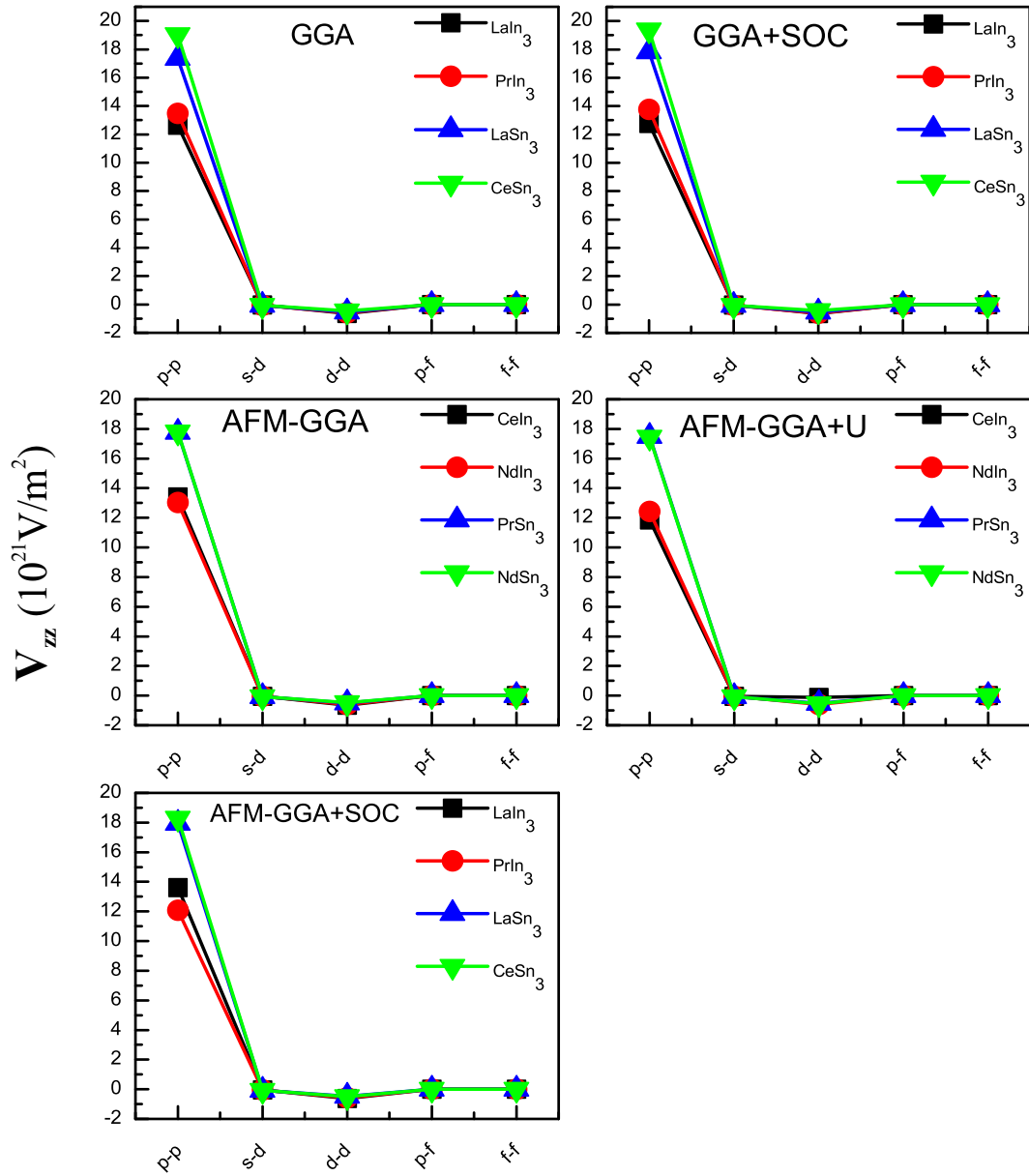


Figure 4.8: Decomposition of the valence EFG into $p-p$, $s-d$, $d-d$, $p-f$ and $f-f$ contributions calculated for nonmagnetic and AFM phases with GGA, GGA+U and GGA+SOC

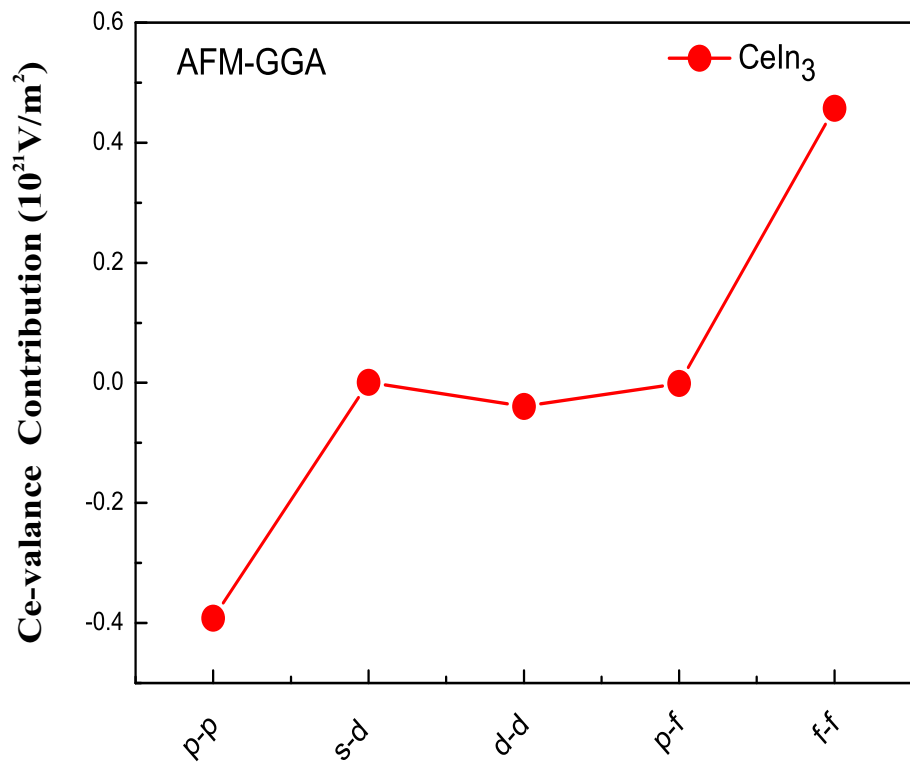


Figure 4.9: Decomposition of valence EFG at Ce site for AFM phase

Chapter 5

Conclusions

In this thesis, first principle calculations have been performed to theoretically study the structural, elastic, mechanical, and electronic properties of LnIn_3 and LnSn_3 ($\text{Ln} = \text{La-Gd}$, $\text{X} = \text{In, Sn}$) compounds using PF-LAPW+lo method within DFT. The structural properties calculated with different exchange and correlations functional of these compounds are consistent with the experimental results. Our calculated results show the divalency in $4f$ series (EuIn_3 and EuSn_3) and nicely confirm the lanthanides contraction in both LnIn_3 and LnSn_3 cases.

The density of states and band structures reveal the intermetallic nature of these compounds. The Hubbard U potential (GGA + U and LDA + U) shifts the $4f$ peaks towards lower energies and open the gap between occupied and unoccupied states. The SOC further split $4f$ state into two states with changing the energy position of $4f$ states. It is concluded that the SOC effect, which is a correction to Schrödinger wave equation, increases as one goes from La to Nd in a compound, which demonstrates interesting nature of SOC in the lanthanides series. We also observed the influence of the spin-orbit coupling strength on the band structure.

The elastic and mechanical properties show that these compounds are elastically stable. The higher values of Young's modulus than Bulk modulus and shear modulus indicate that these compounds are stiffer. The higher value of B/G (> 1.75) for all LnIn_3 and LnSn_3 compounds show a ductile behavior except SmSn_3 . The positive Cauchy's pressure values indicate the metallic bonds and hence high mobility characteristics in these materials. The values of Poisson's ratios indicate that these materials are less compressible and are stable against external deformation. Poisson's ratios also show that the intra-atomic forces in these compounds are central forces. The deviations from unity specify that these compounds are not elastically isotropic and their properties vary strongly in different directions.

The thermo-physical properties like longitudinal v_l , transverse v_s , average sound velocities v_m , and Debye temperatures $\theta(D)$ of the LnIn_3 and LnSn_3 compounds under study are also investigated. The higher Debye temperatures indicate that these compounds exhibit high thermal conductivity.

We have calculated the EFG parameters for LnIn_3 and LnSn_3 ($\text{Ln} = \text{La, Ce, Pr and Nd}$) by means of DFT using FP-LAPW + lo method. The calculated EFG parameters are consistent with the experimental values. Our analysis suggests that the main contributions to In and Sn sites come mainly from $5p$ state. At rare-earth site the valance EFG is predominantly from $4f$ states. From the orbital contributions it is evident that the p - p contribution is dominant at In and Sn sites in case of all approximations for both nonmagnetic and AFM phases.

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