ELECTRONIC PROPERTIES OF TOPOLOGICAL SEMIMETALS, AND WIDE-GAP OXIDE SEMICONDUCTORS USING HYBRID DENSITY FUNCTIONAL THEORY

by

Shoaib Khalid

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Winter 2022

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Shoaib Khalid

Approved: _

Edmund Nowak, Ph.D. Chair of the Department of Physics and Astronomy

Approved: _____

John A. Pelesko, Ph.D. Dean of the College of Arts and Sciences

Approved: _____

Louis F. Rossi, Ph.D. Vice Provost for Graduate and Professional Education and Dean of the Graduate College I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Anderson Janotti, Ph.D. Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Yi Ji, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Xi Wang, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Chitraleema Chakraborty, Ph.D. Member of dissertation committee

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- "Strong band gap reduction in highly mismatched alloy InAlBiAs grown by molecular beam epitaxy" J Zhang,Y Wang, S Khalid, A Janotti, G Haugstad, J M O Zide. J. Appl. Phys. 126, 095704 (2019)
- "Identifying the fingerprints of topological states by tuning magnetoresistance in a semimetal: The case of topological half-Heusler $Pt_1 xAu_xLuSb$ " S Chatterjee, F Lima, J A Logan [et al, including S Khalid] Phys. Rev. Mater. 5(12), 124207 (2021)
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ABSTRACT

Computational materials science is at the forefront of discovering new materials and predicting novel material properties with much improved efficiency. In this work we used first principles methods based on density functional theory to explore a wide range of material properties with an objective to develop and optimize materials properties for a range of applications. We studied the electronic structure, carrier densities and band alignments in rare-earth monopnictides (RE-V), effects of hydrostatic pressure and epitaxial strain on their band structures, the formation of 2D hole gas at the interface between LuSb and GaSb, defect-controlled Fermi-level tuning in half-Heusler topological semimetals (LuPtSb, LuPtBi), and electronic properties of corundum-structured Ir_2O_3 , Ga_2O_3 and their alloys for high power electronic devices and heterojunctions.

The electronic and magnetic properties of rare-earth monopnictide (RE-V) have long been studied both experimentally and by theory, but there have been notable contradictions in the experimental characterization of the electronic properties of these materials. Previous theoretical work was able to clarify only a few specific properties of some RE-V compounds, yet general agreement with experiments for the complete series was not satisfactory. Motivated by this, we focused on RE-V compounds, with RE=La, Gd, Er, and Lu, and V=As, Sb, and Bi, and analyzed the effects of spinorbit coupling and treating the RE 4*f* electrons as valence electrons. Our calculations predict that all the RE-V compounds are semimetals with electron pocket at X point and hole pocket at Γ point. The predicted carrier densities are in good agreement with available experimental data. Based on our understanding of rare-earth monopnictide (RE-V), we explored the effects of hydrostatic pressure on the electronic properties of LaAs. We find that in DFT-GGA, under the calculated equilibrium lattice parameter, LaAs displays a crossing between the highest As p band and the lowest La d band near the X point due to the overestimated p-d band overlap. Such crossing does not occur when the band overlap is corrected in the HSE06 hybrid functional calculation, in agreement with experiments. However, we find that the p-d crossing can be induced in LaAs under hydrostatic pressure, showing a topological phase transition at ~7 GPa. The rocksalt crystal structure of LaAs is predicted to be stable under applied pressure up to 20 GPa, in good agreement with experimental observations. We also showed that non-trivial topological phase can be introduced in LaSb under the effect of epitaxial strain. We show that under compressive epitaxial strain, the La d band crosses the Sb p band near the Z point in the Brillouin zone, stabilizing a topologically nontrivial phase, opening unique opportunities to probe epitaxially strained thin films.

In a joint project with an experimental group at the University of California Santa Barbara, we explored emergent phenomena in rare-earth monopnictide (RE-V) thin films via quantum confinement. We show that quantum confinement lifts carrier compensation and differentially affects the carrier density of the electron and hole-like carriers resulting in a strong modification in its large, non-saturating magnetoresistance behavior. We predicted a 2D interfacial hole gas due to the bonding mismatch at hetero-epitaxial interface of the semi-metal (LuSb) and a semiconductor (GaSb) which is accompanied by a charge transfer across the interface creating opportunity to tune magnetoresistance and engineer hetero-epitaxial interface.

Motivated from the recent experimental work on half-Heusler topological semimetals, we investigate how point defects impact the Fermi level position in two representative half-Heusler topological semimetals, PtLuSb and PtLuBi; we explore how intrinsic defects can be used to tune the Fermi level, and explain recent observations based on Hall measurements in bulk and thin films. Under typical growth conditions we show that Pt vacancies are the most abundant intrinsic defects, leading to excess hole densities that place the Fermi level significantly below the expected position in the pristine material. Suggestions for tuning the Fermi level by tuning chemical potentials are discussed. Finally, we worked on corundum phase of Ir_2O_3 , Ga_2O_3 and their alloys. α -Ga_2O_3 is ultra-wide band gap semiconductor that can be easily doped *n*-type, but not *p*-type. Finding a lattice matched p-type material is highly desirable for device applications. In this context, we studied Ir_2O_3 and its alloys with α -Ga_2O_3. The stability and electronic structure of α -(Ir_xGa_{1-x})₂O₃ alloys are studied along with variations of band edge positions with Ir/Ga concentrations. Our results indicate that Ir_2O_3 can be made *p*-type, and the predicted band alignment at the Ir_2O_3/Ga_2O_3 interface is in good agreement with experimental data, opening up opportunities for *p*-type Ir_2O_3 -based heterojunctions for high power electronic devices.

Chapter 1 INTRODUCTION

1.1 Rare-earth monopnictides

Rare-earth elements and their compounds have been studied for more than 8 decades. The interest in rare-earth compounds increased during 1960s mainly motivated by the search of ferromagnetic semiconductors. Rare-earth monopnictides (RE-V) are very attractive for research because of their simple rock-salt crystal structure and the occupation of their 4f shell ranges from 0 to 14 through the series La to Lu, which means these compounds can have variety of magnetic and electronic properties. RE-V compounds display interesting electronic, magnetic, optical and magneto-optical properties, with applications including thermoelectrics [26], tunnel junctions [27], photoconductive switches, and terahertz detectors [28]. Their rock salt crystal structure is compatible with the zinc blende structure of III-V semiconductors. It has been demonstrated that RE-V compounds can be epitaxially grown on III-V semiconductors [29, 30, 31, 32], to which RE-V have been explored as the ultimate ohmic contacts with high structural quality due to the small lattice mismatch [33]. For instance, ErAs and TbAs have lattice parameters very close to those of GaAs and InGaAs alloys [34, 35, 36], respectively. Some of the RE-V compounds have been investigated due to their non-trivial topological band structures [37, 38, 39], and have shown effects of extreme magnetoresistance [40, 41] and superconductivity [42] at low temperatures.

The electronic and magnetic properties of RE-V have long been studied both experimentally [42, 10, 2, 31, 32] and by theory [43, 44, 45, 39]. There have been notable contradictions in the experimental characterization of the electronic properties

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<u>К</u> 37	Ca 38	39 39	40 Ti	41 41	42 42	Mn 43	Fe 44	45	Ni 46	47 47	<u>Zn</u>	Ga 49	Ge 50	As 51	52 52	Br 53	Kr 54
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	1	Xe
°°Cs	Ba	Lantha- nides	Hf	Ta	Ŵ	Re	⁷⁶ Os	″lr	Pt	Âu	⊮ Hg	TI	Pb	ืBi	Po	At	₿ Rn
⁸⁷ Fr	⁸⁸ Ra	Acti- nides	Z														
		Lantha- nides	₅ La	⁵⁸ Ce	Pr	⁶⁰ Nd	Pm	⁶² Sm	Eu	⁶⁴ Gd	55 Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	Lu

Figure 1.1: Periodic table showing rare-earth lanthanides (yellow) and the pnictides (blue).

of these materials. Early measurements of electrical resistivity have shown metallic as well as semiconducting behavior [46], while optical measurements have shown signs of a semiconducting band gap [47]. Previous theoretical work were limited to semiclassical treatment of the crystalline field[48], or simplified models that account for the *p*-*f* mixing [49], *d*-*f* coulomb interaction [50], and an effective point-charge model for the crystalline field [51]. These models could clarify only few specific properties of some RE-V compounds, yet general agreement with experiments for the complete series was not satisfactory [5]. Using an augmented plane wave method with the Slater X_{α} exchange potential [52] and treating the 4*f* electrons as core electrons, Hasegawa and Yanase [5] claimed that GdN is a semiconductor with a band gap of 1 eV and all the other Gd monopnictides are semimetallic.

A remarkable feature of RE-V compounds is the presence of occupied 4f electronic states near to or resonant in the valence band. As the number of 4f electrons increases from La (no f electrons) to Lu (fully occupied 4f shell), the RE-V series displays a variety of magnetic and electronic effects. The coexistence of partially filled 4f shell along with itinerant p and d charge carriers has been quite challenging to an accurate description of the electronic structure of RE-V compounds. Petukhov *et al.* [1] performed first-principles calculations using the linear-muffin-tin-orbital (LMTO)

method within local spin-density approximation for ErAs and $\text{Er}_{1-x}\text{Sc}_x\text{As}$, treating the Er 4f electrons as core-like electrons. They found cyclotron masses in good agreement with experimental data [10], however, the Fermi surface dimensions were significantly overestimated. Subsequently, Petukhov *et al.* [53] studied the electronic properties of GdX and ErX (X = N,P,As), performing test calculations for ErAs and GdAs with 4f electrons in the valence and in the core. They reported that treating the 4f electrons in the valence leads to strong perturbation of the bands near the Fermi level, and incorrectly predicts that these compounds are not semi-metals. They also claimed that GdN is metallic for one spin channel and semiconducting in the other. Later studies treated 4f as core electrons [5, 54] while some others highlighted the need of including the f electrons in the valence [55, 56].

More recently, a combination of DFT and dynamical mean-field theory (DMFT) calculations indicate the importance of including the 4f electrons in the valence to correctly describe the dimensions of the Fermi surface pockets, carrier concentration, and Shubnikov-de Haas (SdH) oscillation frequencies [8]. These calculations are rather computationally expensive, and finding other more computationally affordable methods that correctly describe the effects 4f electrons on the electronic structure of RE-V compounds is highly desirable. We studied the electronic structure of RE-V compounds using the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06), focusing on the effects of spin-orbit coupling and treating the 4f as valence electrons.

In general, rare-earth monopnictides LnX (where Ln is a rare-earth, and X=As, Sb, Bi) all display complex magnetic and electrical properties [44, 54], including extreme magnetoresistance (XMR)[15, 16, 18] and superconductivity [42, 57]. They are all reported to be semimetals and, except for LaX, YX, and LuX, they are also antiferromagnetic at low temperatures [58, 59, 60, 53, 3, 4, 1] because of the rare-earth partially filled f orbitals. In analogy to topological insulators, with conducting surface states due to non-trivial topology of their bulk band structure[61, 62], some LnX compounds also display topologically protected surface states. Topological semimetals have been classified as Weyl, Dirac and nodal-line semimetals [63, 64, 65]. A necessary

condition for the stability of these topological phases is the presence of certain symmetries. For example, a Dirac point of a Dirac semimetal is only stable if the material preserves time reversal (TRS) and space inversion symmetry [66]. If any one of these symmetries is broken, the Dirac point splits into two Weyl points with opposite chiralities [66]. There is also a class of topological systems called Z_2 topological semimetals [67]. Even though they do not display a gap in the bulk band structure, as in the case of LaBi[41, 18], they are still characterized by non-trivial Z_2 invariant which requires TRS to protect their non-trivial topological properties. The existence of a direct gap at each k point in the bulk Brillouin zone enables the definition of the Z_2 invariant for these materials.

LaBi, LaSb, and LaAs have shown XMR effects, making them promising for sensors and spintronic devices [68, 69, 70, 71], yet the cause of which remains unsettled. Currently proposed models are based either on the complete electron-hole compensation[72] or on the presence of non-trivial topology in their band structures [73]. There is also a recent report on YSb [74], a semimetal with rock salt crystal structure and lack of topologically protected surface states, where XMR is observed and attributed to a combination of near electron-hole compensation and very different electron and hole mobilities. Electron-hole compensation likely plays an important role in XMR as seen in recent studies of LaSb and LaBi [40, 41]. In the context of a topological spectrum, LaBi is on one side with non-trivial topology, whereas LaAs would be on the other side, possibly displaying trivial topology, and LaSb would be on the border line of being a topological semimetal[15, 75].

Whether LaSb is a topological semimetal has been somewhat debated in the literature [41, 75, 37]. Guo *et al.*[41] performed DFT-GGA and meta-GGA (MBJ) calculations for the band structure of LaSb, finding different results for the two functionals. While DFT-GGA calculations indicate that LaSb is a topological semimetal, MBJ calculations, where the overlap of the La d-band and Sb p-band is supposedly corrected, indicate that LaSb is a trivial semimetal. More recently, Guo *et al.*[76] performed HSE06 hybrid functional calculations, finding that LaSb is a trivial semimetal.

Experimental results have also been controversial. Niu *et al.* [37] reported the observation of linear-dispersion states near the Fermi level in LaSb using ARPES, yet their measurements could not identify whether an odd or even number band crossings lie below the Fermi level due to the proximity to the bulk bands. On the other hand, ARPES measurements by Nummy *et al.*[75] indicate that LaSb shows a trivial band structure, yet it is on the verge of becoming a topological semimetal, in disagreement with their own DFT-GGA calculations.

In this work we show that LaSb and LaAs are indeed topologically trivial semimetals, with LaSb being very close to become a topological semimetal, in agreement with angle resolved photoelectron spectroscopy (ARPES) measurements[15, 75] and recent calculations [76]. We also predict that applying hydrostatic pressure leads to non-trivial topology in LaAs. We find that LaAs becomes topologically non-trivial at around 7 GPa, while preserving the electron-hole compensation and crystal structure undisturbed, making it an interesting testing case for the two competing models to understand XMR effects in these materials.

In the past few years, many reports appeared on the topological properties of rare-earth pnictides [67, 37, 38, 77]. Insulators can be categorized into normal or trivial band insulators and non-trivial topological insulators in the presence of time reversal symmetry [78, 62], with the latter showing surface states that are spin-momentum locked and robust against any time reversal invariant local perturbation [78, 62]. Similarly, semimetals can be classified in trivial and topological non-trivial, and the latter are divided into Weyl, Dirac and nodal-line semimetals [63, 64, 65]. These topologically non-trivial semimetals are directly related to each other in a way that a Dirac semimetal transforms into a Weyl semimetal by splitting a Dirac point into two Weyl points provided that the time reversal symmetry or spatial inversion symmetry is lifted [66]. In analogy to the Dirac-cone surface states in the bulk band gap of topological insulators, the surface states of Weyl and Dirac semimetals are characterized by the presence of Fermi arcs [79, 80, 81, 82]. The absence of bulk band gap in the non-trivial semimetals makes it more difficult to probe the Dirac-like cone surface states due to

the overlap with the bulk states. These topological semimetals are characterized by the non-trivial Z_2 invariant using parity analysis provided that space inversion symmetry and time reversal symmetry are preserved and there exists a bulk band gap at each of the k point in the Brillouin zone.

Recent experiments on LaX (X=As, Sb and Bi) showed large magnetoresistance of up to 100,000% with resistivity plateau at low temperatures [16, 15, 18], pointing to potential applications in sensor and spintronic devices [68, 69, 70, 71]. Experiments and first-principles calculations indicated the presence of topological surface states in LaBi, while LaAs was clearly shown to behave as a trivial semimetal [67, 37, 38, 77]. Controversial results were reported for LaSb: first-principles calculations based on the density functional theory (DFT) within the generalized gradient approximation (GGA) predicted that LaSb is a topological semimetal with a crossing between the La d and the Sb p bands near the X point [75], while meta-GGA MBJ [41] and hybrid density functional calculations [77] showed that such crossing does not occur, in agreement with ARPES measurements [75]. These results fuelled the debate of whether the observed magnetoresistance is due to the non-trivial topological properties of the band structure of LaSb and LaBi, or due to complete compensation of the electron and hole pockets [72, 73, 74].

In fact, LaX (X=As, Sb and Bi) are compensated semimetals with equal electron and hole carrier concentrations [18, 40, 15]. LaBi is a non-trivial topological semimetal with three Dirac cones on the surface [67, 38, 75]. LaAs is a trivial semimetal as shown in recent experimental studies [15, 75], but it can be made topologically non-trivial under hydrostatic pressure[77]. Whether LaSb is a trivial or a topological semimetal and whether its band structure can be changed from trivial to topologically non-trivial by applying small perturbations are still matter of debate. The HSE hybrid functional gives an accurate description of the electronic structure of rare-earth pnictides, predicting carrier densities that are in very good agreement with experimental data [6, 23, 7, 18, 15, 16]. It correctly describes the topologically trivial ground state of LaAs, and predicts the observed non-trivial topology of LaBi band structure [67, 37, 38, 77]. Here we use HSE hybrid functional to describe the electronic structure of LaSb, and show that LaSb is indeed a semimetal with a trivial topological band structure. We then predict that LaSb can be turned into a topological semimetal under reasonably small epitaxial strain, reporting the bulk electronic structure of epitaxially strained LaSb and identifying the Dirac cone and spin texture of the surface states.

1.2 Half-Heusler materials

Fritz Heusler was the first to synthesize Cu₂MnAl by mixing Cu, Mn and Al in 1903; this material later named after him. Interestingly, each of the individual elements were non-magnetic and the compound showed ferromagnetic behavior. After Fritz Heusler, more than 1000 of these compounds have been made with general formula XYZ for Half-Heusler and X₂YZ for Full Heusler. Half-Heusler (h-H) compounds form a class of ternary intermetallics with diverse electrical and magnetic properties, that includes semiconductors [83], semimetals [84], half-metals, and topological semimetals. Having a structure that can be viewed as zinc-blende with filled tetrahedral interstitial sites with robust chemical flexibility for occupying the three inequivalent sites gives h-H compounds a range of interesting and tunable physical properties. Recent reports of h-H semimetals with band structure featuring non-trivial topology, such as in PtLuSb [85, 86] and PtLuBi, generated great interest in exploring the charge and spin transport properties of these materials for novel technological applications. Topological semimetals, which are generally classified as Dirac, Weyl, or node-line semimetals, are characterized by the topological stability of surface states with the presence of band touching points (and Dirac cones), nodes, where two or more bands are exactly degenerate at particular values of the crystal momentum in the first Brillouin zone, or line nodes, where bands are degenerate along closed lines in momentum space. Having these topological features placed at or sufficiently near the Fermi level is key to the observation and utilization of the exotic properties in devices. More often than not, these features are either buried deep in the occupied bands or too high in the conduction band relative to the Fermi level. Therefore, finding ways to tune the Fermi level, by

100	20																GC
н			Half-Heusler compounds XYZ														He
Li	Be		ŀ	Heus	ler c	omp		В	С	Ν	0	F	Ne				
Na	Mg							AI	Si	Р	S	CI	Ar				
К	Ca	Sc	Ti	۷	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1	Xe
Cs	Ва	1	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
Fr	Ra	11															
		11	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
		1	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.2: Periodic table showing possible elements of Half and full Heusler compounds.

adding impurities (doping) or deliberately introducing intrinsic defects that minimally perturb the underlying band structure, is crucial for harvesting the full potential of these interesting class of materials.

In the case of PtLuSb and PtLuBi, the Fermi level in bulk and thin films is located well below the expected position in the perfect crystal, with extra charge carriers in the bulk that mask the observation of the topological surface states. The origin of the bulk carriers, if intrinsic defects or impurities, is still unknown. Using first principles calculations based on the density functional theory we investigate the impact of intrinsic defects and impurities on the Fermi level position with respect to that expected in perfect crystalline material, searching for an explanation for the observed extra holes and Fermi level position in these materials and designing possible ways to tune the Fermi level by adding specific impurities or changing the atomic chemical potentials during growth to control the concentration of specific defects that strongly affect the the Fermi level position. We find that the presence of Pt vacancies in both PtLuSb and PtLuBi can explain the observed hole carrier densities and discuss how this effect can be reversed and the Fermi level controlled by adding impurities.

1.3 Ga_2O_3 -Ir₂O₃ alloys

In 1952, there was the first report of Al₂O₃-Ga₂O₃-H₂O system in which different polymorphs of Ga₂O₃ were studied. In 1965 optical absorption and photoconductivity studies were conduced on β -Ga₂O₃ which showed that it is a large band gap material with a bandgap of ~4.7 eV. By 1990s, few methods had been developed to grow bulk single crystal and epitaxial Ga₂O₃ thin film, yet its application in devices remained unexplored. More recently, Ga₂O₃ has been established as an emerging ultra-wide band gap semiconductor with a band gap energy of 4.5-5.6 eV (depending on its structure), which is significantly larger than the band gaps of GaN and SiC (3.4 eV and 3.3 eV respectively). Ga₂O₃ is now considered a promising candidate for high power electronic devices, solar-blind photodetectors[87], thin film high voltage field effect transistors[88, 89], gas sensors[90, 91, 92], deep-UV transparent contacts[93] and Schottky barrier diodes[94].

The monoclinic, β -phase is the most stable phase among other polymorphs (α , γ , δ , ϵ) of Ga₂O₃[95, 96] and it is now the most studied phase. The Corundum α -Ga₂O₃ on the other hand has the advantage that it can be epitaxially grown on sapphire (α -Al₂O₃) substrate by well established methods such as chemical vapor deposition (CVD) technique[97, 98, 99, 100]. It also opens up the venue for band gap engineering in relatively wider range and possible interface engineering with other corundum structure materials[99, 101].

By now, there are lot of studies on *n*-type Ga_2O_3 unipolar devices[101, 102, 103, 104] but achieving *p*-type conductivity in Ga_2O_3 has been proven quite difficult, making *p*-*n* homojunction not possible. The search for *p*-type materials is going on to make good quality heterojunction with *n*-type Ga_2O_3 . There have been reports of fabricating heterojunction diodes using *n*-type β -Ga₂O₃ with *p*-type face-centered cubic cuprite copper(I) oxide (Cu₂O)[105], nickel(II) oxide(NiO)[106] and corundum α -Cr₂O₃[107]. There is no known *p*-type semiconductor having the same structure as that of β -Ga₂O₃. For α -Ga₂O₃ there are several corundum-structured semiconducting oxides[108] available among which there can be a possible candidate of *p*-type material for p-n heterojunction.

There are some reports on corundum α -Rh₂O₃[109] and α -Ir₂O₃[110] showing *p*-type conductivity measured using Seeback effect. Although rutile IrO₂ is the most stable oxide of Ir, Kane *et al.*[111] was able to grow single crystal α -Ir₂O₃ thin films and verified their *p*-type conductivity without any dopant using Hall effect measurements. They also demonstrated the *p*-*n* heterojunction with *p*-type α -Ir₂O₃ and *n*-type α -Ga₂O₃. The lattice mismatch between α -Ir₂O₃ and α -Ga₂O₃ was found to be much smaller than the lattice mismatch between α -Ga₂O₃ and sapphire (α -Al₂O₃) substrate, enabling a good quality heterojunction. Hao *et al.*[112] also recently reported on charge transport mechanism and interface engineering in α -Ir₂O₃/ α -Ga₂O₃ *p*-*n* heterojunction. Here we explore the electronic structure and stability of α -Ir₂O₃ and its alloys with α -Ga₂O₃ aiming at developing a fundamental understanding of these material system for device application.

Chapter 2

THEORY AND COMPUTATIONAL APPROACH

2.1 Density Functional Theory

Density functional theory (DFT) is one of the most successful quantum mechanical approaches for understanding the structure and electronic structure of materials. It became really popular among materials physics and quantum chemistry community in 1990's. The reason for this popularity was the useful balance between accuracy and computational cost because of approximate functionals. basically, it is now possible to study larger systems (typically a few hundred atoms) without losing much accuracy in the description of structure, chemical, and electronic properties. In 1998 Walter Kohn received the Nobel prize in Chemistry for his work on the development of DFT. The number of publications that uses DFT has increased a lot since 1990 showing the significance of his work. DFT is not limited to solving only the Schrödinger equation but it also provides an alternate route to solve any interacting problem by mapping it into much easier non-interacting problem. Apart from its usage in materials physics and chemistry it is now being used in fields like biology and mineralogy. In this chapter we will first discuss why it is difficult to solve many-body (electrons and nuclei) interacting systems, then introduce DFT and discuss different approximations that are used in DFT, i.e., the exchange correlation functionals that are used in DFT and its applications in practical systems.

2.1.1 Many-body Schrödinger Equation

In quantum mechanics, the time independent Schrödinger equation that explains the electronic structure of solids with many electrons and nuclei is written as,

$$\hat{H}_{tot}\Psi(r_1, r_2...r_N, R_1, R_2...R_M) = \hat{E}_{tot}\Psi(r_1, r_2...r_N, R_1, R_2...R_M),$$
(2.1)

where Ψ is the wavefunction of many-body system, \hat{E}_{tot} is the total energy and \hat{H}_{tot} is the Hamiltonian of the system with N electrons and M nuclei. The Hamiltonian \hat{H}_{tot} , in atomic units, is written as:

$$\hat{H}_{tot} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \frac{1}{2} \sum_{I=1}^{M} \frac{1}{M_{I}} \nabla_{I}^{2} - \sum_{i=1}^{N} \sum_{I=1}^{M} \frac{Z_{I}}{r_{iI}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{I=1}^{M} \sum_{J>I}^{M} \frac{Z_{I}Z_{J}}{R_{IJ}}, \quad (2.2)$$

where the index i, j and I, J runs from 1 to N and from 1 to M respectively, Z is the atomic number of the nucleus of the atom and M represents the mass. r_{ij} , r_{iI} , R_{IJ} represents the distance between electrons i and j, electron i and nucleus I, nucleus Iand nucleus J respectively. If we can solve equation 2.1 and get its ground state energy, then we can calculate all the equilibrium properties like formation enthalpies, phase diagrams, and thermal properties of that specific system, but it is practically impossible to solve this simple equation. To get an idea, lets take silicon, which is a semiconductor material, as our model system. The volume of unit cell of silicon is $a^3/4$ where a =5.43 Å is the lattice constant. To solve the equation above for the electrons and nuclei in the unit cell of silicon, lets do a discretization of unit cell with $\Delta x = 0.1$ Å. The grid required to describe the unit cell will have $N_{\rm p} = (a^3/4)/(\Delta x)^3 \sim 10^4$ points. Silicon has two atoms in its unit cell with each atom having four valence electrons, i.e., N+M= 10 particles. To write the wavefunction Ψ for silicon we would need $N_{\rm P}^{N+M} = 10^{40}$ complex numbers. It is impossible to do matrix operation with this many complex numbers and the complexity increases exponentially with the increase in size of the system. This is also known as 'exponential wall' in solving the Schrödinger equation. This, in order to solve Schrödinger equation for practical systems some approximations need to be made which will be discussed in the next sections.

2.1.2 Born-Oppenheimer Approximation

Eq. 2.1 is a general equation that can be applied to solids, liquids, and gases. In these systems, the nuclei can be considered as immobile in the time scale of the electrons, as they are relatively heavier than electrons, so we can focus on electronic part of Eq. 2.1. For that a sensible assumption would be to write total wave function Ψ in Eq. 2.1 as a product of electronic wavefunction ψ_R and nuclear wave function χ as in Eq. 2.3 below.

$$\Psi(r_1, r_2...r_N, R_1, R_2...R_M) = \psi_R(r_1, r_2...r_N)\chi(R_1, R_2...R_M),$$
(2.3)

where $(r_1, r_2...r_N)$ and $(R_1, R_2...R_M)$ are coordinates for electronic and nuclear wave functions respectively. The interesting part of this assumption is that we can determine the electronic wave function for a fixed nuclear coordinates and than we can allow nuclear wave function to relax accordingly. Hence we can separate the many-body Schrödinger equation into an electronic and nuclear parts,

$$\left[-\frac{1}{2}\sum_{i=1}^{N}\nabla_{i}^{2}+\sum_{i=1}^{N}V_{n}(r_{i};R)+\frac{1}{2}\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|r_{i}-r_{j}|}\right]\psi_{R}=E_{R}\psi_{R}$$
(2.4)

and

$$\left[-\frac{1}{2}\sum_{I=1}^{M}\frac{1}{M_{I}}\nabla_{I}^{2}+\frac{1}{2}\sum_{I=1}^{M}\sum_{J>I}^{M}\frac{Z_{I}Z_{J}}{R_{IJ}}+E(R_{1},R_{2}...R_{M})\right]\chi=E_{tot}\chi.$$
(2.5)

In Eq. 2.4, the subscript R in the total electronic energy shows that it is implicitly a function of nuclear coordinates and the second terms $V_n(r_i; R)$ gives the interaction between electron and nuclei. Eq. 2.5 represents the many-body Schrödinger equation for nuclei only, where the effect of electrons are included in $E(R_1, R_2...R_M)$ term and it behaves like an effective potential for the nuclei. The total potential felt by the nuclei is the sum of potential due to nucleus-nucleus interaction and total energy of electrons at fixed nuclear coordinates. This decoupling into electronic and nuclear part of the Schrödinger equation is known as Born-Oppenheimer approximation (Born and Oppenheimer, 1927). In this approximation we assume that as the nuclear coordinates change the electron evolve from its initial ground state to the electronic ground state associated with the final nuclear coordinates. The electrons adjust themselves with change in nuclear coordinates such that they remain in electronic ground state as they are far more mobile than the nucleus making their adiabatic evolution. This electronnucleus adiabatic transformation is taken from adiabatic processes in thermodynamics (Fermi 1956) and because of that Born-Oppenheimer approximation is also known as adiabatic approximation.

2.1.3 Hartree-Fock Equation

We can rewrite Eq. 2.4 in much simpler operator form,

$$\hat{H}\psi = E\psi, \qquad (2.6)$$

where \hat{H} is the Hamiltonian operator for the electrons and ψ is the electronic wave function. The \hat{H} operator can be written as a sum of kinetic energy operator \hat{T} , \hat{V}_{ext} due to the interaction between electrons and nuclei and \hat{V}_{ee} due to electron-electron interaction, i.e.,

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee},$$
 (2.7)

where

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2, \qquad (2.8)$$

$$\hat{V}_{ext} = \sum_{i=1}^{N} V_n(r_i; R),$$
(2.9)

and

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|}.$$
(2.10)

Using the independent electron approximation, we can write the electronic wave function as a product of single-electron wave function:

$$\psi(r_1, r_2...r_N) = \phi(r_1)\phi(r_2)...\phi(r_N).$$
(2.11)

Electrons are Fermions and they follow Pauli-exclusion principle and Fermi-Dirac statistics. So the electronic wave function must be anti-symmetric, i.e., if you exchange two electrons the total electronic wave function ψ must change sign or, in other

words, the two electrons can not occupy the same quantum state. To satisfy this condition we can write the total electronic wave function in the form of Slater determinant, as follows:

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \dots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \dots & \phi_N(r_2) \\ & \ddots & \ddots & & \ddots \\ & \ddots & & \ddots & & \ddots \\ & \ddots & & \ddots & & \ddots \\ & \ddots & & \ddots & & \ddots \\ \phi_1(r_N) & \phi_2(r_N) & \dots & \phi_N(r_N) \end{vmatrix},$$
(2.12)

where ϕ_i are single-particle electronic wave functions. The total energy of electrons can then be written in Dirac notation, i.e.,.

$$E = \langle \psi_{HF} | \hat{H} | \psi_{HF} \rangle \tag{2.13}$$

If we minimize the total electronic energy E with respect to the single-particle wave function ϕ_i using variational principle and require that these wave functions are orthonormal,

$$\frac{\delta E}{\delta \phi_i^*} = 0, \tag{2.14}$$

$$\int \phi_i^*(r)\phi_j(r)\,dr = \delta_{ij},\tag{2.15}$$

where δ_{ij} is Kronecker delta and $\delta_{ij} = 1$ if i=j and $\delta_{ij} = 0$ if $i\neq j$, we obtain the Hartree–Fock equation (Fock, 1930b),

$$\left[-\frac{\nabla^{2}}{2} + V_{n}(r) + V_{H}(r)\right]\phi_{i}(r) + \int V_{X}(r,r')\phi_{i}(r')\,dr' = \epsilon_{i}\phi_{i}(r), \qquad (2.16)$$

with

$$n(r) = \sum_{i} |\phi_i(r)|^2, \qquad (2.17)$$

and

$$\nabla^2 V_H(r) = -4\pi n(r), \qquad (2.18)$$

where $V_n(r)$ is the external potential between the electron and nuclei, $V_H(r)$ is Hartree potential felt by the *n*th electron due to the mean field field created by n-1 electrons
and $V_X(r, r')$ is the Fock exchange potential which is due to anti-symmetric electronic wave function, and it can be expressed as:

$$V_X(r,r') = -\sum_j \frac{\phi_j^*(r')\phi_j(r))}{|r-r'|},$$
(2.19)

where the sum j is over all the occupied single particle states. Basically, in the Hartree-Fock equations we introduced the Pauli exclusion principle for electrons which added an extra exchange potential in the electronic part of the Schrödinger equation, so we moved from classical description of electrons to quantum mechanical description. If we look closely at this Fock-exchange potential $V_X(r, r')$, it is non-local in nature and it includes integration over an additional variable r' which causes a lot of complication in practice for solving the Hartree–Fock equations.

2.1.4 Hohenberg-Kohn Theorem

Before Hohenberg-Kohn theorems, researchers were trying to figure out a way to utilize the electronic density n(r) in electronic structure calculations using approximate forms for the exchange and correlation terms, but it was Hohenberg and Kohn that formalized it in 1964 by putting forward two simple theorems. These theorems provided a link between electron density n(r), external potential $V_{ext}(r)$, Hamiltonian \hat{H} and wave function Ψ .

2.1.4.1 Theorem I

The first theorem states that the total external potential $V_{ext}(r)$ of a system with interacting particles can be uniquely determined by the ground-state electronic density $n_0(r)$, or the external potential $V_{ext}(r)$ is a unique functional of the density $n_0(r)$, where $V_{ext}(r)$ is the interaction between electrons and nuclei as discussed in section 2.1.3. To prove the first theorem, lets suppose that there are two external potentials $V_{ext}^{(1)}(r)$ and $V_{ext}^{(2)}(r)$ that differ from each other by more than a constant and create same ground-state density $n_0(r)$. According to Eq. 2.7, these two potentials will give rise to two different Hamiltonians, which we can name as $\hat{H}^{(1)}(r)$ and $\hat{H}^{(2)}(r)$. These two Hamiltonians will have two different ground states $\psi^{(1)}(r)$ and $\psi^{(2)}(r)$ respectively and which gives same ground-state density $n_0(r)$ according to our assumption. The ground state energy for each of the Hamiltonian is given by the following equations,

$$E^{(1)} = \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle, \qquad (2.20)$$

and

$$E^{(2)} = \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle.$$
(2.21)

Since $\hat{H}^{(1)}(r)$ and $\hat{H}^{(2)}(r)$ are two different Hamiltonians, which means $\psi^{(1)}(r)$ is not a ground-state wave function of $\hat{H}^{(2)}(r)$, so we can write,

$$E^{(2)} < \langle \psi^{(1)} | \hat{H}^{(2)} | \psi^{(1)} \rangle \tag{2.22}$$

The right hand side of Eq. 2.22 can be rewritten as,

$$\langle \psi^{(1)} | \hat{H}^{(2)} | \psi^{(1)} \rangle = \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{H}^{(2)} - \hat{H}^{(1)} | \psi^{(1)} \rangle , \qquad (2.23)$$

which gives

$$\langle \psi^{(1)} | \hat{H}^{(2)} | \psi^1 \rangle = E^{(1)} + \int dr [V_{ext}^{(2)}(r) - V_{ext}^{(1)}(r)] n_0(r).$$
 (2.24)

Using Eq. 2.22

$$E^{(2)} < E^{(1)} + \int dr [V_{ext}^{(2)}(r) - V_{ext}^{(1)}(r)] n_0(r), \qquad (2.25)$$

if we exchange labels in Eq. 2.25 or start with $E^{(1)}$ instead of $E^{(2)}$, we get

$$E^{(1)} < E^{(2)} + \int dr [V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)] n_0(r).$$
(2.26)

Adding Eq. 2.25 and Eq. 2.26 gives $E^{(2)} + E^{(1)} < E^{(1)} + E^{(2)}$, which is incorrect and a contradiction. Hence our assumptions that two different external potentials can give rise to a unique ground-state density is not possible. The ground-state density $n_0(r)$ is uniquely determined by the external potential $V_{ext}(r)$.

2.1.4.2 Theorem II

The second Hohenberg-Kohn theorem states that a functional F[n] which gives the ground-state energy of the system gives the ground-state energy if and only if the input density in F[n] is the true ground-state density $n_0(r)$. From the first theorem we already proved that the ground-state density $n_0(r)$ uniquely determines the external potential $V_{ext}(r)$ and, hence, all the ground-state properties including the total energy,

$$E[n] = T[n] + E_{ee}[n] + E_{eN}[n]$$
(2.27)

where the first, second and third term represents kinetic energy of electrons, electronelectron interaction term and electron-nuclei interaction as a functional of density. So, we have

$$E[n] = T[n] + E_{ee}[n] + \int dr V_{ext}(r)n(r), \qquad (2.28)$$

$$E[n] = F[n] + \int dr V_{ext}(r)n(r),$$
 (2.29)

where

$$F[n] = T[n] + E_{ee}[n].$$
(2.30)

F[n] is a universal functional and it is independent of external potential $V_{ext}(r)$. In the ground state, the ground-state density $n_0(r)$ determines the ground-state energy, i.e.,

$$E_0 = E[n_0] = \langle \psi^{(0)} | \hat{H} | \psi^{(0)} \rangle .$$
(2.31)

Using the variational principle, any other density n(r) will give the energy E[n] greater than the ground-state energy E_0 ,

$$E_0 = E[n_0] = \langle \psi^{(0)} | \hat{H} | \psi^{(0)} \rangle < \langle \psi | \hat{H} | \psi \rangle = E[n].$$
(2.32)

Thus, the energy given in Eq. 2.29 for the ground-state density $n_0(r)$ will be lower than for any other density n(r). So if the functional F[n] in Eq. 2.29 is known, then by minimizing the total energy E[n] with respect to n(r) will gives us ground-state energy and ground-state density.

2.1.5 Kohn-Sham Equations

As discussed in section 2.1.4 the Hohenberg–Kohn theorem states that the total ground-state energy of a system containing many electrons is a functional of electron density. The information about how to formulate such a functional is missing in Hohenberg–Kohn theorems but there are several approximations that have been developed over the years, even though the exact form of this functional is still unknown. We can rewrite Eq. 2.28 as:

$$F[n] = T[n] + V_{ee}[n] + \int dr V_{ext}(r)n(r), \qquad (2.33)$$

where E = F[n]. Ee can also write the kinetic energy T[n] and electron-electron interaction term V_{ee} in terms of wave function, i.e.,

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle + \int dr V_{ext}(r) n(r).$$
(2.34)

It can be seen that the last term in Eq. 2.34, which includes the external potential $V_{ext}(r)$, explicitly depends on the electron density n, whereas the dependence of first term on electronic density n is only implicit. In 1965 Kohn and Sham came with an idea to describe the implicit term in Eq. 2.34 with kinetic energy and Coulomb energy of independent electrons as discussed in section 2.1.3 plus an extra term which contains the difference:

$$E = F[n] = -\sum_{i} \int dr \phi_{i}^{*}(r) \frac{\nabla^{2}}{2} \phi_{i}(r) + \frac{1}{2} \int \int dr dr' \frac{n(r)n(r')}{|r-r'|} + \int dr V_{ext}(r).n(r) + E_{xc}[n]$$
(2.35)

The first three terms in Eq. 2.35 are kinetic energy, Hartree energy and electron-nuclei interactions, respectively, for an independent electron system, whereas the last term accounts for everything that was not included in independent electron approximation and it is known as exchange and correlation energy $E_{xc}[n]$. Practically, the many-body problem in Eq. 2.34 is mapped into an independent electron problem in Eq. 2.35. The ground-state density n_0 minimizes the total energy E = F[n], i.e.,

$$\left. \frac{\delta F[n]}{\delta n} \right|_{n_0} = 0. \tag{2.36}$$

This variational principle is similar to Eq. 2.14 which was used to write the Hartree-Fock equation (Eq. 2.16). If we put a constraint for independent electron wave functions $\phi_i(r)$ to be orthonormal, that would lead us to the Kohn-Sham equation:

$$\left[-\frac{\nabla^2}{2} + V_{ext}(r) + V_H(r) + V_{xc}(r)\right]\phi_i(r) = \epsilon_i\phi_i(r), \qquad (2.37)$$

.

(2.38)

where the first term is the kinetic energy, $V_{ext}(r)$ is the external potential, $V_H(r)$ is the Hartree potential and $V_{xc}(r)$ is exchange correlation potential, represented by:

 $V_{xc}(r) = \frac{\delta E_{xc}[n]}{\varsigma}$

$$On |_{n(r)}$$

$$V_{nuc} \text{ known/constructed}$$
Initial guess $n(r)$
Generate
$$new$$

$$n(r)$$

$$V_{eff}(r) = V_{nuc}(r) + V_{H}(r) + V_{XC}(r)$$





The Kohn-Sham equations provide a powerful instrument to calculate materials properties that are derived from the ground-state charge density and energy. It is interesting to note that these equations reduce the complexity of the many-body problem with 3N dimension to a much simpler problem with three dimensional electronic charge density n(r). The next question is how to solve Kohn-Sham equations in order to get the total ground state energy of any system. For that purpose we can start with Eq. 2.37 which is a standard single particle Schrödinger equation with eigenvalues ϵ_i and eigenfunction ϕ_i . The Hartree potential $V_H(r)$ and exchange correlation potential $V_{xc}(r)$ in Eq. 2.37 depend on the density n and the density n depends on the unknown wave functions ϕ_i according to Eq. 2.17, which means we need to solve the Kohn-Sham equations self-consistently as shown in Fig. 2.1. First we start with nuclear coordinates which gives us $V_{ext}(r)$ and then from a trial electron density we get the initial estimate for $V_H(r)$ and $V_{xc}(r)$. After that, Eq. 2.37 is solved selfconsistently until the new charge density matches with the input charge density. After obtaining the groundstate charge density the outer loop runs over the atomic coordinates until all the atoms are in their relaxed positions. The atomic relaxations are treated classically and once both the electrons and the atoms are in their ground state we obtain the equilibrium ground-state energy of the system as shown in Fig. 2.1.

To apply the Kohn-Sham equations in crystalline solids, we need to use Bloch theorem (Bloch 1928). This theorem states that the singe-particle electronic wave function can be written in terms of periodic function in the unit cell $u_{ik}(\mathbf{r})$ and plane waves $e^{i\mathbf{k}\cdot\mathbf{r}}$ as:

$$\phi_i(\mathbf{r}) \to \phi_{i\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r}), \qquad (2.39)$$

where i is the imaginary unit and i is the eigenstate index and $u_{ik}(\mathbf{r})$ is given by

$$u_{i\mathbf{k}}(\mathbf{r} + \hat{\mathbf{T}}) = u_{i\mathbf{k}}(\mathbf{r}), \qquad (2.40)$$

and

$$\hat{\mathbf{T}} = n_1 \tilde{\mathbf{a}}_1 + n_2 \tilde{\mathbf{a}}_2 + n_3 \tilde{\mathbf{a}}_3, \qquad (2.41)$$

where n_1, n_2, n_3 are integers, $\hat{\mathbf{T}}$ is the translation operator and $\tilde{\mathbf{a}}_1$, $\tilde{\mathbf{a}}_2$, $\tilde{\mathbf{a}}_3$ are lattice vectors. Putting the Blöch wave function in Kohn-Sham equation 2.37 gives us:

$$\left[-\frac{(\nabla + i\mathbf{k})^2}{2} + V_{ext}(r) + V_H(r) + V_{xc}(r)\right]u_{i\mathbf{k}}(r) = \epsilon_{i\mathbf{k}}u_{i\mathbf{k}}(r).$$
(2.42)

It is interesting to note that Eq. 2.42 does not have the exponential $e^{i\mathbf{k}\cdot\mathbf{r}}$ and it is expressed only in terms of the periodic part $u_{i\mathbf{k}}(\mathbf{r})$. The normalization condition of this periodic part gives one electron per unit cell for each wave function.

$$\int_{UC} dr |u_{i\mathbf{k}}(r)|^2 = 1, \qquad (2.43)$$

Similarly the density n(r) in equation 2.17 can be expressed in terms of periodic function $u_{ik}(\mathbf{r})$

$$n(r) = \sum_{i} \int_{BZ} \frac{d\mathbf{k}}{\Omega_{BZ}} f_{i\mathbf{k}} |u_{i\mathbf{k}}(r)|^2$$
(2.44)

where the occupation number f_{ik} is 1 for occupied states and 0 for unoccupied states and Ω_{BZ} is the volume of first Brillouin zone in reciprocal space. In this work we used Vienna *ab initio* simulation package (VASP) [113, 114] for our calculations, which expands the perodic bloch functions $u_{ik}(\mathbf{r})$ in terms of plane waves and it uses projectoraugmented wave potential (PAW) [115] method. In this method the calculations are only done on valence electrons. The wave functions of these valence electrons near the ion cores have very rapid oscillations as they need to be orthogonal to core state requiring a lot of fourier components making it computationally inefficient. The PAW method replaces these oscillatory wave function with much smoother wave functions increasing the computational efficiency and also provides a way to escribe the all electron wave function in terms of these smoother wave functions.

2.2 Exchange and Correlation Functionals

After the introduction of Kohn-Sham theory in 1965, a lot of work was done to construct the exchange and correlation functionals $E_{xc}[n]$, $V_{xc}[n]$ accurately for solving the Kohn-Sham equations. There are several different approximations available today. Here we will discuss some of the approximations that were used to calculate material properties in subsequent chapters.

2.2.1 Local Density Approximation (LDA)

One of the first and most simplest approximation for exchange and correlation functional is the local density approximation (LDA) (Ceperley and Alder, 1980; Perdew and Zunger, 1981). It is assumed in this approximation that the exchange-correlation energy functional at each point in space depends upon the density only. This functional was applied first on a simple system like *homogeneous electron gas* related closely to free electron gas, where a gas of N electrons is constrained in a box with volume V under a fix potential of the nuclei. In homogeneous electron gas an additional interaction is included in the form of Coulomb repulsion between the electrons, and it is assumed that the electrons are uniformly distributed in the volume V. It is possible to calculate the exchange energy exactly for homogeneous electron gas, whereas the correlation energy can be approximated using numerical techniques. The eigenstates and eigenenergy for free electron gas can be written as:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \mathbf{e}^{\mathbf{i}\mathbf{k}.\mathbf{r}},\tag{2.45}$$

$$\epsilon_{\mathbf{k}} = \frac{|\mathbf{k}|^2}{2},\tag{2.46}$$

where k is the wave vector of a stationary wave, the eigenvalue corresponding to highest occupied state is ϵ_F and the related wave vector is known as Fermi wave vector k_F , where $\epsilon_F = k_F^2/2$. The interesting thing about this simple model is the dependence of all the physical properties on electron density n=N/V. The dependence of Fermi wave vector k_F , exchange energy E_x and exchange potential V_x on density n is given by the equations below:

$$k_{\rm F} = (3\pi^2 n)^{\frac{1}{3}},\tag{2.47}$$

$$E_x = -\frac{3}{4} (\frac{3}{\pi})^{\frac{1}{3}} n^{\frac{4}{3}} V, \qquad (2.48)$$

$$V_x(r) = -\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}(r).$$
(2.49)

It is not possible to get the exact expression for correlation energy E_c as it was the case for exchange energy as shown in Eq. 2.48. However, the correlation energy E_c can be calculated by solving many-body Schrödinger equation using the stochastic numerical method and the obtained expression is shown below:

$$E_c = nV \begin{cases} 0.0311 \ln r_s - 0.0480 + 0.002r_s \ln r_s - 0.0116r_s, & if r_s < 1, \\ \frac{-0.1423}{1+1.0529\sqrt{r_s} + 0.3334r_s}, & if r_s \ge 1. \end{cases}$$
(2.50)

where r_s is the Wigner-Seitz radius and it is defined as the radius of the sphere occupied by one electron on average,

$$\frac{V}{N} = \frac{4\pi}{3}r_s^3 = \frac{1}{n}.$$
(2.51)

The total exchange correlation energy E_{xc} for LDA can be obtained by adding exchange energy E_x and correlation energy E_c ,

$$E_{xc}^{LDA}[n] = E_x^{LDA}[n] + E_c^{LDA}[n] = \int n(r)\epsilon_{xc}^{homo}[n(r)]dr, \qquad (2.52)$$

where ϵ_{xc}^{homo} is the exchange correlation energy per electron for homogeneous electron gas.

2.2.2 Generalized Gradient Approximation (GGA)

The second level of approximation is the generalized gradient approximation which is more involved than the simple local density approximation (LDA). In this approximation the exchange-correlation energy not only depends on the density n but also on the gradient of density ∇n , and it can be written as,

$$E_{xc}^{GGA}[n] = \int f(n(r), |\nabla n(r)|) dr, \qquad (2.53)$$

$$E_{xc}^{GGA}[n] = \int n(r)\epsilon_{xc}^{homo}[n(r), |\nabla n(r)|]dr \equiv \int n(r)\epsilon_{x}^{homo}(n)F_{xc}(n, |\nabla n|)dr, \quad (2.54)$$

where ϵ_x^{homo} is the exchange energy per electron for homogeneous electron gas and the functional F_{xc} is dimensionless and can be written as $F_{xc}=F_x+F_c$, where F_x is given by,

$$F_x = 1 + \frac{10}{81}s_1^2 + \frac{146}{2025}s_2^2 + \dots,$$
(2.55)

where the reduced density gradient s_i can be defined as:

$$s_i = \frac{|\nabla^i n|}{(2k_F)^i n} = \frac{|\nabla^i n|}{2^i (3\pi^2)^{i/3} (n)^{1+i/3}}.$$
(2.56)

There are several versions of F_x . Perdew and Wang (PW91) [116], Perdew, Burke and Ernzerhof (PBE) [117] and Perdew, Burke, Ernzerhof revised for solids (PBEsol) [118] functionals used different forms of F_x . These functionals are implemented in several codes which give material properties quite accurately. In this work we used PBE and PBEsol functionals as discussed in the next chapters. The correlation term F_c is much smaller than the exchange term and it can be written as,

$$F_c = \frac{\epsilon_c^{LDA}(n)}{\epsilon_x^{LDA}(n)} (1 - 0.219s_1^2 + ...).$$
(2.57)

2.2.3 Hybrid Functionals

The GGA functional discussed in previous section is a semi-local functional. As the LDA, the GGA systematically underestimates the band gap of semiconductors and insulators [119, 120, 121]. GGA functional fails to explain materials with highly localized partially occupied d or f electrons and it also overestimates the size of electron or hole pockets in case of semimetals, which will be discussed in subsequent chapters. Hybrid functionals tends to partially overcome these problems by combining a part of Hartree-Fock (HF) exchange with LDA or GGA exchange-correlation functional [122, 123, 124]. Hybrid functionals are computationally more expensive as compared to LDA or GGA because of the non-local nature of Hartree-Fock (HF) exchange. The exchange-correlation energy for PBE0 hybrid functional can be written as,

$$E_{xc}^{PBE0} = 0.25E_x^{HF} + 0.75E_x^{PBE} + E_c^{PBE}.$$
(2.58)

In the PBE0 hybrid functional, the exchange energy is divided into two parts with 25% contribution from Hartree-Fock (HF) exchange and 75% contribution from PBE or GGA exchange, whereas the correlation energy is the same as in PBE. The exchange energy in HSE (Heyd–Scuseria–Ernzerhof) is calculated using a error function screened Coulomb potential increasing the accuracy in the description of metallic systems, as

compared to PBE0. In HSE the exchange part is divided into short range (SR) and long range (LR) part as follows:

$$\frac{1}{r} = \frac{1 - erf(\omega r)}{r} + \frac{erf(\omega r)}{r}.$$
(2.59)

The first and second term represent the short range (SR) and long range (LR) part, respectively, where screening parameter is ω and the error function erf(x) is defined as,

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt.$$
 (2.60)

The exchange-correlation energy for HSE is thus given by:

$$E_{xc}^{HSE} = a E_x^{HF,SR}(\omega) + (1-a) E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}, \qquad (2.61)$$

where a is the mixing parameter used for mixing Hartree-Fock (HF) exchange and PBE exchange in the short range part. The long range part has only PBE exchange term. For HSE06 hybrid functional the value of a=1/4 comes from perturbation theory [125] whereas the value of screening parameter is set to $\omega=0.2$ Å⁻¹. The upper limit of $\omega \rightarrow \infty$ gives us the PBE functional, whereas the lower limit of $\omega \rightarrow 0$ leads us to PBE0 functional.

Chapter 3

RARE-EARTH MONOPNICTIDES - BULK AND THIN FILMS

As introduced in section 1.1, rare-earth monopnictides (RE-V) display interesting properties including thermoelectricity[26], extreme magnetoresistance [16, 15, 18] and non-trivial topological electronic structure properties[15, 75], and are promising for photoconductive switches[28]. In this chapter we will discuss electronic properties, RE-V/III-V semiconductor interfaces, and topological properties of RE-V materials. Most of the work in this section is discussed from theoretical point of view but comparison with experiment is made wherever needed. The experimental results shown in this section are courtesy from our experimental collaborators from University of California Santa Barbara.

3.1 Crystal Structure



Figure 3.1: (a) Rock salt crystal structure of rare earth monopnictide (b) First Brillouin zone of RE-V.

RE-V compounds have simple rock salt crystal structure consisting of two type of atoms, where one of the atom is from rare-earth (Lanthanides) family and the other comes from the pnictide (As, Sb, Bi) family as represented by green and red spheres in Fig. 3.1(a). The space group of rock-salt crystal structure is $Fm\bar{3}m$ where each of the atom separately forms a face-centered cubic lattice and alternatively it can be viewed as a face-centered cubic lattice with the secondary atom in its octahedral interstitial sites. The Brillouin zone of the two-atom primitive cell along with high symmetry points are shown in Fig. 3.1(b).

3.2 Bulk Electronic Properties

In this section we will discuss the structural parameters and electronic structure of rare-earth pnictides calculated using density functional theory (DFT) with the Heyd, Scuseria, and Ernzerhof (HSE06) screened hybrid functional. We focus on RE-V compounds, with RE=La, Gd, Er, and Lu, and V=As, Sb, and Bi, and analyze the effects of spin-orbit coupling and treating the RE 4*f* electrons as valence electrons in the projector augmented wave approach. The results of HSE06 calculations are compared with DFT within the generalized gradient approximation (GGA) and other previous calculations. We find that all these RE-V compounds are semimetals with electron pockets at the X point and hole pockets at Γ . Whereas in DFT-GGA the carrier density is significantly overestimated, the computed carrier densities using HSE06 is in good agreement with the available experimental data.

3.2.1 Lattice parameters of RE-V

The calculated lattice parameters of RE-V compounds using HSE06 along with the results from GGA calculations and experimental values are listed in Table 3.1. The results shown were obtained by treating the 4 f electrons as core and valence electrons. We note that the HSE06 results are systematically closer to the experimental values than the results from the DFT-GGA, which typically slightly overestimates lattice parameters.

We note from Table 3.1 that for a given rare earth, the lattice parameter a increases going from As, Sb, to Bi, i.e., as the atomic size of the pnictide atom increases.

On the other hand, the lattice parameter decreases by going from La, Gd, Er, to Lu, due to the lanthanide contraction effect on the atomic size [126].

3.2.2 Electronic band structures of RE-V

The analysis of the electronic structure of the RE-V compounds starts with the results using HSE06 without spin-orbit coupling and without including the 4f electrons in the valence, shown in Fig. 3.2. In this approximation, all the RE-V studied are semi-metallic except for LaAs which shows a very small band gap of 5 meV. All RE-V compounds have hole pockets at Γ point and electron pockets at the X point. The hole pocket bands are composed mostly of pnictide p orbitals while the electron pocket bands are derived mostly from the rare-earth d orbitals. For a given rare-earth we note that the size of the hole pocket increases going from As to Bi. This trend is explained by the relative energy of the valence p orbitals of the pnictide atoms, which increases from As to Bi [127]. The gap at X point opens up as we go from La to Lu largely due to the dispersion of the pnictide p band that increases as the lattice parameter decreases due to the lanthanide contraction effect.

3.2.2.1 Effects of spin-orbit coupling on the electronic structure of RE-V

The effects of spin-orbit coupling are expected to be very significant for the RE-V compounds, which are composed of heavy elements and the bands of interest, situated near the Fermi level, are derived from pnictide p and lanthanide d orbitals. Previous first-principles calculations have already pointed out the importance of spin-orbit coupling in the description of the electronic structure of RE-Vs [128, 129]. The threefold degenerate pnictide p band at Γ splits into 2+1 bands due to spin-orbit coupling. Also the splitting increases from As to Bi as the atomic number increases. The spin-orbit coupling also causes a splitting of the highest occupied pnictide p band at the X point, and this splitting also increases going from As to Bi. Interestingly, as shown in Fig. 3.3 for the case of Er-V, we find that in ErBi the Bi 6p band is very close to Er 5d band at the X point, but it avoids any band crossing making it topologically

Material	DFT-GGA	HSE06	HSE06	Exp.
	(4f in the core)	(4f in the core)	(4f in the valence)	
	a (Å)	a (Å)	a (Å)	a (Å)
LaAs	6.187	6.173	6.173	6.137
LaSb	6.540	6.514	6.514	6.488
LaBi	6.654	6.625	6.625	6.578
GdAs	5.879	5.838	5.882	5.854
GdSb	6.247	6.192	6.245	6.217
GdBi	6.373	6.314	6.368	6.295
ErAs	5.769	5.737	5.766	5.732
ErSb	6.148	6.105	6.160	6.106
ErBi	6.281	6.233	6.269	6.206
LuAs	5.701	5.670	5.697	5.679
LuSb	6.091	6.056	6.081	6.055
LuBi	6.231	6.185	6.220	6.159

Table 3.1: Calculated equilibrium lattice parameters a for the RE-V compounds using the HSE06 hybrid functional. The results obtained using DFT-GGA and the experimental values are also shown for comparison [1, 2, 3, 4, 5, 6, 7]. For the La-V compounds, the 4f shell is empty so the results using HSE06 with the 4f in the core or valence are the same. For Gd, Er, and Lu, treating the 4f as core electrons or as valence electrons give slightly different lattice parameters.



Figure 3.2: Calculated electronic band structure of (a)LaAs, (b) LaSb, (c) LaBi, (d) GdAs, (e) GdSb, (f) GdBi, (g) ErAs, (h) ErSb, (i) ErBi, (j) LuAs, (k) LuSb, and (l) LuBi using HSE06 without spin-orbit coupling and treating the 4f electrons as core electrons. The Fermi level is set to zero.

trivial semi-metal. This results doesn't change if we include 4f as valence electrons as shown in Fig. 3.4.



Figure 3.3: Calculated electronic band structure of (a)LaAs, (b) LaSb, (c) LaBi, (d) GdAs, (e) GdSb, (f) GdBi, (g) ErAs, (h) ErSb, (i) ErBi, (j) LuAs, (k) LuSb, and (l) LuBi using HSE06 with spin-orbit coupling and treating the 4f electrons as core electrons. The Fermi level is set to zero.

3.2.3 Effects of including 4f as valence electrons on the electronic structure of RE-V

In this section we will show how the electronic structure of RE-V change if we include 4f as valence electrons. In most of the previous calculations of RE-V compounds using DFT-LSDA or GGA the 4f electrons were taken as core electrons. Treating the 4f as valence electrons in these approximations would lead to incorrect description of the bands near the Fermi level [53]. To overcome this problem, an extra Coulomb interaction is often added to the 4f orbitals as in the LDA+U method, with U typically used as an adjusting parameter. This added electron-electron repulsion term splits the occupied and unoccupied 4f bands, pushing them out of the Fermi level region [128, 130, 8]. Here, instead, we show that the HSE06 hybrid functional also improves the description of the electronic structure of RE-V compounds, compared to DFT-LSDA or GGA, including the effects of 4f electrons being treated self-consistently as valence electrons. The results for GdAs, ErAs, and LuAs are shown in Fig. 3.4.



Figure 3.4: Calculated electronic band structure of (a) GdAs, (b) GdSb, (c) GdBi, (d) ErAs, (e) ErSb, (f) ErBi, (g) LuAs, (h) LuSb, and (i) LuBi with 4f as valence electrons using HSE06.

For GdAs, the 4f shell is half filled, resulting in flat bands occupied well below the Fermi level, whereas the empty 4f bands lie well above the Fermi level. The occupied 4f bands are located around 8 eV below the Fermi level and the unoccupied 4f states lie around 4-5 eV above the Fermi level, in qualitative agreement with the results of Petukhov *et al.* [53], and in good agreement with experimental data [131] and quasiparticle *GW* results [9].

In the case of ErAs, the filled 4f bands lie between -9.0 eV and -5.7 eV, while the three unoccupied 4f bands lie near 2 eV above the Fermi level, with a spread of around 0.5 eV. It is worth mentioning that the filling of 4f bands follows Hund's rule, as in previous LDA+U results [128, 130, 8]. Note that our results do not capture the multiplet features shown in the LDA+DMFT results [8] due to the single-particle nature of the HSE06 functional. It is interesting to note that in the case of Lu-V (V = As, Sb, Bi) all the 4f bands are occupied so the electronic structure does not change upon he inclusion of 4f bands as shown in Fig. 3.4. Experimental angleresolved photoemission spectroscopy (ARPES) E - k spectral map for LuSb along both $\bar{\mathbf{M}} - \bar{\Gamma} - \bar{\mathbf{M}}$ and $\bar{\mathbf{X}} - \bar{\Gamma} - \bar{\mathbf{X}}$ directions of the surface Brillouin zone for the hole pockets and along $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ for the electron pocket are found to be in excellent correspondence with our HSE06 calculations shown in Fig. 3.5. The experimental effective masses are determined from parabolic fittings of the band dispersions at the Fermi level, which are in agreement with our calculations as shown in Table 3.2. Three hole-like bands are observed near the $\overline{\Gamma}$ point with the third band (γ) completely below the Fermi level in agreement with our calculations. The use of generalized gradient approximation (GGA) erroneously predicts that all three hole-like bands in LuSb cross the Fermi level, in clear disagreement with the ARPES data. The extracted Fermi wave vector k_F and effective mass m^{*} at the Fermi level from both experiment and our calculations are shown in Table 3.2 for comparison.

3.2.3.1 Magnetic moments and band widths

We find the spin, orbital and total moment to be $2.9\mu_B$, $6.0\mu_B$, and $8.9\mu_B$, respectively, in the case of ErAs, using HSE06 as in LDA+U [8]. The total moment

FS^1	l	\mathbf{k}_F (Å ⁻¹)			m^*	
10	SdH	ARPES	DFT	SdH	ARPES	DFT
α	$0.11(a), 0.34(b)^2$	0.1(a), 0.38(b)	0.11(a), 0.37(b)	0.19	0.09(a), 1.02(b)	0.11(a), 1.16(b)
β	0.15	$0.12(1), 0.12(\bar{1})^3$	$30.15(1), 0.15(\bar{1})$	0.22	$0.26(1), 0.26(\bar{1})$	$0.23(1), 0.21(\bar{1})$
δ	0.22	$0.21(1), 0.19(\bar{1})$	$0.24(1), 0.19(\bar{1})$		$0.45(1), 0.36(\bar{1})$	$0.54(1), 0.31(\bar{1})$

 Table 3.2:
 Fermi Surface of LuSb

¹ FS denotes Fermi surface.

 2 a and b indicates directions along the semi-minor and semi-major axes of the elliptical α pocket, respectively.

³ 1 and $\overline{1}$ indicates [100] and [110] crystallographic directions, respectively.

Table 3.3: Exchange splitting (in meV) of the As 4p hole bands at Γ and the Er 5d electron bands at the X point in the HSE06 calculations compared to previous LDA+U and LDA+DMFT results from Ref. [8] and quasi-particle GW results from Ref. [9].

band/k-point	LDA+U	GW	LDA+DMFT	HSE06
$hh @ \Gamma$	66	40	11	64
$lh @ \Gamma$	242	120	80	387
$sh @ \Gamma$	112	153	65	369
$e^- @ X$	124	150	65	223

is in good agreement with the experimental values for high magnetic field, but slightly different from the low applied magnetic field value according to the LDA+DMFT results [8]. The results for the exchange splitting in the semi-metallic As 4p hole bands at Γ (*hh*, *lh*, and *sh*) and the Er 5*d* electron bands at the *X* point are listed in Table 3.3. Overall, HSE06 gives larger exchange splittings due to the closer proximity of the unoocupied 4f bands to the semi-metallic As 4p and Er 5*d* bands, compared to LDA+U, *GW*, and LDA+DMFT [9, 8], except for the *hh* band that HSE06 gives a similar value to the LDA+U result[8].

Finally, we note that the width of the As 4p hh band, measured along Γ -X



Figure 3.5: ARPES spectra of LuSb thin films(from our collaborators). (a) Bulk three-dimensional Brillouin zone of LuSb and its surface projection showing high-symmetry points. (b) Two-dimensional Fermi surface map near the bulk Γ point showing both hole-like(β,δ) and electron-like(α) Fermi surface sheets. (c) Two-dimensional map near the bulk Γ point at a binding energy of 0.495eV illustrating anisotropy of the δ pocket. (d) E - k spectral map along Γ-M-Γ as indicated by brown arrows in panel (b). E - k spectral maps along (e) M-Γ-M and (f) X-Γ-X indicated by (e) blue and (f) red arrows in (c). Red dotted lines are calculated dispersions from DFT.

is ~1.5 eV, very close to the GW result[9], and much larger than the value of ~1.1 eV in the LDA+U and LDA+DMFT results[8]. This is attributed to the improved description of the band dispersion of uncorrelated bands in HSE06 and GW, as in the case of band gaps and band dispersions in semiconductors. In the LDA+DMFT calculations, the As 4p bands are not corrected.

3.2.4 Carrier concentration in RE-V

The rare-earth pnictides are compensated semimetals with equal electron and hole concentrations. The free carrier concentration in these materials is determined by the overlap in energy of the electron and hole pockets. The volume of the Fermi surface

	10, 11, 10, 15, 2	[0, 21, 22].	
Material	DFT-GGA	HSE06	Exp.
	$n(10^{20} \text{ cm}^{-3})$	$n(10^{20} \text{ cm}^{-3})$	$n(10^{20} { m cm}^{-3})$
LaAs	0.94	0.25	0.46[15]
LaSb	2.28	1.44	1.10[16]
LaBi	4.04	3.72	3.78 [17, 18]
GdAs	5.13	3.00	2.10[19]
GdSb	6.55	4.39	4.20[19]
GdBi	7.18	6.09	-
ErAs	5.59	3.3	1.8[10, 11], 4.69[12, 13], 3.3[10, 11, 14]
ErSb	6.68	4.53	-
ErBi	8.06	6.88	-
LuAs	5.86	2.63	1.52[20]
LuSb	6.57	4.35	4.35, 5.07[21]
LuBi	8.24	6.44	6.61, 6.99[22]

Table 3.4: Calculated carrier concentration n for the RE-V compounds using the HSE06 hybrid functional, including spin-orbit coupling (SOC) and treating the f electrons as core (DFT-GGA) or valence (HSE06) electrons Experimental results are also listed for comparison[10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22].

for ErAs calculated using LSDA [1] is almost three times larger than the experimental value [12]. The reason behind this disagreement is the fact that LSDA overestimates the band overlap between As p and Er d bands, overestimating the dimensions of the electron and hole pockets and resulting in higher carrier concentrations than in experiment. Here we computed the carrier concentration using different approximations, i.e., GGA, HSE06, including SOC, and treating the 4f as core electrons. The carrier concentrations are calculated using the wannier90[132] and SuperCell K-space Extremal Area Finder(SKEAF) codes [133]. The results are shown in Table 3.4. Only the results including SOC should be compared to the experimental data.

3.2.5 Band alignments at RE-V/III-V interfaces

Due to the common group-V fcc sublattice and similar lattice parameters of RE-V and conventional III-V semiconductors, we expect that the later can serve as substrates for epitaxial growth of RE-V, as demonstrated in the case of (In)GaAs/ErAs [30, 34, 35] and GaSb/LuSb [31, 32]. In this context, it is important to know the workfunction of these materials to understand the formation of Schottky barriers and any possible charge transfer across the III-V/RE-V interfaces. So we calculated the band alignment at the ErAs/GaAs and LuSb/GaSb, which are two systems of current interest, and display small lattice mismatches [134, 31]



Figure 3.6: Calculated band alignment at the ErAs/GaAs and LuSb/GaSb interfaces. The band alignment between GaAs and GaSb was taken from the literature [24].

The band alignments between the Fermi level in the semimetal and the band edges in the semiconductor are calculated as follows [134]. First, we calculated the Fermi level position in the semimetal and the band edges in the semiconductor with respect to the respective averaged electrostatic potential through bulk calculations using their primitive cells. Then we aligned the averaged electrostatic potential in the two materials by performing an interface calculation using a superlattice geometry with two equivalent interfaces, as described previously. The superlattice consisted of 9 monolayers of each material, along the non-polar [110] direction in order to minimize the effect of charge transfer across the interface. In order to remove the effects of strain due to the small lattice parameters, we used the in-plane lattice parameter of the semiconductor and adjusted the out-of-plane lattice parameter of the semimetal to give its equilibrium volume. In this way, the calculated band alignments should be regarded as natural band alignments. In any case, effects of small strain on the absolute position of the Fermi level in the semimetal were shown to be negligible [134].

For the superlattice, we used a $6 \times 6 \times 1$ Gamma-centered mesh of special k points for the integration over the Brillouin zone. We note than for GaAs our calculated band gap using the HSE06 hybrid functional is 0.11 eV lower than the experimental value of 1.42 eV, while for GaSb our calculated band gap is 0.06 eV larger than the experimental value of 0.67 eV. The results for the band alignments are shown in Fig. 3.6.

We find that the Fermi level of the semimetal lies within the band gap of the semiconductor in the cases of ErAs/GaAs and LuSb/GaSb. The band alignment between GaAs and GaSb was taken from the literature [24]. In the case of ErAs/GaAs we find that the Fermi level in ErAs is 0.58 eV above the valence band of GaAs, and in the case of LuSb/GaSb the Fermi level of LuSb is 0.36 eV above the valence band of GaSb. From the transitivity rule, we obtain the Fermi level of LuSb 0.47 eV higher than that of ErAs, consistent with the Sb 5p orbitals being higher in energy than the As 4p orbitals. Note that our results for position of the Fermi level in ErAs with respect to the valence band edge in GaAs is slightly higher than previous uncorrected DFT value by 0.3 eV [134], yet only ~0.1 eV lower than the reported experimental value [29].

In summary, we performed HSE06 hybrid functional calculations for the electronic structure of RE-V compounds, where RE= La, Gd, Er, Lu and V = As, Sb, Bi. The HSE06 gives equilibrium lattice parameters in very close agreement with experimental data. All the studied compounds are semi-metals with the size of hole pocket increasing from As to Bi, whereas the gap at X point increases with increase in atomic number of the rare-earth element. We show that using HSE06 gives a good description of the electronic structure of RE-V including the 4f electrons explicitly as valence electrons. In particular, we find reasonable agreement with LDA+DMFT and GW calculations for ErAs. We also show that HSE06 gives hole and electron concentrations that are closer to the observed values, correcting the overestimation of the electron and hole pockets overlap in the DFT-GGA calculations. Our results for the band alignment at the ErAs/GaAs interface is in good agreement with experimental data, and it is a significant improvement over previously reported DFT calculations within local spin density approximation.

3.3 Effects of pressure on the electronic structure of La-V

In this section we will study the effects of hydrostatic pressure on the electronic properties of LaAs using density functional theory (DFT) calculations with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06). We focus on the band crossing near the X point that can make LaAs a topological semimetal, discussing results of both DFT within the generalized gradient approximation (GGA) and the HSE06 hybrid functional. As introduced in section 1.1 we find that in DFT-GGA, under the calculated equilibrium lattice parameter, LaAs displays a crossing between the highest As p band and the lowest La d band near the X point due to the overestimated p-d band overlap. Such crossing does not occur when the band overlap is corrected in the HSE06 calculation. However, we find that the p-d crossing can be induced in LaAs under hydrostatic pressure, showing a topological phase transition at ~7 GPa. The rocksalt crystal structure of LaAs is predicted to be stable under applied pressure up to 20 GPa, in good agreement with experimental observations.

In this study, we used plane-wave basis set with 300 eV kinetic-energy cutoff. For the Brillouin-zone sampling, we use a $8 \times 8 \times 8$ Γ -centered k-point mesh. In the calculations of the crystal under pressure, we use a variable cell relaxation at different applied pressures, in the range of 0-28 GPa. The effects of spin-orbit coupling (SOC) were included only in the band structure calculations, not in the cell optimization. Since LaAs in the rock-salt crystal structure has both time-reversal symmetry and inversion symmetry, the Z_2 topological invariant is calculated from the parity of the occupied bands at the eight time-reversal invariant momentum (TRIM) points [135].

3.3.1 Electronic band structure of LaAs

LaAs is one of the member of RE-V family and it is stable in rock-salt structure at ambient pressure. The calculated equilibrium lattice parameter using DFT-GGA is 6.187 Å, and 6.173 Å using HSE06, in good agreement with the experimental value of 6.137 Å [7]. The calculated electronic band structure of LaAs using DFT-GGA and HSE06 are shown Fig. 3.7. We focus on the bands within 2 eV of the Fermi level. The partially occupied bands at Γ (hole pockets) are derived mainly from As 4p orbitals, and the partially occupied bands at the X point (electron pockets) are derived mainly from La 5d orbitals. The band inversion near the X point would be a sign of topologically non-trivial band structure, as in the case of LaBi, a similar material for which such band inversion has been established theoretically and experimentally [38].

Previous calculations have reported qualitatively different results for the electronic structure of LaAs[136, 15], depending on the exchange-correlation functional employed. In standard DFT-GGA calculations [15], LaAs is a semimetal with the As pand La d bands crossing near the X point. By applying an external repulsive potential U=1.63 eV to the La d in the DFT-GGA+U method, the overlap between the As p-La d is reduced to 0.20 eV, and the crossing disappears [15]. By employing the modified Becke-Johnson meta-GGA for the exchange potential [137], LaAs is a semiconductor with an indirect band gap of 0.20 eV [15]. In recent HSE06 hybrid functional calculations, it was found that LaAs is a semiconductor with a small indirect band gap of 0.12 eV [136]. However, these HSE06 results did not include the effects of spin-orbit coupling. We performed test calculations using HSE06 without spin-orbit coupling, and find a gap of 0.01 eV. In our calculations, both DFT-GGA and HSE06 show an overlap between the La d band and As p bands indicating that LaAs is a semimetal,



Figure 3.7: Electronic band structure of LaAs in rock-salt structure using (a) DFT-GGA functional and (b) the HSE06 hybrid functional with spin-orbit coupling. The Fermi level is set to zero.

in agreement with ARPES measurements [15, 75]. In the DFT-GGA calculations we find that the La d band touches the As p band near the X point, in agreement with previous calculations, while in the HSE06 this band inversion does not occur, with a separation of ~0.3 eV between the As p band and La d band near the X point.

Therefore, LaAs is predicted to show different behavior, depending on the functional used in the calculations. In DFT-GGA, it is predicted to be topological semimetal, while in HSE06, LaAs is predicted to be a normal, topologically trivial semimetal. We note that ARPES measurements [15, 75] in LaAs bulk shows the absence of any band crossing in the band structure, in agreement with our HSE06 calculations, and in contrast to DFT-GGA which overestimates the overlap between the As p and La d bands.



Figure 3.8: Electronic band structures of (a) LaAs (b) LaSb (c) LaBi calculated using the HSE06 hybrid functional with spin-orbit coupling. The Fermi level is set to zero.

3.3.2 Comparison between La monopnictides(La-V)

In Fig. 3.8 we show the band structures of LaAs, LaSb, and LaBi calculated using HSE06. LaBi, LaSb and LaAs are quite similar materials, in the sense that they share the same crystal structure and are non-magnetic members of the rare-earth monopnictide family as discussed in 1.1. Thus, we expect their band structure to be similar. However, the spin-orbit coupling is much stronger in LaBi than in LaSb and LaAs, and the Bi p band is much higher in energy at Γ point than the Sb and As pbands. As consequence, the LaBi is predicted to be a topological semimetal with a crossing of the La d and Bi p bands near the X point, in agreement with previous calculations [41, 75] which clearly show the presence of three Dirac cones [67, 38] in the surface band structure, and also verified by ARPES measurements [67, 37, 75].

The calculated carrier densities in LaAs, LaSb and LaBi are listed in Table 3.5. The results are in good agreement with experimental values [15, 16, 18, 7, 23, 6]. For LaSb, which experimentally is found on the verge of being a topological semimetal, we find a small separation of ~0.17 eV between the Sb p and the La d bands and it will be discussed in detail in next section. For LaBi, our calculated band structure is in quantitative agreement with the reported ARPES results [75].

Material	a((Å)	$n(\mathrm{cm}^{-3})$		
	HSE06	Expt.	HSE06	Expt.	
LaAs	6.173	6.137	$2.49 \mathrm{x} 10^{19}$	$4.60 \mathrm{x} 10^{19}$	
LaSb	6.514	6.488	$1.44 \mathrm{x} 10^{20}$	$1.10 \mathrm{x} 10^{20}$	
LaBi	6.625	6.570	3.72×10^{20}	3.78×10^{20}	

Table 3.5: Calculated carrier concentration n for the La-V compounds using the HSE06 hybrid functional, including spin-orbit coupling (SOC). Experimental results are also listed for comparison. [15, 16, 18, 7, 23, 6].

3.3.3 Structural phase transition in LaAs under pressure

In general, applying pressure to a material will change its bond lengths and, consequently, band width and band gap, without any sort of chemical doping or stoichiometry modification. As discussed earlier in section 3.3.1, at ambient conditions, LaAs is stable in the rock-salt structure, shown in Fig. 3.9(a), but it goes a structural phase transition under hydrostatic pressure, transforming to a body-centered tetragonal (*bct*) structure, shown in Fig. 3.9(b).

We calculate the enthalpy of LaAs in these two crystal structures for a wide range of pressures. The structure with minimum enthalpy for a given pressure will be the most stable structure at that pressure. Enthalpy is defined as H = E + PV, where E is the total energy, P is pressure and V is volume of unit cell. The enthalpy of both structures increases with increase in pressure, but the enthalpy of the rock-salt structure rises faster than that of the *bct* structure. We find that at around 20 GPa, the rock-salt structure becomes less stable than the (*bct*) structure, as shown in Fig. 3.9(c). This result is in good agreement with experimental observations [7]. The change in relative volume of LaAs under applied pressure is shown in Fig. 3.9(d) along with the experimental data [7].



Figure 3.9: Crystal structures of LaAs: (a) ground-state rock-salt structure and (b) body-centered tetragonal (bct) structure. (c) Enthalpies of LaAs in rock-salt and tetragonal structures as a function of pressure showing a transition from rock-salt to bct at 20 GPa.(d) Relative changes in volume as a function of pressure in LaAs. The experimental data were extracted from Ref. [7].

3.3.4 Change in electronic band structure of LaAs under pressure

We also compute the band structure of LaAs under different pressure conditions, for up to 10 GPa, focusing on the behavior of La d and As p bands near the Fermi level. For the band structure calculations we limited our attention to the rock-salt structure as this is the stable crystal structure up to 20 GPa. We find that for up to 6 GPa, there is no sign of band inversion, and that starting at 7 GPa, the La d and As p bands cross near the X point. Therefore, we expect a topological phase transition in LaAs to occur at about 7 GPa. The band structure of LaAs along Γ -X direction for hydrostatic pressures of 6 GPa and 7 GPa are shown in Fig. 3.10.

To verify the non-trivial topology of the band structure of LaAs under pressure we also calculate the Z_2 invariant. There are four Z_2 invariants in the case of three dimensional materials. For a material with both time-reversal and inversion symmetry, such as LaAs in the rock-salt structure, the Z_2 invariant can be calculated from the parities of all the occupied bands at the TRIM (time reversal invariant momentum) points [135], through the relation:

$$(-1)^{v_{0}} = \prod_{m=1}^{8} \delta_{m}, \qquad (3.1)$$

where the index ν_0 defines the topological class of the material and δ_m is the parity product of all the occupied bands at the *m*-th TRIM point. The parity of a band can be determined by a symmetry analysis of the orbitals that compose it.

For up to 6 GPa, the valence band of LaAs near the X point is derived from As p orbitals while the conduction band is derived from La $d(t_{2g})$ orbitals. At the X point, the parity of the As p band is X_7^- (odd), while the parity of the La d band is X_7^+ (even). When the two bands cross at 7 GPa, Fig. 3.10(b), the parity is also switched at the X point.

The parities of all the relevant bands at eight TRIM points just before the topological phase transition (6 GPa) and just after the phase transition (7 GPa) are shown in Tables 3.6 and 3.7 respectively. Hence, due to the inversion of the As p and La d bands at the X point, the Z_2 topological invariant v_0 changes from 0 to 1 making LaAs a non-trivial topological semimetal at applied pressure of 7 GPa. Since the As p and La d t_{2g} bands belong to the same irreducible representation of the C_{4v} double group, the band crossing opens up a gap when spin-orbit coupling is included, as shown



Figure 3.10: Electronic band structure along Γ -X- Γ direction of LaAs under (a) 6 GPa and (b) 7 GPa hydrostatic pressure.(c) Zoomed in view at 7 GPa near the crossing of the La d and As p bands. The symmetries and parities of the two bands that cross near the X point are indicated. The Fermi level is set to zero.(d) Z_2 topological invariant (ν_0) plotted as a function of hydrostatic pressure for LaAs in the rock-salt structure, calculated using the HSE06 hybrid functional.

No.	Γ	L	L	L	L	X	X	X	Total
1	-	-	-	-	-	-	-	-	+
3	-	-	-	-	-	-	-	-	+
5	-	-	-	-	-	-	-	-	+
7	+	-	-	-	-	+	+	+	+
9	-	+	+	+	+	-	-	-	+
11	-	+	+	+	+	-	-	-	+
13	-	+	+	+	+	-	-	-	+
Total	+	+	+	+	+	+	+	+	+

Table 3.6: Parities at time reversal invariant momenta (TRIM) points in the first Brillouin zone of LaAs in the rock-salt crystal structure for all the occupied bands just before the topological phase transition (6 GPa).

in Fig. 3.10(c). These results indicate that LaAs is not a Dirac semimetal, but due to the inversion of the two bands at X with opposite parities it can be classified simply as a non-trivial topological semimetal. The calculated ν_0 as a function of pressure, shown in Fig. 3.10(d), switches from 0 to 1 at 7 GPa due to the band crossing near the X point.

In summary, magnetotransport measurements in LaAs bulk samples show XMR effects [15], although reduced in magnitude compared to LaSb and LaBi [75]. In LaAs, the XMR is clearly unrelated to non-trivial band topology, as LaAs is not a topological semimetal at ambient pressure. This is similar to YSb, another rock-salt structure monopnictide, where XMR has been observed without any sign of non-trivial band topology [74]. It was argued that XMR in YSb is caused by the difference in electron and hole mobilities, yet this conclusion relies on the simple semi classical two-band model [138, 139]. In topological semimetals such as LaBi, the observed XMR could be induced by the breaking of time reversal symmetry in the presence of magnetic field, yet

No.	Γ	L	L	L	L	X	X	X	Total
1	-	-	-	-	-	-	-	-	+
3	-	-	-	-	-	-	-	-	+
5	-	-	-	-	-	-	-	-	+
7	+	-	-	-	-	+	+	+	+
9	-	+	+	+	+	-	-	-	+
11	-	+	+	+	+	-	-	-	+
13	-	+	+	+	+	+	+	+	-
Total	+	+	+	+	+	-	-	-	-

Table 3.7: Parities at time reversal invariant momenta (TRIM) points in the first Brillouin zone of LaAs in the rock-salt crystal structure for all the occupied bands after the topological phase transition (7 GPa).

a direct relationship is still missing since LaBi also shows electron-hole compensation and possibly large differences in electron and hole mobilities.

Our calculations for the electronic structure of LaAs using DFT-GGA and the screened hybrid functional HSE06 show that HSE06 calculations corrects the overestimated overlap between valence and conduction bands compared to DFT-GGA. HSE06 correctly predicts no band inversion at the X, which makes LaAs a topologically trivial semimetal, in agreement with the experiments under ambient pressure. The calculated charge carrier concentration is also in good agreement with experiments. The electronic band structure of LaAs can be tuned by applying pressure, and it becomes a topologically non-trivial semimetal under hydrostatic pressure of \sim 7 GPa. This pressure is well below the structural phase transition to a *bct* crystal structure which is predicted to occur at \sim 20 GPa. Studying the XMR effect as a function of pressure in LaAs could shed light on the evolution of the XMR with carrier concentration (which

tends to increase with applied pressure) and the emergence of non-trivial band topology at 7 GPa, revealing the role of non-trivial topology in XMR. Therefore, LaAs can be a test material to find the relationship between electron-hole compensation and non-trivial topology as competing models to explain the observed XMR in rare-earth monopnictides.

3.4 Effects of epitaxial strain on the electronic structure of rare-earth monopnictides

In this section we will study the effects of epitaxial strain on the electronic strucfure of LaSb. The combination of magneto-transport and topological properties has brought great attention to rare-earth monophic semimetals. For some of them, like LaSb, it is unclear whether they show non-trivial topology or not based on density functional theory calculations and angular resolved photoemission spectroscopy measurements. Here, we use hybrid density functional theory to demonstrate that LaSb is in fact a trivial topological semimetal, in agreement with experiments, but on the verge of a transition to a topological phase. We show that under compressive epitaxial strain, the La d band crosses the Sb p band near the X₃ point in the Brillouin zone, stabilizing a topologically non-trivial phase, opening unique opportunities to probe the inter-relation between magneto-transport properties and the effects of band topology by examining epitaxially strained and unstrained thin films of the same material.

For the calculations of epitaxial strain we first use an eight atom cubic unit cell to simulate the epitaxial strain (fixing a=b and relaxing c), from which we extract a two atom primitive cell for band structure calculations, thus avoiding the effects of band folding. To sample the Brillouin zone we use $8 \times 8 \times 8$ Γ -centered k-point mesh for the 2-atom cell calculations. Effects of spin-orbit coupling (SOC) are included only in the band structure calculations, not in the cell optimization. Owned to the inversion symmetry and time-reversal symmetry at equilibrium and under epitaxial strain, the Z_2 topological invariant can be calculated from the product of parities at the timereversal invariant momentum (TRIM) points [135]. The wannier90 code [140] is used to obtain maximally localized Wannier functions (MLWF) and to parameterize a tight binding (TB) hamiltonian. The WannierTools code [141] is used to obtain surface band structure and spin texture based on the TB hamiltonian interfaced with wannier90.

3.4.1 Electronic band structure of LaSb

Like the other rare-earth pnictides, LaSb is stable in the rock-salt crystal structure with space group $Fm\bar{3}m$. The calculated equilibrium lattice parameter of LaSb is 6.540 Å using DFT-GGA and 6.514 Å using HSE06, in good agreement with experimental lattice parameter of 6.488 Å [6]. The calculated electronic band structure of LaSb using DFT-GGA and HSE06 are shown in Fig. 3.11, focusing on the region within ± 2 eV of the Fermi level. The partially occupied bands near Γ (hole pockets) are derived mostly from Sb 5*p* orbitals, whereas the partially occupied bands at the *X* point are derived from La 5*d* orbitals. With the inclusion of spin-orbit coupling the 3-fold degenerate bands at Γ split into a doubly degenerate band and a non degenerate band, whereas the La *d* band at *X* remains unchanged.



Figure 3.11: Electronic band structure of LaSb using (a) HSE06 hybrid functional and (b) the DFT-GGA functional with spin-orbit coupling. The zero in the energy axis corresponds to the Fermi level..

The electronic structure of LaSb is still under debate as the calculations by Guo et al. [41] predict different results using DFT-GGA and meta-GGA (MBJ). The DFT-GGA functional predicts LaSb to be a topological semimetal with a band inversion
at the X point, whereas the meta-GGA predicts a topologically trivial behavior by decreasing the La d-Sb p band overlap. HSE06 hybrid functional calculations by Guo *et al.* [76] also predict a topologically trivial band structure. ARPES measurements by Nummy *et al.*[75] showed no sign of band inversion, whereas results by Niu *et al.* [37] were not conclusive regarding the non-trivial topological nature of LaSb.

Our DFT-GGA and HSE06 calculations show an overlap in energy between La d band and Sb p band thus confirming the semimetallic nature of LaSb in agreement with previous calculations [41, 76] and experiments [40, 75, 16]. However, the HSE06 calculations reveal that the La d band lies higher in energy than the Sb p bands at each k along the $\Gamma - X$ direction, while in the DFT-GGA there is a crossing between the La d and Sb p bands along the $\Gamma - X$ direction. We note that our HSE06 calculations correct the overestimated La d-Sb p band overlap in DFT-GGA and also correctly describes the trivial nature of LaSb band structure in agreement with previous HSE06 calculations [76] and experiments[75, 40]. Note also that the order to the La d band and the pnictogen p band can be reversed if the spin-orbit coupling is stronger as in the case of LaBi [77, 67, 38], which is a similar material with a topologically non-trivial band structure.

3.4.2 Effect of epitaxial strain on electronic band structure of LaSb

In this section we will discuss how the electronic band structure evolve under applied epitaxial strain. The electronic structure of a material can be changed without adding any extraneous chemical species or doping. As discussed in section 3.3.4, applying hydrostatic pressure leads to an inversion of the La d and the pnictogen p bands at the X point in LaAs[77] and LaSb[76], turning them into topologically non-trivial materials. Epitaxial strain, such as in coherently strained films grown or deposited on lattice mismatched substrates, can also be employed to alter the electronic structure of materials. It reduces the space group symmetry from $Fm\bar{3}m$ to I4/mmm, yet keeping the inversion symmetry. Here we show that compressive epitaxial strain can be used as an effective tool to change the topological properties of the LaSb band structure. Epitaxial strain has been demonstrated in the growth of rare-earth pnicitides on III-V semiconductors using molecular beam epitaxy (MBE) [31, 32]. Compressive epitaxial strain of up to 3% has already been realized in III-V semiconductors[142], and we expect that similar strains can be achieved in the rocksalt rare-earth pnictides. Note that effects of charge transfer at the interface between the substrate and the LaSb thin film may affect the carrier compensation; the amount of charge will depend on the band alignment, the interface termination, and the doping type and level in the semiconductor.



Figure 3.12: Crystal structure and Brillouin zone of (a) LaSb at equilibrium and (b) under compressive epitaxial strain (the later was exaggerated for easy visualization). The shaded area in yellow shows the projection of the bulk Brillouin zone on the (001) surface Brillouin zone (SBZ), with symmetry points in the SBZ displayed in red.

In Fig. 3.12 we show how the Brillouin zone of LaSb changes under epitaxial strain. Under equilibrium, the Brillouin zone has the shape of a truncated octahedron, which is common for face-centered cubic or rocksalt crystal structures, with Γ at the center and three independent X points at the center of the square faces. The shape of the Brillouin zone changes when we apply compressive epitaxial strain as the three independent X points split into two in-plane X points and one out-of-plane Z point. It is important to note that the spacial inversion symmetry is preserved in LaSb under epitaxial strain, and it is reflected in the inversion symmetry of the distorted Brillouin zone shown in Fig. 3.12(b).

The calculated electronic band structure of LaSb under compressive epitaxial strain is shown in Fig. 3.13, along the $\Gamma - X - \Gamma$ and $\Gamma - Z - \Gamma$ directions. Using the HSE06 functional we find that under equilibrium the three independent X points are equivalent, and the band structure along the in-plane and out-of-plane $\Gamma - X$ directions are the same. However, under epitaxial strain the three independent X points are split into two in-plane X and one out-of-plane Z point. In the case of compressive epitaxial strain of 1%, the La d band gets closer to the Sb p bands as the overall volume of the crystal is decreased. However, the La d and Sb p bands along the out-of-plane $\Gamma - Z$ direction, but still there is no crossing between the La d and Sb p bands. At 1.6% compressive epitaxial strain we observe a band inversion along the out-of-plane $\Gamma - Z$ direction, whereas the La d and Sb p bands along the $\Gamma - X$ still avoid crossing.

Note that the crossing between the La d and Sb p bands only occur in the case of compressive epitaxial strain, not for tensile strain. For compressive strain, the La dband and Sb p bands approach each other along both the $\Gamma - Z$ and $\Gamma - X$ directions because the overall volume/cell of the crystal decreases. The out-of-plane c lattice parameter changes according to the calculated Poisson's ratio, $\nu = -\frac{\varepsilon_{zz}}{\varepsilon_{xx}} = 0.26$, where $\varepsilon_{xx} = \varepsilon_{yy}$ is the change of the lattice parameters along the in-plane a and b directions, and ε_{zz} is the change of the lattice parameter along the out-of-plane c direction under epitaxial strain. For tensile epitaxial strain, the La d and Sb d bands are further



Figure 3.13: Electronic band structures of LaSb with (a) 0% (b) 1% and (c) 1.6% applied compressive epitaxial strain. The top row shows the bands along the in-plane direction, the middle row shows the bands along an out-of-plane direction, whereas the bottom row shows the bands along the Γ -X- Γ direction for the case of 0% applied compressive epitaxial strain, and along the Γ -Z- Γ direction for the cases of 1.0% and 1.6% applied compressive epitaxial strain all calculated using the HSE06 hybrid functional with spin-orbit coupling. The Fermi level is set to zero.

separated from each other due to the overall increase in the volume/cell of the crystal.

3.4.3 Parity analysis and surface band structure of LaSb

To shed light on the bulk band inversion and its relationship with the non-trivial topology in LaSb under epitaxial strain, we calculated the Z_2 invariant, which is given

No.	Γ	L	L	L	L	X	X	X	Total
1	-	-	-	-	-	-	-	-	+
3	-	-	-	-	-	-	-	-	+
5	-	-	-	-	-	-	-	-	+
7	+	-	-	-	-	+	+	+	+
9	-	+	+	+	+	-	-	-	+
11	-	+	+	+	+	-	-	-	+
13	-	+	+	+	+	-	-	-	+
Total	+	+	+	+	+	+	+	+	+

Table 3.8: Parities of all the occupied bands at TRIM points in the first Brillouin zone of LaSb under 0% applied compressive epitaxial strain.

Table 3.9: Parities of all the occupied bands at TRIM points in the first Brillouin zone of LaSb under 1.6% applied compressive epitaxial strain).

No.	Γ	L	L	L	L	X	X	Z	Total
1	-	-	-	-	-	-	-	-	+
3	-	-	-	-	-	-	-	-	+
5	-	-	-	-	-	-	-	-	+
7	+	-	-	-	-	+	+	+	+
9	-	+	+	+	+	-	-	-	+
11	-	+	+	+	+	-	-	-	+
13	-	+	+	+	+	-	-	+	-
Total	+	+	+	+	+	+	+	-	-

by the product of parities of all the occupied bands at the TRIM points[135] through the following relation:

$$(-1)^{v_0} = \prod_{m=1}^8 \delta_m \tag{3.2}$$

where ν_0 indicates the topological nature of the material and δ_m is the parity product at *m*-th TRIM point for all the occupied bands. For the LaX (X=As,Sb,Bi) compounds, this Z_2 invariant actually depends upon the product of parities of the occupied bands at the X points, which in the case of epitaxial strain will be X and Z points.

In LaSb at equilibrium, the valence band is mostly composed of Sb p orbitals,



Figure 3.14: Electronic band structure of (a) LaSb at equilibrium along M- Γ -M and (c) M-X-M directions and (b) LaSb under 1.6% compressive epitaxial strain along M- Γ -M and (d) M-X-M directions in the (001) surface Brillouin zone (SBZ). The bar on the right shows the intensity of surface states. The Fermi level is set to zero. The Dirac cone and Dirac point are indicated in (b). The spin textures of the bands crossing at 0.5 eV below the Fermi level of LaSb under equilibrium and LaSb under 1.6% compressive epitaxial strain are shown in (e) and (f), respectively.

whereas the conduction band has most of the contributions from La d orbitals. The parity of La d band is X_7^+ which is even, while the parity of Sb p band is X_7^- which is odd at two inequivalent X point and one Z point as shown in Table 3.8. Under compressive epitaxial strain of ~1.6%, the parity at the Z point is interchanged, whereas the parity at the two in-plane X points remains unchanged as shown in Table 3.9. Due to the change in parity at the Z point under applied compressive epitaxial strain the Z_2 invariant switches from 0 to 1 which is a sign of a non-trivial topological semimetal.

To further characterize the topologically non-trivial nature of LaSb under epitaxial strain we calculated the (001) surface band structure. From previous work [67], we learned that LaBi is a topologically non-trivial material under equilibrium. LaBi has bulk band inversion at three inequivalent X points, so that the surface states show three Dirac cones related to the bulk band inversions that are projected onto the surface Brillouin zone. Two in-plane X points are projected onto M points in the surface Brillouin zone (SBZ), and the third, out-of-plane, X(Z) point is projected onto Γ .

Since the bulk band inversion in LaSb under the effect of compressive epitaxial strain occurs only at the Z point (i.e., the out-of-plane X point), we expect only one Dirac cone to appear at the surface, located at the Γ point. In Fig. 3.14(a) and (b) we show the LaSb(001) surface electronic band structure along M- Γ -M direction. We see that a Dirac cone is missing at the Γ point when LaSb is at equilibrium, indicating of the trivial behavior in agreement with previous results [41, 76, 75, 40]. However, a gapless Dirac cone appears at the Γ point in LaSb under compressive epitaxial strain of 1.6%, in agreement with parity analysis. In Fig. 3.14(c) and (d) we also show the surface band structure along the M-X-M direction and, as expected from the discussion above, there is no sign of surface Dirac cones even under compressive epitaxial strain.

Another feature of non-trivial band structures is the presence of helical spin texture. To demonstrate that, we determined the spin texture for the surface band structures of LaSb at equilibrium and under 1.6% compressive epitaxial strain, the results of which are shown in Fig. 3.14(e) and (f), respectively. The spin textures are calculated at an energy cut of 0.5 eV below the Fermi level. In Fig. 3.14(e), we see that the helical spin texture is missing, with all spins aligned in one direction, whereas in Fig. 3.14(f) we observe a helical spin texture, further corroborating our analysis above. These calculations clearly demonstrate that under reasonably small compressive epitaxial strain, of 1.6%, LaSb becomes a topological semimetal. The ability to coherently grow and characterize thin films of LaSb on lattice matched and lattice mismatched substrates that offer such relatively small strains could shed light on the role of carrier compensation and non-trivial topology in the observed extreme magnetoresistance effects. In summary, using first-principles calculations we studied the electronic structure of LaSb using DFT-GGA and the screened hybrid functional HSE06. We verify that HSE06 rectifies the overestimated band overlap between conduction and valence bands in DFT-GGA. Using HSE06 we showed that LaSb is a topologically trivial semimetal under equilibrium, in agreement with the experiments. We also show that compressive epitaxial strain can be used to turn LaSb films into topological semimetal, creating unique opportunity to probe the inter-relationship between the occurrence of non-trivial topological properties, compensation of electrons and holes, and extreme magnetoresistance in rare-earth pnictides.

3.5 Tuning magnetoresistance in LuSb

As introduced in section 1.1, semi-metallic rare-earth monopnictide compounds offer an exciting platform to realize exotic quantum states of matter and novel material properties [143, 144, 86, 85, 145, 146]. Large, non-saturating magnetoresistance is one such example that has generated great interest in the recent years [16, 147, 148], where spin-orbit coupling [147], linearly dispersive states [149], charge compensation [150, 40] and charge inhomogeneity [151, 152, 153] have been proposed as possible mechanisms for its origin. Though electronic structure is expected to play a key role, demonstration of controlling the magnetoresistance via electronic structure modification remains elusive, which might also allow us to distinguish between the different proposed scenarios. To address this outstanding issue we calculated the electronic band structure of LuSb with different film thickness. Though LuSb is found to be a compensated semimetal in the bulk [31, 21], we establish that dimensional confinement differentially alters the occupation of electron and hole-like bands lifting carrier compensation. Loss of carrier compensation along with an overall reduction in carrier mobility in thinner films dramatically modifies their magnetoresistance behavior establishing the importance of carrier compensation. However, no evidence is found for the predicted semimetallic to semiconducting phase transition [154] in dimensionally confined thin films of LuSb, which remain semimetallic in the ultrathin limit. Heteroepitaxial interfaces offer another potential route to control electronic properties in few atomic layer geometries and can lead to emergent ground states not realizable in the bulk[155, 156, 157, 158]. We show that the local coordination and chemical bonding at the technologically relevant (001) interface, between rock-salt (LuSb) and zinc-blende (GaSb) crystal structure[159] provides a novel route to realize a two-dimensional hole gas, which remains tightly bound to the interface. This is accompanied by a charge transfer across the interface, which significantly affects the electronic structure and transport properties in LuSb in the ultra-thin limit. The experimental results discussed in this section are courtesy from our experimental collaborators from University of California Santa Barbara.

The LuSb/GaSb(001) interface was simulated using (i) a slab geometry with LuSb/GaSb/LuSb layers with 7.5 layers of Ga-terminated GaSb sandwiched between two 6-monolayer thick LuSb with a ~15 Å thick vacuum layer, and (ii) a LuSb/GaSb(001) superlattice with 17 layers of LuSb and 7.5 layers of GaSb. In both cases there are two equivalent, yet rotated with respect to each other, LuSb/Ga-terminated interfaces. LuSb(001) thin films were simulated using periodic slabs with 7, 13, 21, and 41 monolayers (ML). The odd numbers of layers are chosen to ensure inversion symmetry, making it easier to analyze the band structures. These calculations were performed using the DFT-GGA functional with $12 \times 12 \times 1$ special k-points; HSE06 calculations for these slabs are prohibitively expensive given the size of the supercell and the large number of k-points required to describe metallic systems.

3.5.1 Discrepancy between transport and ARPES data in experiment

Our experimental collaborators were able to grow thin films of LuSb with 6, 12, 20 and 40 monolayer (ML) thickness using MBE. Results of charge transport measurements, in Fig. 3.15, show interesting features. The arrow in Fig. 3.15(a) indicates the temperature below which the resistance is dominated by LuSb. So for film thickness down to 20 ML, the longitudinal resistance decreases with temperature, but for ultra thin films it does not change much. Magnetoresistance (MR) in these thin films

changes in both magnitude and shape with film thickness. MR decreases rather sharply from 120% for 40ML to around 10% in the thinner layer as shown in Fig. 3.15(b). For the Hall resistance a multi-carrier Hall behavior was observed in 40 and 32ML films, which changes to electron like behavior in 20 and 12Ml films as evident from the linear negative slope, whereas for 8 and 6Ml thin films p-type Hall conductivity was observed as seen from the positive slope as shown in Fig. 3.15(c). At that time, the origin of this p-type Hall conductivity was puzzling. The quantum oscillation data also indicate that dimensional confinement induces change in electronic structure, which differently affects electron- and hole-like bands. As shown in Fig. 3.15(e), there is a significant decrease in oscillation of the δ hole band for 32ML film compared to 40 ML, and for 20ML the oscillation for the δ band disappears, whereas the oscillation of electron band does not change in the same way, which is a sign that electron-hole compensation is lifted.

The angle resolved photoemission spectroscopy (ARPES) data indicate a decrease of the hole pocket as the film thickness decreases, whereas the electron pocket more or less stays the same. For the 40ML thick film the electron and hole concentrations obtained from the Fermi wave vector k_F values in ARPES are almost equal, giving ratio $\frac{n}{p} \approx 1.01$, which shows that electron-hole compensation is still present in 40Ml film. The same ratio for 6Ml thick film gives $\frac{n}{p} \approx 1.6$ which shows higher concentration of electron carriers than hole carriers, and a deviation from electron-hole compensation which could also explain the significant decrease in magnetoresistance (MR) for thin films. So the contradiction here is that from the ARPES data we have more electronlike carriers in 6ML thin films whereas from the Hall measurements we get *p*-type conductivity. This apparent contradiction between the two types of measurements we reconciled by our first-principles DFT calculations.

3.5.2 Surface electronic structure of LuSb

To explain this discrepancy discussed in section 3.5.1, we started with DFT calculations for LuSb(001) slabs to see how the electron and hole pockets change with



Figure 3.15: Experimental transport properties of LuSb/GaSb (001) thin films. (a) Temperature dependence of resistance in thin films of various thicknesses. R_Ξ is the resistance at the sample temperature below which film resistance is dominated by LuSb layer. Temperatures corresponding to R_Ξ are indicated for all film thicknesses. (b) Evolution of magnetoresistance with film thickness. Inset highlights saturating magnetoresistance behavior at high fields for 8- and 6-ML-thick samples. All data taken at 2 K.(c) Hall resistance measured at 2 K as a function of film thickness. (d) Crystal structure of LuSb and its Fermi surface, calculated using hybrid DFT. (e) Fast Fourier transform of the quantum oscillations for the 40-, 32-, and 20-ML-thick films



Figure 3.16: Experimental photoemission spectroscopy measurements of LuSb/GaSb(001) thin films. (A) Three-dimensional and surface Brillouin zone of LuSb showing the high-symmetry points. Red and blue lines show the cut directions along which ARPES measurements are taken for (C-F) and (G-J), respectively. (B) Fermi surface map showing both the electron and the hole pockets and the ARPES cut directions. *E-k* spectral map at the bulk Γ point (top panels) along $\overline{M} - \overline{\Gamma} - \overline{M}$ (red line in **A**) of the surface Brillouin zone for thin films of thickness (C) 40ML (D) 20ML (E) 12ML and (F) 6ML, and at the bulk X point (bottom panels) along $\overline{\Gamma} - \overline{M} - \overline{\Gamma}$ (blue line in **A**) of the surface Brillouin zone for (G) 40ML (H) 20ML (I) 12ML and (J) 6ML thick films. All data taken at 70K.

film thickness. In Fig. 3.17 we show the electronic band structure for LuSb slab along $\overline{M} - \overline{\Gamma} - \overline{M}$ high symmetry direction. We note that the choice of using odd numbers of layers in the LuSb slab calculations, for instance 7, 13, 21, and 41 ML shown in Fig. 3.17 instead of 6, 12, 20, and 40 in the experiments was to ensure inversion symmetry and facilitate the analysis of band structures, and does not affect our results and conclusions. For different thickness we see a decrease in size of hole pocket at $\overline{\Gamma}$ point with decrease in film thickness, agreeing very well with the ARPES data, but the electron pocket at \overline{M} is strongly affected by quantum confinement, contrary to the experimental data shown in Fig. 3.16. We attribute this discrepancy to the

excess charge due to the specific termination at the interface between the GaSb(001) substrate and the LuSb(001) film and will be discussed in next section. These results are summarized in terms of Fermi wave vector k_F obtained from both ARPES data and the calculations as shown in Fig. 3.17(d) and Fig. 3.17(c), respectively, where k_F corresponds to the size of the Fermi pocket.



Figure 3.17: LuSb slab calculations.(a) LuSb slab along (001) direction. (b)Bulk Brillouin zone and its projection on surface. (c-d) Evolution of Fermi wave vectors (k_F) with film thickness from calculations and ARPES respectively. Calculated electronic structure of free-standing LuSb (001) films as a function of film thickness (number of monolayers or ML) for (e) 7ML, (f) 13ML, (g) 21ML, and (h) 41ML.

The ARPES and quantum oscillation measurements along with LuSb slab calculations does establish the loss of electron-hole compensation in thinner films, but dimensional confinement alone is not sufficient to explain the experimental data. To understand these contradictory behavior we started thinking about the effect of the GaSb/LuSb interface and what is the impact of this buried interface on the experimental observations.

3.5.3 Simulating the LuSb/GaSb heterostructure

To investigate the effects of the interface, we created LuSb/GaSb heterostructures along (001) direction. We used two interfaces in order to avoid any dipole effects which can create undesired electric field. In Fig. 3.18 we show the structural characterization of the interface. The TEM image shows Ga termination in GaSb zinc blende lattice at the interface. Our calculations predict a distortion of Lu atoms at the interface due to bonding mismatch and this is also observed in experimental TEM image. The Lu-Lu interatomic distance in the out of plane direction is smaller at the interface and is consistent with the atomic layer buckling. This provides further evidence for the validity of our slab calculations in understanding the experimental results.

Our DFT calculations reveal the existence of a 2D hole gas at the LuSb/GaSb(001)interface. In Fig. 3.19(a), we show the electronic band structure of the LuSb/GaSb/LuSb(001) slab. We find two interfacial bands crossing the Fermi level, mostly composed of s orbital of the Ga atoms at the interface, corresponding to one band with Ga-s character per interface. These two bands show different dispersions along $\Gamma - \bar{X}_1 - \bar{M}$ and $\Gamma-\bar{X}_2-\bar{M}$ because the corresponding Ga-Sb bonds at the two equivalent interfaces are rotated with respect to each other by 90° due to the symmetry of the zinc blende structure of GaSb. The Fermi-level crossings of these two bands and the resulting Fermi surface are shown in Fig. 3.19(d), respectively, indicating a hole-like behavior, which explains experimental observation. The estimated carrier concentration, based on the Luttinger volume, is 0.7 hole per 2D unit-cell area per interface. We note that the estimated Luttinger volume depends marginally on the functional used in the calculation and should be considered as a lower bound due to the use of generalized gradient approximation (GGA) in the slab calculations. The calculated projected density of states, shown in Fig. 3.20, also indicates that these interface bands are associated with the Ga atoms at the interface. The charge density distribution (Fig. 3.19(b)), corresponding to the square of the single-particle states at the maximum of the hole band along $\bar{X}_2 - \bar{M}$ (highlighted by blue circles in Fig. 3.19), reveals the 2D character of these two bands, which are highly localized out of plane vet uniformly distributed in



Figure 3.18: LuSb/GaSb heterostructure. (a) LuSb/GaSb/LuSb(001) slab.(b) Average atomic positions along a-b, shown in d, plotted as a function of the distance from a, calculated by averaging those atomic columns that terminate with a Lu atom at the interface between a-b and a^* b^* . Inset shows the evolution of the Lu-Lu inter-atomic distance as a function of the distance from the interface. Lu-Lu inter-atomic pairs are numbered away from the interface, as shown in b.(c) A closeup of the HAADF-STEM image in d and a ball-and-stick model of the proposed interface showing the atomic arrangement at the interface. Distortion of the Lu atoms at the interface is evident from the change in the bond angle and from a reduced Lu-Lu inter-atomic distance between the 1st and the 3rd LuSb monolayer (violet arrow) as opposed to the 3rd and the 5th monolayer (brown dashed arrow). (d) HAADF-STEM image along [110] zone-axis.

the plane of the interface.

The charge density of this two-dimensional hole gas and associated charge transfer to the LuSb atomic layers can also be estimated based on a simple electron counting argument. In Fig. 3.19(c), we show the valence charge density profile of the LuSb/GaSb/LuSb(001) slab system. The excess charge on the LuSb layer on the top or at the bottom of the GaSb layer is defined as the macroscopically averaged charge density along the heterostructure direction in the LuSb region (indicated in



Figure 3.19: Origin of the two-dimensional hole gas at a rock salt/zinc blende interface. Electronic structure of a LuSb/GaSb/LuSb(001) slab showing (a) Interface bands that originate from Ga s-orbitals at the interface. The two-dimensional unit cell and the surface Brillouin zone is also shown. (b) Charge density distribution of the single-particle state at the maximum of the hole bands crossing the Fermi level along the X
₁-M and X
₂-M directions. (c) Valence charge density distribution of the LuSb/GaSb/LuSb (001) slab along the direction perpendicular to the interface. (d) Fermi surfaces of the two interface bands associated with the two equivalent interfaces, yet rotated, corresponding to the structure used in the simulation, shown in a.



Figure 3.20: Origin of \mathbf{the} two-dimensional hole gas \mathbf{at} a rock salt/zincblende interface. Electronic structure of a LuSb/GaSb/LuSb (001) slab showing (a) Interface bands that originates from s orbital of the Ga atom at the interface; (b) 3D view of the two interface bands associated with the two equivalent interfaces, yet rotated, the structure used in the simulation. (c) Charge density distribution of the single-particle state at the maximum of the hole band crossing the Fermi level along the \bar{X}_2 - \bar{M} direction. (d) Valence charge density distribution of the LuSb/GaSb/LuSb (001) slab along the direction perpendicular to the interface. (e) Density of states (DOS) calculation for the GaSb region in the LuSb/GaSb/LuSb (001) slab. (f) Density of states (DOS) calculation for the GaSb bulk.



Figure 3.21: Evolution of Fermi wave vectors (k_F) with film thickness.(a) Fermi wavevectors for both the elliptical electron-like pocket (α) and quasi-spherical hole-like pockets (β, δ) as a function of film thickness obtained from (a) ARPES measurements (b) LuSb slab calculations after adding a charge transfer of 0.25 electrons/2D unit cell into the LuSb atomic layers.

Fig. 3.19(c)) and the corresponding charge density of charge neutral LuSb bulk. The calculated excess charge density on the LuSb film amounts to 0.45 electrons/2D unit cell area. Assuming that an excess charge of 1.5 electrons is expected at the interface due to the valence mismatch, i.e. in an ionic picture of GaSb, each Ga layer transfers 3/2 electrons to each of the neighbouring Sb layers, we obtain 1.5 - 0.45 = 1.05 electrons/2D unit cell area would remain at the interface. Discounting the electrons that are transferred to the bulk of GaSb, which is only 0.045 electrons/2D unit-cell area per interface according to the results shown in Fig. 3.19(c), this will amount to ~ 1 excess electrons per unit-cell area per interface. Assuming that this electron partially occupies an interface band, we have about 1 hole per unit-cell area in the interface band. This estimation of 1 hole/2D unit cell can be considered as an upper bound value as GaSb bonds have strong covalent character.

The estimated values of 0.7 - 1 hole per 2D unit-cell, based on the DFT calculations, corroborates the experimental value of 0.8 hole/2D unit cell. Furthermore, following our understanding based on the calculations, observation of 0.8 hole/2D unit cell at the interface implies 0.25 excess electrons transferred to the LuSb atomic layers. Calculated k_F values for the LuSb slabs after inclusion of the charge transfer across the interface were found to be in close agreement with those extracted from ARPES, shown in Fig. 3.21. This underscores the importance of the interfacial effects, in addition to the quantum confinement effects, in understanding the evolution of the electronic structure with film thickness in heteroepitaxial semimetallic thin films. Finally, in Fig. 3.20 we show that the existence of a two-dimensional hole gas at the LuSb/GaSb (001) interface does not depend on the LuSb surface, where we plotted the band structure of the LuSb/GaSb(001) superlattice with 17 ML of LuSb and 7 ML of GaSb, without a vacuum layer. The interface bands with Ga-s character in LuSb/GaSb(001) superlattice are very similar to those obtained in the LuSb/GaSb/LuSb(001) slab shown in Fig. 3.19.

We note that an alternate explanation for the 2D hole gas at the LuSb/GaSb(001) interface could be due to band bending and surface charge accumulation in the GaSb interfacial layer resulting from the Fermi level at the GaSb surface being pinned in the valence band. We rule this out for the following reasons. First, the surface Fermi level pinning position of uncovered GaSb surfaces is known to lie 0.2 eV above the valence band[160]. Second, both photoemission results from metal/GaSb heterostructures and electrical measurements of metal/GaSb Schottky barriers indicate a surface Fermi level position within the GaSb band gap[161, 162, 163, 164, 165]. Finally, the density of such electrostatically induced 2D hole gases is typically $\leq 5 \times 10^{12}$ holes/cm²[166, 167], which is two orders of magnitude lower than the hole density observed in this work. Therefore, the 2D hole gas observed in our studies is of novel origin arising due to bonding mismatch at the interface, which should be a generic feature of such heterointerfaces.

In summary, using DFT calculations we studied in detail the concept of controlling the electronic properties via band structure engineering in semimetals where, utilizing LuSb as a model system, we show that quantum confinement lifts carrier compensation and differently affects the carrier density of the electron and hole-like carriers resulting in a strong modification in its large, non-saturating magnetoresistance behavior. Bonding mismatch at the heteroepitaxial interface of the semimetal (LuSb) and a semiconductor (GaSb) leads to the emergence of a novel, two-dimensional, interfacial hole gas and is accompanied by a charge transfer across the interface that provides another avenue to modify the electronic structure and magnetotransport properties in the ultra-thin limit. Our work lays out a general strategy of utilizing confined thin film geometries and hetero-epitaxial interfaces to engineer electronic structure in semi-metallic systems, which allows control over their magnetoresistance behavior and, simultaneously, provides insights into its origin.

Chapter 4

HALF-HEUSLER TOPOLOGICAL SEMIMETALS

As introduced in section 1.2, half-Heusler compounds display a wide range of physical properties which also includes non-trivial topology in LuPtSb and LuPtBi. Three-dimensional topological semimetals host a interesting quantum phenomena related to band crossing and band touching that give rise to Dirac or Weyl fermions, and could be engineered into novel technological applications. Harvesting the full potential of these materials in applications will depend on our ability to position the Fermi level near the symmetry-protected band crossings or touchings so that exotic spin and charge transport properties are manifest. Using first-principles calculations based on density functional theory, we investigate how point defects impact the Fermi level position in two representative half-Heusler topological semimetals, PtLuSb and PtLuBi; we explore how intrinsic defects can be used to tune the Fermi level, and explain recent observations based on Hall measurements in bulk and thin films. Under typical growth conditions we show that Pt vacancies are the most abundant intrinsic defects, leading to excess hole densities that place the Fermi level significantly below the expected position in the pristine material. Suggestions for tuning the Fermi level by tuning chemical potentials are discussed.

We used three atom primitive cell to calculate the equilibrium lattice parameters and band structures, with a $16 \times 16 \times 16$ Γ -centered mesh of k points for integrations over the Brillouin zone. For the defect calculations, we used a cubic supercell containing 96 atoms which corresponds to a $2 \times 2 \times 2$ repetition of the conventional 12-atom cubic unit cell of LuPtSb(Bi), with $4 \times 4 \times 4$ mesh of special k points for integrations over the Brillouin zone. All calculations were performed using a kinetic-energy cutoff of 400 eV for the plane-wave basis set. The completely filled 4f shell of Lu was treated in the core. Previous calculations for band structures of LuSb and LuBi show that the occupied 4f bands are well below the Fermi level (more than 8 eV) and do not affect their structural and electronic properties [168]. Tests with supercells containing 324 and 768 atoms show that formation energies change by less than 0.02 eV. The effects of spin-orbit are included in all calculations.

4.1 Crystal Structure of LuPtSb and LuPtBi

The structure of half-Heusler compounds ABC (A= Lu; B= Pt; C= Sb or Bi) can be visualized as three interpenetrating fcc lattices with the atomic positions (0.5,0.5,0.5)a, (0.25,0.25,0.25)a and (0,0,0) for A, B and C respectively, where a is the lattice parameter; Lu and Sb(Bi) form a rock salt structure while Pt and Sb form a zinc blende structure, as shown in Fig. 4.1. The calculated lattice parameters for LuPtSb and LuPtBi are 6.443 Å and 6.572 Å, in good agreement with the experimental values of 6.457 Å and 6.578 Å [169, 85, 170].



Figure 4.1: (a) Crystal structure C1_b of half-Heusler comprising of three interpenetrating face centered cubic sub lattices, where the green, blue and brown spheres denoting Pt, Lu and Sb(Bi) atoms respectively.(b) Bulk Brillouin zone of half-Heusler compound.

4.2 Electronic band structure of LuPtSb and LuPtBi

The electronic structure of half-Heusler compounds is closely related to the number of valence electrons. These compounds exhibit semiconducting properties similar to that of conventional semiconductor GaAs when the total number of valence electrons per formula unit is equal to 8 or 18 (closed shell) also known as 8 or 18 electron rule. To understand the topological properties in semimetallic members of this family such as LuPtSb and LuPtBi the band structure of HgTe can serve as a starting point. HgTe is a well known topological semimetal with a band inversion between Hg-s state (Γ_6) and Te-p state (Γ_8) at the Γ point. The Fermi level in the intrinsic material is located at the point where conduction band touches the valence band at Γ . Similar band inversion occurs in LuPtSb and LuPtBi, as shown in the orbital-resolved electronic band structure shown in Fig. 4.2(a-e). For LuPtSb the occupied bands near the Fermi level originate mostly from the Sb atom, with the inversion between Γ_8 (p-character) and Γ_6 (s-character) making it topological non-trivial as shown in Fig. 4.2(c), in agreement with previous studies [171, 85, 172]. The Lu-d orbitals mostly contribute to the bands 2-4 eV above the Fermi level, whereas Pt-d occupied bands are around 4 eV below the Fermi level. The calculated band inversion strength (BIS) for LuPtSb is 0.23 eV in agreement with previous studies [171, 85, 172]. The band structure of LuPtBi is qualitatively similar, with the Γ_8 band well above the Γ_6 band, as shown in Fig. 4.2(df), in agreement with the previous studies [171, 172]. The calculated band inversion strength (BIS) for LuPtBi is 1.55 eV, being significantly larger than in LuPtSb due to the stronger spin-orbit coupling.

4.3 Defects and Stability Phase Diagram

Defects are modelled by removing, adding, or replacing an atom in a supercell using periodic boundary conditions. The results of defect calculations reported here are obtained using a supercell with 96 host atoms, and convergence tests for the lowest energy defects using supercells of 324 and 768 atoms, show that formation energies



Figure 4.2: Electronic band structures of (a-c) LuPtSb and (d-f) LuPtBi where the first row represents projection on (a) Lu (b) Pt and (c) Sb, the second row shows projection on (d) Lu (e) Pt and (f) Bi respectively starting from left to right. The Fermi level is set to zero.

change by less than 0.05 eV, and do not change our conclusions. The formation energy for a defect X is given by:

$$E^{f}[X] = E_{tot}[X] - E_{tot}[host] + n_i \sum_{i} (E_{tot}[X_i] + \mu_i), \qquad (4.1)$$

where $E_{tot}[X]$ is the total energy of the supercell containing the defect X, $E_{tot}[host]$ is the total energy of the perfect crystalline host material using the same supercell, n_i is the number of atoms that are removed/added to the supercell to form the defect X, and μ_i is the atomic chemical potential, i.e., the energy of the atomic reservoir for the species added/removed, referenced to the total energy of the respective elemental phases $E_{tot}[X_i]$, and can be related to the experimental growth or processing conditions. The chemical potentials μ_i are not free parameters, but are bound to the stability condition of the host material (LuPtSb or LuPtBi, in this case) and the need to avoid the formation of possible secondary phases, such as LuSb, LuPt, PtSb₂, and LuPt₃, in the case of LuPtSb, through the following relations:

$$\mu_{\rm Lu} + \mu_{\rm Pt} + \mu_{\rm Sb} = \Delta H^f [\rm LuPtSb], \qquad (4.2)$$

$$\mu_{\rm Lu} + \mu_{\rm Sb} < \Delta H^f [{\rm LuSb}], \tag{4.3}$$

$$\mu_{\rm Lu} + \mu_{\rm Pt} < \Delta H^f [{\rm LuPt}], \tag{4.4}$$

$$\mu_{\rm Pt} + 2\mu_{\rm Sb} < \Delta H^f [\text{PtSb}_2], \tag{4.5}$$

$$\mu_{\rm Lu} + 3\mu_{\rm Pt} < \Delta H^f [{\rm LuPt}_3], \tag{4.6}$$

with $\mu_{Lu} \leq 0$, $\mu_{Pt} \leq 0$, and $\mu_{Sb} \leq 0$ representing the upper limits set by the respective elemental phases. Similar equations are considered for LuPtBi. The range of chemical potentials in the plane μ_{Lu} vs μ_{Pt} for LuPtSb and LuPtBi are shown in Fig. 4.3, where the relevant regions for the discussion are indicated. The calculated formation energies of all the native point defects, i.e., vacancies, interstitials, and antisites, on the three sublattices in LuPtSb and LuPtBi are listed in Table 4.1 and Table 4.2 for points A, B, C, and D indicated in the diagrams of Fig. 4.3.

The accessible atomic chemical potential region for LuPtSb is relatively larger than for LuPtBi. In the phase stability diagram of LuPtSb, we see that $V_{\rm Pt}$ is the lowest formation energy defect along the line bordering the formation of LuSb (segment 4) in Fig. 4.3(a), from Sb-rich to Lu-rich (point B), whereas Lu_{Pt} has the highest formation energy equal to 6.451 eV. The formation energy of LuSb at point A, also corresponding to Sb-rich limit, is slightly higher (0.635 eV). The formation energies for all the point defects are found to be greater than 1 eV at point C and D. Overall, we predict that $V_{\rm Pt}$ is the most likely defect to form in LuPtSb, corresponding to $\mu_{\rm Lu} = -2.0$ eV, $\mu_{\rm Pt} = -1.5$ eV, and $\mu_{\rm Sb} = 0$ eV (Sb-rich limit) near the point A.

In case of LuPtBi, the stability region [Fig. 4.3(b)] is relatively smaller yet the results are qualitative similar to those of LuPtSb. In the region close to point C, all the point defects have formation energies greater than 1 eV. At the point D, all the defects have $E^f > 1$ eV except Bi_{Lu}. At points A and B along the LuBi line V_{Pt} is the lowest energy defect with formation energy equal $E^f=0.592$ eV, as listed in Table 4.2. Moving along the Bi-rich line toward the Lu poor region, we find Bi_{Lu} to be another

Defect	Form	ation ene	ergy (eV)	
2 01000	A(Sb-rich)	В	С	D
$\mathrm{Sb}_{\mathrm{Lu}}$	1.096	3.281	2.607	1.097
$\mathrm{Sb}_{\mathrm{Pt}}$	4.452	5.438	6.112	5.810
$\mathrm{Pt}_{\mathrm{Lu}}$	4.090	5.289	3.942	2.733
$\mathrm{Pt}_{\mathrm{Sb}}$	3.500	2.514	1.841	2.143
$\mathrm{Lu}_{\mathrm{Sb}}$	4.075	1.890	2.564	4.074
$\mathrm{Lu}_{\mathrm{Pt}}$	6.451	5.252	6.600	7.809
Sb_{i}	4.501	5.558	5.558	4.953
Pt_{i}	2.975	3.046	2.372	2.070
Lu_i	5.048	3.920	4.594	5.500
$V_{ m Lu}$	1.914	3.042	2.368	1.462
V_{Pt}	0.635	0.564	1.238	1.540
$V_{\rm Sb}$	4.148	3.091	3.091	3.696

Table 4.1: Calculated formation energies $E^{f}[X]$ of native point defects in LuPtSb at
the boundaries of the phase stability diagram in Fig. 4.3(a).

Defect	Fo	rmation of	energy (e	eV)
	A(Bi-rich)	В	С	D(Bi-rich)
$\mathrm{Bi}_{\mathrm{Lu}}$	1.325	2.188	1.530	0.568
$\mathrm{Bi}_{\mathrm{Pt}}$	3.867	4.298	4.916	4.718
$\mathrm{Pt}_{\mathrm{Lu}}$	4.226	4.658	3.386	2.619
$\mathrm{Pt}_{\mathrm{Bi}}$	2.966	2.534	1.917	2.115
$\mathrm{Lu}_{\mathrm{Bi}}$	2.446	1.583	2.240	3.202
$\mathrm{Lu}_{\mathrm{Pt}}$	5.515	5.083	6.358	7.122
Bi_{i}	4.047	4.479	4.465	4.079
Pt_i	2.720	2.720	2.089	1.900
Lu_{i}	3.627	3.195	3.840	4.415
$V_{ m Lu}$	1.883	2.314	1.669	1.094
V_{Pt}	0.592	0.592	1.219	1.411
$V_{\rm Bi}$	3.726	3.295	3.308	3.695

Table 4.2: Calculated formation energies $E^{f}[X]$ of native point defects in LuPtBi at the boundaries of the phase stability diagram in Fig. 4.3(b).



Figure 4.3: The allowed chemical potential region(yellow shading) in μ_{Lu} versus μ_{Pt} plane along with some of the other competing phases for (a) LuPtSb and (b) LuPtBi.

point defect with the low formation energy of $E^f = 0.568$ eV. So, for chemical potentials near the Bi-rich and Pt-poor lines (near the LuBi phase), the lowest energy defect is by far the Pt vacancy, as in LuPtSb. Experimentally, thin-film growth of LuPtSb by molecular beam epitaxy (MBE) [85, 169] or bulk growth of LuPtBi [173, 174] were carried out in Sb/Bi-rich environments, and were most likely to happen near point A in the stability diagrams of Fig. 4.3.

Given the prevalence of the Pt vacancy as the defect of low formation energy in

large part of the stability phase diagram of LuPtSb and LuPtBi, and, in particular, near the region where growth were carried out, we expect it to play major role in determining the electronic characteristics of the reported bulk and thin films. Considering that Pt and Sb compose a zinc blende sublattice within LuPtSb, removing a Pt atom leads to Sb dangling bonds, and according to the electronic band structures in Fig. 4.2, we expect Sb dangling bonds to introduce partially occupied bands near the Sb-related 5pbands just below the Fermi level, and lead to excess hole carriers, i.e., a predominant p-type behavior, compared to the compensated pristine perfect material where electron and hole concentrations are the same. Similarly, Pt vacancies in LuPtBi would also lead excess holes. This is consistent with the behavior of Pt vacancies in half-Heusler semiconductors, which were predicted to act as acceptors [175]. Thus, our results are also consistent with the experimental observations in LuPtSb[85, 169], and LuPtBi[173, 174], where excess holes have been observed in thin films and bulk single crystals grown or deposited under Sb- and Bi-rich conditions.

Each Pt vacancy in LuPtSb and LuPtBi is then expected to result in three holes, taking the oxidation state Sb³⁻ in the pristine materials. Assuming that the measured hole concentrations in LuPtSb and LuPtBi, of 2-3x10²⁰ cm⁻³, [169, 85] and 2-4x10¹⁹ cm⁻³[173, 174], determined from Hall measurements, originate from Pt vacancies incorporated during growth at temperatures in the range $T=450^{\circ}$ C (thin films) to $T=800^{\circ}$ C, we can invert the equation for the concentration of Pt vacancies ($c = N_{sites} \exp(-E^f/k_{\rm B}T)$, where N_{sites} is the number of sites per cubic centimeter that the vacancy can be incorporated on) to obtain vacancy formation energies of 0.375 eV for LuPtSb (taking from thin-film growth at T=450°C[169, 85]) and 0.562 eV for LuPtBi (bulk growth at T=650°C[173, 174]). These values are close to the calculated formation energies near the A points in the phase diagrams of Fig.4.3(a) and (b) respectively, close to the Sb- or Bi-rich limit. Better agreement is found for the Pt vacancy in LuPtBi, which is bulk growth at higher temperature, i.e., closer to thermodynamic equilibrium.

Such hole concentrations in LuPtSb thin films and LuPtBi bulk single crystals

place the Fermi level at significantly lower positions compared to the expected value in the compensated pristine materials, as shown in Fig.4.4 for the case of LuPtSb. For the measured hole concentrations of $2-3 \times 10^{20}$ cm⁻³ [169, 85], The Fermi level is positioned at 305-360 meV below the Fermi level in the ideal material. In order to shift the Fermi level upward by 200 meV, for example, the hole density would have to decrease to 2.8×10^{-19} cm⁻³. Assuming that these holes come from Pt vacancies and each Pt vacancy contributes with 3 holes, we would have to increase the defect formation energy by 132 meV by increasing $\mu_{\rm Pt}$ by the same amount ($\Delta \mu_{\rm Pt} = 132$ meV). In an attempt to translate this number to the experimental control during growth (Lu/Pt/Sb fluxes) in the MBE chamber), we can estimate the change in partial pressure of Pt, assuming an ideal gas. We note that this is a simplification of the experimental situation, where the fluxes in MBE are controlled by the temperature of the Knudsen cells, and relative changes are important. Yet, one can imagine that during growth the Pt atoms at the surface are in equilibrium (or close enough to equilibrium) with a flux of Pt atoms that is idealized here as an ideal gas. Keeping these approximations in mind, we estimate that a change of Fermi level by 200 meV would correspond to $\Delta \mu_{\rm Pt} = 132$ meV, and that corresponds in a reduction of a factor of ~ 8 in the Pt partial pressure, or abundance of Pt during growth.

These results also provide an strategy for tuning the Fermi level in these materials. Since Pt vacancy is by far the lowest energy defect in most part of the allowed chemical potential region, increasing the chemical potential μ_{Pt} is a "straightforward" way of increasing the Pt vacancy formation energy, and therefore, decrease the hole density towards the pristine materials. Another way, is to use aliovalent species containing an additional electron and that replaces Pt, filling the Pt vacancies and resulting in extra electrons. This will also raise the Fermi level, eventually beyond the position in the pristine material, leading to n-type conductivity, as has been recently reported in Au-doped LuPtSb[169].

In summary, we studied the impact of native point defects on the electronic



Figure 4.4: Calculated density of states (DOS) and hole concentration [p] as function of Fermi level in LuPtSb, taking the Fermi level E_F in the compensated perfect material as reference.

properties of the topological semimetals LuPtSb and LuPtBi using first-principles calculations. We find that Pt vacancy is by far the lowest energy defect in most of allowed chemical potential region in which these compounds are stable, and therefore, the most likely point defect to form during growth of thin films or bulk single crystals. The Pt vacancy leads to Sb dangling bond states that lie below the Fermi level, resulting in acceptor-like states and, thus, excess holes in these otherwise compensated semimetals. The calculated formation energies of the Pt vacancy are consistent with the observed hole concentrations in both LuPtSb and LuPtBi in undoped materials. Finally our results provides a guide to the experiments to refine and pinpoint individual point defects that can affect the transport and magnetoresistance properties in these topologically non-trivial half-Heusler compounds.

Chapter 5

Ir₂O₃, Ga₂O₃, AND THEIR ALLOYS IN THE CORUNDUM STRUCTURE

In this last chapter we discuss the electronic properties of Ir₂O₃ and Ga₂O₃Ga₂O₃ in the α phase, i.e., the same as that of Al₂O₃. Ga₂O₃ is a well known ultra-wide band gap semiconductor promising for high power electronic devices. Corundum α -Ga₂O₃ has a band gap of ~ 5.14 eV and exhibits hexagonal structure. Relatively high band gap, small electron effective mass, higher Baliga's figure of merit and higher breakdown field makes it an ideal candidate for p-n heterojunctions. Ga₂O₃ is easy to dope n type, but impossible to dope p type, impeding the realization of some electronic device designs. Developing a lattice matched *p*-type material that forms a high-quality heterojunction with n-type Ga_2O_3 would open new opportunities in device design. In this work we studied Ir_2O_3 , which is a possible candidate that can serve this purpose. Using hybrid density functional theory calculations we calculated the electronic band structure of α -Ir₂O₃ and α -Ga₂O₃. The stability of α -(Ir_xGa_{1-x})₂O₃ alloys are studied along with their band gap and band-edge positions. We also discuss the band offset between the two materials and compare with recently available experimental data. We find that the Ir-d bands that compose the top of the valence band in α -Ir₂O₃ are much higher in energy than O-p bands that compose the top of the valence band in α -Ga₂O₃, Which is an indication that α -Ir₂O₃ could be made *p*-type. Our results provides an insight into possibility of using lattice matched p-type Ir_2O_3 as promising material to realize bipolar power devices and heterojunctions.

In our computational approach, we considered Ga d electrons in the valence and, and used a plane wave cutoff of 400 eV. All the structures are relaxed using generalized gradient approximation of Perdew-Burke-Ernzerhof (PBEsol)[176]. Using



Figure 5.1: (a) Conventional unit cell of corundum-structured Ir₂O₃ and Ga₂O₃ where all the cation sites are equivalent.(b) Primitive cell used for band structure calculation containing four cation atoms (green) and six oxygen atoms (red).

mcsqs code of the Alloy Theoretic Automated Toolkit (ATAT)[177] we generated the special quasirandom structures (SQS)[178] to simulate α - $(Ir_xGa_{1-x})_2O_3$ random alloys. This method use annealing loop with an objective function simulated in Monte Carlo that looks for perfectly matched correlation functions in order to generate periodic supercell analogous to real disordered structures[177].

5.1 Electronic band structure of α -Ga₂O₃ and α -Ir₂O₃

A typical corundum structured unit cell with R $\overline{3}$ c symmetry comprising of six formula units is shown in Fig. 5.1(a). The oxygen is closely hexagonally packed, whereas the cation metal atoms occupy octahedral sites. Each metal octahedron is connected with one face and three edges of the other three neighboring octahedron. To relax the structure we used the PBEsol functional; the calculated equilibrium lattice parameters are compared with experimental data as shown in Table 5.1. The experimental band gap of α -Ga₂O₃ is measured in the range of 4.9-5.6 eV[111, 112, 179, 180]. Using 33% and 30% nonlocal exchange for α -Ga₂O₃ and α -Ir₂O₃ respectively, the calculated indirect band gaps are in good agreement with the experimental results. The or-

	α-Ir	$_{2}O_{3}$	α -Ga ₂ O ₃		
	Calc.	Expt.	Calc.	Expt.	
$a(\text{\AA})$	5.194	-	5.004	4.983^{a}	
$c(\mathrm{\AA})$	13.730	-	13.452	13.433 ^a	
$\Delta H({\rm eV/f.u.})$	-3.220	-	-9.493	-	
$E_{\rm g}({\rm eV})$	3.05	3.00^{b}	5.13	5.14^{c}	

Table 5.1: Calculated lattice parameters, formation enthalpy (ΔH) and indirect band gaps $E_{\rm g}$ of α -Ir₂O₃ and α -Ga₂O₃.

^b Ref. [111]

 $^{\rm c}$ Ref.[112]

bital resolved electronic band structures of α -Ga₂O₃ and α -Ir₂O₃ using HSE hybrid functional are shown in Fig. 5.2. It can be seen that the conduction band (CB) of α -Ga₂O₃ is mainly composed of delocalized Ga 4s derived states, giving rise to a highly dispersive band with a low electron effective mass, while the valence band (VB) has most of the contribution from O 2p orbital which is highly localized and shows very less dispersion resulting in large hole effective mass in good agreement with previous experimental[182, 111, 112] and theoretical studies[183, 184, 185]. It should be noted that the conduction-band minimum (CBM) in α -Ga₂O₃ occurs at Γ point whereas valence-band maximum (VBM) occurs along the $\Gamma - X$ drection and it is 0.245 eV above local maximum at Γ . In case of α -Ir₂O₃ the VBM occurs along the $\Gamma - Z$ and $\Gamma - L$ and the highest valence band shows a larger dispersion that in Ga₂O₃. The oxygen 2p orbitals in α -Ir₂O₃ lie around 5 eV below the VBM and, in contrast to α -Ga₂O₃. The lowest-energy conduction bands in α -Ir₂O₃ is also composed of Ir 5d and shows a much less dispersion that the conduction band in Ga₂O₃. The Ir 4s bands appear a



Figure 5.2: Orbital-resulved electronic band structures of (a) α -Ga₂O₃ and (b) α -Ir₂O₃ where the bar on the right side shows the projection of different orbitals. The Fermi level is set to zero.

bit higher than CBM as shown by green band in Fig. 5.2(b). The calculated position of Ir 5d and O 2p bands below the VBM are in good agreement with the experimental XPS data[112].

5.2 Band offset between α -Ga₂O₃ and α -Ir₂O₃

Besides knowing the band gaps of the two materials, it is essetion to know the band offset between them, since this is a fundamental parameter in the design of heterojunction-based devices [186]. Band offsets determine carrier confinement and which side of the heterojunction electrons and holes will reside. For the band offset calculation, first the position of VBM and CBM was calculated with respect to the average electrostatic potential for both materials[187]. In the second step the average electrostatic potential of the two materials is aligned with respect to each other by doing the interface calculations. For the interface we used a supercell with 12 layers of each material with two similar interfaces. To avert any polar discontinuity at the heterojunction interface we created the superlattice along a non-polar [100] direction. The two materials have slightly different lattice parameters so in order to accomodate the lattice mismatch at the interface we used average in plane lattice parameters and the out of plane lattice parameters are adjusted with respect to the equilibrium volume of each each material in the superlattice. Using this method we obtain a staggered-gap (type-II) band alignment between the two materials.

Our calculated band offsets of 3.19 eV and 1.11 eV for VBM and CBM, respectively, are in good agreement with recent experimental studies[112, 111]. It can be seen that around 74.4% band offset arise from discontinuity in valence band, whereas around 25.6% band offset arise from the conduction band. Achieving *p*-type conductivity in α -Ga₂O₃ is usually difficult because of its low valence band energy. Our result shows that the VBM in α -Ir₂O₃ is 3.19 eV above than that of α -Ga₂O₃ making α -Ir₂O₃ much more likely to be doped *p*-type and an excellent candidate for *p*- α -Ir₂O₃/*n*- α -Ga₂O₃ heterojunction.

5.3 α -Ga₂O₃/ α -Ir₂O₃ alloys

For the calculations of α -(Ir_xGa_{1-x})₂O₃ alloys, we use a 120-atom supercell to generate special quasirandom structures (SQS) that approximate the random distribution of Ir and Ga atoms[178]. In α -Ga₂O₃ or α -(Ir_xGa_{1-x}), all the metal-atom sites are equivalent; so Ir/Ga occupy metal sites randomly. The volume dependence of α -(Ir_xGa_{1-x})₂O₃ alloy on the Ir composition is shown in Fig. 5.4(a). Since Ir has larger atomic radius compared to Ga, it can be seen that the volume of the alloy increases almost linearly with increase in Ir content, following the Vegard's law.

In Table 5.1 we show the formation enthalpies of α -Ga₂O₃ and α -Ir₂O₃, which is defined as the total energy of the elemental bulk phases subtracted from the total energy of the parent compounds. The alloy formation enthalpy, or mixing enthalpy, of the α -(Ir_xGa_{1-x})₂O₃ alloys are defined as the total energy of the ally supercell minus the weighted total energy of the parent compopunds, as follows:

$$\Delta H[(\mathrm{Ir}_x \mathrm{Ga}_{1-x})_2 \mathrm{O}_3] = E[(\mathrm{Ir}_x \mathrm{Ga}_{1-x})_2 \mathrm{O}_3] - xE[(\mathrm{Ir}_2 \mathrm{O}_3] - (1-x)E[(\mathrm{Ga}_2 \mathrm{O}_3], (5.1)]$$

where $E[Ir_2O_3]$ and $E[Ga_2O_3]$ are the total energies of the parent compounds Ir_2O_3 and Ga_2O_3 , respectively, in the 120-atom corundum-structured supercell, and $E[(Ir_xGa_{1-x})_2O_3]$


Figure 5.3: Calculated band offset between α -Ga₂O₃ and α -Ir₂O₃.

is the total energy of the random alloy in the same-size supercell. The results are shown in Fig. 5.4(b).

Note that the hightest formation enthalpy of α -(Ir_xGa_{1-x})₂O₃ alloy at x=0.5 is only 104 meV/f.u., which is significantly lower than 300 meV/f.u.[188] for α -(In_xGa_{1-x})₂O₃, yet higher than that of α -(Al_xGa_{1-x})₂O₃ which is around 55 meV/f.u.[189]. The relatively small values of formation enthalpy indicate that α -(Ir_xGa_{1-x})₂O₃ alloys might be realized for all Tr/Ga compositions.

We also studied the electronic structure of α -(Ir_xGa_{1-x})₂O₃ alloys. In Fig. 5.5(a) we show the band gap of α -(Ir_xGa_{1-x})₂O₃ alloys with different Ir composition. The results are different from the reported values by Kaneko *et al.* [25] who determined



Figure 5.4: (a) Calculated equilibrium volume and (b) formation enthalpy of α - $(Ir_xGa_{1-x})_2O_3$ alloys as a function of Ir concentration (x).

the band gap for alloys between x=0.51 and 0.63 using XPS data for thin films and Tauc plot fit to optical absortion for a thicker films. We argue that these type of measurements for the band gap can incurr in large errors and that our results is justified as discussed below.

In our calculations for the band gap of the alloys, we use HSE functional with 33% mixing parameter, obtaining good agreement with experiments [25] for the parent compounds α -Ga₂O₃ (x=0) and α -Ir₂O₃. However, we do not find a smooth variation of the band gap as function of Ir content as the authors of Ref. [25] suggest. Instead we find that the band gap of α -(Ir_xGa_{1-x})₂O₃ alloy decreases sharply from 5.3 eV to 2.9



Figure 5.5: Band gap of α -(Ir_xGa_{1-x})₂O₃ as a function of Ir concentration (x). (b) CBM and VBM position in α -(Ir_xGa_{1-x})₂O₃ as a function of Ir concentration (x). The experimental data is taken from Ref. [25]

eV even for a small Ir composition of 12.5% and does not change much for up to 50% Ir composition(x = 0.5). Above x=0.5, the band gap increases almost linearly with Ir concentration to reach 3.3 eV for x=1.

The band gap of α -(Ir_xGa_{1-x})₂O₃ alloy changes very differently from that of α -(Al_xGa_{1-x})₂O₃ [189] and (In_xGa_{1-x})₂O₃ [188] alloys mostly because of "unique" electronic structure of α -Ir₂O₃. As discussed earlier the VBM in α -Ir₂O₃ is composed of Ir d orbital whereas for α -Ga₂O₃, α -Al₂O₃ and In₂O₃ the VBM is oxygen 2p and metal d states lie deep inside the valence band. From the band alignment study in Fig. 5.3 we show that Ir 5d states in α -Ir₂O₃ are 3.19 eV higher in energy than that of oxygen

2p states in α -Ga₂O₃, so a very small composition of Ir (x > 0) pushes the VBM of α -(Ir_xGa_{1-x})₂O₃ alloy to higher energy resulting in a sharp decrease in band gap. The slight increase in band gap for Ir compositions greater than 50% (x > 0.5) can be explained in terms of relative increase in band dispersion with increase in Ir composition. Fig. 5.5(b) shows the change in position of CBM and VBM as a function of Ir composition x. For all the alloy compositions the position of VBM and CBM is aligned with respect to oxygen 2s states. The conduction-band edge changes slightly with Ir composition x, whereas most of change occurs in the valence band edge. It can be seen that with introduction of samll concentrations of Ir in α -Ga₂O₃, the valence-band edge moves really sharply to higher energy and does not move much with the increase in Ir composition afterwards, and this is due the the d nature of the VBM in Ir₂O₃.

In summary, we calculated the electronic structure of α -Ir₂O₃ and α -Ga₂O₃. The band offset between these materials show that α -Ir₂O₃ is a promising candidate for *p*-type oxide to compose *p*-*n* heterojunction with *n*-type Ga₂O₃, opening up unique opportunities in device design. The calculated band offset at at the α -Ir₂O₃/ α -Ga₂O₃ interface is in good agreement with the available experimental data, and the enthalpy of formation of α -(In_xGa_{1-x})₂O₃ are relatively small to expect that these alloys can be made to all Ir/Ga composition range. We also find that the band gap of α -(Ir_xGa_{1-x})₂O₃ alloys decreases rather sharply with even small Ir concentration, with most of the changes in valence-band edge, because of the localized nature of Ir *d* states in the Ga₂O₃ matrix.

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