2018

Structural prediction and theoretical characterization of Bi-Sb binaries: Spin-orbit coupling effects

Sobhit Kumar Singh

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Structural prediction and theoretical characterization of Bi-Sb binaries: Spin-orbit coupling effects

Sobhit Kumar Singh

Dissertation submitted
to the Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Physics

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2018

Keywords:

Bi-Sb alloys, Structural search, Minima hopping method, Rashba effect,
Thermoelectrics, Spintronics, Weyl semimetals, Elastic properties, Auxetics

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Abstract

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Bismuth antimonides or Bi-Sb binaries ($\text{Bi}_x\text{Sb}_{1-x}$) have attracted immense attention of researchers due to their diverse range of technological applications. Some notable features of these binaries include excellent low-temperature thermoelectricity, large Rashba-Dresselhaus effect, auxeticity, and topological quantum effects. In fact, Bi-Sb binaries are considered as the first generation topological insulators. In the present work, I will discuss the novel properties of several low-energy crystal structures of Bi-Sb binaries predicted from the *first-principles* structural search calculations. Some of the predicted structures are good thermoelectrics, whereas some of them are novel topological insulators, Weyl semimetals, ferroelectrics, and giant Rashba semiconductors. Interestingly, we demonstrate that one can create Weyl fermions and tune their dynamics in the momentum space of BiSb crystal by utilizing an interlink between the large spin-orbit coupling of the constituent atoms and the intrinsic ferroelectric polarization. In two-dimensions, BiSb monolayer inherits large Rashba effect with tunable Rashba parameters. A detailed analysis of the elastic and mechanical properties of Bi-Sb binaries is presented. Our calculations reveal that spin-orbit interaction effects soften the elastic stiffness. Notably, we find that three monoclinic structures of Bi-Sb binaries exhibit significantly large auxeticity (negative Poisson's ratio), which arises due to the special geometric arrangement of covalent bonds.

“Live to learn and help others to learn.”

Acknowledgements

This thesis is based on the research that I have carried out under the supervision of Prof. Aldo H. Romero at West Virginia University. The time I spent during my Ph.D. would remain as one of the most wonderful and rewarding time for me. I still feel like I started my Ph.D. a few months ago. Time flies so fast indeed! The reason behind the wonderful time that I had in last five years is only because of the awesome people who entered in my life and helped me in various ways. Without their love and support, it would have been impossible to complete this thesis. Therefore, I would like to take this opportunity to thank these awesome people for their generosity, love, support and encouragement.

First and foremost, I would like to thank my advisor Aldo for his mentorship, friendship, and great supervision. He has been amazingly kind to me. He was always there whenever I needed any help or guidance. I was very fortunate to learn a tremendous amount of knowledge and skills from him while doing research with him as well as attending his lectures. Thank you Aldo for being so patient and listening to all my vacuous ideas. Thank you for supporting and encouraging me to travel, to attend conferences and workshops, and to interact with the scientific community. I would also like to thank Taty, Mattias and Camila (Aldo's family) for their love and affection at all times.

I would like to express my sincere gratitude and utmost respect to Prof. Mohindar S. Seehra for his invaluable guidance, patient mentorship, encouragement and support. Thank you Professor Seehra for letting me work in your lab and nurturing my professional abilities. You have always been a great source of inspiration to me. The role that you played in my academic life is invaluable and it will remain unmatched. Thank you for being an outstanding mentor, collaborator and friend.

I owe my profound gratitude and sincere thanks to my master's thesis advisor Prof. Subhash Thota for introducing me to materials science. His supervision and friendship has played a key role in shaping my research career, and making me what I am today.

A special thanks note must be extended to my committee members: Prof. Cheng Cen, Prof. Matthew B. Johnson, and Prof. David S. Mebane, for their time and efforts in assessing my thesis.

I would like to thank Irais Valencia-Jaime for being an amazing friend and mentor. She has been incredibly patient to teach me the ABC of *first-principles* calculations when I switched from an experimental research group to a theoretical research group. It was all because of her tremendous efforts and mentorship that I managed to learn new techniques in a timely fashion.

Life of a Ph.D. student is not ‘*perfectly*’ complete without the friendship and assistance of post-docs. I would especially like to thank Guillermo Avendaño-Franco, Wilfredo Ibarra-Hernandez, and Andres Camilo Garcia-Castro for being awesome friends and always being so helpful.

I would like to thank the distinguished physicists who were very benevolent to collaborate with me and help me in learning new things and developing new skills. These kind-hearted people are: Francisco Muñoz (Chile), Alexey Soluyanov (ETH Zurich), Sergio Ulloa (Ohio), Matthieu Verstraete (Liège, Belgium), Zeila Zanolli (RWTH Aachen), Eric Bousquet (Liège, Belgium), Jorge Sofo (Penn State University), Cecil Ouma (Pretoria, South Africa), Camilo Espejo (Bogotá, Colombia), QuanSheng Wu (EPFL Lausanne), Madhav Ghimire (IFW, Dresden), Abdulrahman Al Sharari (Ohio), Alan Bristow (West Virginia), Mikel Holcomb (West Virginia). I am indebted to all of you for your friendship, collaboration, and support.

I am very grateful to my friends and colleagues: Adam, Olivia, Pedram, Uthpala, Saeed, Robbyn, Mina, Navid, Raju bhai, Kelly, Vishal Narang, Usha, Prativa, Deep Chandra, Sayan, Ayan, Sana, Sravan, Sruthi, Haresh, Anitha, Sandeep and Vinod Mishra.

I want to extend my sincere gratitude and thankfulness to my very dear friends who were more like a family to me in Morgantown. Thank you Apoorva, Pragya, Swathi, Srikanth, Vikas, Ashok, and Panpan for your love and friendship. My most beautiful memories in Morgantown belong to you.

I must thank the friends who helped me to stay healthy and physically fit through recreational activities. Thank you Marriah, Apoorva, and Demian for being awesome dance partners. I truly enjoyed hanging out with you guys. I will miss going out for late night dinner after dance classes. Together we established the West Virginia University (WVU) Latin Dance Club which is now in full swing. Thank you for your love, affection and support all these years. Every moment spent with you has been pleasing. I would also like to thank the friends for joining me on the badminton and racquetball courts regularly all these years. Thank you Matteo, Josh, Bin, Julian, Prakash and Ghadendra for all the joy and fun you have brought in my life at WVU rec center.

During my Ph.D. life, I have been blessed to receive support of various scholarships, awards and honors in WVU. In particular, I received support from the Arthur Weldon Prize, Oleg D. and Valentina P. Jefimenko Physics Fellowship, Robert T. Bruhn Research Award, Seehra Research Award, and WVU Foundation Distinguished Doctoral Scholarship. I would like to sincerely thank the donors of these research awards.

My Ph.D. research has been supported by the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation Grant

No. ACI-1053575. I acknowledge the support from Texas Advances Computer Center (TACC) and Super Computing System (Mountaineer and Spruce) at West Virginia University. I also acknowledge support from the Donors of the American Chemical Society, Petroleum Research Fund under Contract No. 54075-ND10, the National Science Foundation (NSF) DMREF-NSF Project No. 1434897, the U.S. Department of Energy Project No. DE- SC0016176, and funds from the WVU Downtown Campus Library.

I owe a debt of gratitude to the administrative staff of department for patiently assisting me with a tremendous amount of paper work. Thank you Viola, Beena, Sherry and Vicki for always being there whenever I needed any help, and for being so proficient at your job.

I am deeply grateful to all my teachers who taught me at various stages of my life since the kindergarten. I would never be able to come this far without their support and great tenderness. Thank you J. K. Mishra sir for teaching me the first lessons of physics, and sowing seeds of science in me.

I will always be indebted to my loving parents, and fabulous sisters for having faith and trust in my dreams. I am nothing without their love, kindness and incredible support. Thank you very much from the bottom of my heart for always being there by my side.

Lastly and most importantly, I would like to thank myself for not giving up, for being persistent through the hard times, and for chasing my dreams and goals on the way of continuous pursuit of knowledge. I heartily congratulate myself on the completion of my Ph.D. degree.

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Abbreviations

DFT	D ensity F unctional T heory
KS	K ohn S ham
GGA	G eneralized G radient A pproximation
LDA	L ocal D ensity A pproximation
XC	E Xchange C orrelation
PBE	P erdew B urke E rnzerhof
PAW	P rojected A ugmented W ave
VASP	V ienna A b-initio S imulation P ackage
BEP	B ell E vans P olanyi
MHM	M inima H opping M ethod
MD	M olecular D ynamics
PES	P otential E nergy S urface
DOS	D ensity o f S tates
ELF	E lectron L ocalization F unction
SOC	S pin O rbital C oupling
CBB	C onduction B and B ottom
VBT	V alence B and T op
WSM	W eyl S emi M etal
WP	W eyl P oint
BTE	B oltzmann T ransport E quations
CRTA	C onstant R elaxation T ime A pproximation

Scientific Contributions

List of Publications

1. On the Cubic Phase Stability and Magneto-Optical Properties of Cu-doped Zirconia Nanocrystals
[Journal of Physics D: Applied Physics 51 \(22\), 225304 \(2018\)](#)
P. Pramanik, **Sobhit Singh**, D. C. Joshi, A. Mallick, K. Pisane, Aldo H. Romero, S. Thota, and M. S. Seehra.
2. Elastic, mechanical, and thermodynamic properties of Bi-Sb binaries: Effect of spin-orbit coupling
[Physical Review B 97, 054108 \(2018\)](#)
Sobhit Singh, Irais Valencia-Jaime, Olivia Pavlic, and Aldo H. Romero.
3. Giant tunable Rashba spin splitting in two-dimensional BiSb monolayer and BiSb/AlN heterostructures
[Physical Review B 95, 165444 \(2017\)](#)
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4. Controlling the magnetic and optical response of MoS₂ monolayer by lanthanide substitutional doping: a first principles study
[Physical Chemistry Chemical Physics 19, 25555-25563 \(2017\)](#)
Cecil N. M. Ouma, **Sobhit Singh**, K. O. Obodo, G. O. Amolo, and A. H. Romero.

5. Size-dependent structural, magnetic and optical properties of MnCo_2O_4 nanocrystallites

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7. A core-shell-surface layer model to explain the size dependence of effective magnetic anisotropy in magnetic nanoparticles

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8. Unusual enhancement of effective magnetic anisotropy with decreasing particle size in maghemite nanoparticles

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12. Synthesis, structural characterization and magnetic properties of Fe/Pt core-shell nanoparticles
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18. Topological Thermoelectricity in Metals
submitted (2018)
Sobhit Singh, QuanSheng Wu, Changming Yue, Aldo H. Romero, and Alexey Soluyanov.
19. Thermoelectric properties of bismuth bulk and monolayer: new low energy crystal phases
submitted (2018)
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20. Surface recombination in ultra-fast carrier dynamics of perovskite oxide $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films
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21. Systematic design of 2D quantum spin Hall insulator and 3D topological insulator using topologically trivial Rashba semiconducting layers
manuscript in preparation (2018)
Sobhit Singh, M. P. Ghimire, M. Richter, and Aldo H. Romero
22. Thermoelectric properties of bulk and monolayer BiSb
manuscript in preparation (2018)
Sobhit Singh, and Aldo H. Romero.
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27. A review on 2D Rashba semiconductors and ferroelectrics

in preparation (2018)

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- Topological phase transition and charge-transfer in Graphene/MoS₂ van der Waals heterostructures

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- Nature of magnetic ordering in cobalt based spinels

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[InTech Publishers ISBN: 978-953-51-5029-9](#) (2017)

Subhash Thota, and **Sobhit Singh**.

Journals Peer Reviewed

- Scientific Reports (A Nature publication)
- Crystal Growth & Design (An ACS journal)
- European Physical Journal B
- Semiconductor Science and Technology (IOP Publishing)
- Materials Research Express (IOP Publishing)
- Advances in Condensed Matter Physics

Total number of papers reviewed: 11

*Dedicated to
my parents, my teachers, and my country India*

Introduction

Prediction and design of novel materials for a given application has been the central theme of computational material research. Development of advanced supercomputing facilities, Density Functional Theory (DFT), and sophisticated software packages relying on the principles of quantum mechanics has greatly helped us to realize this theme. Simulation has now become an indispensable tool in the design and characterization of new materials. It has remarkably served its primary purpose of overcoming the tedious Edisonian approach, where thousands of different materials and compositions were tried and tested for a particular application (trial and error method). In past few decades, national and international research funding agencies have realized the importance of simulations in the accelerated materials discovery, and provided adequate funds to open new research centers to pursue research in this direction. Strikingly, the *first-principles* DFT-based crystal structure prediction methods have made successful predictions which have been verified in experiments. These methods have been applied to predict new structures of many complex alloys and compounds. Among many other known alloys, bismuth and antimony based alloys (Bi-Sb alloys) have retained a unique place in the thermoelectric cooling industry. A thermoelectric cooler has no moving parts, and is more compact, reliable and light weight than the mechanical coolers.

Bi-Sb binary alloys ($\text{Bi}_{1-x}\text{Sb}_x$) have been known and widely studied since past few decades because of their excellent thermoelectric performance and refrigeration [15–21]. In fact, these are one of the best known thermoelectrics at low temperatures (below 90 K) [15, 18–20]. Low temperature refrigeration has many important applications in

the cooling of superconductors, laser diodes, IR detectors, etc. However, the industrial use of thermoelectrics has been limited due to the limited efficiency of thermoelectric materials.

Thermoelectric properties of Bi-Sb alloys were first measured by Gehlhoff and Neumeier in 1913. [22] Later, Jain studied the electrical properties of zone-levelled single crystals of Bi-Sb alloys in 4.2 K to 300 K temperature range, and reported semi-metallic behaviour arising due to the overlapping conduction and valence bands in these alloys. [23] Based on the de Haas-van Alphen measurements, Shoenberg and Uddin found that the Fermi energy in Bi-Sb alloys decreases with addition of Sb. [24] This observation was associated with decrease in the overlap of conduction and valence bands as we add Sb in Bi lattice. [25, 26] Some early experiments revealed opening of an energy bandgap in Bi-Sb alloys at Sb concentrations greater than 4%. [26–34] Thanks to the opening of a narrow bandgap (decreasing overlap) in the Sb composition range $x = 7\text{--}22\%$, Bi-Sb binaries exhibit remarkable thermoelectric cooling at low temperatures and are considered to be one of the best n-type thermoelectrics. [15, 17, 21, 30, 35–39] Teramoto et al. reported increase in the Seebeck coefficient with decreasing overlap between conduction and valence bands. [40] In another independent study, Tanuma also observed increase in the thermoelectric power or Seebeck coefficient with increasing Sb-concentration. [26] Therefore, the thermoelectric performance of Bi-Sb alloys can be significantly tuned by controlling the Sb-concentration (x). [41, 42]

Researchers have utilized the magnetic-field dependence of the thermoelectric properties of Bi-Sb crystals with aim to achieve better thermoelectric response of these materials near room temperature. Magnetic-field effects are reported to significantly enhance the thermoelectric response and magneto-Seebeck coefficient of Bi-Sb alloys in the vicinity of room temperature. [43–48]

Lenoir et al. [35] prepared the single crystals of bismuth-antimony alloys for various different stoichiometries using the traveling heater method. This method requires a precise knowledge of the binary phase diagram of Bi-Sb. They further performed the thermoelectric characterization of the prepared crystals and reported figure of merit (zT) $\approx 0.46 \pm 0.04$ over a wide range of temperature ($80\text{ K} \leq T \leq 270\text{ K}$). [35] Smith and Wolfe studied the thermoelectric properties of the Bi-Sb single crystals having different compositions (in the range of 1% – 40% antimony), and reported that the highest zT in

Bi-Sb system occurs at a temperature between 70 K and 100 K. [15] A high $z = 5 - 7 \times 10^{-3} K^{-1}$ was reported at around 80 K in BiSb alloys for 9–16% Sb concentration. [17, 35, 36, 38, 49, 50]

In addition to exhibit good thermoelectric performance at bulk, these binaries also exhibit remarkable enhancement in their thermoelectric performance under reduced dimensions [42, 51–57]. Dresselhaus’s research group at Massachusetts Institute of Technology (Cambridge, United States) thoroughly studied the properties of Bi-Sb nanowires and nanosheets [53, 58–61], and concluded that Bi-Sb nanostructures are very suitable for low-temperature thermoelectric applications. The trigonal axis is reported to be the most favorable wire orientation for thermoelectric applications. [59] Robin et al. reported an enhanced thermoelectric figure of merit (ZT) up to 2.5 for cylindrical $Bi_{1-x}Sb_x$ nanowires. [60] Furthermore, Lin et al. observed an enhanced ZT of 5 in pristine Bi nanowires of diameter 10 nm. [62] Experimental details related to the synthesis and characterization of Bi-Sb nanowires can be obtained in Refs. [52, 58, 62–65].

Low temperature properties of these binaries strongly depend upon the purity of the crystal. Crystal purity is particularly an important factor in the semiconducting region. In the presence of impurities/defects, additional impurity/defect bands merge with the conduction band near Fermi-level and bury the semiconducting features of Bi-Sb alloys. [18, 50, 66–68] Moreover, Volckmann et al. [69] reported that the thermal conductivity of the polycrystalline sintered Bi-Sb samples decreases with decreasing grain size. Consequently, the grain size significantly influences the thermoelectric properties of Bi-Sb alloys. [39, 55, 70–73] Datta and Nolas prepared $Bi_{1-x}Sb_x$ nanocrystals using a low temperature polyol synthesis process. [74] This process allows a better control over the stoichiometry, high crystallinity, and size of the nanocrystals. Datta and Nolas observed that the melting point of $Bi_{1-x}Sb_x$ nanocrystals was shifted towards higher temperature with increasing Sb content. [74]

Lopez et al. studied the mechanical alloying conditions on the Sb homogeneity in Bi-Sb alloys for 7%, 10%, 12%, 15% and 22% Sb concentrations. [75, 76] The homogeneity of the powder samples has been reported to considerably depend up on the milling parameters. [10, 55, 75] Landschreiber et al. observed strong influence of the pressing conditions on the thermoelectric properties of $Bi_{1-x}Sb_x$ nanoparticles prepared by mechanical alloying. [55]

Zemskov et al. have grown single crystals of Bi-Sb binaries by the Czochralski method with Sb feed and with different orientations. [77] Kitagawa et al. reported that a highly homogeneous single crystal of Bi-Sb binaries can be obtained by the quenching and annealing process. [38] Brown and Heumann proposed a zone-melting technique to grow the homogeneous crystals of Bi-Sb alloys. [78] They further describe the necessary conditions to grow large macro- and micro- homogeneous single-crystals of Bi-Sb binaries with Sb concentration ranging from 5% to 14%. Short and Schott also discovered some techniques to eliminate the inhomogeneity in the Bi-Sb crystal growth, and prepared homogeneous single-crystals of Bi-Sb alloys. [79]

Chaudhuri and Dey measured the thermal conductivity of Bi-Sb single crystals containing 1.77, 3.2, and 9.33 atomic % Sb in the temperature range 4.2–300 K, and observed that increasing Sb concentration enhances the scattering mechanism from purely phonon-phonon scattering to predominantly impurity scattering by phonons. [80] They also reported dominant contribution of electronic thermal conductivity over the lattice thermal conductivity to the total thermal conductivity in the high temperature region. This study [80] is consistent with the observations of Yazaki [81]. Yazaki reported that the most of the heat is transported by the charge carriers above 200 K with minimal contribution from the phonons. [81] Fenton et al. measured the low-temperature electrical resistivity of pure Bi and Bi-Sb single crystals at low Sb-concentrations and reported decrease in the free-carrier concentration with increasing Sb-content. [82] They also report a phonon-mediated electron-electron scattering (Frohlich-BCS type) in Bi-Sb crystals.

A recent work reveals that nanoporous Bi-Sb alloys, fabricated by dealloying of ternary Mg-based precursors, exhibit an ultralong cycling performance for sodium ion battery applications. [83] Moreover, these alloys show enhanced electrochemical performance towards Na storage. [83]

In 2007, Fu and Kane theoretically predicted that $\text{Bi}_{1-x}\text{Sb}_x$ could be a 3D topological insulator hosting gapless surface states [84]. One year later, Hsieh et al. [85] experimentally observed the signatures of the robust gapless surface states in $\text{Bi}_{1-x}\text{Sb}_x$ crystals using angle-resolved photoemission spectroscopy (ARPES). These two seminal works paved the way for discovery of a new class of materials that could host topological quantum phases [86, 87]. $\text{Bi}_{1-x}\text{Sb}_x$ alloys are often regarded as the first generation 3D topological insulators, which were later superseded by Bi_2X_3 ($\text{X} = \text{Te}, \text{Se}$) compounds

because of the large bandgap (0.3 eV for Bi_2Se_3) and better crystallographic ordering in Bi_2X_3 compounds [87, 88]. Tang and Dresselhaus also reported that an anisotropic single-Dirac cone can be realized in $\text{Bi}_{1-x}\text{Sb}_x$ thin films. [89]

Pure Bi crystal has semi-metallic character, which arises due to the small overlapping of the conduction bottom band and the valence top band. Such overlapping of the orbitals can be attributed to the huge spin-orbit coupling (SOC) present in Bi. Compared to Bi, Sb has weak SOC due to smaller atomic size ($\text{SOC} \propto Z^4$, where Z is the atomic number), same crystal symmetry and same number of valence electrons. Doping of Sb reduces the net strength of SOC in $\text{Bi}_{1-x}\text{Sb}_x$ alloys which lifts up the overlapping orbitals and drives the system into a semiconducting phase. However, the semiconducting phase exists only for a narrow region of Sb doping concentration in the $\text{Bi}_{1-x}\text{Sb}_x$ alloys ($x = 0.07\text{--}0.22\%$). [32, 34, 49, 90]

Based on the *ab-initio* calculations, Zhang et al. proposed an efficient way to make the bulk $\text{Bi}_{1-x}\text{Sb}_x$ semiconducting for larger Sb-doping concentrations [91]. They predicted that application of uniaxial pressure along c -axis of unit cell could enhance the indirect bandgap in the bulk $\text{Bi}_{1-x}\text{Sb}_x$ systems for broader range of x . In order to observe the topological insulating phase, a positive bulk bandgap is a fundamental requirement.

Here, it is important to mention that not all the phases and stoichiometries of Bi-Sb binaries were explored in the aforementioned studies. A complete theoretical phase-diagram of Bi-Sb binaries was undetermined. The novel properties of Bi-Sb alloys hint that different stoichiometries and crystal structures of Bi-Sb binaries can potentially inherit more intriguing topological phases and novel electronic properties that were not yet known.

Although pure Bi and pure Sb crystals have been extensively studied, a systematic investigation of $\text{Bi}_{1-x}\text{Sb}_x$ phase diagram was still lacking in literature, when I started working on these binary alloys in 2014. Figure 1.1 shows the theoretical convex hull of Bi-Sb binaries calculated using the reported structures of Bi-Sb binaries gathered from the various open-source material databases, namely - Materials Project [92], OpenQMD [93] and AFLOW [3]. One can notice that all the structures on the convex-hull have positive formation energy, which implies that Bi and Sb atoms could never form a compound since a compound formation requires negative formation energy. [94, 95]. However, the

previous experimental studies suggest otherwise. As I mentioned above, many experimental research groups have successfully synthesized Bi-Sb single crystals in laboratory using various different methods. These experimental works indicate that there must be several low-energy crystal structures of Bi-Sb binaries with negative formation energy on the convex-hull.

FIGURE 1.1: The theoretical convex-hull calculated for existing crystal phases of Bi-Sb binaries. These structures were obtained from the open access crystal structure databases.

A complete phase diagram of $\text{Bi}_{1-x}\text{Sb}_x$ is strongly needed for both experimentalists and theorists to study this system properly. Being an alloy, $\text{Bi}_x\text{Sb}_{1-x}$ has random substitutional disorder, which makes its electronic structure and surface states very complex with as many as five or more band crossings at the Fermi energy surface [91]. Due to such complexity of electronic structure, it is very difficult to describe the electronic properties of $\text{Bi}_x\text{Sb}_{1-x}$ alloys using simple theoretical models and its electronic structure can only be defined within the mean field or the coherence potential approximation. Since the electronic properties of materials mainly depend on their crystal structure, it is very important to find the stoichiometric crystals of $\text{Bi}_{1-x}\text{Sb}_x$ with ordered atomic configurations, preferably layered crystal structures so that it has well-defined electronic structure with simpler surface states, which can be explained by simple theoretical methods.

In this work, I explored the full phase diagram of Bi-Sb binaries, by performing *first-principles* structural search calculations, with aim to discover and identify new structures of Bi-Sb lying on the convex-hull with negative formation energy, which could be useful

for technological applications. I further studied the novel properties of the predicted Bi-Sb structures and discussed the origin of the novel phenomenon in these structures. These properties include: thermoelectric effects, negative Poisson's ratio (auxeticity), Rashba effect, ferroelectricity, Weyl semimetallic phase, and topological insulating phase.

In addition to my thesis work on Bi-Sb binaries, I have been actively involved in several other collaborative research projects. Detailed information about these projects can be found in Refs. [96–107].

Thesis Outline The remainder of this thesis consists of 8 chapters, including the Introduction chapter. In chapter 2, the essential details of the theoretical methodologies used to carry out the present research are described.

In chapter 3, a theoretical convex-hull of Bi-Sb binaries is presented. We employed the minima hopping method (MHM) [108, 109] to explore the potential energy surface of 35 different stoichiometries of Bi-Sb binaries. Several low-energy structures with negative formation energy were identified. A detailed analysis of the structural, electronic and vibrational properties of the selected low-energy structures is presented. The results of this chapter are published in Ref. [110].

In chapter 4, we evaluate the thermoelectric performance of several selected low-energy structures of Bi-Sb. As expected, we find that some of the predicted structures exhibit very good thermoelectric properties, which are comparable to the best known thermoelectric materials. These results are published in Ref. [110].

In chapter 5, we carried out a comprehensive analysis of the electronic structure of BiSb (space group #160), which is the lowest energy structure on the Bi-Sb phase diagram. This structure shows large Rashba-Dresselhaus effects due to the broken inversion-symmetry and large spin-orbit interactions of the constituting elements. We further find that a Weyl semimetallic phase can be realized in this particular structure under application of an external pressure in 4–6 GPa range. Pairs of opposite Weyl fermions appear in this structure at 4 GPa pressure *via* pair-creation. With increasing pressure Weyl fermions move and meet each other at 6 GPa, and eventually annihilate each other at 6 GPa pressure due to pair-annihilation. We also demonstrate that two opposite Weyl fermions can be switched by exploiting an interlink between the electric polarization and spin-orbit coupling. These results are published in Ref. [111].

In chapter 6, we discuss the properties of BiSb in two-dimensions. Our calculations reveal that BiSb monolayer is energetically, mechanically, vibrationally and thermodynamically stable at 0 K and at 300 K. BiSb monolayer exhibits very large Rashba spin-splitting in 2D, which can be controlled by means of an electric field, external strain or substrate effects. These results are published in Ref. [112].

In chapter 7, we discuss the elastic, mechanical and thermodynamic properties of the selected low-energy structures of Bi-Sb binaries. We further study the role of spin-orbit interactions on the elastic stiffness. Interestingly, we find that three monoclinic structures of Bi-Sb binaries inherit negative Poisson ratio, *i.e.* auxetic features. We proposed a possible mechanism to explain the possible origin of the auxetic effects in solid state materials. The findings of this chapter are published in Ref. [113].

Finally, we conclude by highlighting the main findings of this work in chapter 8, and discuss the future research scope in this area.

Theoretical Background

In this chapter, we introduce several essential concepts and methods that are used to carry out the research presented in this thesis. We start with a brief discussion on the many-body problem for quantum systems and then introduce Density Functional Theory (DFT) which is the main workhorse in this research. We also discuss different approximations that are often used to carry out DFT calculations. Afterwards, the concepts behind the potential energy surface (PES), structural relaxation and minima hopping method (MHM) for structural search are presented.

2.1 Many-body problem

Since everything is made of atom, it is fundamentally important to get a good grasp of the distinct properties of atoms, which govern the properties of materials. All atoms consist of a positive nucleus and a negatively charged electron cloud surrounding the nucleus in such a way that the total charge on an atom is neutral. In solids, multiple identical or non-identical atoms are arranged in a periodic or non-periodic fashion forming different crystal structures. In bulk solid state materials, there exists a large number of atoms ($\sim 10^{23}$ atoms) and a sea of electrons distributed in a certain way. In order to understand the properties of materials, it is important to understand the distribution of electrons in crystals *i.e.* the electronic structure of matter.

Our current understanding of electronic structure primarily relies on the principles of quantum mechanics [114–122]. In 1926, Schrödinger proposed an equation to understand the behaviour of quantum mechanical systems [120]. The equation is a type of wave equation which predicts the time evolution and movement of waves. Since all particles including electrons have wave characteristics, the Schrödinger’s equation can be applied to understand various properties of these particles. The most general form of Schrödinger’s equation is:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2.1)$$

Here, $\hat{H}$ represents the Hamiltonian operator acting on a quantum wave function $|\Psi\rangle$ yielding a proportionality constant E , which is the total energy of that quantum system. $\hat{H}$ can be written as the summation of operators corresponding to the kinetic energy $\hat{T}$ and potential energy $\hat{V}$:

$$\hat{H} = \hat{T} + \hat{V} \quad (2.2)$$

For a system composed of nuclei and electrons,

$$\hat{H} = \hat{T}_{\text{el}} + \hat{T}_{\text{nucl}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{nucl-nucl}} + \hat{V}_{\text{el-nucl}}, \quad (2.3)$$

where, kinetic energy of electrons:

$$\hat{T}_{\text{el}} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 \quad (2.4)$$

kinetic energy of nuclei:

$$\hat{T}_{\text{nucl}} = -\frac{\hbar^2}{2M_I} \sum_{I=1}^N \nabla_I^2 \quad (2.5)$$

m_e and M_I represent the mass of electron and nucleus (ion), respectively. $\hbar$ is the Planck’s constant. I and i are indices for nuclei and electrons, respectively.

Negatively charged electrons and positive charged nuclei interact *via* Coulombic interaction. The Coulomb interaction potential for nuclei-nuclei ($V_{\text{nucI-nucI}}$), electron-electron ($V_{\text{el-el}}$), and electron-nuclei ($V_{\text{el-nucI}}$) are given as follows:

$$\hat{V}_{\text{el-el}} = \frac{e^2}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.6)$$

$$\hat{V}_{\text{nucI-nucI}} = \frac{e^2}{2} \sum_{I=1}^N \sum_{J \neq I}^N \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.7)$$

$$\hat{V}_{\text{el-nucI}} = -e^2 \sum_{I=1}^N \sum_{i=1}^n \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (2.8)$$

Here, $\mathbf{R} = \{\mathbf{R}_I\}$ ($I = 1, \dots, N$) represents a set of N nuclear coordinates, and $\mathbf{r} = \{\mathbf{r}_i\}$ ($i = 1, \dots, n$) represents a set of n electronic coordinates. Z_I and M_I are the atomic number and mass of the I^{th} nucleus, respectively.

The non-relativistic time-independent Schrödinger equation for such system can be written as follows:

$$\hat{H}\Psi_i(\mathbf{r}, \mathbf{R}) = E_i\Psi_i(\mathbf{r}, \mathbf{R}) \quad (2.9)$$

where, $\Psi_i(\mathbf{r}, \mathbf{R}) \equiv \Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$

Since solids contain a large number of atoms ($\sim 10^{23}$ atoms), the real Hamiltonian is very complex and practically impossible to solve using the currently available computing resources. Therefore, it is important to simplify the above Eq. 2.3 using successive layers of plausible approximations.

2.2 Born-Oppenheimer approximation

Born-Oppenheimer approximation [123] is the very first approximation that we make to isolate the coordinates of nuclei and electrons. In this approximation, we use the fact that electrons are much lighter compared to nuclei (ions), *i.e.* $m_e \ll M_I$, and therefore electrons respond much faster than ions to any potential. It can be assumed that electrons move almost instantaneously (adiabatically) with respect to the motion

of nuclei. This is the Born-Oppenheimer approximation [123]. Since nuclei are much heavier than electrons ($\frac{M_I}{m_e} \sim 4627$ for Bi), $\hat{T}_{\text{nuc}}$ is much smaller (negligible) compared to the $\hat{T}_{\text{el}}$. Therefore, nuclei can be treated as frozen classical particles and their kinetic energy can be neglected in the evaluation of Eq. 2.3. Once we fix the position coordinates of nuclei ($\mathbf{R}_I$), the Coulombic interaction of nuclei with each other ($\hat{V}_{\text{nuc}-\text{nuc}}$) becomes a constant term, which would simply cause a scalar shift in the energy eigen values. $\hat{V}_{\text{nuc}-\text{nuc}}$ is also known as the Madelung energy, and it can be easily computed using the methods described in Ref. [124]. Now, electronic motion can be described independently of the nuclear coordinates as electrons move in a fixed Coulombic potential generated by nuclei. Therefore, the electronic structure is calculated for a given atomic geometry (crystal structure), and the nuclei are then moved according to the laws of classical mechanics.

After Born-Oppenheimer approximation, we are left with only three terms in the main Hamiltonian:

$$\hat{H} = \hat{T}_{\text{el}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{el-nuc}}, \quad (2.10)$$

The above equation encapsulates the electronic structure problem, and solving above equation is the central theme in the electronic structure community. Notably, the first and second terms in Eq. 2.10 ($\hat{T}_{\text{el}} + \hat{V}_{\text{el-el}}$) are universal for any electronic structure problem. It is the third term ($\hat{V}_{\text{el-nuc}}$) that varies with the specifications of the system.

According to the Born-Oppenheimer approximation, the $\hat{V}_{\text{el-nuc}}$ term can be represented only as a function of the electron degree coordinates and can be treated independent of the nuclear coordinates since nuclei are assumed fixed. Therefore, we can write the last term in Eq. 2.10 as an external potential acting on the electrons due to the interaction with positive nuclei.

$$\hat{V}_{\text{ext}} = \sum_{i=1}^n V_i(\mathbf{r}_i) \quad (2.11)$$

Thus, Eq. 2.10 simplifies to the below equation:

$$\hat{H} = \hat{T}_{\text{el}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext}}, \quad (2.12)$$

and now the Schrödinger equation involving the electronic Hamiltonian can be expressed as:

$$\hat{H}_{elec}\Psi(\{\mathbf{R}, \mathbf{r}\}) = E_{elec}(\mathbf{R})\Psi_{elec}(\mathbf{R}, \mathbf{r}). \quad (2.13)$$

Here, the electronic wavefunction $\Psi_{elec}(\mathbf{R}, \mathbf{r})$ depends explicitly on the electronic coordinates but parametrically depends on the nuclear coordinates ($\mathbf{R}_I$). Hamiltonian is also parameterized in $\mathbf{R}$. Even after considering the aforementioned approximations, the above equation is still enormously complicated to be solved exactly due to the “curse of dimensionality”. For an N electron system in 3D, there are $3N$ independent variables in the electronic wavefunction Ψ_{elec} , which make the problem numerically challenging.

Let us assume that we can express the wavefunction of a single electron using M basis functions, then an N electron system would require $N \times M$ basis functions. Since electrons are identical fermions, one must obey the Fermi-Dirac statistics while writing the manybody wavefunction for electrons, which can be done using the Slater’s determinant [125]. For M basis sets and N electron system, the number of determinants would be ${}^M C_N$ [125]:

$${}^M C_N = \frac{M!}{N!(M-N)!} \simeq e^{pN}, \quad (2.14)$$

where, p is a positive number. Evidently, the problem scales exponentially with increasing N . Troyer and Wilson reported it to be a nondeterministic polynomial (NP) hard problem [126]. Density functional theory is an alternative tool to tackle this problem by simplifying *the curse of dimensionality*.

2.3 Density Functional Theory (DFT)

DFT is one of the most successful quantum theories that are often used to solve the electronic structure problem in materials. It is chiefly formulated on the principles led by Hohenberg-Kohn [127] and Kohn-Sham [128] in years 1964 and 1965, respectively. The central idea in DFT is to replace the many-body electron wavefunction by electronic

density $n(\mathbf{r})$, which is a function of only three spatial coordinates ($\mathbf{r} \equiv x, y, z$) rather than $3N$ coordinates. Density of electrons and the electronic wavefunction can be related using the Born's rule [118]:

$$n(\mathbf{r}) = |\Psi_{elec}(\mathbf{R}, \mathbf{r})|^2 = \Psi_{elec}^*(\mathbf{R}, \mathbf{r}) \Psi_{elec}(\mathbf{R}, \mathbf{r}) \quad (2.15)$$

Here, $n(\mathbf{r})$ parametrically depends upon $\mathbf{R}$. When $n(\mathbf{r})$ is integrated over total volume, it yields the total number of electrons (N_e) present in the system.

$$N_e = \int |\Psi_{elec}(\mathbf{R}, \mathbf{r})|^2 d^3\mathbf{r} \quad (2.16)$$

where, $d^3\mathbf{r}$ is the volume of system.

It is worthy to mention that Thomas [129] and Fermi [130] first independently used the electron density (in year 1927) as a basic variable to write the ground state energy functional $E[n(\mathbf{r})]$. They demonstrated that the total kinetic energy of a multi-electron system can be written as an explicit function of $n(\mathbf{r})$. However, they both neglected the exchange and correlation effects among the electrons. Three years later Dirac formulated the local approximation for exchange in 1930 [131]. Therefore, one can argue that the original DFT for a multi-electron quantum system was first proposed by Thomas and Fermi.

2.3.1 Hohenberg-Kohn Theorems

The modern formulation of DFT stands on the foundations of two theorems proposed by Hohenberg and Kohn in 1964 [127]. In these theorems, $n(\mathbf{r})$ was introduced as a 'basic variable', and it was demonstrated that any property of a multi-electron system can be represented as an unique functional of the ground state density $[n_0(\mathbf{r})]$ of electrons. Later, Mermin extended this idea to finite temperature canonical and grand canonical ensembles [132]. The Hohenberg-Kohn theorems state the following:

Theorem 1: The external potential (V_{ext}) for any system of interacting electrons can be uniquely determined by the ground state density of electrons, up to an arbitrary constant.

Theorem 2: For a given V_{ext} , a universal function for energy $E[n(\mathbf{r})]$ can be defined in terms of $n(\mathbf{r})$. The exact ground state density $E[n_0(\mathbf{r})]$ of system minimizes the total energy functional $E[n(\mathbf{r})]$, *i.e.* ground state energy $E_0 = E[n_0(\mathbf{r})]$.

Flow chart shown in Fig. 2.1 illustrates the Hohenberg-Kohn formalism. The proofs of above two theorems are beyond the scope of this chapter. For additional details regarding the above two theorems, I would refer the reader to Refs. [125, 127].

Using Eq. 2.12 we can write:

$$E = \langle \Psi_{\text{elec}} | \hat{H} | \Psi_{\text{elec}} \rangle = \langle \Psi_{\text{elec}} | \hat{T}_{\text{el}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext}} | \Psi_{\text{elec}} \rangle \quad (2.17)$$

or

$$E = \langle \Psi_{\text{elec}} | \hat{T}_{\text{el}} + \hat{V}_{\text{el-el}} | \Psi_{\text{elec}} \rangle + \langle \Psi_{\text{elec}} | \hat{V}_{\text{ext}} | \Psi_{\text{elec}} \rangle \quad (2.18)$$

Above equation can also be expressed in terms of electron density $n(\mathbf{r})$:

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{\text{ext}} n(\mathbf{r}) d\mathbf{r} \quad (2.19)$$

Here $F[n(\mathbf{r})]$ is a functional of density which is associated with the kinetic and potential energy of electrons. Even at this stage, numerical evaluation of $F[n(\mathbf{r})]$ is extremely challenging due to the complexity of $\hat{V}_{\text{el-el}}$ term. One year after the publication of Hohenberg-Kohn theorems, Kohn and Sham proposed an ingenious way to handle this issue [128].

FIGURE 2.1: Schematic representation of the Hohenberg-Kohn formalism.

2.3.2 Kohn-Sham Ansatz

In 1965, Kohn-Sham gave *an ansatz* to numerically solve the complicated equations of DFT for ground state electron density in real electronic systems [128]. Thanks to this work for making the practical applications of DFT possible. The main idea behind this *ansatz* is to replace the original complicated problem of many-body *interacting* electron system by a relatively simple problem of an auxiliary *non-interacting* single particle system. It can be assumed that a non-interacting electron (Kohn-Sham electron) experiences an effective local potential $V_{eff}(\mathbf{r})$ at some point in space $\mathbf{r}$.

Then, we can write the single-electron Schrödinger equation (or Kohn-Sham equation) as follows:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\psi_i = \epsilon_i\psi_i, \quad (2.20)$$

where,

$$V_{eff} = V_{ext} + V_{Hartree} + V_{xc}, \quad (2.21)$$

$$V_{Hartree} = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.22)$$

$V_{Hartree}$ is the classic electrostatic potential (Hartree potential) for electrons and V_{xc} corresponds to the so-called exchange-correlation energy E_{xc} . The exchange-correlation energy term contains all the missing information that we lost during the mapping of the real interacting multi-electron problem into an auxiliary non-interacting problem. This includes all many-body effects of exchange and correlation present in interacting multi-electron systems. Therefore, in principle, the solution of above equation would yield the exact ground state density if the exact form of exchange-correlation energy term is known. Unfortunately, this is not the case. The exact form of E_{xc} is not yet known, however, there exists several good approximations to evaluate this term. The exchange-correlation potential is defined as a functional derivative of the exchange energy E_{xc} :

$$V_{xc} = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (2.23)$$

In Eq. 2.20, ψ_i represents the Kohn-Sham states and ϵ_i represents Kohn-Sham energy eigen values, which are different than that of for the real electronic states. Nonetheless,

there is a restriction on the total number of particles in the system. The total number of particles (N_e) in the system is fixed, *i.e.*:

$$N_e = \int n_{KS}(\mathbf{r}) d\mathbf{r} \quad (2.24)$$

where,

$$n_{KS}(\mathbf{r}) = \sum_i |\psi_i^{KS}(\mathbf{r})|^2, \quad (2.25)$$

Now we can solve the uncoupled Kohn-Sham equations for independent Kohn-Sham particles (Eq. 2.20) provided V_{eff} is known. *Another problem arises here.* Complete knowledge of V_{eff} requires information about $V_{Hartree}$, which can be calculated only when $n(\mathbf{r})$ is known (see Eq. 2.21 and Eq. 2.22). In order to evaluate $n(\mathbf{r})$, we need to know ψ_i , which is obtained after solving Kohn-Sham equations (Eq. 2.20). Evidently, this is a self-consistent problem, which can be solved iteratively. For instance, one can construct V_{eff} using a trial electron density $n(\mathbf{r})$. Afterwards, solve the non-interacting Kohn-Sham equations (Eq. 2.20) to get the single-particle Kohn-Sham wave-functions ψ_i . Now calculate $n_{KS}(\mathbf{r})$ using Eq. 2.25 and compare the calculated $n_{KS}(\mathbf{r})$ with the initial electron density. If the difference between two electronic densities (initial and final) is less than a pre-defined criterion (ideally zero), stop the self-consistent cycle, otherwise use the new electron density as the starting point [trial $n(\mathbf{r})$] of the new self-consistent iteration. Repeat these steps until the initial and final electronic densities become same, which then implies that thus obtained electronic density is the true ground state density of the system. Figure 2.2 shows a flow-chart of the self-consistent cycle that is generally utilized to solve the Kohn-Sham equations.

In principle, DFT is an exact theory. But since the exact analytical form of V_{xc} is not yet known, approximations for exchange-correlation energy are generally made in practice.

2.4 Approximations for exchange-correlation energy

The exchange-correlation energy contains information about the difference in the *non-interacting* Kohn-Sham problem and the *interacting* real multielectron problem. It takes into account the quantum mechanical exchange and electron-electron correlation effects

FIGURE 2.2: A flow chart of the Kohn-Sham iteration scheme.

present in the real multielectron system, which are not considered in the non-interacting Kohn-Sham electrons. It also accounts for the differences in the kinetic energy of the real interacting electrons and kinetic energy the non-interacting Kohn-Sham electrons. The exchange energy term arises due to the anti-symmetric nature of electronic (fermionic) wave function, which is associated with interchange of two electrons. In fact, exchange energy is the energy needed to interchange two electrons with the same spin. The correlation term refers to the fact that real electrons interact with each other, and this term could be non-local in nature.

$$E_{XC} = \frac{1}{2} \int \int \frac{n(\mathbf{r}) \tilde{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.26)$$

where $\tilde{n}_{xc}(\mathbf{r}, \mathbf{r}')$ is the average *exchange-correlation hole density*. It describes the effect of the inter-electronic repulsion considering the fact that an electron present at point $\mathbf{r}$ reduces the probability of finding another electron at $\mathbf{r}'$. Since the exact analytical form of E_{XC} is not yet known, there exists several approximations for this term.

2.4.1 Local Density Approximation (LDA)

LDA is the very first and one of the most widely used approximations for the exchange-correlation energy E_{xc} [128, 131, 133, 134]. In this approximation, one assumes that $E_{xc}[n(\mathbf{r})]$ at each point in space depends upon the local electronic density of homogeneous electron gas at that point $[n_o(\mathbf{r})]$ [133].

$$E_{XC}^{LDA} = \int n(\mathbf{r}) \epsilon_{XC}^{LDA}[n_o(\mathbf{r})] d\mathbf{r} \quad (2.27)$$

where, $\epsilon_{XC}[n_o(\mathbf{r})]$ is the exchange-correlation energy per particle in a homogeneous uniform gas. LDA works well for solids in which electronic density is fairly uniform and varies slowly in space. LDA predicts stronger chemical bonding than that for the actual strength of bonds. Therefore, bulk modulus is overestimated, and bond-length and lattice parameters are generally underestimated in LDA [134].

2.4.2 Generalized Gradient Approximation (GGA)

GGA is a natural extension of LDA. In GGA, the $E_{xc}[n(\mathbf{r})]$ functional depends on the local density as well on the local gradient of density $\nabla n(\mathbf{r})$ [135–137].

$$E_{XC}^{GGA} = \int n(\mathbf{r}) \epsilon_{XC}^{GGA}[n_o(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r} \quad (2.28)$$

Many different non-empirical and empirical forms of GGA functionals have been proposed in literature, since there is no unique way to determine the gradient dependence of the uniform electron gas. Different forms of GGA are optimized for different cases.

Perdew, Burke and Ernzerhof (PBE) approximation is one of the most widely used GGA functional [136]. Generally, PBE-GGA predicts slightly overestimated bond lengths and lattice parameters, and underestimated bulk modulus. However, the PBE-GGA predicted values are usually in good agreement with the experimental data.

Following a similar trend (from LDA to GGA), one could keep adding higher order derivatives of electron density to better describe the spatial variation of electronic density. In meta-GGA, we consider up to second order derivatives of $n(\mathbf{r})$ [138], *i.e.*

$$E_{XC}^{meta-GGA} \equiv E_{XC}[n_o(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r})] \quad (2.29)$$

However, there exists no convincing proof (to the best of my knowledge) stating that including higher order derivatives of the electron density in the same fashion is ever going to converge to the exact exchange-correlation energy functional. Another route is to use a new functional, often called as hybrid functional, which is an appropriate mixture of the different exchange and correlation terms from LDA and GGA, and exact Hartree-Fock exchange [125].

2.5 Bloch's Theorem and Plane Wave Basis Set

In solids, electrons enjoy a periodic potential. Therefore, electronic wavefunction in solids $\Psi_k^n(\mathbf{r})$ can be written using the Bloch's theorem [139, 140]:

$$\Psi_k^n(\mathbf{r}) = u_k^n(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.30)$$

where, $u_k^n(\mathbf{r})$ is a potential that obeys the periodicity of lattice, $e^{i\mathbf{k}\cdot\mathbf{r}}$ represents plane waves, $\mathbf{k}$ is the crystal momentum, and n is index for electronic bands. Due to the periodicity, we can decompose $u_k^n(\mathbf{r})$ into a set of plane waves whose wave vectors are reciprocal lattice vectors ($\mathbf{G}$) of the crystal:

$$u_k^n(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_{\mathbf{G}} C_k^n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.31)$$

Here, Ω_{cell} and C_k^n represent the cell volume and the Fourier series coefficients for plane waves. $\mathbf{G}$ vectors are defined by $\mathbf{G} \cdot \mathbf{R} = 2\pi m$, where $\mathbf{R}$ represents a lattice vector in the real space of crystal and m is an integer. Therefore, each electronic wavefunction (in plane wave expansion) can be written as follows:

$$\Psi_k^n(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}}^n e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (2.32)$$

In principle, infinite $\mathbf{G}$ vectors are required to expand the wavefunctions with infinite accuracy. However, in practical computations, we use a limited finite number of plane waves having energy lower than a cut-off energy value (E_{cut}).

$$\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 < E_{cut}. \quad (2.33)$$

Evidently, larger number of plane waves, *i.e.* higher E_{cut} , would yield better accuracy in the DFT predicted values. However, beyond a certain E_{cut} , change in the numerical value of the predicted properties (such as- total energy of system) becomes negligible. This process is commonly known as the energy cutoff convergence, and the converged E_{cut} is used in the DFT calculations. In general, the planes waves with smaller kinetic energy play a more important role in determining the material properties compared to that of the plane waves with higher kinetic energy.

In addition to a well-converged E_{cut} value, a proper sampling of points in the reciprocal space (k -points) is equally important in the *first-principles* calculations. Using the Bloch's theorem, we have mapped the problem of infinite number of electrons distributed in a lattice with periodic boundary conditions onto a problem of describing the electronic wavefunction in terms of an infinite number of reciprocal space vectors within the first Brillouin zone of the periodic cell. The Born-von Karman boundary conditions allow us to represent an infinite periodic crystal lattice from real space in form of another periodic lattice in the reciprocal space utilizing the translational symmetry properties of the real lattice [139, 140]. First Brillouin zone is the smallest building block in the construction of the reciprocal lattice, and it always contains the same number of k -states as the number of primitive unit cells in the crystal lattice. In practice, we sample the Brillouin zone using special sets of points, often known as k -points. The electronic wavefunctions at

each k -point are expressed using plane waves, where the upper limit of required number of plane waves at each k -point is set by E_{cut} (see Eq. 2.33).

In DFT calculations, an accurate evaluation of charge density is crucial. Determination of charge density requires summation over the k -points in Brillouin zone (BZ) and the occupied electronic bands, as shown below:

Charge density,

$$n(\mathbf{r}) = \frac{\Omega_{cell}}{(2\pi)^3} \int_{BZ} n_k(\mathbf{r}) d\mathbf{k} \quad (2.34)$$

where,

$$n_k(\mathbf{r}) = \sum_{n=1}^N \Psi_{n,k}^*(\mathbf{r}) \Psi_{n,k}(\mathbf{r}) \quad (2.35)$$

Calculation of $n(\mathbf{r})$ requires evaluation of $n_k(\mathbf{r})$ at each k -point in a carefully chosen k -mesh which samples the BZ. Using the space group symmetry operations, one can reduce the total k -points required for computation. Results of one k -point can be used for another k -point related with symmetry operations. There exists several different methods to generate the special set of k -points with given weighing factors that efficiently sample the irreducible BZ [141, 142]. Evidently, a larger size of k -mesh (*i.e.* denser k -mesh) would give better numerical accuracy. For instance, a k -mesh of size $10 \times 10 \times 10$ might be sufficient to converge the results for an insulating system, while a $30 \times 30 \times 30$ k -mesh might not be dense enough for a metallic system.

2.6 Pseudopotential Approximation

Since the electronic wavefunction oscillates rapidly near the nucleus (core electrons region) and varies relatively slow in the interstitial region (valence electrons region), we need a large E_{cut} *i.e.* a large number of plane waves to capture the wiggleness of the wavefunction near nucleus. This increases the computational cost of DFT simulations. Pseudopotential approximation overcomes this issue by separating the electronic states into core states and valence states. Atomic orbitals work well to describe the wavefunction of the core states, whereas plane waves are more suitable for description of the valence states. Mostly, the core states do not contribute in chemical bonding and in determining various properties of materials. Hence, one could in principle construct a potential that encapsulates the features of the nucleus and the core states. This effective

potential will be seen by the valence electrons. The main advantage of this approximation is that it considerably reduces the number of total electrons in the *first-principles* calculations. Usually, the computational complexity scales as $O(N^3)$, where N is the number of electrons in calculation.

Another advantage of the pseudopotential approximation lies in the fact that the pseudo wavefunction has no radial nodes or rapid fluctuations in the core region (see Fig. 2.3). Also, the pseudopotential is smoother than the actual Coulombic potential in the core region and it becomes identical with the actual Coulombic potential beyond a certain cutoff radius (r_c). These features of the pseudopotential approximation allows one to compute the Kohn-Sham wavefunctions for valence electrons using a relatively smaller number of plane waves.

The pseudopotential approximation was first proposed by Hellman in 1935 [143], and later refined by Phillips and Kleinman in 1959 [144]. Nowadays, there exists several different pseudopotential approximations that are well-suited for different tasks [145–151].

2.7 Projected Augmented Wave (PAW) method

PAW method was first proposed by Blöchl in 1994 to improve the numerical accuracy of the *first-principles* calculations [152]. This method allows one to keep information about all core electronic wavefunctions into consideration *via* a mathematical linear transformation approach. Consequently, it sustains the information that is normally lost in the pseudopotential approximation, which influences the calculation of properties associated with nucleus, such as hyperfine parameters, and electric field gradients. In other words, PAW method unifies all-electron and pseudopotential approaches. As we mentioned earlier, the electronic wavefunctions inherit rapid oscillations in the vicinity of the nucleus due to the orthogonality requirement. This situation demands a large number of Fourier components to describe the wavefunction accurately near the nucleus. The PAW method proposes a way to transform the rapidly oscillating electronic wavefunctions of all core electrons into smooth wavefunctions that are easier to compute numerically.

An all electron Kohn-Sham wavefunction (not the many-body wavefunction) Ψ can be transformed into a fictitious pseudo wavefunction $\tilde{\Phi}$ by a linear transformation operation

FIGURE 2.3: Schematic representation of the pseudopotential and the pseudo wavefunction. The real and the pseudopotential match beyond a given cutoff radius r_c . Notice that the pseudo wavefunction is nodeless before r_c and the pseudopotential is much weaker than the real potential in the core region. [Figure adopted with permission from Ref. [1]]

$\hat{\tau}$, with an aim to find smooth pseudo wavefunction $\tilde{\Phi}$ that can be represented as a some atom-like partial wave basis set:

$$|\Psi\rangle = \hat{\tau}|\tilde{\Psi}\rangle \quad (2.36)$$

In practice, we combine PAW method with pseudopotential approximation for computational benefits [153–155]. Since within the pseudopotential approximation we isolate the core wavefunction (within cutoff radius r_c) and the valence wavefunctions, $\hat{\tau}$ operates only on the core wavefunctions within radius r_c .

$$\hat{\tau} = 1 + \sum_{r_c} \hat{\tau}_R \quad (2.37)$$

$\hat{\tau}_R$ is non-zero only within a sphere of radius r_c centered at nucleus, and is defined in such a way that there is no overlap of the augmentation spheres of neighboring atoms. Inside each augmentation spheres, we expand the true wave function in a smooth complete partial waves basis set $|\tilde{\Phi}\rangle$.

$$|\tilde{\Psi}_n\rangle = \sum_i |\tilde{\Phi}_n\rangle \langle \tilde{p}_i | \tilde{\Psi}_n \rangle \quad (2.38)$$

Here, $\tilde{p}_i$ are the projector functions which form a smooth complete basis set within the augmentation spheres. Thus, projector functions act as a probe for the character of the pseudo wavefunction. The above-mentioned transformation (Eq. 2.37) can be applied to any operator to determine the expectation value using smooth pseudo-waves while retaining the information of all-electron wavefunction.

$$\langle \hat{A} \rangle = \sum_n \langle \Psi_n | \hat{A} | \Psi_n \rangle = \sum_n \langle \tilde{\Psi}_n | \tau^\dagger \hat{A} \tau | \tilde{\Psi}_n \rangle \quad (2.39)$$

2.8 Potential Energy Surface (PES)

PES or potential energy landscape refers to the potential energy of a collection of atoms or molecules as a function of their relevant generalized coordinates, such as - atomic coordinates, bond-length, bond angle, etc. In solids, a PES can be defined as: $E = E(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_N)$, where $\mathbf{R}_i$ represents the coordinates of atom i within the unit cell. It is important to note that PES contains information only about the potential energy, not the kinetic energy. At 0 K temperature, the kinetic energy of atoms is zero, therefore atoms tend to arrange themselves in such a way that they attain the lowest energy configuration (minima) on the PES. An schematic of PES in 1D is shown in Figure 2.4. Fig. 2.4 shows the potential energy curve of two atoms forming a covalent bond as a function of the inter-atomic distance (r). At point A on this curve, atoms feel an attractive force ($F = -\frac{\partial V}{\partial r}$) due to the positive slope of $V(r)$ curve, and therefore atoms move close to each other. Whereas, at point B, atoms experience a strong repulsion (*i.e.* positive force) due to the negative slope of $V(r)$ curve, and hence tend to move away from each other. However, at the extremum point C, the slope of $V(r)$ curve is zero, which implies zero net force on atoms. Therefore, atoms would prefer to vibrate

around this equilibrium inter-atomic distance (r_c) because of their thermal energy. Here r_c would denote the length of the covalent bond.

FIGURE 2.4: Illustration of a potential energy profile of two atoms forming a covalent bond of length r_0 in one dimension. $V(r)$ represents the potential energy as a function of the inter-atomic distance r .

The PES could be very complex in multi-dimensions. Nonetheless, the same idea described above can be utilized to evaluate the forces and discover the local minimum energy configurations on the potential energy landscape. Figure 2.5 shows an illustration of PES in two dimensions with multiple local energy minima and valleys.

In solid state crystals, atoms prefer to obtain the ground state relaxed geometry on the PES, which means the lowest energy minimum (global minimum) on PES, so that atoms experience no net force and enjoy the minimum energy state (see Figure 2.6). This global minimum can be associated with the ground state crystal structure of atoms in a given stoichiometry. In addition to the lowest energy ground state structure, atoms can also arrange themselves in metastable states (local minima) that are higher in energy than that of the global minimum. These metastable states can be realized in experiments at certain conditions of temperature, pressure, doping, etc. For instance, diamond is a metastable state configuration of carbon atoms at room temperature and pressure. Given “enough time” and activation energy, diamond would eventually transform into graphite which is the most stable global minimum energy configuration of carbon atoms at ambient conditions.

FIGURE 2.5: Illustration of potential energy surface in a two dimensional coordinate space (r_1, r_2) . Red (Blue) color depicts the regions of high (low) potential energy.

Exploration of PES in DFT calculations requires evaluation of forces and Hessian matrices ($\mathbf{H}_{i,j} = \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$). The determinant of the Hessian matrix is often referred as Hessian. The Hessian matrix describes the local curvature of a multidimensional PES. At a local minimum (*i.e.* stationary point), Hessian matrix has no negative eigen values, which implies that any perturbation from the stationary point would yield a higher energy configuration on the PES (see Fig. 2.6). Negative eigen values of Hessian matrix correspond to the negative force constants or negative curvature of PES (*i.e.* negative vibrational frequencies). This is often associated with structural phase transitions. At a transition state, which is also known as first-order saddle point, Hessian matrix has a single negative eigen value. In principle, there could be higher-order saddle points with more than one negative Hessian eigen values. Consequently, one can define an index, Hessian index (h), denoting the number of negative Hessian eigen values. $h = 0$ for a stationary point, $h = 1$ for a first-order saddle point, and $h > 1$ for higher-order saddle points. This index also indicates the total number of negative phonon modes present in the system.

FIGURE 2.6: Illustration of potential energy surface in one dimension with several local minima separated by energy barriers. A local minimum with the lowest energy refers to the global minimum. All configurations within a basin relax to the same local minimum of that basin after completion of structural relaxation calculations. All configurations within a funnel relax to the global minimum of that funnel given finite activation energy required to escape the local minima present in that funnel. Transition state (or saddle point) separates two funnels. [Figure adopted with permission from Ref. [2]]

2.9 Structural Relaxation

The purpose of structural relaxation is to find the local energy minimum on the PES of the system under consideration. This is an important step in DFT calculations to get information regarding the equilibrium crystal geometry related properties, such as - lattice parameters, bond length, bond angle, coordination number, etc. In a nutshell, forces on atoms are computed from a self-consistent single-point DFT calculation, and atoms are moved in the direction of forces until they achieve the equilibrium configuration with vanishing forces (within the numerical tolerance). The shape and size of unit cell can also be varied according to the net stresses on the unit cell.

In DFT, we employ the Hellmann-Feynman theorem to determine forces [156, 157]. According to this theorem, once the spatial distribution of the electrons (*i.e.* electron density) has been determined by solving the self-consistent Kohn-Sham equation under the Born-Oppenheimer approximation, forces on each atom can be calculated using classical electrostatics. In DFT calculations, the Hamiltonian is parameterized in $\mathbf{R}$ because of the frozen atomic coordinates ($\mathbf{R}$) assumed in the Born-Oppenheimer approximation.

Hellman-Feynmann theorem:

$$\mathbf{F}_{\mathbf{I}} = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_{\mathbf{I}}} = -\langle \Psi(\mathbf{r}, \mathbf{R}) | \frac{\partial \hat{H}_{\mathbf{R}}}{\partial \mathbf{R}_{\mathbf{I}}} | \Psi(\mathbf{r}, \mathbf{R}) \rangle \quad (2.40)$$

where, $\Psi(\mathbf{r}, \mathbf{R})$ is the ground state Kohn-Sham wavefunction.

2.10 Minima Hopping Structural Search Method

The minimum hopping method (MHM) is an efficient dynamical algorithm that explores the PES and searches for local minima as well as the global minimum on the PES of complex condensed matter systems. This method was first proposed by Goedecker in 2004 [158], tested for several complicated system including 216 atom crystals, and was proven very efficient in exploration of the configurational space compared to the other known structural search methods. The main goal of MHM is to search as many as possible local minima on the PES without revisiting the same minimum in a timely fashion. In order to escape one minimum, the searcher has to overcome the energy barrier separating that minimum with the neighboring local minima (see Figure 2.6). In 2010, Amsler and Goedecker generalized MHM to periodic systems using a variable cell shape molecular dynamics (MD) simulations [108]. Here the idea is to direct the Car-Parrinello MD [159] escape moves in such a way that new lower energy minima can be obtained.

The MHM algorithm can be divided into two main parts: (i) *inner part*, and (ii) *outer part*. The *inner part* is responsible for jumping the searcher from one local minimum to a neighboring minima in an efficient manner, whereas the *outer part* is responsible for making decisions whether to accept or reject the new minima proposed by the *inner part*. This method can be employed just by the knowledge of the stoichiometry of any system.

In practice, we start with an initial configuration for a given stoichiometry and given number of atoms in a periodic unit cell. In other words, we create a unit cell containing desired number of atoms required for a given stoichiometry. Since such creation of unit cell does not guarantee that the structure would be in a stationary state, *i.e.* in a local minimum and atoms might be feeling residual forces, DFT calculations are

performed for structural relaxation. This step ensures that the structure attains the local minimum of that basin. Afterwards, short MD escape moves are performed to overcome the energy barrier ($E_{barrier}$) between two neighboring local minima. Here we utilize random Boltzmann velocity distribution to add a kinetic energy (E_{kin}) in order to assist the searcher to overcome the $E_{barrier}$ and escape the local minimum. Generally, we start with a small E_{kin} and make an attempt to escape the local minimum, if the searcher manages to escape the $E_{barrier}$ (*i.e.* $E_{kin} > E_{barrier}$), MD step stops. Otherwise, algorithm increases E_{kin} with an aim to cross the $E_{barrier}$. The algorithm also stores the history of the visited local minima. If the searcher lands into a local minima after MD escape move that has already been visited, the algorithm further increases the E_{kin} with aim to find a new local minima. Thus, $E_{barrier}$ is continuously adjusted during the MD simulations.

The MHM exploits the Bell-Evans-Polanyi (BEP) principle [160] to determine the direction of forces on atoms (*i.e.* velocities) required for the MD escape move. This principle states that highly exothermal reactions will have a low activation energy barrier. That means, it is more likely to find a lower energy local minimum if we align the MD escape move in such a way that searcher crosses the energy barrier through the lowest slope of the energy landscape rather than pushing the searcher through steep hills on the energy landscape [161, 162]. The direction of the lowest slope (*soft mode*) can be determined from the Hessian matrix. The algorithm aligns the velocity vectors on each atom during the MD escape move along the direction which corresponds to the Hessian eigen vector with the lowest Hessian eigen value. This ensures that the searcher is crossing the $E_{barrier}$ through a soft mode direction [162]. Once a new local minima is obtained, MD step stops and geometrical optimization is performed for relaxation of the crystal structure.

The *outer part* of algorithm accepts or reject the local minima proposed by the *inner part* as follows: If the energy of the new minimum (E_{new}) is lower than the energy of previous minimum (E_{old}) by a difference of energy parameter E_{diff} ($E_{diff} > 0$), *i.e.* $E_{new} < E_{old} + E_{diff}$, the new minimum is accepted. During the simulation, E_{diff} is continuously adjusted in such a way that the *outer part* accepts only half of the minima proposed by the *inner part*. This ensures that the structural search is always directed towards the lower energy local minima on the PES.

The MHM method has been employed to explore the PES of several condensed matter systems, such as Si_2H_6 [163], carbon [163–166], phosphorus-hydride [167], Li-Al [168], Au-Na [169], LiAuH_4 [170], Si [171], Li-Si [172], Mg-Li [173], CuBO_2 [174], boron [175], $\text{NaSc}(\text{BH}_4)_4$ [176], nitride perovskites [177], and ternary oxides [178]. This method has remarkably predicted new low energy stable and metastable structures of many compounds, and it has also recovered the already known experimental structures of a wide range of materials. In addition to the periodic solid state crystals, this method has been applied and proven successful for nanoparticles, molecules, and two-dimensional systems [175, 179–182]. In principle, the MHM can also be applied to explore the PES of complex systems at finite pressure conditions. In this case, instead of PES, *i.e.* $E(\mathbf{R})$, we explore the enthalpy space: $H = E + PV$, where P is the pressure, V is the volume, E is the internal energy, and H is enthalpy of the system.

Investigation of Novel Crystal Structures of Bi-Sb Binaries Predicted by Minima Hopping Method

3.1 Introduction

Semi-conducting alloys $\text{Bi}_x\text{Sb}_{1-x}$ have emerged as a potential candidate for topological insulators and are well known for their novel thermoelectric properties. In this work, we present a systematic study of the low-energy phases of 35 different compositions of $\text{Bi}_x\text{Sb}_{1-x}$ ($0 < x < 1$) at zero temperature and zero pressure. We explore the potential energy surface of $\text{Bi}_x\text{Sb}_{1-x}$ as a function of Sb concentration by using the *ab-initio* minima hopping structural search method. Even though, Bi and Sb crystallize in the same $R\bar{3}m$ space group, our calculations indicate that the $\text{Bi}_x\text{Sb}_{1-x}$ alloys can have several other thermodynamically stable crystal structures. In addition to the configurations on the convex hull, we also find a large number of metastable structures which are dynamically stable. The electronic band structure calculations of several stable phases reveal the presence of strong spin-orbit interaction leading to the Rashba-Dresselhaus spin-splitting of bands which is of great interest for spintronics applications.

The electronic bandstructure calculations predict the topological insulating nature and the presence of giant Rashba-Dresselhaus spin-splitting effect [183–185] in Bi-rich compositions. In 2011, Bahramy et al. [186] theoretically predicted the existence of giant

Rashba effect in bulk BiTeI which was experimentally corroborated as well [187]. They proposed three necessary conditions for realization of giant Rashba effect in bulk: (i) large SOC in an inversion-asymmetric system, (ii) a narrow bandgap, and (iii) the presence of valence band top (VBT) and conduction band bottom (CBB) of symmetrically the same character. We find that most of our Bi-Sb structures satisfy these three conditions and consequently, exhibit giant Rashba effect in the bulk. The Rashba spin-splitting is large in the Bi-rich compound due to presence of strong SOC in the system. However, due to the bulk inversion-asymmetry, a Dresselhaus contribution [183] in the spin-splitting of bands can not be denied and we do notice the evidence of Dresselhaus effect in the spin-texture calculations. An excellent review of these two effects can be found in Ref. [188].

3.2 Computational Details

Several different global structure search methods have been proposed in literature in the last few years. Some of the most popular structure search methods are: random search [189], metadynamics [190, 191], simulated annealing [192, 193], basin hopping [194], evolutionary metadynamics [195], genetic algorithm [196–198], particle swarm [199] and firefly method [200]. Computational discovery of new crystal structure requires a systematic exploration of the potential energy surface of a given composition, and to achieve so, we use the global search methods. In this work, we use the Minima Hopping Method (MHM) [108, 158] to find the low-energy phases of Bi-Sb binaries. This method is coupled with Density Functional Theory (DFT) and it employs an efficient dynamical algorithm to explore the PES of a given composition by performing short Molecular Dynamics (MD) simulations. The MD escape moves help the searcher to overcome a minima and move to a different minima. To improve the efficiency of each escape move, the initial velocities of the MD simulations are aligned along the soft-mode directions. A local geometric relaxation of the atomic coordinates and the cell parameters has been performed after each MD escape move (see chapter 2 for more details).

We employ MHM method to sample the PES of $\text{Bi}_x\text{Sb}_{1-x}$ ($0 < x < 1$) at zero temperature and zero pressure. We perform structure search for 35 different stoichiometries of $\text{Bi}_x\text{Sb}_{1-x}$, ranging from pure Sb to pure Bi. We used cells containing up to 20 atoms for all structural search calculations presented in this paper. To obtain the energy and forces

for each system, we used Vienna Ab-initio Simulation Package (VASP) implementation of DFT [201, 202]. The Projector Augmented Wave (PAW) method [203] was used to describe the valence and core electrons. We considered fifteen valence electrons of Bi ($5d^{10}6s^26p^3$) and five valence electrons of Sb ($5s^25p^3$) in the PAW pseudo-potential. The generalized gradient approximation (GGA) as parametrized by Perdew-Burke-Ernzerhof (PBE) [136] was used for the exchange-correlation functional. A plane wave energy cut-off of 650 eV was used together with a Monkhorst-pack k -mesh [141] of different sizes (depending up on the size of the cell). However, for hexagonal and trigonal structures, we used a Γ -type k -mesh to sample the Brillouin zone. After structural search runs for each stoichiometry, all obtained structures were further re-optimized using an automatically determined dense k -mesh. For all calculations, the size of k -mesh was sufficient to ensure the numerical convergence of the total energies to less than 2 meV/atom. All forces were converged better than 10^{-4} eV/Å. A theoretical convex-hull was generated from the resulting structures of the reoptimization step.

We select all the low-energy structures, which are either lying at the convex-hull or are very close to the convex-hull, and consider them for further characterization. To study the thermodynamical stability of the selected structures, we performed the phonon calculations using frozen phonon approach [204]. PHONOPY code [205] was used to calculate the force-constants for $2 \times 2 \times 2$ supercell of each structure. It is worth to mention that SOC was not included in the phonon calculations as well as in the relaxation of the cell used for phonon calculation. However, for all other results presented in this paper, SOC was included during the relaxation of internal coordinates and cell parameters for each structure. Large SOC present in Bi and Sb atoms plays a crucial role in determining the electronic properties of the Bi-Sb binaries. Therefore, we have studied the effect of SOC on the electronic bandstructure of each structure.

3.3 Results and Discussions

Figure 3.1 shows the calculated convex-hull, consisting of all low-energy structures of the different stoichiometries of $\text{Bi}_x\text{Sb}_{1-x}$ ($x = \text{Bi}/(\text{Bi}+\text{Sb})$) binaries at zero temperature and zero pressure. These structures were obtained after the MHM simulations for each composition followed by a geometrical reoptimization of each structure with a tighter

convergence criteria for forces and stress. In order to study the effect of exchange-correlation functional on the convex-hull, we performed the reoptimization step using two different approximations for the exchange-correlation functional. We calculated the convex-hull using local density approximation (LDA) [133] and GGA (PBE) [136] approximations for the exchange-correlation functional. We find a large number of structures having negative formation energy. Blue ‘plus’ symbols correspond to the low-energy structures calculated using PBE approximation, while red ‘cross’ symbols represent the low-energy structures calculated using LDA approximation (Fig. 3.1). The chemically stable structures (structures lying on the convex-hull) are marked with blue circles and red triangles for PBE and LDA approximations, respectively. The solid blue line represents the convex-hull calculated using PBE approximation and the red dotted line represents the convex-hull calculated using LDA approximation. For both PBE and LDA approximations, we did not find any new lower-energy phase for each composition, only the energy values were slightly modified which is due to the difference in methodology used in the different approximations. We do not see any significant change in the shape of the convex-hull for different approximations, which indicates that the same compositions are chemically stable for both PBE and LDA approximations. A very small change in the shape of the convex-hull at Bi_7Sb_1 and Bi_9Sb_1 compositions can be ascribed to the numerical accuracy of our calculations. The difference in the lowest-energy of these compositions corresponding to different functionals is less than the total energy convergence criteria.

We notice that the lowest-energy phase of Bi_3Sb_1 composition is not lying exactly on the convex-hull, however, it is very close to the convex-hull for both LDA and PBE approximations. Therefore, we consider this composition for further characterization. Along with the chemically stable structures, we also find a large number of metastable structures, which can be experimentally synthesized by means of temperature, pressure, doping, etc.

Furthermore, we have calculated the convex-hull for all previously reported structures of $\text{Bi}_x\text{Sb}_{1-x}$ (see Fig. 1.1). These structures were obtained from the Materials Project [92], OpenQMD [93] and AFLOW [3] open crystal structure databases. In the convex-hull of the databases phases, we did not find any structure with negative formation energy. On the contrary, in the MHM structural search runs we did find several new structures of $\text{Bi}_x\text{Sb}_{1-x}$ having negative formation energies. In addition to the prediction

FIGURE 3.1: Convex hull of the $\text{Bi}_x\text{Sb}_{1-x}$ binary system. Blue solid line represents the convex-hull calculated using GGA (PBE) approximation while the red dotted line represents the convex-hull calculated using LDA approximation. Blue plus (+) and red cross (x) symbols show the low-energy phases obtained after MHM structural search runs for each composition. The phases lying on the convex-hull are energetically stable and all the other phases above convex-hull are metastable.

of new structures, we were also able to reproduce the experimentally known structures of $\text{Bi}_x\text{Sb}_{1-x}$.

Table-I contains a summarized crystallographic information of all chemically stable structures along with some interesting metastable structures, which are very close to the convex-hull. Wyckoff positions and simulated x-ray diffraction patterns for all the selected interesting structures are given at the end of this chapter. We find that the Bi_1Sb_1 composition in $R3m$ space group has the lowest-energy amongst all the different phases of Bi-Sb binaries. Thus, this structure is chemically the most stable structure of the $\text{Bi}_x\text{Sb}_{1-x}$ compounds. Indeed, we found experimental evidences of the same structure in Refs. [17, 206, 207].

In the following sections, we systematically present crystallographic, electronic and vibrational properties of each structure mentioned in the Table-I.

3.3.1 Bi_1Sb_7

$P1m_1$ (space group number-06) phase:— Figure 3.2(a) shows the crystal structure of Bi_1Sb_7 composition in $P1m_1$ space group. The primitive cell contains one atom of Bi

TABLE 3.1: Composition, number of atoms in cell, space group (space group number), lattice parameters ($\text{\AA}$), angles (degree), and formation energy of the lowest-energy stable structures (ground state) along with some interesting metastable structures

Composition	Number of atoms in cell	space group	a	b	c	α	β	γ	Formation-energy (in meV/atom) (for PBE)
Bi ₁ Sb ₇	8	$P1m_1$ (06)	6.369	4.373	9.381	90.00	93.40	90.00	-8.74 (ground state)
Bi ₁ Sb ₁	6	$R3m$ (160)	4.516	4.516	11.885	90.00	90.00	120.00	-14.9 (ground state)
	4	$Imm2$ (44)	4.474	6.413	4.873	90.00	90.00	90.00	-5.64 (metastable)
	12	$R\bar{3}m$ (166)	4.618	4.618	28.052	90.00	90.00	120.00	-5.04 (metastable)
Bi ₃ Sb ₁	12	$R3m$ (160)	4.559	4.559	23.984	90.00	90.00	120.00	-6.3 (ground state)
Bi ₇ Sb ₁	16	$C1m_1$ (08)	9.632	9.175	7.954	90.00	56.69	90.00	-3.03 (ground state)
Bi ₉ Sb ₁	10	$C1m_1$ (08)	12.208	8.134	8.134	147.02	120.00	60.00	-3.4 (ground state)

and seven atoms of Sb. Bi (Sb) atoms are shown in purple (gold) color. We follow the same color representation for Bi and Sb atoms in the rest of the chapter. The nearest Sb-Sb and Bi-Sb bond lengths in the relaxed cell are 2.96 and 3.03 Å, respectively. Thus, the bond between two nearest Sb atoms is 2.3 % shorter than the bond length between nearest Bi and Sb atom. This is expected due to the fact that Bi has larger atomic radius than that of Sb. To gain further insight into the bonding nature of Bi and Sb atoms, we investigate the electron localization function (ELF) plot as shown in Fig. 3.2(c). A covalent type of bonding can be seen between Sb-Sb and Bi-Sb atoms. The contour plot of ELF calculated in (110) plane reveals that electrons are more localized near Sb-atoms. The calculated phonon bandstructure is shown in figure 3.2(d). The k-path is chosen along the high symmetric directions in the momentum space. We do not see any significantly large imaginary frequency phonon mode in the phonon spectra, which implies that this structure is thermodynamically stable. By including SOC and choosing a larger supercell in the phonon calculation, we can get rid of the small imaginary frequencies present near Γ -point.

The electronic bandstructure and density of states calculations reveal the semi-metallic nature of this system. The electronic bandstructures calculated along the high symmetry lines of the Brillouin zone are shown in Fig. 3.2(e) (for without-SOC) and Fig. 3.2(f) (for with-SOC). Due to SOC, we notice that each band gets split into two spin non-degenerate bands and the system remains semi-metallic due to the crossing of the Fermi-level by conduction and valence bands. A weak Rashba type spin-splitting of valence bands can be noticed near the A-point (Fig. 3.2(f)). Since the SOC strength of Sb is weaker than that of Bi and this is a Sb-rich composition, therefore, we do not see a large spin-splitting in the bands. However, this is not the case for Bi-rich compositions of $\text{Bi}_x\text{Sb}_{1-x}$. Figure 3.2(g) shows the projected electronic density of states (DOS) for Bi_1Sb_7 compound. From DOS plot, the presence of a small but non-zero DOS at the Fermi-level can be noticed. We do notice effect of this semimetallic nature in the thermoelectric properties of this composition. We also see that majority of the states near Fermi-level are coming from the Sb-atom which is as expected for a Sb-rich composition.

FIGURE 3.2: a) Monoclinic crystal structure of Bi_1Sb_7 in $P1m1$ space group. Bi (Sb) atoms are shown in purple (gold) color. b) Brillouin zone of this structure obtained using AFLOW software [3]. c) The electron localization function (ELF) calculated in real space and the distribution of ELF in (110) plane. Red/blue color represents localization/delocalization of electrons. d) The calculated phonon bandstructure. The electronic bandstructure calculated e) without-SOC, f) with-SOC. g) Projected electronic density of states (DOS) calculated using a Monkhorst-pack k -mesh of size $11 \times 11 \times 11$. The dotted line shows the Fermi-level. SOC was included for all DOS calculations reported in this paper.

3.3.2 Bi₁Sb₁

This composition has the lowest-energy structure (ground state) in $R3m$ space group. As we can see in table-I, that this composition has two more interesting metastable phases in $Imm2$ and $R\bar{3}m$ space groups, which are 9.26 and 9.86 meV/atom higher in energy than the ground state energy, respectively. The properties of all these three phases of Bi₁Sb₁ composition are described below:

$R\bar{3}m$ (160) phase:— This non-centrosymmetric structure is energetically the most stable structure of Bi_xSb_{1-x}. In this structure, Bi and Sb atoms are arranged in alternative layers stacked along the c -crystallographic direction of the cell [Fig. 3.3(a)]. The stacking sequence is: Bi-Sb-Bi-Sb-... . Two alternative monolayers of Bi and Sb form a bilayer which is being repeated along (001) direction. The Bi-Sb bond length within a bilayer is 3.04 Å. A hexagonal lattice structure can be observed in Fig. 3.3(b). The lattice parameters of the relaxed cell are given in table-I. Here, it is important to mention that we do not include Van der Waal's correction in the relaxation of this layered structure. We find that without Van der Waal's correction the percentage error between theoretical and experimental values [206, 207] of lattice parameter is ≈ 2.0 %, however, the agreement between the experimental and the theoretical values of lattice parameters worsens if we include the Van der Waal's correction in our calculations. We observe the same behavior in other layered structures reported in this paper. Therefore, we decide not to include the Van der Waal's correction in our first-principles calculations. A more detailed information about the crystal structure, thermodynamical, mechanical and electronic properties of this system is reported in ref [?]. In ref [?] we also reported the presence of a controllable Weyl semi-metallic phase in this system.

The electronic bandstructure was calculated along the high-symmetric directions of Brillouin zone [Fig. 3.3(c)]. Bandstructure calculated without-SOC [Fig. 3.3(d)] tells us that this system is an indirect bandgap semiconductor with an indirect gap of 0.16 eV. The direct bandgap is located at the L-point of Brillouin zone. When we include SOC in our calculation, we notice that each band splits into two spin non-degenerate bands and a Rashba-Dresselhaus spin-splitting occurs near the L-point [Fig. 3.3(e-f)]. Due to Rashba-Dresselhaus spin-splitting, VBT and CBB come close to each other reducing the direct gap at the L-point. We further calculate the S_x , S_y and S_z spin-projections on

the electronic bands using PyProcar code [208] [Fig. 3.3(f)]. Spin-splitting of spin-up and spin-down bands can be observed which gives us the signature of presence of bulk Rashba-Dresselhaus spin-splitting in this system. We further calculate the Rashba energy (E_R) and Rashba constant (α_R) as described in ref. [209]. The obtained values are: $E_R = 147.3$ meV, $\alpha_R = 10.43$ eVÅ for the CBB along the L-H direction and $E_R = 65.9$ meV, $\alpha_R = 4.71$ eVÅ for the VBT along the L-H direction. These values are comparable to that of GeTe compound, which was recently predicted to exhibit giant Rashba effect [209]. The shape of the spin-texture calculated in $k_x - k_y$ plane and centered at the L-point is not circular, as it should be for a pure Rashba case, rather it is elliptical [similar to Fig. 3.6(f)]. The change in the shape of spin-texture is due to the contribution from Dresselhaus effect, which is known to exhibit such kind of spin-texture in bulk materials. [188] Figure 3.3(g) shows the projected electronic DOS for this system. A positive energy gap can be noticed near the Fermi-level. We have also observed a SOC induced band-inversion near the L-point. The presence of a finite positive energy gap and the band-inversion reveals the topological insulating nature of this system.

FIGURE 3.3: a) Trigonal layered crystal structure of Bi_1Sb_1 in $R\bar{3}m$ space group. b) (001) top-view of the crystal showing the hexagonal lattice structure with presence of two different lattice sites. c) Hexagonal Brillouin zone of this structure with high-symmetry points. The Brillouin zone was obtained using AFLOW [3] software. The electronic bandstructure calculated d) without-SOC, e) with-SOC. f) Projection of S_x , S_y and S_z spin-components on the electronic bands along $H \rightarrow L \rightarrow H'$ direction. (001) direction was chosen as the quantization axis. Red color represents projection of spin-up states while blue color represents projection of spin-down states as depicted by the color scale. The black line demonstrates the original bands without any spin-projection. g) Projected electronic DOS calculated using a Γ k -mesh of size $11 \times 11 \times 11$. The dotted line shows the Fermi-level.

Imm2 (44) phase:– The first metastable structure of Bi_1Sb_1 composition is in *Imm2* space group. This metastable state is 9.26 meV/atom higher in energy than the ground state energy of Bi_1Sb_1 . Figure 3.4(a) shows the arrangement of atoms in this space group. This system lacks an inversion center. The bond length between nearest Bi and Sb atoms is 3.01 Å. The distribution of electron localization function in (010) plane of the crystal infers the covalent type bonding between nearest Bi and Sb atoms [Fig. 3.4(b)]. Our phonon calculation suggests that this structure is thermodynamically stable [Fig. 3.4(c)] at the DFT level. The electronic bandstructure calculation without-SOC reveals that this system is an indirect gap semiconductor [Fig. 3.4(d)]. Two electron pockets exist at T and S points. Additionally, two hole pockets can also be seen at W-point and along Γ –X direction.

Inclusion of SOC results in the spin-splitting of each band. Surprisingly, we notice that VBT and CBB cross each other at discrete points in momentum space along $\text{T}(\frac{1}{2}, \frac{1}{2}, 0)$ – $\text{W}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ direction. Such band-crossing between an electron and a hole pocket is very rare in nature. It reveals the existence of novel Weyl semi-metallic phase in this system. [86, 210, 211] Weyl points attracted considerable attention of physicists after the experimental discovery of Weyl fermions in 2015 by three independent experimental groups. [212–215] The two band-crossing points [red dotted circles in Fig. 3.4(e)] represent possible location of two Weyl points. One Weyl point is located above the Fermi-level and the another one is located below the Fermi-level. Such distribution of Weyl points in energy and momentum space leads to novel topological transport properties. [216, 217]

Figure 3.4(f) shows the projected DOS for this system. The semimetallic nature can be observed in this system. One can also notice strong hybridization between *s-s* and *p-p* orbitals of Bi and Sb. Majority of the states near Fermi-level are composed of *p* orbitals of Bi and Sb.

FIGURE 3.4: a) Orthorhombic crystal structure of Bi_1Sb_1 in $Imm2$ space group. b) Distribution of the electron localization function in (010) plane of this crystal. Blue color (0) represents the delocalization of electrons while the red color (1) represents the localization of electrons. c) The calculated phonon bandstructure. The electronic bandstructure, d) without-SOC e) with-SOC, calculated along the high symmetry lines of the Brillouin zone of $Imm2$ space group. We use Bilbao Crystallographic Server [4–8] to find the Brillouin zone. Dotted red circles along T-W path depict the possible location of type-II Weyl points. f) Projected electronic DOS calculated using a Γ k -mesh of size $15 \times 15 \times 15$. Dotted line represents the Fermi-level.

$R\bar{3}m$ (166) phase:– This metastable structure is very interesting because of the presence of inversion-center. To the best of our knowledge, this is the only structure of $\text{Bi}_x\text{Sb}_{1-x}$ compounds which has inversion-symmetry. Pure Bi and Sb semimetals have same symmetry ($R\bar{3}m$) in their ground state and both possess inversion-centers. Intuitively, in Bi_1Sb_1 composition, one replaces a Bi-atom by a Sb-atom in the cell and thus,

breaks the inversion-symmetry of the original crystal. Therefore, we expect an inversion-asymmetric ground state structure for Bi_1Sb_1 compound. Indeed, the obtained ground state phase ($R\bar{3}m$) of Bi_1Sb_1 has broken inversion-symmetry. Properties of the ground state structure have been discussed above. Since the electronic properties mainly depend up on the crystal symmetry, therefore, we expect different electronic properties for Bi_1Sb_1 in $R\bar{3}m$ space group.

Figure 3.5(a) shows the crystal structure of Bi_1Sb_1 composition in $R\bar{3}m$ space group. The primitive cell contains two atoms of Bi and two atoms of Sb. The stacking sequence along the (111) direction of primitive cell is: Sb-Bi-Bi-Sb-... Energetically, this structure is 9.86 meV/atom unfavorable than the ground state of Bi_1Sb_1 . The bond length between two nearest Bi and Sb atoms is 3.04 Å. The interlayer gap between two adjacent Bi-Sb, Sb-Sb and Bi-Bi layers is 1.6, 2.18 and 2.52 Å, respectively. The large atomic radius of Bi-atom is responsible for the large Bi-Bi interlayer gap. Figure 3.5(b) shows the distribution of electron location function in (101) plane of the primitive cell. Following the color scale, we infer that electrons are more localized near the Sb-atoms and delocalized near the Bi-atoms. Evidently, there is a covalent-type of bonding between Bi and Sb atoms of a Bi-Sb bilayer. Two adjacent Bi-Sb and Sb-Bi bilayers weakly interact. Moreover, two nearest Sb-Bi and Bi-Sb bilayers show weak Van der Waal's interaction due to the large interlayer separation between Bi-Bi planes. Therefore, we can consider this system as a stacking of Bi-Sb-Sb-Bi quadruple layers [see Fig. 3.5(b)], which are being repeated along (111) direction of the primitive cell. Interestingly, we find that this structure is thermodynamically stable at the DFT level [Fig. 3.5(c)].

FIGURE 3.5: a) Trigonal layered crystal structure of Bi_1Sb_1 in $R\bar{3}m$ space group. b) The distribution of electron location function in (101) plane of the primitive cell. Stacking of the Bi-Sb-Sb-Bi quadruple layers can be noticed. c) The calculated phonon bandstructure. The electronic bandstructure calculated d) without-SOC, e) with-SOC along the high symmetry directions in momentum space. Path in k -space was obtained using the Bilbao Crystallographic Server [4–8]. f) Projected electronic DOS calculated using a Γ k -mesh of size $15 \times 15 \times 15$. Dotted line represents the Fermi-level.

The electronic structure calculations are shown in Fig. 3.5(d-f). The bandstructure and DOS calculations manifest the semi-metallic nature of this system. In DOS, strong hybridization can be observed between s - s and p - p orbitals of Bi and Sb [Fig. 3.5(f)]. For without-SOC case, VBT and CBB bands touch each other along $\text{FA}(0, \frac{1}{2}, -\frac{1}{2})$ – $\text{T}(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ and Γ –FA directions in the momentum space. Along the Γ –FA path, we notice the linear dispersion of spin-degenerate bands in k -space exhibiting signature of the Dirac cone near the band crossing point. It is similar to the Dirac cone in case of

graphene, except for the fact that this crossing is not located at any high-symmetry point. Additionally, another band-crossing takes place exactly at the Fermi-level along the FA–T direction. This could yield some new intriguing phenomenon in this system, particularly, novel transport properties. When we turn on SOC in our calculations, we see that the VBT and CBB bands repel each other and the band-crossings disappear. The SOC opens an energy gap in the bandstructure and the system behaves like an indirect gap semiconductor. An electron-pocket exists at the FA-point and a hole-pocket can also be traced along the FA–T direction. The direct energy gap is located at the FA-point with a small energy gap of 50.7 meV. Moreover, we do not see any spin-splitting of the bands in presence of SOC, which is as expected for a centrosymmetric crystal. The inversion-symmetry of the crystal preserves the spin-degeneracy of bands.

3.3.3 Bi₃Sb₁

***R3m* (160) phase:**– The layered crystal structure of this non-centrosymmetric system is shown in Fig. 3.6(a). In this structure, we have a stacking sequence Sb-Bi-Bi-Bi... along the c-crystallographic direction of cell. We notice two kinds of bilayers, Bi-Sb and Bi-Bi bilayers. The bond length between nearest Bi and Sb atoms in a Bi-Sb bilayer is 3.03 Å, while the bond length between two nearest Bi atoms is 3.09 Å in the another Bi-Bi bilayer. Figure 3.6(b) shows the distribution of electron localization function in (110) plane of the crystal. In this figure., we can see that electrons are more localized at Sb-atomic sites and delocalized at the Bi-atomic sites. Furthermore, one can see there is covalent type of bonding between Sb-Bi and Bi-Bi atoms located within each bilayers. However, two adjacent bilayers interact by weak Van der Waal's interaction. In the calculated phonon frequency spectrum, we observe that all phonon frequencies are positive, except one phonon-branch. This branch has imaginary frequencies close to the Γ -point, which indicates that this structure is thermodynamically unstable at the DFT-level. However, it can be stabilized under suitable laboratory conditions, i.e by means of temperature, pressure, doping, etc.

FIGURE 3.6: a) Trigonal layered crystal structure of Bi_3Sb_1 in $R3m$ space group. b) Distribution of the electron localization function in (110) plane of this crystal. Blue color (0) represents the delocalization of electrons while the red color (1) represents the localization of electrons. c) The calculated phonon bandstructure. The electronic bandstructure d) without-SOC, e) with-SOC calculated along the high symmetry lines of the hexagonal Brillouin zone. f) The spin-texture calculated at a constant energy surface $E = 0.20$ eV above the Fermi-level. g) Projected electronic DOS calculated using a Γ k -mesh of size $11 \times 11 \times 7$. Dotted line represents the Fermi-level.

The electronic bandstructure calculations reveal the semi-metallic nature of this system. The bandstructure calculated without-SOC [Fig. 3.6(d)] shows the presence of a hole-pocket along the $K \rightarrow \Gamma$ direction. Also, one can see the evidence of an electron-pocket located at the M-point of Brillouin zone. The direct bandgap is located at the M-point $(\frac{1}{2}, 0, 0)$ with an energy gap of 0.17 eV. In presence of SOC, each band splits into two spin non-degenerate bands and the direct bandgap at M-point decreases due to large SOC of Bi and Sb atoms. The Kramer's degeneracy is still preserved at the time-reversal invariant points of Brillouin zone. We observe a Rashba-Dresselhaus type spin-splitting of bands near the M-point. The spin-projection on bands along $K \rightarrow M \rightarrow K'$ direction is similar as shown in Fig. 3.3(f). Fig. 3.6(f) shows the spin-texture calculated in $k_x - k_y$ plane centered at the M-point. Red color shows the projection of spin-up states, while blue color shows the projection of spin-down states. One can clearly see the splitting of different spin-states in $k_x - k_y$ plane. The shape of the spin-texture confirms the existence of Rashba-Dresselhaus spin-splitting in this system. The calculate values of spin-splitting parameters are: $E_R = 73.4$ meV and $\alpha_R = 7.87$ eV-Å for the CBB along M-K direction. Fig. 3.6(g) represents the projected DOS, which reveals the semimetallic nature of this system.

3.3.4 Bi₇Sb₁

C_1m_1 (08) phase:— The monoclinic crystal structure of Bi₇Sb₁ composition in C_1m_1 space group is shown in Fig. 3.7(a). Figure 3.7(b) shows the calculated phonon spectra. We do not see any imaginary frequency in the phonon spectrum, which suggests that this structure is thermodynamically stable. Chemically this structure is equivalent to Bi₈₈Sb₁₂ and this composition has been well studied by many experimental groups. The electronic bandstructure and DOS calculation reveal the semi-metallic nature of this system. From bandstructure calculation without-SOC [shown in Fig. 3.7(c)] one can notice that an electron-pocket exists at the L-point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with a small direct energy gap at the L-point. However, the presence of SOC leads to the spin-splitting of the bands [Fig. 3.7(d)]. Spin-splitting has more pronounced effects on the bandstructure close to the L-point. We further notice that band-inversion takes place in presence of SOC which yields novel topological features in this Bi-rich compound [Fig. 3.7(e-f)]. Electronic DOS calculation (shown in Fig. 3.7(g)) reveal the presence of a small energy gap which is a fundamental requirement to realize a topological insulating phase.

FIGURE 3.7: a) Monoclinic crystal structure of Bi_7Sb_1 in C_{1m1} space group. b) The calculated phonon bandstructure. The electronic bandstructure, c) without-SOC d) with-SOC. Figure e) and f) depict the p -orbital projection of Bi and Sb atoms for without SOC and with-SOC case, respectively. Red circles represent Bi- p orbitals while green circles represent Sb- p orbitals. The high symmetric k -path was obtained using the AFLOW [3] software. g) Projected electronic DOS calculated using a Monkhorst-pack k -mesh of size $11 \times 11 \times 7$. Dotted line represents the Fermi-level.

FIGURE 3.8: a) Monoclinic crystal structure of Bi_9Sb_1 in C_{1m1} space group. b) The calculated phonon bandstructure. The electronic bandstructure, c) without-SOC d) with-SOC. e) Projection of S_x , S_y and S_z spin-components on the electronic bands along $\Gamma \rightarrow Y \rightarrow F$ direction. f) Projected electronic DOS calculated using a Monkhorst-pack k -mesh of size $7 \times 7 \times 9$. Dotted line represents the Fermi-level.

3.3.5 Bi₉Sb₁

C_1m_1 (08) phase:– The crystal structure of Bi₉Sb₁ in C_1m_1 space group is shown in Fig. 3.8(a). The primitive cell contains one Sb and nine Bi atoms. The phonon calculation shows that this structure is thermodynamically unstable at 0 K due to the presence of small imaginary frequencies near Γ -point. However, one might stabilize the unstable phonon modes at higher temperature. The electronic bandstructures calculated without-SOC and with-SOC are given in Fig. 3.8(c-d). We observe that strong SOC of this Bi-rich composition lifts the spin-degeneracy of bands and leads to the band-inversion near Y-point ($\frac{1}{2}, \frac{1}{2}, 0$) of Brillouin zone. This band-inversion yields topological insulating phase in this system which has already been experimentally demonstrated [85, 218]. We further calculate the projection of S_x , S_y and S_z spin-components on the electronic bands (Fig. 3.8e). A Rashba-Dresselhaus type spin-splitting can be noticed near the Y-point. Calculated values of the spin-splitting parameters are: $E_R = 16.26$ meV, $\alpha_R = 2.25$ eVÅ for CBB along Γ -Y direction; and $E_R = 29.94$ meV, $\alpha_R = 5.96$ eVÅ for CBB along Y-F direction.

3.4 Simulated x-ray diffraction patterns and Wyckoff positions

In order to assist experimentalists in the detection of interesting Bi-Sb phases, we present the simulated x-ray diffraction (XRD) patterns and Wyckoff positions of all the considered phases of Bi-Sb binaries. XRD patterns were simulated using Mercury software [219] for the optimized crystal structures using following parameters:– x-ray wavelength = 1.54056 Å; and full width at half maxima (FWHM) of peaks = 0.1. All the reported Wyckoff positions also correspond to the optimized crystal structures.

Bi₁Sb₇ (P_1m_1 space group no. – 06)

FIGURE 3.9: Simulated X-ray diffraction pattern of Bi_1Sb_7 in P_1m_1 space group.TABLE 3.2: Wyckoff positions for Bi_1Sb_7 in P_1m_1 space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	1b	0.071	0.500	0.716
Sb2	1b	0.603	0.500	0.685
Sb3	1a	0.109	0.000	0.446
Sb4	1a	0.568	0.000	-0.032
Sb5	1a	0.101	0.000	-0.072
Sb6	1a	0.574	0.000	0.473
Sb7	1b	0.593	0.500	0.180
Bi1	1b	0.079	0.500	0.221

Bi_1Sb_1 ($R3m$ space group no. – 160)

FIGURE 3.10: Simulated X-ray diffraction pattern of Bi_1Sb_1 in $R3m$ space group. The simulated pattern is consistent with the experimental data reported in Ref. [9].

TABLE 3.3: Wyckoff positions for Bi_1Sb_1 in $R3m$ space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	3a	0.000	0.000	0.353
Bi1	3a	0.000	0.000	0.818

Bi_1Sb_1 ($Imm2$ space group no. – 44)

FIGURE 3.11: Simulated X-ray diffraction pattern of Bi_1Sb_1 in $Imm2$ space group.

TABLE 3.4: Wyckoff positions for Bi_1Sb_1 in $Imm2$ space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	2a	0.000	0.000	0.719
Bi1	2b	0.000	0.500	0.133

Bi_1Sb_1 ($R\bar{3}m$ space group no. – 166)

FIGURE 3.12: Simulated X-ray diffraction pattern of Bi_1Sb_1 in $R\bar{3}m$ space group.

TABLE 3.5: Wyckoff positions for Bi_1Sb_1 in $R\bar{3}m$ space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	6c	0.000	0.000	0.121
Bi1	6c	0.000	0.000	0.612

Bi_3Sb_1 ($R\bar{3}m$ space group no. – 160)

FIGURE 3.13: Simulated X-ray diffraction pattern of Bi_3Sb_1 in $R\bar{3}m$ space group.

TABLE 3.6: Wyckoff positions for Bi_3Sb_1 in $R\bar{3}m$ space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	3a	0.000	0.000	0.063
Bi1	3a	0.000	0.000	0.791
Bi2	3a	0.000	0.000	0.297
Bi3	3a	0.000	0.000	0.564

Bi_7Sb_1 (C_1m_1 space group no. – 08)

FIGURE 3.14: Simulated X-ray diffraction pattern of Bi_7Sb_1 in C_1m_1 space group.

TABLE 3.7: Wyckoff positions for Bi_7Sb_1 in C_1m_1 space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	2a	0.729	0.000	0.737
Bi1	4b	0.232	0.252	0.240
Bi2	4b	0.534	0.245	0.705
Bi3	2a	0.231	0.000	0.745
Bi4	2a	0.0301	0.000	0.209
Bi5	2a	0.537	0.000	0.187

Bi₉Sb₁ (C_1m_1 space group no. – 08)

FIGURE 3.15: Simulated X-ray diffraction pattern of Bi₉Sb₁ in C_1m_1 space group. This data is in excellent agreement with experiments [10].

TABLE 3.8: Wyckoff positions for Bi₉Sb₁ in C_1m_1 space group

site	Multiplicity and Wyckoff letter	x	y	z
Sb1	2a	0.152	0.000	0.413
Bi1	2a	0.684	0.000	0.879
Bi2	2a	0.282	0.000	0.084
Bi3	2a	0.880	0.000	0.284
Bi4	2a	0.089	0.000	0.672
Bi5	2a	-0.052	0.000	0.017
Bi6	2a	0.547	0.000	0.216
Bi7	2a	0.349	0.000	0.816
Bi8	2a	0.752	0.000	0.611
Bi9	2a	0.494	0.000	0.477

3.5 Chapter Summary

In summary, we have performed a systematic structural search for 35 different compositions of $\text{Bi}_x\text{Sb}_{1-x}$ ($0 < x < 1$) using the minima hopping method. We have obtained many metastable structures with negative formation energy. Bi_1Sb_7 , Bi_1Sb_1 , Bi_7Sb_1 and Bi_9Sb_1 compositions lie on the convex-hull and have the lowest energy ground state in P_1m_1 , $R3m$, C_1m_1 and C_1m_1 space groups, respectively. We also find two other interesting metastable structures of Bi_1Sb_1 in $Imm2$ and $R\bar{3}m$ space groups. These metastable structures are thermodynamically stable and show interesting electronic properties. We have further performed the electronic bandstructure calculations of the selected structures and studied the effect of SOC on the bandstructure. We have also found evidence of giant Rashba-Dresselhaus spin-splitting effect in several systems, which is very useful from spintronics device application point of view.

Thermoelectric Properties of Bi-Sb Binaries

4.1 Introduction

In addition to the attractive electronic properties, $\text{Bi}_x\text{Sb}_{1-x}$ binaries also exhibit impressive thermoelectric performance. Even though the thermoelectric properties of Bi, Sb and Bi-Sb solid solutions have been extensively studied by experimentalists [16–18, 20, 220], a detailed theoretical investigation of thermoelectric properties of stoichiometric $\text{Bi}_x\text{Sb}_{1-x}$ binaries is still lacking in literature. Therefore, we also explore the thermoelectric properties of the new structures obtained from the structural search.

We find that the compositions which crystallize in the rhombohedral structure exhibit values of the Seebeck coefficient and power factor similar to that of Bi_2Te_3 at room temperature.

4.2 Computational Details

We perform the calculation of the thermoelectric properties such as the Seebeck coefficient (S) and the power factor ($S^2\sigma/\tau$). These thermoelectric properties were obtained by using the solution of the Boltzmann transport equations (BTE) within the constant relaxation time approximation (CRTA) as implemented in the BOLTZTRAP

code [221, 222]. This theory allows us to calculate the Seebeck coefficient tensor independently of the electronic relaxation time (τ) while the electronic conductivity still depends on τ . The code relies on the rigid band approximation to change the carrier concentration by rigid shift of the chemical potential (μ) into valence or conduction bands while the effect of temperature on the electronic bands is neglected. The results obtained within the BOLZTRAP code have shown very good agreement with experimental measurements, specially for bulk materials [223, 224]. In addition to the bulk systems, it is also possible to predict the thermoelectric behavior in special cases like, nanotubes [225], highly doped narrow-band gap semiconductors [223] and under effect of uni-axial [224] and hydrostatic [226] pressure. It is always good to compare the theoretical values of the Seebeck coefficient with those measured by experimentalists. For $\text{Bi}_x\text{Sb}_{1-x}$, most of the experiments were carried on the thin films and heterostructures, which is not exactly same as the results obtained from bulk. Also, experiments suggest that the carrier concentration varies significantly with temperature (from one to two orders of magnitude in the temperature range 10 - 200 K) [41, 42]. Therefore, we decide to plot the thermoelectric properties as a function of the carrier concentration. We also notice that the values of the Seebeck coefficient are very sensitive to the choice of doping. Therefore, we provide results for the chemical potential dependence of the thermoelectric properties. The power factor is conveniently plotted in units that allow to get the usual units ($\mu\text{W}/\text{cmK}^2$) by multiplying by the relaxation time (τ) which is generally of the order of 10^{-14} seconds.

In the following sections, we present the thermoelectric properties of each structures mentioned in Table-I.

4.2.1 Bi_1Sb_7

P_1m_1 (space group number-06) phase:— Even though this crystal structure is not isotropic, the values of the Seebeck coefficient along three cartesian coordinates are very similar. Therefore, we decide to plot the average of the trace of Seebeck coefficient as a function of the carrier concentration [Fig. 4.1(a)]. Negative values of the carrier concentration are related to the electron doping (shift of the chemical potential inside the conduction band) while positive values refer to the hole doping. We also calculate the power factor at different values of temperature. We find that the Seebeck coefficient

values are relatively small compared to that of Bi_2Te_3 , however, the power factor is comparable at 300 K [221]. This is mainly because of the high electrical conductivity that we obtain in this system which is evident from the DOS plot [Fig. 3.2(g)]. Here, we must remark that even though the BOLTZTRAP code accurately reproduces the experimental values of the Seebeck coefficient, this code usually overestimates the Seebeck coefficient at high temperatures since the theory does not take into account the scattering processes that usually increase with temperature. Nevertheless, the calculated Seebeck coefficient values are, in general, very accurate with increasing pressure [226]. We also observe that the Seebeck coefficient, and the power factor exhibit almost symmetric behavior with respect to the type of carriers. The small differences come from the shift of the Fermi-level towards the valence or conduction bands.

FIGURE 4.1: Carrier concentration dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_7 composition in P_1m_1 space group.

FIGURE 4.2: Chemical potential dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_7 composition in P_1m_1 space group.

4.2.2 Bi₁Sb₁

***R3m* (160) phase:**– The semiconducting character of this structure helps to improve the Seebeck coefficient. Due to the existence of a band gap, the electronic conductivity is smaller compared to Bi₁Sb₇. The *R3m* symmetry yields anisotropic behavior in the transport properties. This has been reported in compounds with similar crystal structure such as Bi₂Te₃ and Sb₂Te₃ which are two of the best known room-temperature thermoelectric materials. Here, the transport properties are degenerate in-plane (along the *x* and *y* directions) while different along out-of-plane (*z*) direction. In our case, as well as for the mentioned tellurides compounds, the in-plane Seebeck coefficient is higher than its out-of-plane counterpart [see Fig. 4.4]. This is due to the fact that the atoms are “stacked” along the *z*-direction which periodically changes the chemical environment. From Figs. 4.3(a-b), we can conclude that the best thermoelectric performance is reached when the compound is doped with holes (positive doping). This is also true for the mentioned tellurides compounds [224, 226]. In Fig. 4.3, we decide to plot the average of the trace for *S* and *S*² σ/τ , because we consider that it is more significant to address the change of the thermoelectric properties as function of temperature. Fig. 4.4 shows the same quantities but as a function of the chemical potential.

FIGURE 4.3: Carrier concentration dependence of a) average of the trace of the Seebeck coefficient, and b) the power factor (*S*² σ/τ) at different values of temperature for Bi₁Sb₁ in *R3m* space group.

***Imm2* (44) phase:**– The anisotropy of the system is present in the electronic transport properties [see Fig. 4.6]. The maximum value of Seebeck coefficient for each of the three coordinates is different. This is because the mobility of carriers differs in each direction. Similar results have been found for BiSb thin films, where the thin film was doped with holes and at certain temperature the Seebeck coefficient goes from

FIGURE 4.4: Chemical potential dependence of a) two non-degenerate cartesian components and the average of the trace of the Seebeck coefficient at 300K, b) the average of the trace of the Seebeck coefficient, and c) the power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_1 in $R3m$ space group.

positive to negative due to the change in the mobility of the minority carriers [41]. Even though the values of the Seebeck coefficient [Fig. 4.5(a)] are rather smaller than those found for the $R3m$ phase of Bi_1Sb_1 , the overall power factor [Fig. 4.5(b)] is comparable between the two phases. This is attributed to the semi-metallic nature of this structure, which increases the mobility of electrons and holes giving it an outstanding electrical conductivity. Fig. 4.6 shows the same quantities but as a function of the chemical potential.

$R\bar{3}m$ (166) phase:— This is the first structure where the thermoelectric performance improves when the system is doped with electrons instead of holes. Even though, the Seebeck coefficient seems to be smaller for n-type doping than for p-type doping [Fig. 4.7(a)]. We attribute this to the presence of the electron pocket located at the FA high symmetry point. Due to the rhombohedral geometry, this metastable configuration also shows anisotropic transport properties similar to that of Bi_1Sb_1 in $R3m$ space group [see Fig. 4.8].

FIGURE 4.5: Carrier concentration dependence of a) average of the trace of the Seebeck coefficient, and b) the power factor ($S^2\sigma/\tau$) at different values of temperature for Bi_1Sb_1 in $Imm2$ space group.

FIGURE 4.6: Carrier concentration dependence of a) three cartesian components of the Seebeck coefficient at 300 K, b) the average of the trace of the Seebeck coefficient, and c) the power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_1 in $Imm2$ space group.

4.2.3 Bi_3Sb_1

$R\bar{3}m$ (160) phase:— At this concentration, the crystal structure is similar to the structure of Bi_1Sb_1 in $R\bar{3}m$ phase. Even though, the rhombohedral crystal structure is anisotropic, here we report the average of the trace of the Seebeck coefficient [Fig. 4.9(a)]

FIGURE 4.7: Carrier concentration dependence of a) the average of the trace of the Seebeck coefficient, and b) the power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_1 in $R\bar{3}m$ space group.

FIGURE 4.8: Chemical potential dependence of a) two non-degenerate cartesian components and the average of the trace of the Seebeck coefficient at 300K, b) the average of the trace of the Seebeck coefficient, and c) the power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_1Sb_1 in $R\bar{3}m$ space group.

and the power factor [Fig. 4.9(b)]. The three cartesian components of the Seebeck coefficient are reported in Fig. 4.10. The overall values are very similar to what we found for Bi_1Sb_1 in space group $R\bar{3}m$. However, for hole doping, we notice that the maximum values of Seebeck coefficient and power factor are smaller in Bi_3Sb_1 than that of in Bi_1Sb_1 . We also observe that the Seebeck coefficient attains larger values for the

hole doping (positive carrier concentration) than compared to the electron doping. This can be explained from the DOS plot. In Fig. 3.6(g), one can notice that the Fermi-level is closer to the valence bands which makes this system very sensitive for the hole doping concentrations.

FIGURE 4.9: Carrier concentration dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_3Sb_1 in $R3m$ space group.

FIGURE 4.10: Chemical potential dependence of a) two non-degenerate cartesian components of the Seebeck coefficient at 300K, b) the average of the trace of the Seebeck coefficient, and c) the power factor ($S^2\sigma/\tau$) for different values of temperature for Bi_3Sb_1 in $R3m$ space group.

4.2.4 Bi₇Sb₁

Even though, this crystal structure is anisotropic, Seebeck coefficients exhibit near isotropic values. Again the maximum values of Seebeck coefficient correspond to the hole doping. Contrary to what we found in the previous configurations of Bi-Sb binaries, this particular structure reaches its maximum value of the Seebeck coefficient at 300 K, and with further increase in the temperature, we observe decrease in the Seebeck coefficient. With electrons as majority carriers, the maximum value of Seebeck coefficient lies at 200 K [Fig. 4.11(a)]. This is close to experimental results on Bi-Sb alloys (for small Sb-concentration) where the maximum is reached at temperatures just above 100 K and with values around $-100\mu\text{V/K}$ [41].

FIGURE 4.11: Carrier concentration dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi₇Sb₁ in C_1m_1 space group.

FIGURE 4.12: Chemical potential dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi₇Sb₁ in C_1m_1 space group.

4.2.5 Bi₉Sb₁

At this concentration, we notice that one can achieve better thermoelectric performance by doping this system with holes instead of electrons. The asymmetry in the power factor plot can be clearly seen in Fig. 4.13(b). It is well known that semiconductors exhibit better thermoelectric performance than metals. The semiconducting nature of this composition makes it a better thermoelectric material for hole doping concentrations. The maximum of the Seebeck coefficient is found at the middle of the band-gap. From Figs. 3.8(g) and 3.7(g) one can observe that the Fermi-level is closer to the valence band for which explains the large Seebeck coefficient for hole doping for both Bi-rich compositions. For Bi₉Sb₁, we find that the maximum Seebeck coefficient is -114 $\mu\text{V/K}$ for electrons and 150 $\mu\text{V/K}$ for holes.

FIGURE 4.13: Carrier concentration dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi₉Sb₁ in C_1m_1 space group.

FIGURE 4.14: Chemical potential dependence of the a) Seebeck coefficient, and b) power factor ($S^2\sigma/\tau$) for different values of temperature for Bi₉Sb₁ in C_1m_1 space group.

4.3 Chapter Summary

Our results show that Bi-Sb binaries can exhibit outstanding thermoelectric performance even at high temperatures. However, we suggest further investigation related to thermal conductivity and electrical conductivity. We encounter the issue that, so far, Bi-Sb alloys were considered for low temperature thermoelectricity applications. Direct comparison of our results with experimental measurements is complicated, since most of the experiments were carried on thin films and we consider bulk systems in our calculations. However, our theoretical results for several systems are in good agreement with previous experimental studies. The systematic shift of the power factor with respect to the carrier concentration is due to the metallicity of mostly of the structures. For all Bi-rich compositions, we notice that the power factor is asymmetric for electron and hole doping concentrations, and it attains larger values for hole doping. Also, Bi-rich compositions inherit a finite positive bandgap, which makes Bi-rich compositions good p-type thermoelectrics.

Prediction and Control of Spin Polarization in a Weyl Semimetallic Phase of BiSb

5.1 Introduction

Weyl fermions have recently attracted the attention of researchers due to their unique intriguing physical properties such as presence of discontinuous Fermi-arcs [210, 227–229], quantized anomalous Hall effect [216, 230], quantum transport [231], anomalous magnetoresistance [232], etc. Weyl fermions are alternative massless solution of two-component Dirac equation, which is also known as Weyl equation [233]. These fermions were initially discovered by the particle physicists to explain the chiral and massless behavior of neutrinos (assuming neutrinos have negligible mass). In condensed matter systems, Weyl fermions can be realized as low-energy excitations near the band touching points of two non-degenerate bands at discrete $\mathbf{k}$ -points in the momentum space of a bulk system. These gapless band touching points are known as Weyl nodes or Weyl points [210]. Close to a Weyl point, bands have linear dispersion in all directions in $\mathbf{k}$ -space. In 3D, Weyl points are similar to the well-known Dirac points except for the fact that Weyl points are spin non-degenerate, but Dirac points have spin-degeneracy. By breaking either the time-reversal (TR) symmetry or space-inversion (I) symmetry, one can lift up the degeneracy of the Dirac points in a Dirac semimetal [234] and realize

a Weyl semi-metal (WSM) with non-degenerate Weyl points in $\mathbf{k}$ -space. Hence, the lack of TR-symmetry or I-symmetry is an essential requirement for realization of WSM phase in 3D systems. However, unlike Dirac points, the Weyl points are robust against small perturbations in the system provided the translational symmetry is preserved, and are topologically protected due to the non-trivial band topology of the system [235].

Each Weyl point can be characterized by an associated chirality (left handedness or right handedness) or a monopole and an antimonopole having charge +1 or -1, respectively. Weyl points are always created in pairs *via* pair-creation of a monopole and an antimonopole [217, 236, 237]. Similarly, they can disappear only *via* pair-annihilation process. Thus, the total charge in $\mathbf{k}$ -space is always zero and the total number of Weyl points is always even. In case of I-symmetric WSMs (broken TR-symmetry), all Weyl points are located at the same energy level and thus, by aligning the Fermi-level to the energy of the Weyl points one can realize a nodal semi-metallic state. On the other hand, I-asymmetric WSMs (with TR-symmetry) have Weyl points separated in both momentum and energy space. This eliminates the possibility of realization of a nodal semi-metallic state by tuning the Fermi-level and thus, separate electron and hole Fermi-surfaces exist in the I-asymmetric WSM systems. Such systems are very interesting and possess novel topological transport properties. Zyuzin et al. [216] have predicted that the application of an external magnetic field along the direction of vector connecting two opposite Weyl points can induce an equilibrium nondissipative current in the system. This current can be measured experimentally and is proportional to both the applied magnetic field and the energy difference between two opposite Weyl points.

In recent years, many different theoretical proposals have been reported for realization of Weyl semimetallic (WSM) phase in inversion (I)-symmetric [211, 227, 238, 239] and I-asymmetric systems [86, 237, 240–247]. Several experimental groups have recently reported the experimental realization of WSM phase in single crystal compounds [248–251] and in photonic crystals [252]. To the best of our knowledge, there is no report of controllable WSM phase in a stable compound. However, ferroelectric-like polar WSM compounds having large spin-orbit coupling (SOC) could open a new avenue of realization of novel transport properties. When we combine SOC with ferroelectricity, we obtain a class of novel multifunctional materials, called Ferro-Electric Rashba Semiconductors (FERSC) [253]. Recently, Picozzi *et al.* have theoretically demonstrated the possible control and switching of the spin-texture by means of an electric field in

GeTe [253, 254]. This prediction was later experimentally corroborated [255]. Furthermore, the recent experimental discovery of ferroelectric-metals has generated huge interest in polar materials [256, 257]. The interplay between SOC and polarity could yield exotic quantum phenomenon in polar ferroelectric-metals [258, 259]. Here, we take advantage of the large SOC of Bi and Sb atoms [260–262] and the ferroelectric polarization of BiSb semiconductor to control the spin-related properties in the present BiSb system.

The $\text{Bi}_{1-x}\text{Sb}_x$ alloys are the first generation topological insulator [87]. In 2013, Kim *et al.* reported experimental evidence of WSM phase in $\text{Bi}_{1-x}\text{Sb}_x$ alloys for $x = 3\%$ by magnetoresistance measurements [232]. In the present work, we report a stoichiometric crystal structure of BiSb with broken I-symmetry. This structure belongs to the space group 160 ($R\bar{3}m$) and has non-trivial band topology. By means of first-principle calculations, we observe a pressure-induced WSM phase transition in the present BiSb system in 4.0 – 6.0 GPa pressure range. We have further exploited the coupling between pressure and electric field to realize and control the chirality of Weyl points in BiSb.

5.2 Computational Details

We used the projected augmented wave (PAW) method implemented in the VASP code to perform all DFT-based first principle calculations [201, 202]. We considered fifteen valence electrons of Bi ($5d^{10}6s^26p^3$) and five valence electrons of Sb ($5s^25p^3$) in the PAW pseudo-potential. For exchange-correlation potential, we used exchange-correlation functional parameterized by Perdew-Burke-Ernzerhof [136]. For all calculations presented in this paper, we used a conventional unit-cell of BiSb (space group 160: $R\bar{3}m$), containing 3 atoms of Bi and 3 atoms of Sb. We used 650 eV as kinetic energy cut-off for the plane wave basis set and a Gamma $10 \times 10 \times 10$ k -point mesh has been employed for all DFT based first principle calculations. For convergence of electronic self-consistent calculations, a total energy difference criterion was defined as 10^{-8} eV. For ionic relaxations, the cell was relaxed, first in the internal coordinates and then in the volume until the total energy difference between two consecutive steps was smaller than 10^{-8} eV and the total residual forces were less than 10^{-5} eV/Å. Spin-orbit interaction was included for all ionic relaxations. We use ABINIT code to calculate phonon spectra [263–265]. We have used a q-mesh of size $4 \times 4 \times 4$ for all phonon calculations. Band-structure

calculations were done (i) with spin-orbit coupling (SOC) and (ii) without SOC. For all pressure dependent electronic structure calculations, we employ isotropic pressure ranging from 1 GPa to 10 GPa on the original unit cell. To visualize the open Fermi-arcs, we have calculated the spin-texture at (001) surface of a BiSb-slab [208]. This 55.6 Å thick slab consists 14-bilayers of BiSb and a vacuum layer of 12.0 Å thickness. VESTA [266], PyProcar [208] and MAYAVI [267] softwares were used to make some figures.

5.3 Results and Discussions

5.3.1 Crystal structure of BiSb (in $R3m$ space group)

In the $R3m$ space group, BiSb has layered structure with alternative layers of Bi and Sb atoms oriented along the c-axis of the rhombohedral unit-cell [Fig. 5.1(a)]. Two alternative layers of Bi and Sb form a bilayer, which is repeated along the c-crystallographic direction of the unit-cell. Lattice parameters of the fully relaxed unit-cell are; $a = b = 4.51$ Å, $c = 11.92$ Å and the angles are; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$. It is worthy to note that this system lacks space-inversion symmetry, while it preserves time-reversal symmetry. Therefore, its bulk bands are in general spin non-degenerate which is the reason of realization of WSM phase in this material. Figure 5.1(b) shows the hexagonal ordering of atoms from (001) direction.

Figure 5.1(c) shows the distribution of electron localization function (ELF) in the real space and Figs. 5.1(d-e) represents the real space contour plots of the calculated electron location function (ELF) along (100) and (110) directions. ELF analysis gives us information about the bonding nature of atoms in the bulk systems. Color scale is same for all ELF plots [Figs. 5.1(c-e)]. The ELF plots span values between 0 (blue) and 1 (red). Blue/Red color corresponds to the depletion/excess of the charges where electrons delocalize/localize. From Fig. 5.1(c), it is evident that the interlayer bonding between the Bi and Sb atoms of a bilayer is of covalent type. However, the bonding between two adjacent bilayers can be characterized by weak Van der Waal's forces. Thus, in principle one can easily exfoliate one bilayer from another and make thin-film of desired numbers of bilayers, which will be of interest for new experiments. The inter-spacing between Bi and Sb monolayers (inside a bilayer) is 1.58 Å, while the intra-spacing between two

FIGURE 5.1: (a) Layered crystal structure of BiSb oriented along c -crystallographic direction. Bi atoms are represented in purple color and Sb atoms are in orange color. (b) Hexagonal lattice structure of BiSb in a - b plane. (c) Distribution of electron localization function in real space. (d, e) Contour plots of electron localization function along (100) and (110) directions, respectively. Red/Blue colors correspond to the localization/delocalization of the electrons.

alternate Bi-Sb bilayers is 2.33 Å [see Fig. 5.1(a)]. The bond length between two nearest Bi and Sb atoms is 3.04 Å.

5.3.2 Phonon bandstructure

To study the dynamical stability of BiSb ($R3m$ phase), we performed phonon calculations using Density Functional Perturbation Theory (DFPT) as implemented in ABINIT code [263–265]. Two different approximations for exchange-correlation functional (LDA and GGA) and a q -mesh of size $4 \times 4 \times 4$ were used for all phonon calculations. Since spin-orbit coupling (SOC) is known to significantly affect the phonon modes of pristine Bi and Sb atoms [260–262], we have calculated phonon modes with and without including SOC for both LDA and GGA approximations. Figure 5.2 shows the calculated

phonons modes at 0.0 , 5.0 and 10.0 GPa applied pressures. We used different approximations for exchange-correlation functional (LDA, LDA+SOC, PBE and PBE+SOC) to compute phonon modes at different values of applied pressure. We notice that phonons are positive till 10.0 GPa for all four approximations of exchange-correlation functional (GGA, GGA+SOC, LDA and LDA+SOC). However, phonon modes start becoming softer at higher pressures which indicates that a pressure-induced structural phase-transition could occur at high pressures. Hence, phonon calculations suggest that this structure is vibrationally stable at the level of DFPT calculations. This structure has already been experimentally synthesized due to its novel thermoelectric properties at low temperatures [17, 206].

FIGURE 5.2: Calculated phonon spectra under (a) GGA, (b) GGA+SOC, (c) LDA and (d) LDA+SOC approximations and at 0.0, 5.0 GPa and 10.0 GPa isotropic pressures. We found that phonon frequencies are positive for all cases.

The electronic bandstructure calculations (shown in Fig. 5.3) reveal that, without-SOC, BiSb is an indirect bandgap semiconductor with indirect energy gap of 0.16 eV. The direct bandgap is located at the L-point of the hexagonal Brillouin zone. In the presence of SOC, each band of BiSb shows spin-splitting. However, the spin-degeneracy of bands still exists at the L-point (Kramers' point), which confirms that BiSb breaks

the I-symmetry but preserves the time-reversal (TR)-symmetry [Fig. 5.4(a)]. For TR-symmetric systems, lack of I-symmetry is an essential requirement for realization of WSM phase. We also notice that the SOC-induced band-inversion takes places along $H \rightarrow L$ direction. Such a band-inversion process yields topologically protected conducting surface states in the bulk insulating system. Thus, the bandstructure calculations exhibit the non-trivial topological nature of bands in the BiSb system.

FIGURE 5.3: Electronic bandstructure of BiSb calculated without-SOC (a), and with-SOC (b). The effect of large SOC can be observed in the spin-splitting of bands near Fermi-level. Projection of Bi-6 p and Sb-5 p orbitals on bands close to the L-point is shown in (c) without-SOC and (d) with-SOC. Violet circles correspond to the projection of Bi-6 p orbitals and orange circles represent the projection of Sb-5 p orbitals.

SOC induced band-inversion can be clearly observed along $H \rightarrow L$ direction.

According to the theoretical model proposed in Ref. [86, 268], one can possibly realize a gapless WSM phase by varying a control parameter m in the effective model Hamiltonian $H(\mathbf{k}, m)$ of a bulk insulating system. For I-asymmetric systems, the gapless WSM phase exists for a finite range of the control parameter m . In the present work, we use isotropic pressure (P) as the control parameter to tune the bulk bandgap. Figure 5.4(a) shows the evolution in the direct bandgap along $H \rightarrow L$ direction for different values of applied pressure. The direct bandgap along $H \rightarrow L$ direction (E_g^L) decreases as we increase pressure up to 3.0 GPa [Fig. 5.4(b)]. Interestingly, with further increase in pressure, E_g^L becomes zero at 4.0 GPa pressure and remains zero until 6.0 GPa. In this pressure range, the conduction band bottom (CBB) and the valence band top (VBT) accidentally touch

each other along $H \rightarrow L$ direction (see Fig. 5.4(a) for 5.0 GPa case). The dispersion of the bands close to the band touching point is linear in $\mathbf{k}$ and the band touching point is not located at any Kramers' points or along any high-symmetry direction of the bulk Brillouin zone. These facts give us signatures of a Weyl semimetallic phase in 4.0 – 6.0 GPa pressure range. When we further increase the external pressure, we observe that the direct bandgap E_g^L reopens. However, the system becomes semimetallic (SM) due to crossing of the Fermi-level by other topologically trivial bands. Thus, a pressure induced non-trivial insulator-WSM-semimetal phase transition takes place in the present BiSb system. A similar pressure induced phase transition has been reported for trigonal Te and Se systems [244].

Figure 5.5(a) shows the projection of spin-components (S_x , S_y , and S_z) on the electronic bands for 5.0 GPa applied pressure. We observe similar behavior of spin-projections for other values of P ($4.0 \leq P \leq 6.0$). Here, we have chosen the (001) direction as the quantization axis for all spin dependent calculations. In Fig. 5.5(a), we calculate the band structure along two different directions in $\mathbf{k}$ -space: $H/2 \rightarrow L \rightarrow H'/2$ and $P/2 \rightarrow L \rightarrow Q/2$ (see Fig. 5.5(c) for directions). Along the $H/2 \rightarrow L \rightarrow H'/2$ direction, one can clearly notice that two non-degenerate gapless points are present in the vicinity of the L-point. Such gapless points in $\mathbf{k}$ -space are called Weyl points or Weyl nodes and unlike Dirac points they are 2-fold degenerate rather than 4-fold. Weyl points (W1) along $H/2 \rightarrow L \rightarrow H'/2$ direction are located near the Fermi-level and are related by TR-symmetry (L-point as Kramers' point). Hence, these two points have the same chirality and topological charge. Bandstructure along $P/2 \rightarrow L \rightarrow Q/2$ direction reveals presence of two more non-degenerate gapless points located slightly below Fermi-level. These two gapless points represent another set of Weyl points depicted by W2. W2 Weyl points are related by TR-symmetry and hence, they share the same chirality and topological charge. Even though two Weyl points can be noticed along $P/2 \rightarrow L \rightarrow Q/2$ direction [Fig. 5.5(a)], only one Weyl point lies inside the first Brillouin zone. Here, it is worthy to mention that P and Q are not high-symmetry points in Brillouin zone, and Q point lies outside of the first Brillouin zone [Fig. 5.5(c)]. To determine the chirality of W1 and W2 Weyl points, we have calculated the Berry flux through a closed surface enclosing only one Weyl point at a time [269, 270]. Our calculations reveal that W1 and W2 have opposite chirality and therefore, they carry opposite topological charges (supplemental information). Consequently, W1 behaves like a monopole and W2 behaves

like an antimonopole in $\mathbf{k}$ -space. These two opposite Weyl points are located at different energy values. Existence of such opposite Weyl points, located at different energies, is attributed to the broken I-symmetry of the present BiSb system. Since W1 and W2 are separated in momentum space as well as in energy, it is impossible to realize a nodal semimetallic phase by tuning the Fermi-level and there always exists a state with separate

FIGURE 5.4: (Color online) Figure (a) represents the evolution of the electronic band structure (with-SOC) for different values of applied isotropic pressure, $P = 0.0, 5.0$, and 10.0 GPa. Figure (b) depicts change in the direct electron bandgap along $H/2 \rightarrow L$ direction as a function of applied pressure, P .

FIGURE 5.5: (a) The spin-projections on bands along $H/2 \rightarrow L \rightarrow H'/2$ (top) and $P/2 \rightarrow L \rightarrow Q/2$ (bottom) directions for 5.0 GPa applied pressure (see figure (c) for directions in k -space). Red and blue color represents projections of up and down spin-orientations, respectively (see the color scale). Weyl points along $H/2 \rightarrow L \rightarrow H'/2$ direction (top) are labelled as W1 while Weyl points along $P/2 \rightarrow L \rightarrow Q/2$ direction (bottom) are labelled as W2. The k -space coordinates of P and Q points are $(\frac{1}{3}, -\frac{1}{3}, \frac{1}{2})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$, respectively. It is important to notice that W1 Weyl points are located near the Fermi-level, however, W2 Weyl points are located slightly below the Fermi-level. Figure (c) shows the locations of all Weyl points situated at $k_z = \frac{\pi}{c}$ plane of the hexagonal Brillouin zone shown in figure (b). Cyan circles represent W1 Weyl points while red circles represent W2 Weyl points. Figure (d) shows the dispersion of bands in $k_x = 0.494$ plane ($k_y - k_z$ plane passing through cut-1 in figure (c)). (e) The (001) surface spin-texture of BiSb calculated at constant energy $E = 0.10$ eV above Fermi-level.

electron and hole Fermi-surfaces. Such a property of WSM is very interesting as it could yield chiral magnetic effect and novel topological transport properties in this system. In recent years, these properties have attracted much theoretical interest [216, 217, 271–276].

Using the symmetry of the crystal the position of all other Weyl points can be determined. Figure 5.5(c) shows the location of all Weyl points present at the $k_z = \frac{\pi}{c}$ surface of the hexagonal Brillouin zone. To further confirm the existence of two W2 Weyl points, located slightly away from the high-symmetry line, we calculate the 3D band-dispersion at constant $k_x = 0.494$ plane [see plane along cut-1 in Fig. 5.5(c)]. Two gapless points can be clearly noticed in Fig. 5.5(d). In $R3m$ space group, each type of Weyl point (W1 or W2) gives total 12 Weyl points due to presence of time-reversal, mirror and C_{3v} rotation symmetries. Thus, in total there are 24 Weyl points in the hexagonal Brillouin zone.

Observation of Fermi-arcs connecting two Weyl points is crucial to confirm the prediction

of a WSM phase. For this purpose, we have performed the spin-texture calculations at (001) surface of a BiSb-slab [208]. The slab was constructed from the primitive cell of BiSb. We observe two trivial Fermi-circles along with two open Fermi-curves [Fig. 5.5(e)]. These open Fermi-curves are reminiscent of Fermi-arcs connecting opposite Weyl points [277].

Having established the existence of WSM phase in BiSb, we will finally comment on the possibility to control the chirality of Weyl points. Here, we take advantage of the large SOC (Bi and Sb atoms are known to exhibit strong SOC [260–262]) and ferroelectric polarization to control the spin-related properties in the present BiSb system.

FIGURE 5.6: The spin-control and switching of Weyl points by means of polar-displacements (P^s) in the system can be observed. Top (Bottom) figure 5.6a (5.6b) shows the spin-projected band dispersions near W_1 and W_2 Weyl points for original (inverted) polarization cell. The change in the polarization is equivalent to the Bi-displacements along up or down directions as shown by the red and blue arrows. Bi and Sb atoms are shown in violet and orange colors, respectively.

At zero pressure, the BiSb material is a narrow-bandgap semiconductor which exhibits Rashba-like spin-splitting as observed in figure 5.4. In order to quantitatively determine the strength of the Rashba spin-splitting at zero pressure, we calculate Rashba energy (E_R) and Rashba parameter (α_R) as described in the corrected version of Ref. [254]. We find that $E_R = 147.3$ meV and $\alpha_R = 10.43$ eVÅ for CBB along L – H direction, while $E_R = 65.9$ meV and $\alpha_R = 4.71$ eVÅ for VBT along L – H direction. Further details about the Rashba spin-splitting in this compound can be obtained in Ref. [110]. In the $R3m$ phase, Bi and Sb atoms are displaced from the ideal rocksalt sites. The polar displacement (λ) of

the Bi atoms along the direction of red arrows (see crystal structure shown in Fig. 5.6a) yields to a ferroelectric-like polarization in the BiSb system at the semiconducting state. The calculated value of the spontaneous polarization (P^s) at zero pressure is $34.46 \mu\text{C}\cdot\text{cm}^{-2}$ (by Berry phase approach [269, 278]) and $28.50 \mu\text{C}\cdot\text{cm}^{-2}$ (by ionic model). The polarization can be switched by reversing the direction of the polar displacement of Bi-atoms from the ideal rocksalt sites [253, 254]. We find that the energy barrier (ΔE) to overcome the transition from the paraelectric phase in $R\bar{3}m$ symmetry [110] ($\lambda = 0$) to the ferroelectric phase in $R3m$ symmetry ($\lambda = \pm 1$) is $\Delta E = 0.141 \text{ eV/f.u.}$ (see figure S5). This energy barrier is comparable with the reported energy barrier values for other proper ferroelectrics such as BaTiO_3 [279], PbTiO_3 [279], LiNbO_3 [280] and the geometric ferroelectrics BaMgF_4 and BaZnF_4 [281], in which reported ΔE is 0.018, 0.200, 0.259, 0.133, and 0.218 eV/f.u., respectively. Therefore, we expect ferroelectric switching to be experimentally feasible in the BiSb compound.

We notice that the spin-polarization of all three spin components of Rashba-like bands gets inverted when we switch the direction of the ferroelectric polarization at the semiconducting phase at zero pressure. This, as expected from the ferroelectric and SOC coupling terms in the Rashba Hamiltonian [282], makes BiSb (in $R3m$ phase) a FERSC material at ambient conditions. After the polarization inversion process, we apply isotropic pressure of 4.0 GPa to reach the WSM phase with inverted spin-polarized bands. Figure 5.6 shows the dispersion of bands along W1 and W2 Weyl points for original and inverted polarization cases. The shape of bands and the location of Weyl points in energy and momentum space is exactly same for both $P_\uparrow^s$ and $P_\downarrow^s$ polarizations. However, after inverting the polarization we found that the spin-projection on the bands changes in spin-orientation which is depicted by switching of the up and down S_x spin-components (Fig. 5.6). We observed similar behavior for S_y and S_z band spin-projections. The band spin-switching happens along both k-directions containing W1 and W2 Weyl points after the polarization is reversed and 4.0 GPa pressure has been applied. As a result, the topological charge and chirality of Weyl points attain opposite values after inverting polarization. This observation suggests the possibility of switching of the monopole and antimonopole charges in a WSM via an electric field. Here, it is important to remark that the WSM-phase will retain the polar-like displacements similar to the case of “ferroelectric-metals” [257].

5.4 Electronic bandstructure at high pressures

FIGURE 5.7: Electronic bandstructure of BiSb calculated without-SOC at (a) 4.0 GPa, (b) 10.0 GPa and (c) 15.0 GPa pressure. Figure (d), (e) and (f) represent electronic bandstructure calculated with-SOC at 4.0, 10.0 and 15.0 GPa pressures, respectively. One can notice that at high pressures electronic bands cross the Fermi-level yielding increase in the semimetallicity of the system. Bandstructures at zero pressure are given in figure 5.3(a-b).

5.5 Ferroelectric switching

FIGURE 5.8: Above figure depicts the double-well potential energy profile as a function of the polar displacements (λ). Here, λ governs the structural transformation from the paraelectric phase ($R\bar{3}m$ symmetry) to the ferroelectric phase ($R3m$ symmetry).

5.6 Computation of topological charge of Weyl points

FIGURE 5.9: Motion of the charge center around the sphere enclosing the gapless Weyl point; (a) represents presence of an antimonopole (Chern no. = -1) and (b) represents presence of a monopole (Chern no. = +1)

The Berry phase was computed by using the method suggested in Ref. [246]. We use Wannier-function based tight-binding model to calculate the Bloch states on the closed spheres around each gapless Weyl point. The corresponding Berry flux was computed on the closed sphere parameterized by θ and ϕ . We discretize the closed sphere into 1D loops and calculate the charge center $\langle \Phi \rangle$ for each of the loops θ_i . The slope of the plot in Fig. 5.9 gives us information about the Chern number or topological charge of the associated Weyl points. In Fig. 5.9, we have calculated topological charge of two opposite Weyl points located near the L-point of the BiSb rhombohedral primitive cell.

5.7 Calculation of the Berry Flux

The Berry flux around L-point was calculated using the PythTB module [270] together with a s^2p^3 basis, and using Slater-Koster parameterization. The parameters were fitted to reproduce the bulk bandstructure as shown in Fig. 5.10. Figure 5.11 shows the calculated Berry flux in a two-dimensional slice of the reciprocal space ($k_z=0.5$ plane) near L-point (0.5, 0.0, 0.5). We observe two W1 Weyl points and four W2 Weyl points. Out of the four W2 Weyl points, only two W2 Weyl points are located within the first Brillouin zone. Red and blue colors depict opposite charges of the Weyl points.

FIGURE 5.10: The electronic band structure (at 5.0 GPa pressure) obtained from the tight-binding approximation using Slater-Koster parameterization.

FIGURE 5.11: The Berry flux calculated near the L-point in the $\vec{b}_1$ - $\vec{b}_2$ plane (at $\vec{b}_3 = 0.5$). Here, $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ are the reciprocal lattice vectors. It is important to stress that $\vec{b}_1$ and $\vec{b}_2$ vectors are not rectangular while the chosen k-mesh was square (L-centered). Due to this reason we see minor shift in the distribution of the Weyl points.

5.8 Chapter Summary

In summary, we presented a stoichiometric layered structure of BiSb which is energetically, vibrationally and mechanically stable at the DFT level. This structure has a bulk insulating gap at zero pressure with non-trivial band topology. Pressure dependent electronic band structure calculations reveal the existence of a WSM phase in the pressure range 4.0 – 6.0 GPa. We have found 12-pairs of Weyl points in the first Brillouin zone. Surface state calculations confirm the presence of WSM phase in BiSb. We further discussed the possibility to control the chirality and topological charge of the Weyl points by means of applied pressure and electric field. The existence of a polar-like Weyl semimetallic phase in this BiSb compound calls for further studies on the underlying exotic quantum phenomena [258].

Giant Tunable Rashba Spin Splitting in Two-Dimensional BiSb Monolayer and BiSb/AlN Heterostructures

6.1 Introduction

Discovery of new materials having large spin-orbit coupling (SOC) is very crucial in the rapidly burgeoning field of spintronics. In spintronics, we exploit the spin-orbit interaction present in materials to tune their electronic properties. The spin-orbit interaction originates due to the relativistic motion of electrons and acts as an effective built-in magnetic field in non-magnetic materials, which functions similar to the external magnetic field in the celebrated quantum Hall effect [283, 284]. Electrons with opposite spins feel opposite magnetic field in their rest frame and this field couples to their magnetic moment. Nevertheless, the net effects do not cancel out but yield a new quantum phenomenon called Rashba effect [285]. Rashba effect appears in systems with broken inversion-symmetry and causes lift in the spin degeneracy of electronic bands. Initially, the Rashba effect was believed to arise at the surfaces and interfaces due to the asymmetry of the confinement potential. However, recent works reveal that the Rashba effect can also be realized in bulk semiconductors [286–292] and hybrid organic-inorganic perovskites [293–295].

The strength of the Rashba effect can be quantized by three key parameters: Rashba energy (E_R), Rashba momentum (k_o) and Rashba constant (α_R). Materials with large Rashba energy and large Rashba constant provide us more opportunities to tune their spintronics properties. Experiments report the presence of 2D Rashba spin-splitting in InAlAs/InGaAs [296] and LaAlO₃/SrTiO₃ [297, 298] interfaces. However, the magnitude of the Rashba constant (α_R) is not large in the mentioned interfaces ($\alpha_R = 0.07$ eVÅ for InAlAs/InGaAs [296] and $\alpha_R = 0.01 - 0.05$ eVÅ for LaAlO₃/SrTiO₃ oxide interface [297, 298]). Currently, surfaces of heavy metals such as Au, Bi, Ir and BiAg(111) alloys are known to exhibit large Rashba spin-splitting. The magnitude of α_R in Au(111) [299], Bi(111) [300], Ir(111) [301] and BiAg(111) [302] surfaces is 0.33, 0.55, 1.3 and 3.05 eVÅ, respectively. Even though these surfaces inherit large Rashba spin-splitting, yet they cannot be used in many spintronics device applications due to the presence of the (semi)metallic surface states. In particular, there is still no stable 2D semiconductor having large Rashba effect which is suitable for spin field-effect transistor applications.

In addition to the spintronics applications, the 2D semiconductors inheriting large Rashba effect are strongly desired to hunt Majorana fermions. A 2D Rashba semiconductor interfaced with an *s*-wave superconductor under broken time-reversal symmetry can be used to build topological heterostructures that can support the long-sought but not yet detected Majorana fermions [303–305]. Majorana fermions manifest themselves as a zero-bias conductance peak [306]. If experimentally realized, Majorana fermions may pave the way for realization of fault-tolerant topological quantum computation [307–309]. Therefore, there is a huge demand to search for new stable materials inheriting large controllable Rashba effect in two-dimensions.

In present work, we study the electronic properties of BiSb monolayer by means of first-principle calculations. Our calculations reveal that BiSb monolayer forms a stable free-standing 2D crystal and exhibits giant controllable Rashba effect. The observed E_R and α_R are 13 meV and 2.3 eVÅ, respectively, which is amongst the largest yet known Rashba spin-splitting parameters in two-dimensional materials [296–302, 310–317]. We demonstrate that the Rashba effect in BiSb monolayer can be efficiently tuned by applying bi-axial strain. The calculated energy bandgap is 1.6 eV, which lies in the visible range. Presence of the giant Rashba spin-splitting together with a large electronic bandgap makes this system of peculiar interest for optoelectronics applications. We further investigate the electronic properties of BiSb monolayer placed in contact

with an AlN substrate. We construct BiSb/AlN heterostructures with two possible layer terminations (Bi and Sb) at the interface. Both BiSb/AlN van der Waal (vdW) heterostructures are found to exhibit direct bandgap semiconducting nature with presence of light mobile two-dimensional electron gas (2DEG) at the interface. Remarkably, we notice signatures of the giant Rashba spin-splitting of 2DEG near the Fermi-level. Our results suggest that BiSb monolayer and BiSb/AlN heterostructure systems could be potentially used to develop highly efficient spin field-effect transistors, optoelectronics and nano-spintronics devices.

6.2 Computational Details

Density Functional Theory (DFT) [127, 128] based first-principle calculations were carried out using the projector augmented-wave (PAW) method as implemented in the VASP code [201, 202]. We used the PBE exchange-correlation functional as parameterized by Perdew-Burke-Ernzerhof [136]. The SOC was employed by a second-variation method implemented in the VASP code. We considered fifteen valence electrons of Bi ($5d^{10}6s^26p^3$) and five valence electrons of Sb ($5s^25p^3$) in the PAW pseudo-potential. The lattice parameters of the monolayer were optimized until the Hellmann-Feynman residual forces were less than 10^{-4} eV/Å per atom. For convergence of the electronic self-consistent calculations, a total energy difference criterion was defined as 10^{-8} eV. We used 650 eV as kinetic energy cutoff of the plane wave basis set and a Γ -type $10 \times 10 \times 1$ k -point mesh was employed to optimize the lattice parameters and the self-energy. The phonon calculations were performed for a $4 \times 4 \times 1$ supercell. The PHONOPY code [318] was used for phonons post-processing. SOC was included in phonon calculations as well as in the optimization of the primitive cell. To verify the stability of BiSb monolayer at room temperature, we performed room temperature molecular dynamics (MD) simulations for more than 6000 fs with a time step of 1 fs. In MD simulations, we employed a supercell of size $4 \times 4 \times 1$ to guarantee the decay of interatomic force constants within the supercell dimensions. To investigate the effect of in-plane bi-axial strain, we varied the a and b lattice vectors from -8% (compression) to $+8\%$ (expansion) while performing relaxation of the inner-coordinates. The screened hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional [319, 320] was used to get a better estimation of the electronic bandgap of BiSb monolayer. The Bi- and Sb-terminated BiSb/AlN heterostructures

were modeled by using supercells of size $(3 \times 3 \times 1)/(4 \times 4 \times 1)$. This combination yields a lattice mismatch of 1.3%. The vdW interaction [321, 322] together with SOC as implemented in the VASP code were included in the structural optimization as well as in the electronic structure calculations reported for BiSb/AlN heterostructures. The heterostructures were optimized until the total residual forces on each atom were less than $0.001 \text{ eV}/\text{\AA}$. A Γ k-point mesh of size $8 \times 8 \times 1$ was used to sample the irreducible Brillouin zone of heterostructures. A vacuum of thickness larger than $15 \text{ \AA}$ was added along c -axis to avoid any interaction between two periodic BiSb and BiSb/AlN geometries. The PyProcar code was used to calculate the constant energy contour plots of the spin-texture [208].

FIGURE 6.1: Figure (a-b) represent the honeycomb crystal structure of BiSb monolayer viewed from top and side directions. Bi atoms are shown in purple color while Sb atoms are shown in orange color. (c) Bonding of Bi-Sb atoms. Here, d represents the Bi-Sb bond length and h represents the buckling height. (d) The phonon spectra of BiSb monolayer calculated along the high symmetry directions of Brillouin zone. (e) The hexagonal 2D Brillouin zone labelled with high symmetry points.

6.3 Results and discussion

6.3.1 Crystal structure and the stability of BiSb monolayer

The bulk BiSb compound is known to exhibit a rhombohedral structure with $R3m$ symmetry in its ground state [110, 111]. In this geometry, Bi and Sb atoms are stacked along the (111) direction of rhombohedral primitive cell. Two alternative Bi and Sb layers strongly interact covalently and form a BiSb bilayer, whereas, two adjacent BiSb bilayers weakly interact due to the weak vdW interaction. Therefore, it is possible to fabricate a stable two-dimensional BiSb monolayer by advanced exfoliation, vapor deposition, or molecular-beam epitaxy techniques. A detailed study of the structural, vibrational, electronic, thermoelectric and topological behaviour of bulk BiSb can be found in Ref. [110, 111]. Bulk BiSb exhibits a giant Rashba effect with presence of the pressure-driven Weyl semimetallic phase [111]. This is one of the first predicted ferroelectric Weyl semimetals which demonstrates tunability of Weyl charges. Such unique and intriguing topological features of bulk BiSb stimulate research in the two-dimensional BiSb.

Fig. 6.1(a-c) shows the crystal structure of an isolated BiSb monolayer. The fully optimized structure exhibits a buckled honeycomb lattice having a three fold rotational symmetry in $P3m1$ space group (156). The optimized lattice parameters are $a = b = 4.255$ Å. The Bi-Sb bond length (d) and the buckling height (h) are 2.98 and 1.69 Å, respectively. The Bi-Sb-Bi bond angle is 91.2° . In order to test the energetic stability of BiSb monolayers, we calculate the formation energy of a single optimized BiSb monolayer using the following expression:

$$E_{formation} = \frac{E_{coh}(BiSb) - xE_{coh}(Bi) - yE_{coh}(Sb)}{(x + y)} \quad (6.1)$$

where, E_{coh} denotes the cohesive energy relative to the free constituent atom, x and y represents the total number of Bi and Sb atoms in the cell, respectively. The calculated formation energy ($E_{formation}$) of a single BiSb monolayer is -2.23 eV/atom, which is lower than the formation energy of most of the previously synthesized single layer transition-metal dichalcogenides [323]. For example, the formation energy of single layer MoS_2 , $MoSe_2$, $MoTe_2$, WS_2 , WSe_2 , WTe_2 , $NbTe_2$ and $NbSe_2$ is -0.83 , -0.75 , -0.30 , -0.91 ,

-0.62, -0.10, -0.42 and -0.88 eV/atom, respectively [324]. However, the formation energy of BiSb monolayer is slightly larger than that of other binary V-V monolayer compounds such as PN, AsN, SbN, AsP, SbP and SbAs [325]. Nonetheless, BiSb monolayer forms an energetically stable crystal structure and therefore, it can be synthesized in laboratory.

We test the dynamical stability of the BiSb monolayer by analyzing the phonon spectra. Fig. 6.1(d) represents the phonon bandstructure calculated along the high symmetry directions of Brillouin zone shown in Fig. 6.1(e). We notice that there are three optical and three acoustical phonon branches, corresponding to total 6 branches due to 2 atoms per cell. The longitudinal acoustic (LA) and transverse acoustic (TA) modes represent in-plane vibrations while the ZA branch corresponds to the out-of-plane vibrations. One can notice that all phonon frequencies are positive, which confirms the dynamical stability of BiSb monolayer at 0 K. It is worthy to note that the ZA phonon branch exhibits a small imaginary frequency having a ‘U’-shape near the Γ -point. This ‘U’-shape feature does not correspond to the lattice instability, nevertheless, it is a signature of the flexural acoustic mode present in two-dimensional systems [326]. The flexural acoustic modes are known to play a crucial role in governing the thermal and mechanical properties of two-dimensional systems. Such ‘U’-shape feature near Γ -point has been observed in many other similar two-dimensional systems studied earlier [325, 327, 328]. Thus, our phonon calculations confirm that BiSb monolayer is dynamically stable and therefore, it can exist as a free standing two-dimensional crystal. Furthermore, we notice that the acoustic and optical phonon branches are well separated, indicating good optical response of BiSb monolayer. There is a wide direct frequency gap ($\Delta\omega$) of 70 cm^{-1} between the optical and acoustic phonon modes at K-point. In the photoexcitation experiments and in the solar cell applications, the excitons (photon excited electron-hole pairs) lose most of their energy by exciting the optical phonons. These excited optical phonons further decay into the acoustic phonons which carry the heat away. Notably, in our case the phonon frequency gap is larger than the frequency of the hardest acoustic phonon mode ($\sim 50 \text{ cm}^{-1}$). This feature significantly avoids the Klemens decay, [329] which indicates the possibility to use such type of materials for the high-efficiency solar cell applications. [330]

From the application point of view, it is important to check the mechanical stability of any new material. Therefore, we have performed first-principle calculations to determine the elastic constants (C_{ij}) of BiSb monolayer. The elastic constants were calculated using

the stress-strain relations as implemented in the VASP code [201, 202]. We used a dense $21 \times 21 \times 1$ Γ k -mesh to reduce the numerical errors caused by in-plane strain of the system. The second Piola–Kirchhoff stress method was used to determine the elastic constants in 2D with units of N/m [331, 332]. We find that $C_{11} = 24.4$ N/m and $C_{12} = 5.8$ N/m. We further calculated the 2D layer modulus (γ), Young’s modulus (Y_S^{2D}) and Poisson’s ratio (ν) using the method suggested by Andrew et al.[333]. The obtained values of γ , Y_S^{2D} and ν are 15.12 N/m, 23.0 N/m and 0.24, respectively. Poisson’s ratio is larger compared to that of h-BN (0.22) and graphene (0.17) monolayers, however, ν is smaller compared to that of buckled Si (0.34) and Ge (0.28) monolayers [333]. γ and Y_S^{2D} values of BiSb monolayer are significantly lower than that of h-BN and graphene. This is due to the fact that Bi-Sb bonds are weaker compared to B-N and C-C bonds. However, all the obtained elastic constants are positive confirming the mechanical stability of BiSb monolayer. A detailed study of the mechanical properties of strained BiSb monolayer will be published elsewhere.

FIGURE 6.2: This figure shows variation in the mean-square displacement of Bi (purple) and Sb (orange) atoms as a function of simulation time at 300 K. Insets show the top and side views of the geometric structures of monolayer at the end of MD simulation at 300 K.

We further perform the *ab-initio* MD simulations to assess the thermal stability of BiSb monolayer at room temperature. Fig. 6.2 shows the mean-square displacement of the Bi and Sb atoms as a function of the simulation time (in ps). The snapshots of the geometric structure at 300 K obtained at the end of the MD simulation (total time =

7.5 ps) are also given in the insets of Fig. 6.2. We see that the mean-square displacement oscillates with an amplitude of about 2% of the total Bi-Sb bond length. Additionally, one can notice that the geometric structures at 0 K (Fig. 6.1) and at 300 K (insets of Fig. 6.2) are quite similar. This confirms the thermodynamical stability of BiSb monolayer at the room temperature, suggesting the possible applicability of this system for room temperature device applications.

It is worthy to mention that, although the energetic stability tests indicate that the proposed BiSb monolayer structure is quite robust against small lattice defects, vacancies, impurities and structural deformations, the situation might change in different ambient environments. Most of the recently discovered 2D systems exhibit significant structural deformations under different ambient conditions. A more detailed investigation is required to understand the effect of the ambient environment on structural stability and electronic properties of BiSb monolayer.

6.3.2 Electronic structure: the giant 2D Rashba spin-splitting

Fig. 6.3 shows the electronic bandstructure of BiSb monolayer calculated using (a) GGA and (b) GGA+SOC approximations. Without-SOC, the bandstructure reveals the semi-conducting nature with presence of a direct bandgap (E_g) of 0.95 eV at the Γ point. However, bulk BiSb is known to exhibit an indirect bandgap semiconducting nature [111]. The thickness dependent transition from an indirect (3D) to direct (2D) bandgap semiconductor is not new in layer-like systems, and it has already been reported for other layer-like systems [334]. In BiSb monolayer, the conduction band bottom (CBB) shows a parabolic nature near Γ point indicating the presence of highly mobile light electrons (nearly free-electrons), while the valence band top (VBT) indicates the presence of relatively heavy holes near Γ point. Since DFT is known to underestimate the energy bandgap, we employ the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional to predict a more reasonable energy bandgap. Fig. 6.3(c) shows the orbital projected DOS calculated using HSE06 approximation (without-SOC) for BiSb monolayer. We find that the HSE06 bandgap is approximately 1.6 eV which is larger than the DFT (GGA and GGA+SOC) predicted bandgap and lies in the visible range of electromagnetic spectrum. This makes this system of peculiar interest for optoelectronic applications. It is worth mentioning that the HSE06 functional only enhances the bandgap without any

notable change in the shape of the electronic bands and the strength of the Rashba spin-splitting [288]. Our calculations further indicate that the bands near Fermi-level (E_F) are mainly composed of Bi 6*p* and Sb 5*p* orbitals.

FIGURE 6.3: The electronic bandstructure of BiSb monolayer, (a) without-SOC (b) with-SOC. (c) The atomic orbital projected DOS calculated using HSE06 approximation and a Γ k-mesh of size $21 \times 21 \times 1$. (d) The enlarged view of Rashba spin-splitting of conduction bands near the Fermi-level. The green dotted line represents Fermi-level.

Inclusion of SOC results in the spin-splitting of the electronic bands [Fig. 6.3(b)]. Remarkably, we notice a Rashba type spin-splitting of CBB near Γ -point, while the VBT remains degenerate (Fig. 6.3(b, d)). Also, the direct DFT bandgap at Γ -point decreases to 0.37 eV. To quantitatively determine the strength of the Rashba spin-splitting, we calculate the Rashba parameters as described in Ref. [288]. We find that $E_R = 13$ meV, $k_o = 0.0113 \text{ \AA}^{-1}$ and $\alpha_R = 2E_R/k_o = 2.3 \text{ eV\AA}$. This is amongst the largest Rashba spin-splitting in two-dimensional materials reported so far. For example: the reported Rashba energy (Rashba constant) for Au(111) surface, InGaAs/InAlAs interface, LaAlO₃/SrTiO₃ oxide interface and Bi(111) surface is 2.1 meV (0.33 eV $\text{\AA}$) [299], 0.98 meV (0.07 eV $\text{\AA}$) [296], <5 meV (0.01–0.05 eV $\text{\AA}$) [297, 298] and 14 meV (0.55 eV $\text{\AA}$) [300], respectively. One can notice that the Bi(111) surface exhibits the largest Rashba spin-splitting ($E_R = 14$ meV) amongst all the above listed systems. However,

the semimetallic nature of Bi(111) surface limits its applications in the spintronics devices [300, 335]. The BiSb monolayer overcomes this limitation due to its direct bandgap semiconducting nature coupled with the large Rashba spin-splitting, which is comparable with the Rashba spin-splitting of Bi(111) surface. Interestingly, we notice that the Rashba spin-splitting of BiSb monolayer is even comparable with some of the known bulk Rashba semiconductors such as BiAlO₃ ($E_R = 7.34\text{--}8.62$ meV, $\alpha_R = 0.39\text{--}0.74$ [292]), BiTeI ($E_R = 100$ meV, $\alpha_R = 3.8$ eVÅ [286]), BiTeCl ($E_R = 18.5$ meV, $\alpha_R = 1.2$ eVÅ [290]), GeTe ($E_R = 227$ meV, $\alpha_R = 4.8$ eVÅ [288]), SnTe ($E_R = 272$ meV, $\alpha_R = 6.8$ eVÅ [289]), LiZnSb ($E_R = 21$ meV, $\alpha_R = 1.82$ eVÅ [291]) and KMgSb ($E_R = 10$ meV, $\alpha_R = 0.83$ eVÅ [291]).

The origin of the large Rashba effect in the present BiSb structure can be understood by looking at the symmetry of the orbitals near Fermi-level. The orbitals projected DOS plot shown in Fig. 6.3(c) reveals that the states near Fermi-level have same orbital symmetry. Therefore, these states could strongly couple and yield large Rashba spin-splitting, as predicted by the $k \cdot p$ theory in Ref. [287]. Thus, after comparing the strength of the Rashba spin-splitting in BiSb monolayer and several other known large Rashba semiconductors, one can realize that the Rashba spin-splitting of the highly mobile light-electrons in BiSb monolayer is indeed remarkable and therefore, this system can be used to make efficient advanced spin-field effect transistors.

Fig. 6.4 shows the constant energy 2D contour plots of spin-texture calculated in a $k_x\text{--}k_y$ plane centered at the Γ -point. Evidently, one can notice the Rashba type spin-splitting of spin-up (red) and spin-down (blue) electronic bands. The concentric spin-texture circles are result of the purely two-dimensional Rashba spin-splitting present above the Fermi-level (conduction bands). A further analysis of the projection of different spin-components (S_x , S_y and S_z) on the electronic bands reveals that only in-plane S_x and S_y spin components are present in the Rashba-spin split bands, without presence of any out-of-plane S_z component. This further confirms that the spin-splitting of electrons in BiSb monolayer has purely two-dimensional Rashba nature. Interestingly, we observe the Rashba spin-splitting at significantly large energies (0.40 and 0.75 eV) above the Fermi-level.

6.3.3 Effect of in-plane bi-axial strain on the electronic properties

It is very important to study the effect of the bi-axial strain on the electronic properties before we shift our concentration to the BiSb/AlN heterostructure systems. Therefore, we study the strained BiSb monolayers by applying bi-axial strain (x) ranging from -8% (compression) to $+8\%$ (elongation) on the a and b lattice vectors. Fig. 6.5 shows change in the with- and without-SOC electronic bandstructures with respect to $x = +2\%$ (solid blue lines), -2% (broken magenta line) and -6% (solid orange lines) bi-axial strains. From Fig. 6.5(a-b), we notice that the system retains its direct bandgap semiconducting nature until $x = -2\%$. However, with further increase in bi-axial strain, it changes to an indirect bandgap semiconductor at -4% and eventually, we realize a metallic phase-transition at $x = -6\%$. Furthermore, the degeneracy of the valence band near Γ -point breaks down at $x = -6\%$ bi-axial compression and a Rashba type spin-splitting appears in the valence band states. Analysis of the Rashba spin-splitting in the strained bands evinces that the Rashba energy (constant) decreases from 13 meV ($2.3 \text{ eV\AA}$) to 9.21

FIGURE 6.4: Spin projected constant energy contour plots of spin-texture calculated in a $k_x - k_y$ plane centered at the Γ -point. Top (Bottom) row represents the spin-textures calculated at an energy surface 0.40 eV (0.75 eV) above the Fermi-level. In the color scale, red color depicts spin-up states while blue color depicts spin-down states.

meV ($1.77 \text{ eV\AA}$) with increase in the bi-axial compression from $x = 0\%$ to $x = -4\%$. However, we observe significant increase in the Rashba spin-splitting parameters with

FIGURE 6.5: The electronic bandstructure of strained BiSb monolayers at an applied in-plane bi-axial strain $x = +2\%$ (stretched), -2% and -6% (compressed) monolayers, (a) without-SOC and (b) with-SOC. The green dotted line represents Fermi-level.

increasing bi-axial elongation (For $x = +6\%$ elongation: $E_R = 33.4$ meV, $\alpha_R = 3.56$ eVÅ). Consequently, one can significantly tune the strength of the Rashba spin-splitting by varying the in-plane bi-axial strain. Nonetheless, in order to experimentally realize the novel direct bandgap Rashba semiconducting properties of the BiSb monolayer, we must grow this system on top of a substrate such that the lattice mismatch is less than 2%. This can be experimentally realized by a proper choice of substrate material.

FIGURE 6.6: Figure represents the relaxed geometric structures of BiSb/AlN heterostructures with two possible terminations at the interface. Fig. (a) shows the top and side views of Bi-terminated interface while Fig. (b) shows the top and side views of Sb-terminated interface.

6.3.4 BiSb/AlN heterostructures

How do the electronic properties of BiSb monolayer change in presence of another substrate material? Can we still realize the Rashba spin-splitting of 2DEG present at the interface of heterostructure systems? How would the energetic stability of an isolated BiSb monolayer change in presence of another contact material? In order to address these questions, we model BiSb/AlN heterostructures and study their electronic properties. To minimize the lattice mismatch between two stackings, we build the heterostructure using a $4 \times 4 \times 1$ supercell of AlN and a $3 \times 3 \times 1$ supercell of BiSb. Thus obtained lattice mismatch is 1.3%. One could also use hexagonal BN or GaN as a substrate material for BiSb monolayer. The lattice mismatch for BiSb($3 \times 3 \times 1$)/BN($5 \times 5 \times 1$) and BiSb($3 \times 3 \times 1$)/GaN($4 \times 4 \times 1$) combinations is 1.7% and 2.15%, respectively. In the present work, we study the BiSb/AlN heterostructure system because this system

FIGURE 6.7: Fig. a (b) shows the electronic bandstructure calculated without-SOC, with-SOC and enlarged conduction bands showing Rashba spin-splitting near Fermi-level for Bi-terminated (Sb-terminated) interface. Fig. c (d) depicts the projected DOS calculated using a Γ k-mesh of size $11 \times 11 \times 1$ for Bi-terminated (Sb-terminated) interface. The vdW interaction was included in all first-principle calculations for BiSb/AlN heterostructures. The green dotted line represents Fermi-level.

exhibits minimum lattice mismatch. Fig. 6.6 shows the BiSb/AlN heterostructures with two possible layer terminations at the interface: first, Bi-termination (Fig. 6.6(a)) and second Sb-termination (Fig. 6.6(b)). The vdW optimized lattice constants for Bi- and Sb-terminated interfaces are 12.541 and 12.536 Å, respectively. In both cases, the BiSb lattice is being compressed by 1.8% while the AlN lattice is being stretched by 0.5%. The interlayer spacing between AlN and BiSb monolayers is 3.45 Å (3.10 Å) for Bi-terminated (Sb-terminated) interfaces. The presence of larger interlayer spacing for Bi-terminated interface can be ascribed to the fact that Bi-atom has larger covalent radius compared to the Sb-atom.

The calculated formation energies for Bi- and Sb-terminated interfaces are -2.59 and

-2.60 eV/atom, respectively. This suggests that the Sb-terminated interface is energetically 10 meV/atom more favorable compared to the Bi-terminated interface. Furthermore, comparing the formation energy of an isolated BiSb monolayer with that of BiSb/AlN system, we notice that the BiSb/AlN heterostructures are energetically more stable than a single sheet of BiSb. One can switch the ferroelectric polarization, and thus the electric field direction at the interface, by switching the Bi and Sb layers. An inverted ferroelectric polarization leads to the complete inversion of the spin-polarized Rashba bands near the Fermi-level. This particular feature has already been investigated for bulk BiSb [111]. We observe that BiSb monolayer exhibits the same behavior upon reversal of the ferroelectric polarization.

FIGURE 6.8: Spin-texture for Bi-terminated interface calculated in a $k_x - k_y$ plane centered at the Γ point and at an energy surface 0.15 eV above the Fermi-level. The red color depicts spin-up states while blue color depicts spin-down states.

The calculated electronic bandstructure and projected DOS of BiSb/AlN heterostructures are shown in Fig. 6.7. Fig. 6.7(a) shows the electronic bands without-SOC, with-SOC and conduction bands near Γ -point showing Rashba spin-splitting for Bi-terminated interface, while Fig. 6.7(b) shows the same but for Sb-terminated interface. Without-SOC, both Bi- and Sb-terminated heterostructures show a direct bandgap of 0.90 and 0.91 eV at the Γ -point, respectively. The CBB of both heterostructures has a free-electron gas like parabolic shape near the Γ -point whereas the top valence bands are quite flat in both heterostructures indicating presence of heavy holes along with existence of light 2DEG at the interface. The direct gap of the heterostructures is lower compared to that of the isolated BiSb-monolayer. Interestingly, we notice a Rashba type spin-splitting of CBB in presence of SOC for both heterostructures. Also, the direct DFT gap of both heterostructures reduces to 0.33 eV (Bi-terminated) and 0.35 eV

(Sb-terminated) due to inclusion of SOC. The calculated strength of the Rashba spin-splitting is $E_R = 6$ meV and $\alpha_R = 1.5$ eVÅ for Bi-terminated interface and $E_R = 5$ meV and $\alpha_R = 1.1$ eVÅ for Sb-terminated interface. The strength of the Rashba splitting is larger at the Bi-terminated interface. This is due to the fact that Bi has larger SOC compared to the Sb atom [226, 260–262]. It is noteworthy that the strength of the Rashba spin-splitting is amongst the largest yet known Rashba heterostructure systems. The reason of such a large Rashba splitting in this heterostructure system can be ascribed to the presence of Bi-6*p* and Sb-5*p* orbitals near the Fermi-level as depicted by the projected DOS plots for both heterostructures (Fig. 6.7(c-d)). The semiconducting nature of both heterostructures is also evident from their respective DOS.

To further confirm the 2D nature of Rashba spin-splitting, we calculate the spin projected spin-texture in a k_x - k_y plane centered at the Γ -point. The constant energy (0.15 eV above Fermi-level) contour plots of the spin-texture for Bi-terminated interface are shown in Fig. 6.8. The spin-texture for Sb-terminated interface exhibits similar shape. The circular shape of the spin-textures confirm the purely 2D nature of Rashba spin-splitting of 2DEG at the interface. Furthermore, we observe that only S_x and S_y spin-components are present in k_x - k_y plane without presence of any S_z component. This indicates that the spin-texture has only in-plane spin-components. These remarkable giant Rashba features make this system suitable for many interesting applications in the spintronics industry. In particular, one can make highly efficient spin field-effect transistors using this system, where we exploit the giant 2D Rashba effect to control the spin-state of 2DEG.

6.4 Chapter Summary

In summary, we have identified a new energetically, dynamically and mechanically stable crystal phase of BiSb monolayer which has buckled honeycomb lattice geometry. Our first principle calculations reveal that this monolayer is a direct bandgap semiconductor having free-electron-like parabolic conduction band features near Γ -point. Inclusion of SOC yields Rashba type spin-splitting of conduction bands near Fermi-level. The obtained Rashba spin-splitting parameters ($E_R = 13$ meV, $\alpha_R = 2.3$ eVÅ) suggest that this system is amongst the largest yet known 2D Rashba semiconductors. The constant energy contour plots of spin-texture confirm the purely two-dimensional nature of Rashba splitting. Both BiSb/AlN heterostructures exhibit direct bandgap semiconducting nature having parabolic conduction bands near Fermi-level, which indicates the presence of 2DEG at the interface. The strength of the Rashba splitting is stronger for the Bi-terminated interface ($E_R = 6$ meV, $\alpha_R = 1.5$ eVÅ) than compared to the Sb-terminated interface ($E_R = 5$ meV, $\alpha_R = 1.1$ eVÅ). The presence of direct bandgap with light electron-like features makes this system interesting for 2D optical device applications. Additionally, the existence of two-dimensional giant Rashba effect together with the electronic bandgap in visible range paves the way to use BiSb-monolayer and BiSb/AlN heterostructure systems in the development of highly efficient spin field-effect transistors and optoelectronics devices in spintronics industry.

The Elastic, Mechanical and Thermodynamic Properties of Bi-Sb Binaries: Effect of Spin-Orbit Coupling

7.1 Introduction

A thorough understanding of the mechanical response of any given material is essential before the technological applications of that particular material can be realized. A good place to start is investigating the elasticity, a fundamental property of a crystal which governs the macroscopic response of the crystal under external forces. The hardness, mechanical strength and the propagation of the sound and elastic waves in a given material can be determined by knowledge of the elastic constants of that particular material. In previous chapters, we demonstrated that the lowest energy structure of BiSb composition (in $R\bar{3}m$ space group) exhibits large ferroelectric behavior along with a giant tunable Rashba-Dresselhaus effect, which is the result of the broken inversion symmetry and the large spin-orbit coupling (SOC) of the constituent Bi and Sb elements [110, 111]. Furthermore, we demonstrated that one can realize a novel Weyl semimetallic phase under external stress of 4–6 GPa [111]. We have also shown that by exploiting an interlink between the large SOC of the constituent atoms and the ferroelectric polarization, one

can tune the dynamics of Weyl fermions in the momentum space of BiSb. This particular property is of notable interest for applications of Weyl semimetals in the forthcoming Weyltronic technology.

BiSb is not only interesting in its bulk phase, but it also shows unique electronic properties in two-dimensions [112, 336, 337]. In particular, a giant tunable Rashba effect along with a large direct bandgap (~ 1.6 eV) has been observed [112]. The existence of the large tunable Rashba effect together with a direct bandgap in the visible region makes this material of peculiar interest for its applications in the optoelectronics and spintronics industry. Recently, Yu et al. [337] investigated the topological properties of monolayer BiSb, and observed the emergence of robust novel quantum spin Hall (QSH) effect under biaxial tensile strain. This finding was further confirmed by the calculation of Z_2 topological invariant and the nontrivial topological edge states. These features make BiSb an attractive candidate for applications in spintronic devices.

Other than the BiSb composition, several other stable compositions of the Bi-Sb binaries have been reported by both theoretical and experimental studies [16, 17, 20, 61, 110, 206, 207, 220, 338]. The formation mechanism and the chemical synthesis procedure of $\text{Bi}_x\text{Sb}_{1-x}$ nanocrystals are given in Refs. [73, 74, 339]. A detailed structural, electronic, vibrational and thermoelectric investigation of the Bi-Sb binaries can be found in Chapter 3 and in Ref. [110]. In Ref. [110], we explored the potential energy surface of Bi-Sb binaries using the minima hopping method [109, 340], and reported the theoretical convex-hull of Bi-Sb. We not only discovered several new energetically and thermodynamically stable crystal structures of Bi-Sb binaries that are located on the convex-hull, but we also recovered the known structures of Bi-Sb binaries in our structural search calculations. In this chapter, we report our investigations on the elastic and thermodynamic response of the stable Bi-Sb binaries.

Changes in the mechanical properties of $\text{Bi}_x\text{Sb}_{1-x}$ single crystals as a function of Sb-concentration have been studied by ultrasonic wave velocities measurements at room temperature as well as at low-temperatures [11, 13, 341–344]. In general, the elastic properties, *i.e.* bulk modulus, Young’s modulus, and shear modulus increase with increasing Sb-concentration in Bi-Sb binaries [11]. Also, the average speed of sound increases with increasing Sb-concentration, however, it decreases with increasing temperature [344]. Although, most of the experiments report monotonous increase in the

elastic moduli with increasing Sb-concentration for larger atomic % of Sb, there exists some anomalies in the variation of the mechanical properties at low Sb concentration, which is consistent with our theoretical findings [11]. Although, the specific heat of pristine Bi [261, 345–347] and pristine Sb [262, 348] has been studied in detail, [261, 262] little attention has been paid to the thermodynamic properties of Bi-Sb binaries [13, 61, 349]. Lichnowski and Saunders reported increase in Debye temperature with increasing Sb-concentration [13]. The effect of SOC on the elastic and mechanical properties of Bi-Sb binaries has not yet been reported in the literature, even though SOC is known to significantly change the electronic, vibrational and thermodynamic properties of Bi and Sb based compounds [260–262].

In the present work, we report a systematic investigation of the elastic and thermodynamic properties of the Bi-Sb binaries calculated using *first-principles*. We study the properties of the following Bi-Sb binary compositions (crystal structures are shown in Fig. 7.2): Bi₁Sb₇, Bi₁Sb₁, Bi₃Sb₁, Bi₇Sb₁ and Bi₉Sb₁, which lie on the convex-hull of the Bi-Sb binary phase diagram (the only exception is the Bi₃Sb₁ composition which lies above, yet very close to the convex-hull) [110]. Our results indicate that the ductility of the structures increases with increasing Bi-concentration, whereas in general, the elastic moduli decrease with increasing Bi-concentration. The bulk modulus (B), shear modulus (G), Young’s modulus (E), Poisson’s ratio (ν) and the elastic stiffness coefficients (C_{ij}) of the studied systems are reported below. We notice that Bi₁Sb₇, Bi₇Sb₁, and Bi₉Sb₁ monoclinic structures exhibit negative Poisson’s ratio along different spatial directions. The Debye temperature and maximum heat capacity are found to increase with decreasing Bi-concentration. Comparison of our theoretical findings with the available experimental data shows excellent agreement between theory and experiments.

7.2 Computational Details

Density Functional Theory (DFT) based *first-principles* calculations were carried out using the projector augmented-wave (PAW) method as implemented in the VASP code [201, 202]. We used the PBE exchange-correlation functional as parametrized by Perdew-Burke-Ernzerhof [136]. We considered fifteen valence electrons of Bi ($5d^{10}6s^26p^3$) and five valence electrons of Sb ($5s^25p^3$) in the PAW pseudo-potential. The lattice parameters of each structure were optimized until the Hellmann-Feynman residual forces

were less than 10^{-4} eV/Å per atom. For convergence of the electronic self-consistent calculations, a total energy difference criterion was defined as 10^{-8} eV. We used 650 eV as kinetic energy cutoff of the plane wave basis set. We employed a Γ -type k -mesh for hexagonal and trigonal structures, while a Monkhorst-pack type k -mesh was used to sample the irreducible Brillouin zone of all other crystal phases. The size of k -mesh was large enough to ensure the numerical convergence of total energy to less than 1 meV/atom.

The elastic constants C_{ij} were calculated using the stress-strain relationship as implemented in the VASP code. Elastic constants were converged better than 1 GPa by increasing the k -mesh size. The bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (ν) quantities were first determined using the Voigt bound [350] and Reuss bound [351] schemes, and then an arithmetic average was computed following the Voigt-Reuss-Hill averaging scheme [352]. This way of evaluating elastic moduli is important since the Voigt and Reuss bounds give an upper and lower estimates of the actual elastic moduli of polycrystalline crystals, respectively. The Voigt bound scheme [350] relies on the assumption of uniform strain throughout the crystal, whereas the Reuss bound scheme [351] relies on the assumption of uniform stress throughout the crystal. Since SOC plays an important role in describing the electronic and vibrational properties of Bi and Sb atoms, [260–262] we decide to investigate the effect of SOC on the elastic and mechanical properties of Bi-Sb binaries. Therefore, we have calculated elastic constants and elastic moduli for each studied structure twice: once with-SOC and once without-SOC. The phonopy code [205, 318] was used to calculate the heat capacity of crystal lattice.

In order to facilitate the analysis of elastic and mechanical properties, an open source python code, MechElastic [353], was developed. This program can be used to evaluate many important physical quantities such as elastic moduli, elastic wave velocities, Debye temperature, melting temperature, anisotropy factors, and perform the mechanical stability test for any crystalline bulk materials.

FIGURE 7.1: Figures (a-e) represent the crystal structure of Bi-Sb binaries located on the Bi-Sb phase diagram [110]. Bi atoms are shown in purple color while Sb atoms are shown in green color. Each crystal structure is shown from two different lattice orientations. The cutoff length for bonds was defined as 3.10 Å in Sb-rich compositions and 3.20 Å in Bi-rich compositions.

7.3 Results and Discussions

7.3.1 Elastic constants

The crystal structures of all the binary compounds under investigation are shown in Fig. 7.2. It is important to first discuss the elastic stiffness constants and define their relationship with the macroscopically measurable quantities that give us information about the elastic and mechanical properties of the system. The bulk modulus (B), Young's modulus (E), shear modulus (G), and Poisson's ratio (ν) are known as the elastic moduli and are macroscopically measurable quantities that give a measure of the elasticity of the material. These quantities can be determined from the elastic constants, C_{ijkl} . These constants are obtained through the use of the generalized stress-strain Hooke's law [354],

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl}, \quad (7.1)$$

where σ_{ij} and ϵ_{kl} are the tensile stress and longitudinal strain, respectively. Utilizing the crystal symmetry operations, the total number of constants can be reduced from 81 to 3, 5, 6 and 13 for cubic, hexagonal, tetragonal, and monoclinic structures, respectively [354]. Table 7.1 lists the values of the relevant elastic constants calculated with and without inclusion of SOC. Although, few non-diagonal elements of the C_{ij} matrix contain negative values for Bi_7Sb_1 and Bi_9Sb_1 binaries, all the six eigen values of the C_{ij} matrix are positive suggesting the elastic stability of these binaries. In fact, all the eigen values of C_{ij} matrix are positive for each studied Bi-Sb binary.

We notice a small yet significant change in the C_{ij} values due to the SOC effects. Notably, SOC is known to considerably change the electronic and vibrational spectra of Bi and Sb based compounds. Ramifications of SOC on the electronic bandstructure chiefly depend upon the crystal symmetry, and therefore, SOC could have different implications on the same composition but with different crystal symmetry [110, 260]. Moreover, Díaz-Sánchez et al. [260] have reported that the dynamical properties and the interatomic force constants of Bi are very sensitive to the strength of SOC. They reveal that SOC softens the phonon modes in Bi by about 10% and yields remarkable agreement when compared to that of the experimental values. However, SOC has much smaller effects on the lattice parameters [260]. In a similar work, Serrano et al. [262] have studied the effects of SOC on the specific heat, the lattice parameter, and the cohesive energy

of Sb. Their calculations reveal that all these quantities depend almost quadratically on the SOC strength [262]. The small change in the C_{ij} values due to SOC can be attributed to the above mentioned reasons. The calculated elastic constant values are consistent with an experimental work reported by Lichnowski et al. [13], where they investigated the elastic properties of $\text{Bi}_{1-x}\text{Sb}_x$ ($0.03 < x < 0.1$) single crystals for small Sb concentration.

Notably, the strength of SOC in Sb is much smaller compared to that of in Bi, consequently, changes in the C_{ij} values for Sb-rich compositions are relatively less (slightly over our convergence criteria of 1.0 GPa) compared to that of in the Bi-rich compositions. However, we do notice considerable SOC induced changes in the C_{ij} values for Bi-rich compositions. The influence of SOC on the C_{ij} (to increase or decrease the C_{ij} and therefore the stiffness) is fairly uniform across all compositions. Even pure Sb and Bi follow the same trends with the exception of C_{12} . These trends indicate that, in general, due to the SOC effects $\text{Bi}_x\text{Sb}_{1-x}$ becomes less stiff along the x and y major axes for deformations along x and y directions, more stiff along the z major axis for deformation along the z direction, and they differ for the transverse forces and responses in the $x - y$ plane. In general, SOC effects cause elastic softening in all directions perpendicular to the z axis. The observed elastic softening could be associated to the SOC induced softening of phonon modes [260]. In a previous work, Arnaud et al. [355] investigated the effect of SOC on the elastic properties of Bi and observed a similar SOC induced elastic softening. Their reported values are in good agreement with our data presented in Table 7.1. Here, we would like to note the peculiar effect of SOC on the Bi rich compound, Bi_9Sb_1 . In Bi_9Sb_1 we see that the aforementioned trends are reversed for most of the C_{ij} values. Also, anomalous changes in the elastic stiffness constants can be observed for Bi_9Sb_1 , which will be discussed in more detail later. These changes support the before mentioned complex relationship between the SOC and the electronic and phonon bandstructure, leading to directional changes in the bonding within the material.

Our calculations indicate that SOC causes small changes (overall less than 1.0 %) in the Bi-Sb, Bi-Bi, and Sb-Sb bond lengths, which when combined with the phonon softening could be held accountable for the observed SOC induced changes in the C_{ij} values. The maximum variation in the bond length due to SOC is within the range of ± 0.03 Å. Further details of the bond-lengths, lattice parameters, electronic bandstructure, and phonon bandstructure of all studied structures can be found in Ref. [110]. Since

TABLE 7.1: List of elastic constants (C_{ij}) calculated with (PBE+SOC) and without SOC (PBE). C_{ij} values (in GPa units) calculated with PBE+SOC are given in parentheses. x represents the concentration of Bi in $\text{Bi}_x\text{Sb}_{1-x}$. The space group of each composition is given in the square brackets.

Composition	x	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
Sb [166] Theory ^a	0.0	92.2		35.8	29.8			21.8	20.3					
		(89.3)		(38.9)	(28.3)			(22.5)	(20.4)					
		91		38	27			24	21					
Bi ₁ Sb ₇ [06]	0.125	98.5	83.1	36.2	36.8	13.0	16.2	6.4	12.7	32.0	15.1	6.4	1.9	6.8
		(95.1)	(81.5)	(37.4)	(34.0)	(13.7)	(15.2)	(7.2)	(13.0)	(30.9)	(13.2)	(5.4)	(2.3)	(6.5)
Bi ₁ Sb ₁ [160]	0.5	75.5		29.1	13.4			21.8	18.0					
		(68.7)		(31.2)	(12.4)			(22.6)	(19.6)					
Bi ₃ Sb ₁ [160]	0.75	67.3		31.0	7.8			27.0	20.7					
		(58.0)		(34.0)	(8.3)			(25.4)	(21.8)					
Bi ₇ Sb ₁ [08]	0.875	61.6	63.4	26.3	4.2	5.8	20.7	23.1	16.9	17.8	1.6	-4.1	-0.6	-4.3
		(54.6)	(58.1)	(29.5)	(3.9)	(4.5)	(18.3)	(23.2)	(18.7)	(18.6)	(0.63)	(-3.3)	(0.6)	(-4.2)
Bi ₉ Sb ₁ [08]	0.9	25.7	64.5	62.4	20.5	8.1	6.6	16.5	16.8	20.9	-0.5	-5.5	5.7	-4.5
		(30.0)	(66.3)	(55.2)	(15.8)	(10.7)	(0.5)	(16.7)	(15.4)	(18.8)	(-4.4)	(-5.6)	(2.9)	(-0.9)
Bi [166] Theory ^a Theory ^b Exp. ^c Exp. ^d	1.0	68.6		31.7	6.0			27.8	21.3					
		(62.6)		(36.1)	(8.8)			(25.6)	(23.3)					
		68		30	10			24	19					
		67.7		40.6	8.7			25.0	24.3					
		69.3		40.4	13.5			24.5	25.4					
		68.7		40.6	12.9			23.7						

^a Ref. [12] data from [materials project database](#).

^b Ref. [355] data from LDA+SOC calculations.

^c Ref. [13] experiment was performed at 4.2 K. For high temperature C_{ij} values for Bi, see Ref. [13] and references therein.

^d Ref. [356] experiment was performed at 4.2 K.

elastic constants are defined in terms of free energy with respect to strain, the following conclusion can be made here: in presence of SOC, electrons in material are redistributed to minimize the total free energy, thereby recovering some of the strain energy and reducing the effective elastic stiffness.

FIGURE 7.2: Mechanical properties of Bi-Sb binaries calculated with and without inclusion of SOC (a) Bulk modulus B (in GPa), (b) Shear modulus G (in GPa), (c) Young's modulus E (in GPa), (d) Poisson's ratio ν , and (e) B/G ratio. Green dotted line in Fig. (e) shows the boundary ($B/G = 1.7$) below (above) which material behaves as brittle (ductile).

^a Experimental data at room temperature from Ref. [11].

^b Theoretical data from Ref. [12].

^c Experimental data at 4.2 K from Ref. [13].

7.3.2 Mechanical properties

We further test the mechanical stability of all the studied structures. A material can be considered mechanically stable if it passes the Born-Huang mechanical stability criteria [354, 357]. This criteria states that in order to be mechanically stable, the Gibbs free energy of any relaxed crystal, *i.e.* in absence of any external load, must be minimum compared to any other state reached by means of an infinitesimal strain. This requires that the elastic stiffness matrix C_{ij} is positive-definite, *i.e.* all the eigenvalues of C_{ij} are positive and the matrix is symmetric. Additionally, all the leading principle minors and any arbitrary set of minors (trailing minors) of C_{ij} must be positive. If a crystal, regardless of its symmetry, satisfies the aforementioned conditions, it can be considered

mechanically stable. The mathematical expressions for these conditions have been reported for different crystal classes by various research groups [358–361]. It is important to mention here that in some of the published papers [358–360] these conditions are incorrectly generalized from the cubic criteria (specially for the lower symmetry structures), which could lead to wrong quantitative analysis. However, it could not change the qualitative picture of mechanical stability of a crystal. For the first time, Mouhat and Coudert correctly generalized the Born-Huang mechanical stability conditions for all crystal classes [361]. Therefore, we refer the reader to the seminal paper of Mouhat and Coudert for further details regarding the necessary and sufficient conditions for the mechanical stability conditions [361]. In our case, we find that all the studied Bi-Sb binary structures pass the Born-Huang mechanical stability test and hence can be considered mechanically stable.

Once the C_{ijkl} constants are calculated, the four moduli (B , G , E , and ν) can be obtained by using relations between the constants [362]. Details of these relations for different crystal systems, and for Voigt and Reuss bound schemes are summarized in Ref. [360]. The bulk modulus represents the volume compressibility of the material and is given by $B = E/3(1 - 2\nu)$ [354]. Young's modulus gives a measure of the stiffness of the system. It is simply ratio of the stress along an axis to strain along that axis. A material is very stiff if it has large E . Poisson's ratio is used as a measure of plasticity as it measures the expansion of material in the transverse direction to the direction of compression. It is calculated using $\nu = (3B - 2G)/2(3B + G)$. The shear modulus, or the modulus of rigidity, describes the deformation of the system under transverse internal forces. It is related to Young's modulus and the Poisson ratio by $G = E/2(1 + \nu)$. A way to measure the brittleness or ductility of a material comes from the ratio of the bulk modulus to the shear modulus, B/G ratio, with values above 1.7 giving ductile behavior [173, 362].

Figures 7.2 (a-c) show the observed variation in the B , G , and E values as a function of Bi-concentration in $\text{Bi}_x\text{Sb}_{1-x}$. Red (Blue) color represents the data points calculated with (without) inclusion of SOC. We notice that B , G , and E values systematically decrease with increasing Bi-concentration, however, change in B is relatively less compared to that for G and E . As expected, the effects of SOC are more dominant towards Bi-rich side than that of towards Sb-rich side. We notice that in all moduli except B , these effects on the Bi-rich compositions are present, and the same reversal in trends mentioned in the previous section can be seen in Bi_9Sb_1 .

The available experimental and theoretical data (given in Fig. 7.2) are in excellent agreement with our theoretical calculations. [11–13] Here, it is important to mention that all the theoretical values are lower than that of the experimental observations. This is due to the fact that we used GGA approximation in all our calculations, and GGA is well-known to underestimate the elastic constant values [360]. We also notice that the Poisson's ratio (ν) and B/G ratio increase with increasing Bi-concentration, indicating increase in the ductile behavior of Bi-rich compositions. This could be associated to decrease in the strength of the covalent bonds in Bi-rich compositions. The Bi-Bi bond length in pristine Bi (3.10 Å) is considerably larger compared to the Sb-Sb bond length in pristine Sb (2.96 Å), thus suggesting stronger covalent bonding in Sb. The average bond length increases with increase in the Bi-concentration. The bond lengths are as follows: in pristine Sb: Sb-Sb bond = 2.96 Å; in Bi₁Sb₇: Sb-Sb bond = 2.98 Å; in Bi₁Sb₁: Bi-Sb bond = 3.04 Å; in Bi₃Sb₁: Bi-Sb = 3.03 Å and Bi-Bi = 3.09 Å; in Bi₇Sb₁: Bi-Sb = 3.02 Å and Bi-Bi = 3.10–3.12 Å; in Bi₉Sb₁: Bi-Sb = 3.05 Å and Bi-Bi = 3.12 Å, and in pristine Bi (Bi-Bi = 3.10 Å). Consequently, the increasing bond-length causes decrease in the elastic moduli and increase in the ν and B/G values. The observed variation in the mechanical properties is consistent with changes in the bond-length. Thus, monotonic decrease in B , G , and E values with increasing Bi-concentration can be correlated with decreasing valence electron density [363]. However, the anomalies observed in the elastic properties of Bi₉Sb₁ composition with low-Sb concentration that are consistent with previous experimental studies [11] warrant for a further investigation of this issue. The *first-principles* calculations using Virtual Crystal Approximation (VCA), which are beyond the scope of the present work, can offer good insights to resolve this issue. The possible reasons behind the observed anomalies in the properties of Bi₉Sb₁ are discussed below.

7.3.3 Negative Poisson's ratio

Materials having negative Poisson's ratio (ν), known as auxetic materials, have attracted special attention of researchers due to their exceptional advantages in the sensing technology [364–370]. As we mentioned earlier, a positive Poisson's ratio defines the ratio of the transverse contraction to the longitudinal extension of a material during the stretching process. Therefore, materials with negative Poisson's ratio, auxetic materials, are

FIGURE 7.3: Top, middle, and bottom panels represent the calculated Poisson's ratio of Bi_1Sb_7 , Bi_7Sb_1 , and Bi_9Sb_1 binaries, respectively. All plots were generated using the ELATE software [14]. Green (red) color corresponds to the positive (negative) values of ν (see text for details).

expected to expand in the transverse direction when stretched in the longitudinal direction. Auxetic materials are quite rare in nature as compared to the non-auxetic materials. However, Baughman et al. [366] reported that the auxetic property is often observed in cubic elemental metals. Interestingly, auxetic materials with lower symmetry are more appealing for technological applications because they yield much larger strain amplification as compared to the highly symmetric auxetic materials [367]. In order to analyze the auxeticity of the studied structures, we thoroughly investigate the elastic tensor of each studied composition calculated with-SOC.

Using the open source ELATE software tool [14, 371], we have analyzed the spatial variation of Poisson's ratio for each studied structures. We observe that three out of seven binary structures exhibit significantly large negative Poisson's ratio along different

spatial directions. All these structure belong to the low symmetry (monoclinic) space groups, therefore, these structures are more advantageous for technological applications. The results are given in Fig. 7.3. Regarding the theoretical details of these plots, we refer the reader to the excellent paper of Gaillac et al. [371]. In spherical coordinates, the determination of ν requires an extra dimension in addition to the $\theta(0, \pi)$ and $\phi(0, 2\pi)$ coordinates, i.e. $\nu(\theta, \phi, \chi)$. The additional dimension can be characterized by an angle $\chi(0, 2\pi)$ [371, 372]. The blue color in Fig. 7.3 represents the surface obtained at the maximum of χ , whereas the green (red) lobes corresponds to the positive (negative) values of ν obtained at the minimum of χ . We find that Bi_9Sb_1 monoclinic structure exhibits the largest negative Poisson's ratio in $y - z$ plane. The minimum value of ν is ~ -0.6 , which is comparable with the value $\nu_{min} = -0.8$ reported for polymer foam structures by Lakes et al. [365]. The other two monoclinic structures, Bi_1Sb_7 and Bi_7Sb_1 , inherit relatively smaller negative Poisson's ratio.

In order to understand the microscopic origin of negative Poisson's ratio, we analyze the geometry of the bonds and the distribution of electron localization function along the bond directions in Bi_9Sb_1 , as shown in Fig. 7.4(a). One can notice that the atomic bonds in Bi_9Sb_1 form hinge or bow-tie like structure in the $y - z$ plane. Such structural arrangement has been reported to yield negative Poisson's ratio in auxetic materials (see figure 1 of ref. [369]). A linear chain of Bi-Bi atoms forming inverted hexagon or hinge like bonds can be noticed in the highlighted region of Fig. 7.4(a). Plotting electron localization function reveals that two adjacent Bi-Bi bonds inherit opposite features in their electron distribution. Along one bond there exists overlap of charges in the mid indicating bonding nature of orbitals from two nearest Bi atoms, whereas, along the consecutive Bi-Bi bond, no such charge overlap is present indicating antibonding feature or presence of a charge nodal plane at the middle of Bi-Bi bond. Such two adjacent bonds could form orthogonal hinges, which are responsible for the observed auxetic behavior in Bi_9Sb_1 . Similar concept can be applied to explain the auxeticity of Bi_1Sb_7 and Bi_7Sb_1 monoclinic structures. Due to the intrinsic hinge structures, in presence of compressive strain along longitudinal direction, these structures tend to shrink in the transverse direction, and vice-versa. Fig. 7.4(b) illustrates the behavior of an auxetic material in presence of compressive or tensile strain.

FIGURE 7.4: (a) Distribution of electron localization function (turquoise color) in monoclinic Bi_9Sb_1 plotted at isosurface value $\eta = 0.25$. Purple color represents Bi atoms and yellow color represents Sb atoms. The hinge structure or bow-tie structure of Bi-Bi bonds can be noticed in the selected region. (b) Illustration of the negative Poisson's effect under compression (left) and expansion (right) on auxetic materials. Dotted square represents the deformed shape of the original structure (solid lines) and the arrows represent the direction of strain.

7.3.4 Elastic wave velocities, Debye temperature and Melting temperature

Knowledge of the elastic wave velocities, Debye temperature and melting temperature is important for practical applications. Therefore, we estimate these quantities using the

MechElastic code. [353]. We calculate the longitudinal (v_l), transverse (v_t), and average (v_m) elastic wave velocities using the following relations [373, 374]:

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad (7.2)$$

$$v_t = \sqrt{\frac{G}{\rho}}, \quad (7.3)$$

$$\frac{1}{v_m} = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}, \quad (7.4)$$

where B and G are the bulk and shear moduli, and ρ is the density of material. Conversely, one can also determine the elastic stiffness constants by measuring the distance traveled by an ultrasonic wave pulse and the corresponding time.

Debye temperature (Θ_D) is another important parameters that we can estimate from the knowledge of the elastic wave velocities and the density of material. Debye temperature correlates with several important physical properties such as specific heat, elastic constants, ultrasonic wave velocities and melting temperature. At low temperatures, acoustic phonons are the only vibrational excitations that contribute to the specific heat. Therefore, at low temperatures the Debye temperature calculated from the elastic constants is same as the Θ_D obtained from the specific heat measurements. We calculate Θ_D using the following equation [373]:

$$\Theta_D = \frac{h}{k_B} \left[\frac{3q}{4\pi} \frac{N\rho}{M} \right]^{1/3} v_m, \quad (7.5)$$

where h is the Planck's constant, k_B is the Boltzmann's constant, q is the total number of atoms in cell, N is the Avogadro's number, ρ is the density, and M is the molecular weight of the solid. The melting temperature was estimated using the empirical relation: $T_{melt} = 607 + 9.3B \pm 555$ [375].

Table 7.2 contains a list of the v_l , v_t , v_m , Θ_D and T_{melt} values calculated with and without inclusion of SOC. We notice that the magnitude of the elastic wave velocities and Θ_D decreases due to the SOC effects, which can be associated to the SOC-induced elastic softening. Figure 7.5 shows variation in the elastic wave velocities and Θ_D as a function

FIGURE 7.5: (a) Elastic wave velocities, and (b) Debye temperature (Θ_D) of Bi-Sb binaries calculated with SOC.

of the Bi-concentration. In general, we observe a monotonic decrease in the mentioned quantities with increasing Bi-concentration. However, anomalies from the monotonic trend can be noticed at low Sb-concentration. This observation is consistent with the previous experimental studies of Gopinathan et al. [11] and Lichnowski et al. [13], where authors investigated the elastic properties of $\text{Bi}_x\text{Sb}_{1-x}$ crystals using ultrasonic waves. The experimental Θ_D values for pristine Sb and pristine Bi at low temperature are ~ 210 K and ~ 112 K, which are in excellent agreement with our theoretical findings.

Anomalous changes in the electronic, thermal, elastic, and mechanical properties of $\text{Bi}_x\text{Sb}_{1-x}$ at very low Sb-concentration have been often noted in experiments. $\text{Bi}_x\text{Sb}_{1-x}$ undergoes a semimetal-semiconductor phase transition in the Sb-concentration range: $0.07 < x < 0.22$, and a topological non-trivial insulator phase appears due to the inverted ordering of bands at the L-point of Brillouin zone [85, 376–378]. Rogacheva et al. [95] studied the effect of low Sb-concentration on the lattice parameters, microhardness, electrical conductivity, magnetoresistance, and the Seebeck coefficient of $\text{Bi}_x\text{Sb}_{1-x}$. Their experiments revealed an anomalous change in the properties of $\text{Bi}_x\text{Sb}_{1-x}$ at small x values, which were attributed to the percolation transition, geometric re-ordering of atoms, and semimetal-semiconductor electronic phase transition. They further argued that at low Sb-concentration, the elastic fields of neighboring atoms begin to overlap causing partial compensation of elastic stress with reversed signs, which leads to an abrupt decrease in the elastic stiffness of the entire crystal [95]. Due to this reason, at low Sb-concentration $\text{Bi}_x\text{Sb}_{1-x}$ exhibits rapid decrease in the microhardness, electrical conductivity, and Seebeck coefficient. Increasing Sb-concentration beyond a critical

value yields formation of new atomic ordering causing enhancement in the elastic and mechanical properties of $\text{Bi}_x\text{Sb}_{1-x}$. Same argument can be used to explain the observed variation in the elastic wave velocities and Debye temperature of $\text{Bi}_x\text{Sb}_{1-x}$ with varying x (see Fig. 7.5).

TABLE 7.2: List of the longitudinal (v_l), transverse (v_t), average (v_m) elastic wave velocities, Debye (Θ_D) and melting temperatures (T_{melt}) calculated with (PBE+SOC) and without SOC (PBE). Values calculated with PBE+SOC are given in parentheses. The space group of each composition is given in square brackets.

Composition	v_l (m/s)	v_t (m/s)	v_m (m/s)	Θ_D (K)	T_{melt} (K)
Sb [166]	3240 (3256)	1946 (1945)	2152 (2152)	202.4 (202.4)	930 (937)
Exp. ^a				209.6	
Exp. ^b				210.0	
Exp. ^c				211.3	
Exp. ^d				211.3	
Bi ₁ Sb ₇ [06]	2941 (2943)	1714 (1712)	1902 (1899)	177.2 (177.0)	904 (906)
Bi ₁ Sb ₁ [160]	2548 (2519)	1432 (1372)	1593 (1531)	145.0 (139.3)	881 (887)
Bi ₃ Sb ₁ [160]	2308 (2260)	1151 (1077)	1291 (1211)	116.5 (109.2)	893 (893)
Bi ₇ Sb ₁ [08]	2123 (2097)	1050 (975)	1179 (1098)	105.0 (98.0)	856 (863)
Bi ₉ Sb ₁ [08]	2158 (1989)	1131 (885)	1265 (999)	112.5 (88.9)	850 (847)
Bi [166]	2197 (2237)	1071 (1102)	1203 (1237)	108.2 (111.3)	901 (908)
Exp. ^e				112	

^a Ref. [379], ^b Ref. [380], ^c Ref. [381] data from specific heat measurements at low temperatures.

^d Ref. [382] data from thermal expansion measurements.

^e Ref. [383] data evaluated from the sound velocity measurements.

7.3.5 Specific heat

After evaluating the elastic properties and mechanical stabilities of the Bi-Sb binaries, we focus our attention on the specific heat (C) of crystal lattice. Before we start our

discussion, it is important to mention that at low temperatures (T) the difference between $C_p(T)$ (at constant pressure) and $C_v(T)$ (at constant volume) is almost negligible and it lies within the uncertainty range of the experiments [384]. Therefore, we do not make any distinction between $C_p(T)$ and $C_v(T)$ in the present work. In the low T limit, the general relationship between $C(T)$ and T can be described using the following expression:

$$C(T) = \gamma T + \beta T^3 + \alpha T^{-2} \quad (7.6)$$

where, first and second terms correspond to the electronic and crystal lattice contributions to the specific heat, whereas, the last term addresses the interaction of the nuclear quadrupole moment with the electric field gradient of electrons and lattice. The last term is very small even at low temperatures, however, it might become substantial below 1 K [262]. Usually at low T , the specific heat follows T^3 power law due to the dominant contribution from the lattice vibrations. Therefore, plotting $C(T)/T^3$ versus T is a good way to determine the contribution of the lattice vibrations in the net heat capacity [262, 384–386]. The peak appearing in this plot is the evidence of the deviation from the Debye behavior that is known to separate the contribution of the acoustic phonons and optical phonons in the total specific heat of material. From the observed position of peak in $C(T)/T^3$ versus T plot, one can estimate the Einstein's oscillator temperature which is typically equal to $\sim 6T_0$, where T_0 is the temperature corresponding to the maximum $C(T)/T^3$ [384, 386].

Figure 7.6 shows the $C(T)/T^3$ versus T plots for all the studied binaries. SOC was not included in the calculation of $C(T)$. The corresponding phonon dispersion for each structure is given in Ref. [110]. Noticeably, the peak height in $C(T)/T^3$ versus T plot significantly increases (more than three times) with increasing Bi-concentration from Bi_1Sb_7 to Bi_9Sb_1 . Also, the peak shifts towards lower T with increasing Bi-concentration indicating decrease in Θ_D as we go towards Bi-rich side. This is consistent with Θ_D obtained from the elastic constants calculations, and it can be associated to the decrease in the average strength of the covalent bonds in Bi-rich binaries. We further compare our results with the available theoretical and experimental reports on the pristine Bi [261, 345–347], pristine Sb [262, 348] and Bi-Sb binaries [13]. Our findings are in remarkable agreement with the reported data in the literature. Lichnowski and Saunders [13] have experimentally observed decrease in Θ_D with increasing Bi-concentration. The accepted T_0 values for pristine Sb and pristine Bi are 7.5 K and 14 K, respectively [261, 262]. In

FIGURE 7.6: $C(T)/T^3$ versus Temperature T data for Bi-Sb binaries.

agreement, we also notice an overall shift of the T_0 towards lower temperatures from 12 K (for Sb-rich composition) to 8 K (for Bi-rich composition).

Finally, we would like to make a remark about the effect of SOC on the specific heat of the studied binaries. Undoubtedly, SOC is expected to have significant effects on the thermodynamic properties of Bi-rich binaries. In particular, the SOC effects in Bi cause an enhancement in the $C(T)/T^3$ peak height and decrement in the Θ_D value by ~ 1 K, thereby reducing the discrepancies between the experimental heat capacity data and *ab initio* results [261]. However, SOC is found to have negligible effects on the thermodynamic properties of pristine Sb [262]. This is the reason why our results (calculated without inclusion of SOC) for Sb-rich binaries compare well with the experimental observations, while there exists a small inconsistency in the data of Bi-rich compositions (for example– Bi_9Sb_1). Including SOC effects in the calculations would yield better agreement with the experimental data, specifically for Bi-rich compositions. Nevertheless, SOC induced changes in the T_0 values are expected to be within ± 1 K range.

7.4 Chapter Summary

In summary, we have investigated the elastic, mechanical and thermodynamic properties of several energetically stable Bi-Sb binary structures. We find that bulk, shear, and Young's moduli increase with increasing Sb-concentration in $\text{Bi}_x\text{Sb}_{1-x}$, and decrease as we move towards Bi-rich side. However, Poisson's ratio and B/G ratio increase with increasing Bi-concentration suggesting more ductile behavior in Bi-rich compositions. Our calculations reveal that Bi_1Sb_7 , Bi_7Sb_1 , and Bi_9Sb_1 monoclinic structures exhibit negative Poisson's ratio indicating auxeticity along different spatial directions. The hinge structure of atomic bonds is the main source of negative Poisson's ratio in these structures. We also probe the effect of SOC on the elastic and mechanical properties of Bi-Sb binaries. In general, the SOC effects cause elastic softening in most of the studied structures which can be ascribed to the fact that in presence of SOC, electrons are redistributed to minimize the total free energy, thereby recovering some of the strain energy and reducing the effective elastic stiffness. Our calculations reveal that Debye temperature and magnitude of the elastic wave velocities monotonically decrease with increasing Bi-concentration. This can be ascribed to the decreasing strength of covalent bonds (*i.e.* larger bond-length) in the Bi-rich compositions. However, we observe some anomalies in the elastic properties of Bi-rich composition Bi_9Sb_1 , which requires further investigation. The peak of $C(T)/T^3$ shifts towards lower temperatures and increases in height with increasing Bi-concentration. We find that SOC plays an important role in the determination of the properties for Bi-rich compositions, while the effects of SOC are very small for Sb-rich compositions. Our overall results are consistent with the available experimental data.

Summary and Outlook

In this research work, we predicted several new low energy stoichiometric crystal structures of $\text{Bi}_x\text{Sb}_{1-x}$ which were obtained from a systematic exploration of the potential energy surface of Bi-Sb binaries using minima hopping method [108, 158]. These structures have negative formation energy and most of the reported structures are thermodynamically stable. In addition to the ground state structures, we obtained several metastable structures that are very close to the convex-hull line. The structural, vibrational, electronic, thermoelectric, elastic, and mechanical properties of the selected crystal phases were further investigated. This research suggests that Bi-Sb binaries can have very useful applications in the spintronics industry, as well as auxetics, and as excellent thermoelectric materials for many everyday applications.

Several structures of Bi-Sb binaries exhibit novel topological quantum phases. From a detailed analysis of the electronic structure of the lowest energy structure on convex-hull, BiSb (space group #160), we noticed that this structure exhibits several intriguing properties, such as - large Rashba-Dresselhaus spin-splitting in bulk, ferroelectric polarization, topological quantum phase, and a Weyl semimetallic phase under pressure. Although Weyl fermions were first experimentally spotted in condensed matter crystals in 2015, a possible control over their dynamics was not realized. For the first time, we theoretically proposed a way to create Weyl fermions in crystal and gain harness over their dynamics by exploiting the aforementioned properties of BiSb crystal. In particular, we demonstrated that Weyl fermions appear in BiSb at 4.0 GPa pressure *via* pair-creation, and they annihilate at 6.0 GPa pressure *via* pair-annihilation. We further

demonstrated that by utilizing an interlink among pressure, ferroelectric polarization and the intrinsic spin-orbit coupling one can tune the dynamics of Weyl fermions in the momentum space of BiSb. By switching the direction of the ferroelectric polarization (*i.e.* by applying electric field), it is possible to switch two opposite Weyl fermions with different chirality. This proposal was later conceptually verified by an independently performed theoretical and experimental study [387]. In Ref. [387], Liang *et al.* reported the appearance of opposite Weyl fermions in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals under pressure. They also reported that opposite Weyl fermions meet and mutually annihilate at a higher pressure. They further observed change in the dynamics of Weyl fermions in the presence of external electric and magnetic fields. Such tunability of Weyl fermions allows us to develop the long-sought but not yet realized Weyltronic technology. In a recent work (2018), Su *et al.* [388] reported theoretical evidences of Weyl fermions in BiSb crystals, thus further corroborating our predictions made in 2016. These studies open the door to the development of Weyltronic technology.

Since Bi-Sb binaries are specially renowned for their excellent thermoelectric performance, we evaluated the thermoelectric properties of the considered Bi-Sb binary structures. Our theoretical study suggests that some obtained low-energy structures inherit very good thermoelectric properties which are comparable to the best known thermoelectrics to date. This implies potential applications of these binaries in low-temperature thermoelectric industry and refrigeration.

Given the potential practical applications of Bi-Sb binaries, it becomes important to understand the elastic and mechanical properties of these binaries before their technological applications can be realized. Due to this reason, we thoroughly scrutinized the elastic, mechanical, and thermodynamical properties of the interesting low-energy phases of Bi-Sb binaries and further studied the effect of spin-orbit coupling on the elastic stiffness. Our calculations indicate that spin-orbit effects soften the elastic stiffness of Bi-Sb binaries. In presence of spin-orbit coupling, electrons are redistributed in material to minimize the total free energy, consequently the system recovers some of the strain energy and minimizes its effective elastic stiffness. Notably, we find that three monoclinic structures of these binaries, Bi_1Sb_7 , Bi_7Sb_1 , and Bi_9Sb_1 , exhibit negative Poisson's ratio indicating auxeticity along different directions in crystal. This feature makes these structure of special interest for applications in the sensing industry. We also uncovered the origin of auxeticity in these structures. Our research shows that the

hinge-like geometric ordering of Bi-Sb covalent atomic bonds plays the key role in governing the auxeticity in these materials. The same mechanism can be applied to explain the origin of auxeticity in other solid state crystals, *e.g.* in Ni-Ti alloys.

Our calculations reveal that the Debye temperature and magnitude of the elastic wave velocities monotonically decrease with increasing Bi-concentration. This is attributed to the decreasing strength of covalent bonds (*i.e.* larger bond-length) in the Bi-rich compositions.

In addition to study the properties of BiSb in bulk, we also investigated the electronic structure of BiSb in two-dimensions. Our *first-principles* calculations reveal that the BiSb monolayer has a direct bandgap (~ 1.6 eV) having a free-electron-like parabolic conduction band feature near the Γ -point. Inclusion of spin-orbit coupling causes Rashba spin-splitting of conduction bands near Fermi-level. The magnitude of the Rashba spin-splitting is quite large in this monolayer system. In fact, it is among the best known 2D Rashba systems. The strength of Rashba effect in BiSb monolayer remains considerably large even when the monolayer is put in contact with another material. The existence of giant Rashba effect together with a large direct bandgap in visible regime paves the way to use BiSb-monolayer in the development of highly efficient spin field-effect transistors and optoelectronics devices.

Very recently, we have noticed signatures of large one-dimensional Rashba effect in BiSb nanowires with considerably large direct bandgap. This is exciting since it allows us to design topological heterostructures consisting of a Rashba nanowire and a superconducting substrate. Such systems have been predicted to host Majorana fermions at the edge of the nanowire [303, 305, 309]. Therefore, it would be a very interesting topic to investigate in future. If experimentally realized, Majorana fermions may pave the way for realization of fault-tolerant topological quantum computation [307, 308].

In collaboration with Madhav Ghimire (IFW Dresden, Germany), we have found that one can design a topological non-trivial structure by stacking trivial layers of Rashba semiconductors in an inverted ordering. We noticed that the quantum tunneling effects between the adjacent Rashba layers plays the key role in the topological phase transition. In particular, BiSb monolayer has broken inversion-symmetry and it is a trivial insulator (Z_2 invariant = 0) inheriting large Rashba effect. By stacking another BiSb monolayer in inverted ordering (*i.e.* SbBi) on top of BiSb monolayer forms an inversion-symmetric

bilayer structure – BiSb-SbBi – and the Rashba effects disappear in this bilayer due to the restored inversion symmetry along z -direction. However, band-inversion occurs at Fermi-level near the Γ point of reciprocal space, and the bilayer structure shows non-trivial topological features (Z_2 invariant = 1). This non-trivial topological phase is robust with increasing thickness of the bilayer heterostructure. We find that Z_2 invariant is 1 for two stacking of such bilayer (*i.e.* BiSb-SbBi – BiSb-SbBi) heterostructure, and same is true for 3, 4, 6, and 9 stacking of the inversion-symmetric bilayer heterostructure. All these two-dimensional structures host a gapless Dirac point at the Γ point of Brillouin zone. The inversion-symmetric structure of BiSb-SbBi in bulk belongs to 166 space group, and it is a strong 3D topological insulator. In future, it would be interesting to check if the same recipe can be utilized to design non-trivial topological structures using the other well-known 2D Rashba systems.

Another topic that would be compelling to study in future is the design of polar heterostructures consisting of BiSb monolayer and a ferroelectric substrate. This way one can further enhance the strength of Rashba spin-splitting in BiSb monolayer. Moreover, ferroelectric polarization of the substrate material can be used to tune the Rashba related properties of the BiSb monolayer. This study could have useful implications in the development of the spin-field effect transistors. We have recently realized considerable control over the Rashba features in BiSb monolayer in presence of an external magnetic field oriented along different directions in our *first-principles* calculations. This hints that use of ferromagnetic substrates could possibly reveal new intriguing quantum phenomenon in this system.

The thermoelectric performance of BiSb monolayer would be worth to study in future. Existence of novel quantum phenomenon, intriguing elastic properties, and excellent thermoelectricity in this system might open a plethora of new intriguing physics that is not yet understood. Some novel topological quantum phases might be hidden in the Bi-Sb binaries that would be uncovered in future. For instance, in a recent work, researchers observed a higher order topological phase in pristine Bi that hosts topologically protected metallic hinge states [389].

Lastly, we present a table (Table 8.1) containing the summary of Bi-Sb binary structures obtained from our MHM structural search calculations together with some experimentally reported structures of Bi-Sb binaries. The x-ray diffraction (XRD) spectra and

Wyckoff positions of all the predicted structures are given in Chapter 3. The simulated XRD patterns are in excellent agreement with experimental reports [9, 10]. Various experimental techniques [72, 390] that have been successfully used to grow Bi-Sb crystals in past are mentioned in Chapter 1.

TABLE 8.1: A summarized list of the MHM predicted low-energy structures of Bi-Sb binaries along with some references reporting these structures in experiments. Lattice parameters (in Å units) and energies E (in meV/atom units) were calculated using PBE-GGA functional.

Composition	Space group	Lattice parameters	$E_{\text{formation}}$	$E_{\text{above-hull}}$	Exp.
Bi ₁ Sb ₇	P_1m_1 (#06)	a = 6.369, b = 4.373, c = 9.381 $\alpha = 90.0$, $\beta = 93.4$, $\gamma = 90.0$	-8.74	0.00	[11, 206, 207]
Bi ₁ Sb ₁	$R3m$ (#160)	a = b = 4.516, c = 11.885	-14.9	0.00	[9, 11, 17, 23, 206]
	$Imm2$ (44)	a = 4.474, b = 6.413, c = 4.873	-5.64	9.26	
	$R\bar{3}m$ (166)	a = b = 4.618, c = 28.052	-5.04	9.86	
Bi ₃ Sb ₁	$R3m$ (#160)	a = b = 4.559, c = 23.984	-6.3	1.2	[206]
Bi ₇ Sb ₁	C_1m_1 (#08)	a = 9.632, b = 9.175, c = 7.954 $\alpha = 90.0$, $\beta = 56.7$, $\gamma = 90.0$	-3.03	0.0	[10, 35, 342]
Bi ₉ Sb ₁	C_1m_1 (#08)	a = 12.208, b = 8.134, c = 8.134 $\alpha = 147.0$, $\beta = 120.0$, $\gamma = 60.0$	-3.4	0.0	[10, 35, 85, 342, 344]

Appendix A

MechElastic Program

This python script can be used to calculate some important physical properties such as elastic moduli, melting temperature, Debye temperature, elastic wave velocities, elastic anisotropy, etc. for all crystalline systems using the VASP output data from an elastic tensor calculation. It can also be used to test the mechanical stability.

This script reads the elastic matrix written in the OUTCAR file. This software can be obtained at github:

<https://github.com/sobhitsinghphy/MechElastic>

NOTE: In order to evaluate accurate elastic properties and mechanical strength, one must well-converge the elastic constants by increasing the size of k -mesh in the VASP calculation.

An example input file (INCAR) for elastic constants calculations in VASP is given below:

```
1 system = Si-227
2 PREC = High
3 NELMIN = 8
4 NELM = 100
5 EDIFF = 1E-07
6 ISIF = 3
7 ENCUT = 450
8 LREAL = .FALSE.
9 NSW = 1
10 ISMEAR = 0
11 SIGMA = 0.02
```

```

12 IBRION = 6
13 POTIM = 0.015
14 NFREE = 2

```

Use the below line to execute the script:

```

1 >> python MechElastic.py OUTCAR cubic

```

The script expects ‘OUTCAR’ file as the first argument and ‘crystal type’ as the second argument. If not provided by user, this script will read the crystal type from the OUTCAR file. Crystal type is needed only to perform the mechanical stability test. If the crystal symmetry is not provided by user, the code will rely on spglib to find it. If OUTCAR file is within the same folder, it will be read by default. Another way to execute the script:

```

1 >> python MechElastic.py

```

*** PROGRAM ***

```

1 #!/usr/bin/env python
2
3 ''' Read elastic constants from OUTCAR, calculate elastic moduli, and
    perform mechanical stability test:
4   Authors: Sobhit Singh and Aldo Romero
5             *smsingh@mix.wvu.edu
6             **alromero@mail.wvu.edu
7   West Virginia University , Morgantown, USA
8   Version: 2017.12.12
9
10  To RUN if you know the crystal type:
11  >> python MechElastic.py OUTCAR cubic
12
13  If the crystal symmetry is not provided by user , then the code will rely
    on spglib to find it
14  >> python MechElastic.py OUTCAR '''
15
16 import numpy as np
17 import spglib
18 import sys
19 from numpy import linalg as LA
20 from prettytable import PrettyTable

```

```

21 import argparse
22
23 # following info about elements has been taken from https://www.lfd.uci.edu
    /~gohlke/code/elements.py.html
24
25 ELEMENTS = { 'H' : 1 , 'He' : 2 , 'Li' : 3 , 'Be' : 4 , 'B' : 5 , 'C' : 6 ,
    'N' : 7 , 'O' : 8 , 'F' : 9 , 'Ne' : 10 , 'Na' : 11 , 'Mg' : 12 , 'Al'
    : 13 , 'Si' : 14
26 'P' : 15 , 'S' : 16 , 'Cl' : 17 , 'Ar' : 18 , 'K' : 19 , 'Ca' : 20 , 'Sc' :
    21 , 'Ti' : 22 , 'V' : 23 , 'Cr' : 24 , 'Mn' : 25 , 'Fe' : 26 , 'Co' :
    27 , 'Ni' : 28
27 'Cu' : 29 , 'Zn' : 30 , 'Ga' : 31 , 'Ge' : 32 , 'As' : 33 , 'Se' : 34 , 'Br'
    ' : 35 , 'Kr' : 36 , 'Rb' : 37 , 'Sr' : 38 , 'Y' : 39 , 'Zr' : 40 , 'Nb'
    ' : 41 , 'Mo' :
28 'Tc' : 43 , 'Ru' : 44 , 'Rh' : 45 , 'Pd' : 46 , 'Ag' : 47 , 'Cd' : 48 , 'In'
    ' : 49 , 'Sn' : 50 , 'Sb' : 51 , 'Te' : 52 , 'I' : 53 , 'Xe' : 54 , 'Cs'
    ' : 55 , 'Ba' :
29 'La' : 57 , 'Ce' : 58 , 'Pr' : 59 , 'Nd' : 60 , 'Pm' : 61 , 'Sm' : 62 , 'Eu'
    ' : 63 , 'Gd' : 64 , 'Tb' : 65 , 'Dy' : 66 , 'Ho' : 67 , 'Er' : 68 , '
    Tm' : 69 , 'Yb' :
30 'Lu' : 71 , 'Hf' : 72 , 'Ta' : 73 , 'W' : 74 , 'Re' : 75 , 'Os' : 76 , 'Ir'
    : 77 , 'Pt' : 78 , 'Au' : 79 , 'Hg' : 80 , 'Tl' : 81 , 'Pb' : 82 , 'Bi'
    ' : 83 , 'Po' :
31 'At' : 85 , 'Rn' : 86 , 'Fr' : 87 , 'Ra' : 88 , 'Ac' : 89 , 'Th' : 90 , 'Pa'
    ' : 91 , 'U' : 92 , 'Np' : 93 , 'Pu' : 94 , 'Am' : 95 , 'Cm' : 96 , 'Bk'
    ' : 97 , 'Cf' :
32 'Es' : 99 , 'Fm' : 100 , 'Md' : 101 , 'No' : 102 , 'Lr' : 103 , 'Rf' : 104
    , 'Db' : 105 , 'Sg' : 106 , 'Bh' : 107 , 'Hs' : 108 , 'Mt' : 109 }
33
34 if len(sys.argv) < 2:
35     print "OUTCAR file is expected as the first argument \n"
36 else:
37     print "reading OUTCAR ....."
38
39 def printMatrix(c):
40     p = PrettyTable()
41     for row in c:
42         p.add_row(row)
43     print p.get_string(header=False, border=False)
44
45 ## Defining useful constants

```

```
46 ## Avogadro number
47 N_avogadro = 6.022140857e+23
48 ## Planck's constant
49 h_Planck = 6.62607004e-34
50 ## Boltzmann constant
51 kB = 1.38064852e-23
52
53
54 f = open(sys.argv[1], 'r')
55 lines = f.readlines()
56 f.close()
57
58 s=np.zeros((6,6))
59 c=np.zeros((6,6))
60
61 nions=-1
62 mass=[]
63 foundcell=0
64 icell=-1
65 iatom=-1
66 lattice=[]
67 positions=[]
68 atomic_numbers=[]
69 symbols=[]
70 for i in lines:
71     word = i.split()
72     if "TOTAL ELASTIC MODULI (kBar)" in i:
73         ii=lines.index(i)
74         if "POMASS" in i and "ZVAL" in i:
75             m=i.split()[2]
76             mass.append(float(m[:-1]))
77         if "volume of cell" in i:
78             vol=float(i.split()[4])
79         if "NIONS =" in i:
80             nions=int(i.split()[11])
81         if "ions per type =" in i:
82             natoms=map(int, i.split()[4:])
83         if "LATTYP" in i:
84             lattyp=i
85         if (icell > -1 and not foundcell):
86             lattice.append(map(float, i.split()[3:])))
```

```

87         icell=icell+1
88         if ( icell == 3):
89             foundcell=1
90         if not foundcell and "direct lattice vectors" in i:
91             icell=icell+1
92         if (nions>0 and iatom> -1):
93             positions.append(map(float ,word))
94             iatom=iatom+1
95             if (iatom==nions):
96                 iatom=-1
97         if nions>0 and "position of ions in fractional coordinates" in i:
98             iatom=iatom+1
99         if "ions per type =" in i:
100             iontype=map(int ,word[4:])
101         if "VRHFIN" in i:
102             symbols.append(i.split()[1][1:-1])
103         if "length of vectors" in i:
104             n=lines.index(i)
105             l=lines[n+1]
106             lattconst = l.split()
107
108     ## cell parameters
109     A = float(lattconst[0])
110     B = float(lattconst[1])
111     C = float(lattconst[2])
112
113
114     print "Lattice parameters (in Angs.): a = %10.5f          b = %10.5f          c =
115           %10.5f" %(A, B, C)
116
117     atomic_numbers=np.zeros(nions ,dtype=np.int32)
118     k=0
119     for i in range(len(iontype)):
120         for j in range(iontype[i]):
121             atomic_numbers[k]=ELEMENTS[symbols[i]]
122             k=k+1
123
124     print "Atomic numbers"
125     print atomic_numbers
126     lattice=np.array(lattice)
127     positions=np.array(positions)

```

```

127 cell=(lattice , positions , atomic_numbers)
128
129 mass=np.array(mass)
130 print "Mass of atoms (in g/mol units): "
131 print(np.array(mass))
132 print "Number of atoms: %d" %np.sum(natoms)
133
134 totalmass=0.0
135 for i in range(len(natoms)):
136     totalmass = totalmass + natoms[i]*mass[i]
137 print "Total mass (in g/mol): %10.4f " %totalmass
138 print "Volume of the cell (in Ang^3 units): %10.4f " %vol
139
140 ## converting the units
141 vol = vol*1.0e-30      ## from Angstrom to meters
142 totalmass = totalmass*1.0e-3 ## from gram to kg
143 density = totalmass/(vol*N_avogadro)
144
145 print '\n Density (in kg/m^3 units ): %10.5f' % density
146
147
148 for i in range(0,6):
149     l=lines[ii+3+i]
150     word = l.split()
151     s[i][:]=word[1:7]
152     c[i]=map(float , s[i][:])
153
154 mc=np.matrix(c)
155 mci=mc.I
156
157 for i in range(0,6):
158     for j in range(0,6):
159         s[i][j]=mci[i,j]
160
161 print "Printing Cij matrix as read from OUTCAR\n"
162 printMatrix(c)
163
164 ## Redefining the Cij matrix into the correct Voigt notation since VASP's
    OUTCAR has a different order
165 ## In VASP: Columns and rows are listed as: 1, 2, 3, 6, 4, 5

```



```

166 ## In this format OUTCAR's C44 values would be actually C66, C55 would be
    C44, and C66 would be C55.
167 ## OUTCAR follows the below order:
168 ## [C11 C12 C13 C16 C14 C15]
169 ## [C21 C22 C23 C26 C24 C25]
170 ## [C31 C32 C33 C36 C34 C35]
171 ## [C61 C62 C63 C66 C64 C65]
172 ## [C41 C42 C43 C46 C44 C45]
173 ## [C51 C52 C53 C56 C54 C55]
174
175 cnew = np.zeros((6,6))
176 snew = np.zeros((6,6))
177 cnew = np.copy(c)
178
179 for j in range(0,6):
180     cnew[3][j] = c[4][j]
181     cnew[4][j] = c[5][j]
182     cnew[5][j] = c[3][j]
183
184 ctemp=np.zeros((6,6))
185 ctemp = np.copy(cnew)
186
187 for i in range(0,6):
188     cnew[i][3] = cnew[i][4]
189     cnew[i][4] = cnew[i][5]
190     cnew[i][5] = ctemp[i][3]
191
192 #### Change the units of Cij from kBar to GPa
193 for i in range(0,6):
194     for j in range(0,6):
195         cnew[i][j] = cnew[i][j]/10.0
196
197 print "\n \n printing CNEW: Modified matrix in correct order (in GPa units)
    ... For example- to generate input for ELATE code [https://github.com/
    fxcoudert/elate]"
198 #np.set_printoptions(precision=3)
199 np.set_printoptions(precision=3, suppress=True)
200 #print(np.matrix(cnew))
201
202 printMatrix(cnew)
203

```

```

204 def check_symmetric(a, tol=1e-8):
205     return np.allclose(a, a.T, atol=tol)
206
207 print('\n Checking if the modified matrix CNEW is symmetric: i.e.  $C_{ij} = C_{ji}$ 
      : %10s' % check_symmetric(cnew))
208
209 def positive_evals(cnew):
210
211     print "\nEigen Values of the matrix CNEW:"
212     evals = LA.eigvals(cnew)
213     print(evals)
214
215     check = 0
216     for i in range(len(evals)):
217         if evals[i] > 0.0:
218             pass
219         else:
220             check = 1
221
222     if check == 1:
223         print "ATTENTION: One or more eigen values are negative indicating
              elastic instability."
224
225     if check == 0:
226         print "All eigen values are positive indicating elastic stability."
227
228 ## calculate elastic properties
229 def main():
230     # elastic_const(cnew,snew)
231     # parser = argparse.ArgumentParser()
232     # parser.add_argument("-d", help="select the dimensionality of the system
233     #                      ")
234
235     # args = parser.parse_args()
236
237     if (sys.argv[3] == '2D'):
238         elastic_const_2D(cnew)
239     else:
240         elastic_const_bulk(cnew,snew)
241
242     positive_evals(cnew)

```

```

242 crystal = np.array(['cubic', 'hexagonal', 'tetragonal', 'rhombohedral-1',
    'rhombohedral-2', 'orthorhombic', 'monoclinic'])
243 if len(sys.argv) == 3:
244     if (np.sum(crystal == sys.argv[2]) > 0):
245         print "Given crystal system: %10s" % sys.argv[2]
246         crystaltype = sys.argv[2]
247         print "\n \t \t Mechanical Stability Test \n"
248         stability_test(cnew, crystaltype)
249     else:
250         buildcellfromOUTCAR()
251         print "\t \t WARNING: crystal symmetry class was not provided
    by user, it will be taken from the OUTCAR"
252         print "\t \t One of the following was expected as the second argument
    : 'cubic', 'hexagonal', 'tetragonal', 'rhombohedral-1', 'rhombohedral
    -2', '
253             crystaltype=''
254             for x in crystal:
255                 if x in lattyp:
256                     crystaltype=x
257             if crystaltype=='':
258                 crystaltype='monoclinic'
259             print 'From OUTCAR the crystal type is = ',crystaltype
260             stability_test(cnew, crystaltype)
261             #print "\t \t To perform the mechanical stability test you need
    to enter the crystal symmetry class: one of the following is expected
    as the sec
262             #print "\t \t 'cubic', 'hexagonal', 'tetragonal', 'rhombohedral
    -1', 'rhombohedral-2', 'orthorhombic', 'monoclinic' "
263 else:
264     print "\t \t WARNING: crystal symmetry class was not provided by
    user, it will be taken from the OUTCAR"
265     print "\t \t One of the following was expected as the second
    argument: 'cubic', 'hexagonal', 'tetragonal', 'rhombohedral-1', '
    rhombohedral-2', 'orthorhombic', 'monoclinic'"
266     crystaltype=''
267     spg=int(spglib.get_spacegroup(cell, symprec=1e-5).split()
    [1][1:-1])
268     if (spg>=1 and spg<=2):
269         crystaltype='triclinic'
270     if (spg>=3 and spg<=15):
271         crystaltype='monoclinic'

```

```

272         if (spg>=16 and spg<=74):
273             crystaltype='orthorhombic'
274         if (spg>=75 and spg<=142):
275             crystaltype='tetragonal'
276         if (spg>=143 and spg<=167):
277             if (spg == 155 or spg == 160 or spg == 166):
278                 crystaltype='rhombohedral-1'
279             else:
280                 crystaltype='rhombohedral-2'
281         if (spg>=168 and spg<=194):
282             crystaltype='hexagonal'
283         if (spg>=195):
284             crystaltype='cubic'
285         print 'From OUTCAR the crystal type is = ',crystaltype
286         stability_test(cnew, crystaltype)
287
288 def elastic_const_bulk(cnew, snew):
289
290     ##Bulk: Voigt
291     KV = (cnew[0][0] + cnew[1][1] + cnew[2][2]) + 2*(cnew[0][1] + cnew[1][2]
292         + cnew[2][0])
293     KV = KV/9.0
294
295     ## Shear: Voigt
296     GV = (cnew[0][0] + cnew[1][1] + cnew[2][2]) - (cnew[0][1] + cnew[1][2] +
297         cnew[2][0]) + 3*(cnew[3][3] + cnew[4][4] + cnew[5][5])
298     GV = GV/15.0
299
300     ## Young's: Voigt
301     EV = (9*KV*GV)/(3*KV + GV)
302
303     ## Poisson's ratio: Voigt
304     Nu_V = (3*KV - EV)/(6*KV)
305
306     ## P-wave modulus, M: Voigt
307     MV = KV + (4*GV/3.0)
308
309     ##### Reuss Method
310     mc_new = np.matrix(cnew)
311     mci_new = mc_new.I

```

```

311     for i in range(0,6):
312         for j in range(0,6):
313             snw[i][j]=mci_new[i,j]
314
315     ## bulk: Reuss
316     KR = (snw[0][0] + snw[1][1] + snw[2][2]) + 2*(snw[0][1] + snw[1][2]
317           + snw[2][0])
318
319     KR = 1.0/KR
320
321     ## Shear: Reuss
322
323     GR = 4*(snw[0][0] + snw[1][1] + snw[2][2]) -4*(snw[0][1] + snw[1][2]
324           + snw[2][0]) + 3*(snw[3][3] + snw[4][4] + snw[5][5])
325
326     GR = 15.0/GR
327
328     ## Young's: Reuss
329
330     ER = (9*KR*GR)/(3*KR + GR)
331
332     ## Poisson's ratio: Reuss
333
334     Nu_R = (3*KR - ER)/(6*KR)
335
336     ## P-wave modulus, M: Reuss
337
338     MR = KR + (4*GR/3.0)
339
340     #### Voigt-Reuss-Hill Approximation: average of both methods
341     ## VRH
342
343
344     Kvrh = (KV + KR)/2.0
345     Gvrh = (GV + GR)/2.0
346     Evrh = (EV + ER)/2.0
347     Nu_vrh = (Nu_V + Nu_R)/2.0
348     Mvrh = (MV + MR)/2.0
349     KG_ratio_V = KV/GV
350     KG_ratio_R = KR/GR
351     KG_ratio_vrh = Kvrh/Gvrh
352
353     ## Elastic Anisotropy
354     ## Zener anisotropy for cubic crystals only
355     Az = 2*cnew[3][3]/(cnew[0][0] - cnew[0][1])
356
357     ##Ranganathan and Ostoja-Starzewski method: Phys. Rev. Lett. 101, 055504
358     (2008).

```

```

349  ## for any crystalline symmetry: Universal anisotropy index
350  AU = (KV/KR) + 5*(GV/GR) - 6.0
351
352  #"""Note: AU is a relative measure of anisotropy with respect to a
      limiting value. For example, AU does not prove that a crystal having AU
      = 3 has double
353
354  ## log-Euclidean anisotropy parameter by Christopher M. Kube, AIP
      Advances 6, 095209 (2016)
355  #"""AL CV , CR is based on the distance between the averaged
      stiffnesses CV and
356  #CR , which is more appropriate. Clearly, AL CV , CR is zero when the
      crystallite is isotropic.
357
358  AL = np.sqrt(5)*2.303*np.log(1 + (AU/5))
359
360  print "\n \n                               Voigt      Reuss      Average"
361  print "_____"
362  print "Bulk modulus      (GPa)  %9.3f %9.3f %9.3f " % (KV, KR, Kvrh)
363  print "Shear modulus    (GPa)  %9.3f %9.3f %9.3f " % (GV, GR, Gvrh)
364  print "Young modulus     (GPa)  %9.3f %9.3f %9.3f " % (EV, ER, Evrh)
365  print "Poisson ratio      %9.3f %9.3f %9.3f " % (Nu_V, Nu_R, Nu_vrh)
366  print "P-wave modulus    (GPa)  %9.3f %9.3f %9.3f " % (MV, MR, Mvrh)
367  print "Bulk/Shear ratio    %9.3f %9.3f %9.3f (%s) " % (KG_ratio_V,
      KG_ratio_R, KG_ratio_vrh, ductile_test(KG_ratio_vrh) )
368  print "_____"
369
370  print " \n \n \t \t Elastic Anisotropy \n "
371  print "Zener anisotropy (true for cubic crystals only) Az = %10.5f" %Az
372  print "Universal anisotropy index (Ranganathan and Ostoja-Starzewski
      method; PRL 101, 055504 (2008)) Au = %10.5f" %AU
373  print "Log-Euclidean anisotropy parameter by Christopher M. Kube, AIP
      Advances 6, 095209 (2016) AL = %10.5f " %AL
374
375  ## Calculation of elastic wave velocities and Debye temperature using
      the values obtained from the Voigt-Reuss-Hill Approximation
376
377  G = Gvrh*1.0e+9  ## converting from GPa to Pascal units (kg/ms^2)
378  K = Kvrh*1.0e+9
379
380  ## transverse velocity: Navier's equation

```

```

381     vt = np.sqrt((G/density))
382
383     ## longitudinal velocity: Navier's equation
384     vl = np.sqrt(((3*K + 4*G)/(3.0*density)))
385
386     ## average
387     vm=1.0/(np.cbrt((1./3.)*(2./(vt*vt*vt)+1./(vl*vl*vl))))
388
389     ## Debye temperature calculated using Orson Anderson's proposal [Ref- J.
390         Phys. Chem. Solids (1963) 24, 909-917]
391     q = np.sum(natoms)
392     theta = (h_Planck/kB)*vm*np.cbrt((3*q*N_avogadro*density)/(4*(np.pi)*
393         totalmass))
394
395     ## melting temperature using empirical relation from Ref: Johnston I,
396         Keeler G, Rollins R and Spicklemire S 1996
397     ## Solid State Physics Simulations, The Consortium for
398         Upper-Level Physics Software (New York: Wile
399     Tm = 607 + 9.3*Kvrh
400
401     print "\n \t \t Elastic wave velocities calculated using Navier's
402         equation (in m/s units) \n"
403     print "_____ "
404     print "Longitudinal wave velocity (vl) : %10.5f " %vl
405     print "Transverse wave velocity (vt) : %10.5f " %vt
406     print "Average wave velocity (vm) : %10.5f " %vm
407     print "Debye temperature (in K) : %10.5f " %theta
408     print "\nMelting temperature calculated from empirical relation: Tm
409         = 607 + 9.3*Kvrh \pm 555 (in K)"
410     print "Tm (in K)= %10.5f (plus-minus 555 K) " % Tm
411     print "_____ "
412
413     def ductile_test(ratio):
414         if(ratio > 1.75):
415             return "ductile"
416         else:
417             return "brittle"
418
419     def stability_test(matrix, crystaltype):
420         c = np.copy(matrix)

```

```

416 if(crystaltype == "cubic"):
417     print "Cubic crystal system \n"
418     print "Born stability criteria for the stability of cubic system are : [
419         Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
420
421     print "(i)  $C_{11} - C_{12} > 0$ ; (ii)  $C_{11} + 2C_{12} > 0$ ; (iii)  $C_{44} > 0$  \n "
422
423     ## check (i) keep in mind list starts with 0, so c11 is stored as c00
424     if(c[0][0] - c[0][1] > 0.0):
425         print "Condition (i) satisfied."
426     else:
427         print "Condition (i) NOT satisfied."
428
429     if(c[0][0] + 2*c[0][1] > 0.0):
430         print "Condition (ii) satisfied."
431     else:
432         print "Condition (ii) NOT satisfied."
433
434     if(c[3][3] > 0.0):
435         print "Condition (iii) satisfied."
436     else:
437         print "Condition (iii) NOT satisfied."
438
439 if(crystaltype == "hexagonal"):
440     print "Hexagonal crystal system \n"
441     print "Born stability criteria for the stability of hexagonal system are
442         : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
443     print "(i)  $C_{11} - C_{12} > 0$ ; (ii)  $2C_{13}^2 < C_{33}(C_{11} + C_{12})$ ; (iii)  $C_{44} > 0$  \n "
444
445     ## check (i) keep in mind list starts with 0, so c11 is stored as c00
446     if(c[0][0] - c[0][1] > 0.0):
447         print "Condition (i) satisfied."
448     else:
449         print "Condition (i) NOT satisfied."
450
451     if(2*(c[0][2]*c[0][2]) < c[2][2]*(c[0][0] + c[0][1])):
452         print "Condition (ii) satisfied."
453     else:
454         print "Condition (ii) NOT satisfied."
455
456     if(c[3][3] > 0.0):

```



```

454     print "Condition (iii) satisfied."
455 else:
456     print "Condition (iii) NOT satisfied."
457
458 if(crystaltype=="tetragonal"):
459     print "Tetragonal crystal system \n"
460     print "Born stability criteria for the stability of Tetragonal system
         are : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
461     print "(i)  $C_{11} - C_{12} > 0$ ;    (ii)  $2*C_{13}^2 < C_{33}(C_{11} + C_{12})$ ;    (iii)  $C_{44} > 0$ ;
         (iv)  $C_{66} > 0$ ;    (v)  $2C_{16}^2 < C_{66}*(C_{11}-C_{12})$  \n "
462
463     ## check (i)    keep in mind list starts with 0, so c11 is stored as c00
464     if(c[0][0] - c[0][1] > 0.0):
465         print "Condition (i) is satisfied."
466     else:
467         print "Condition (i) is NOT satisfied."
468
469     if(2*(c[0][2]*c[0][2]) < c[2][2]*(c[0][0] + c[0][1])):
470         print "Condition (ii) is satisfied."
471     else:
472         print "Condition (ii) is NOT satisfied."
473
474     if(c[3][3] > 0.0):
475         print "Condition (iii) is satisfied."
476     else:
477         print "Condition (iii) is NOT satisfied."
478
479     if(c[5][5] > 0.0):
480         print "Condition (iv) is satisfied."
481     else:
482         print "Condition (iv) is NOT satisfied."
483
484     if(2*c[0][5]*c[0][5] < c[5][5]*(c[0][0] - c[0][1])):
485         print "Condition (v) is satisfied."
486     else:
487         print "Condition (v) is NOT satisfied."
488
489 if(crystaltype=="rhombohedral-1"):
490     print "Rhombohedral (class-1): i.e. structures with point group:  $3m$ ,  $-3m$ 
         and  $32$  \n"

```

```

491     print "Born stability criteria for the stability of Rhombohedral-1 class
        system are : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
492     print "(i) C11 - C12 > 0;    (ii) C13^2 < (1/2)*C33(C11 + C12);    (iii)
        C14^2 < (1/2)*C44*(C11-C12) = C44*C66;    (iv)  C44 > 0; \n "
493
494     ## check (i)    keep in mind list starts with 0, so c11 is stored as c00
495     if(c[0][0] - c[0][1] > 0.0):
496         print "Condition (i) is satified."
497     else:
498         print "Condition (i) is NOT satisfied."
499
500     if((c[0][2]*c[0][2]) < (0.5)*c[2][2]*(c[0][0] + c[0][1])):
501         print "Condition (ii) is satified."
502     else:
503         print "Condition (ii) is NOT satisfied."
504
505     if(c[0][3]*c[0][3] < 0.5*c[3][3]*(c[0][0] - c[0][1])):
506         print "Condition (iii) is satified."
507     else:
508         print "Condition (iii) is NOT satisfied."
509
510     if(c[3][3] > 0.0):
511         print "Condition (iv) is satified."
512     else:
513         print "Condition (iv) is NOT satisfied."
514
515     if(crystaltype=="rhombohedral-2"):
516         print "Rhombohedral (class-2): i.e structures with point group: 3, -3 \n
        "
517         print "Born stability criteria for the stability of Rhombohedral-1 class
        system are : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
518         print "(i) C11 - C12 > 0;    (ii) C13^2 < (1/2)*C33(C11 + C12);    (iii)
        C14^2 + C15^2 < (1/2)*C44*(C11-C12) = C44*C66;    (iv)  C44 > 0; Note:
        C15 is added.. \
519
520         ## check (i)    keep in mind list starts with 0, so c11 is stored as c00
521         if(c[0][0] - c[0][1] > 0.0):
522             print "Condition (i) is satified."
523         else:
524             print "Condition (i) is NOT satisfied."
525

```

```

526     if(c[0][2]*c[0][2] < (0.5)*c[2][2]*(c[0][0] + c[0][1])):
527         print "Condition (ii) is satisfied."
528     else:
529         print "Condition (ii) is NOT satisfied."
530
531     if(c[0][3]*c[0][3] + c[0][4]*c[0][4] < 0.5*c[3][3]*(c[0][0] - c[0][1]))
532         :
533         print "Condition (iii) is satisfied."
534     else:
535         print "Condition (iii) is NOT satisfied."
536
537     if(c[3][3] > 0.0):
538         print "Condition (iv) is satisfied."
539     else:
540         print "Condition (iv) is NOT satisfied."
541
542 if(crystaltype == "orthorhombic"):
543     print "Orthorhombic crystal system.... \n"
544     print "Born stability criteria for the stability of Orthorhombic systems
545         are : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014)] \n"
546     print "(i) C11 > 0;    (ii) C11*C22 > C12^2;    (iii) C11*C22*C33 + 2C12*
547         C13*C23 - C11*C23^2 - C22*C13^2 - C33*C12^2 > 0;    (iv) C44 > 0;    (v)
548         C55 > 0 ;    (vi
549     ## check (i)    keep in mind list starts with 0, so c11 is stored as c00
550     if(c[0][0] > 0.0):
551         print "Condition (i) is satisfied."
552     else:
553         print "Condition (i) is NOT satisfied."
554
555     if(c[0][0]*c[1][1] < c[0][1]*(c[0][1])):
556         print "Condition (ii) is satisfied."
557     else:
558         print "Condition (ii) is NOT satisfied."
559
560     if(c[0][0]*c[1][1]*c[2][2] + 2*c[0][1]*c[0][2]*c[1][2] - c[0][0]*c
561         [1][2]*c[1][2] - c[1][1]*c[0][2]*c[0][2] - c[2][2]*c[0][1]*c[0][1] > 0
562     ):
563         print "Condition (iii) is satisfied."
564     else:
565         print "Condition (iii) is NOT satisfied."

```

```

561     if(c[3][3] > 0.0):
562         print "Condition (iv) is satisfied."
563     else:
564         print "Condition (iv) is NOT satisfied."
565
566     if(c[4][4] > 0.0):
567         print "Condition (iv) is satisfied."
568     else:
569         print "Condition (iv) is NOT satisfied."
570
571     if(c[5][5] > 0.0):
572         print "Condition (iv) is satisfied."
573     else:
574         print "Condition (iv) is NOT satisfied."
575
576 if(crystaltype=="monoclinic"):
577     print "Monoclinic crystal system.... \n"
578     print "Born stability criteria for the stability of monoclinic systems
579     are : [Ref- Mouhat and Coudert, PRB 90, 224104 (2014), and Wu et al.
580     PRB 76, 054115 (200
581     print "(i) C11 > 0; (ii) C22 > 0; (iii) C33 > 0; (iv) C44 > 0; (v)
582     C55 > 0 ; (vi) C66 > 0 "
583     print "(vii) [C11 + C22 + C33 + 2*(C12 + C13 + C23)] > 0; (viii)
584     C33*C55 - C35^2 > 0; (ix) C44*C66 - C46^2 > 0; (x) C22 + C33 - 2*
585     C23 > 0 "
586     print "(xi) C22*(C33*C55 - C35^2) + 2*C23*C25*C35 - (C23^2)*C55 - (C25
587     ^2)*C33 > 0 "
588     print "(xii) 2*[C15*C25*(C33*C12 - C13*C23) + C15*C35*(C22*C13 - C12*
589     C23) + C25*C35*(C11*C23 - C12*C13)] - [C15*C15*(C22*C33 - C23^2) + C25*
590     C25*(C11*C33 - C1
591     print "          where, g = [C11*C22*C33 - C11*C23*C23 - C22*C13*C13 -
592     C33*C12*C12 + 2*C12*C13*C23 ] "
593
594 for i in range(0, 6):
595     if(c[i][i] > 0.0):
596         print "Condition (%2d) is satisfied." % (i+1)
597     else:
598         print "Condition (%2d) is NOT satisfied." % (i+1)
599
600 if(c[0][0] + c[1][1] + c[2][2] + 2*(c[0][1] + c[0][2] + c[1][2]) > 0 ):
601     print "Condition (vii) is satisfied."

```

```

593     else :
594         print "Condition (vii) is NOT satisfied."
595
596     if (c[2][2]*c[4][4] - c[2][4]*c[2][4] > 0):
597         print "Condition (viii) is satisfied."
598     else :
599         print "Condition (viii) is NOT satisfied."
600
601
602     if(c[3][3]*c[5][5] - c[3][5]*c[3][5] > 0.0):
603         print "Condition (ix) is satisfied."
604     else :
605         print "Condition (ix) is NOT satisfied."
606
607
608     if(c[1][1] + c[2][2] - 2*c[1][2] > 0.0):
609         print "Condition (x) is satisfied."
610     else :
611         print "Condition (x) is NOT satisfied."
612
613
614     if(c[1][1]*(c[2][2]*c[2][4] - c[2][4]*c[2][4]) + 2*c[1][2]*c[1][4]*c
        [2][4] - c[1][4]*c[1][4]*c[2][2] > 0.0):
615         print "Condition (xi) is satisfied."
616     else :
617         print "Condition (xi) is NOT satisfied."
618
619     g = (c[0][0]*c[1][1]*c[2][2]) - (c[0][0]*c[1][2]*c[1][2]) - (c[1][1]*c
        [0][2]*c[0][2]) - (c[2][2]*c[0][1]*c[0][1]) + 2.0*(c[0][1]*c[0][2]*c
        [1][2])
620     h1 = 2*(c[0][4]*c[1][4]*(c[2][2]*c[0][1] - c[0][2]*c[1][2]) + c[0][4]*c
        [2][4]*(c[1][1]*c[0][2] - c[0][1]*c[1][2]) + c[1][4]*c[2][4]*(c[0][0]*c
        [1][2] - c[0][1])
621     h2 = (c[0][4]*c[0][4]*(c[1][1]*c[2][2] - c[1][2]*c[1][2]) + c[1][4]*c
        [1][4]*(c[0][0]*c[2][2] - c[0][2]*c[0][2]) + c[2][4]*c[2][4]*(c[0][0]*c
        [1][1] - c[0][1]*c[
622     x = h1 - h2 + c[4][4]*g
623
624     if(x > 0.0):
625         print "Condition (xii) is satisfied."
626     else :

```

```

627     print "Condition (xii) is NOT satisfied."
628
629 def elastic_const_2D(cnew):
630
631     """Convert the units from GPa or N/m2 to N/m for two-dimensional
        systems
632         1 GPa = 10^9 N/m2
633
634         Here, we use second Piola–Kirchhoff stress method to express the 2D
        forces per unit length in N/m units.
635         Ref: [Peng et al., Acta Mechanica 223 (2012), 2591–2596; Comput.
        Mater. Sci. 68, 320 (2013); Mech. Mater. 64, 135 (2013). ]
636         [Singh et al., Phys. Rev. B 95, 165444 (2017)]
637
638         We multiply elastic tensor by the thickness of the simulation cell
        to eliminate the artifacts due to the vacuum.
639         In 2D: Cij = bulk_Cij * C_latticevector (final units N/m)
640
641         For example: if bulk_Cij = 15 GPa and C = 10 Angs.
642             Then 2D_Cij = [15*10^9 N/m2] * [10*10^-10 m] ; i.e
        15*0.1*C N/m
643         This portion will be updated later.
644     """
645     c2d=np.zeros((6,6))
646
647     for i in range(0,6):
648         for j in range(0,6):
649             c2d[i][j]=cnew[i][j]*0.1*float(lattconst[2])
650     ## TO DO — extract the vacuum thickness automatically in thicker
        slabs.
651     print "\n \n Elastic tensor for two-dimensional system in N/m units
        \n"
652     np.set_printoptions(precision=3, suppress=True)
653     printMatrix(c2d)
654
655     ## Elastic properties
656     ## Layer modulus: represents the resistance of a 2D sheet to stretching;
        Lm = (1/4)*[c11 + c22 + 2*c12] [Ref: Andrew et al.; Phys. Rev. B 85,
        125428 (20
657     Lm = 0.25*(c2d[0][0] + c2d[1][1] + 2*c2d[0][1] )
658

```

```

659  ## 2D Young's modulus or in-plane stiffness: Y[10] = [c11c22 - c12^2]/[
        c22], Y[01] = [c11c22 - c12^2]/[c11]
660  Y10 = (c2d[0][0]*c[1][1] - c[0][1]*c[0][1])/(c[1][1])
661  Y01 = (c2d[0][0]*c[1][1] - c[0][1]*c[0][1])/(c[0][0])
662
663  ## 2D Poisson's ratio; nu10 = c12/c22, nu01 = c12/c11
664  nu10 = c2d[0][1]/c2d[1][1]
665  nu01 = c2d[0][2]/c2d[0][0]
666
667  ## 2D shear modulus; G2d = C66
668  G2d = c2d[5][5]
669
670  print "\n\n Elastic properties in two-dimensions\n"
671  print "[Useful refs. Andrew et al.; Phys. Rev. B 85, 125428 (2012), Peng
        et al., Acta Mechanica 223 (2012), 2591-2596; Comput. Mater. Sci. 68,
        320 (2013)]"
672  print "
673  print "-----"
674  print "2D layer modulus (N/m) : %10.3f " % Lm
675  print "2D Young's modulus Y[10] (N/m) : %10.3f " % Y10
676  print "2D Young's modulus Y[01] (N/m) : %10.3f " % Y01
677  print "2D Shear modulus G (N/m) : %10.3f " % G2d
678  print "2D Poisson ratio v[10] : %10.3f " % nu10
679  print "2D Poisson ratio v[01] : %10.3f " % nu01
680  print "-----"
681
682  if __name__ == '__main__':
683      main()
684
685  *****

```

LISTING A.1: MechElastic program

Professional Presentations

B.1 Invited Talks

1. Oak Ridge National Laboratory, TN, USA; *Friday, March 23, 2018*
“Prediction and computational design of novel structures of Bismuth antimonides:
for applications ranging from classical thermoelectrics to quantum spintronic ma-
terials ”

B.2 Contributed

1. **Sobhit Singh**, Quang Sheng Wu, Changming Yue, Alexey Soluyanov, and Aldo H. Romero
“Coexistence of topological fermions and topological bosons in special triple-point-
metals ”
APS March Meeting, March 5-9, 2018; Los Angeles, CA, USA. TALK

2. **Sobhit Singh**, and M. S. Seehra
“Size dependence of the effective magnetic anisotropy in metallic nanoparticles:
Validation of the core-shell-surface layer model for Fe, Co, Ni and magnetite
nanoparticles”
*Annual conference on magnetism and magnetic materials (MMM), Nov 06-10,
2017; Pittsburgh, USA. TALK*

3. **Sobhit Singh**, Madhav P. Ghimire, and Aldo H. Romero
“A systematic design of the 2D quantum spin Hall insulator using topologically trivial Rashba semiconducting monolayers of BiSb: a first-principles study”
Ab initio Spin-orbitronics, Psi-k/CECAM research conference, September 25-29, 2017; Pescara/Montesilvano, Italy. POSTER
4. **Sobhit Singh**, and Aldo H. Romero
“BiSb: A giant tunable Rashba semiconductor and quantum spin Hall insulator in two-dimensions”
CANADIAN-AMERICAN-MEXICAN (CAM) Graduate Student Physics Conference, August 2017, Washington DC, USA. TALK
5. **Sobhit Singh**, K. L. Pisane, and M. S. Seehra
“Unusual enhancement of effective magnetic anisotropy with decreasing particle size in core-shell nanoparticles: a new model”
17th IEEE International Conference on Nanotechnology (IEEE NANO 2017), July 25 - 28, 2017, Pittsburgh, USA. TALK
6. **Sobhit Singh**, and Aldo H. Romero
“Giant tunable Rashba spin splitting in two-dimensional BiSb monolayer and BiSb/AlN ”
Joint IMPRS Workshop on Condensed Matter, Quantum Technology and Quantum Materials, 03 - 07 April 2017, Max Planck Institute for the Physics of Complex Systems (MPIPKS), Dresden, Germany. POSTER
7. **Sobhit Singh**, A. C. Garcia-Castro, I. Valencia-Jaime, W. Ibarra-Hernández, F. Muñoz, and Aldo H. Romero
“Electronic properties of giant ferroelectric Rashba semiconductor BiSb: A first-principle study of bulk and monolayer”
APS March Meeting, March 13-17, 2017 New Orleans, USA. TALK

8. **Sobhit Singh**, M. S. Seehra, P. Pramanik, and S. Thota
“Surface and finite-size effects on the optical and magnetic properties of MnCo_2O_4 nanostructures”
APS March Meeting, March 13-17, 2017 New Orleans, USA. POSTER
9. **Sobhit Singh**, Irais Valencia-Jaime, A. C. Garcia-Castro, Francisco Muñoz, and Aldo H. Romero
“Pressure induced Lifshitz and Weyl Phase Transitions in BiSb”
APS March Meeting, March 14-18 (2016), Baltimore, USA. TALK
10. **Sobhit Singh**, Irais Valencia-Jaime, A. C. Garcia-Castro, Francisco Muñoz, and Aldo H. Romero
“Prediction of Weyl semi-metallic phase in inversion- asymmetric BiSb”
2nd Annual Meeting of the Mid-Atlantic Section of the APS, West Virginia University, USA (2015). TALK
11. **Sobhit Singh**, Irais Valencia-Jaime, A. C. Garcia-Castro, Francisco Muñoz, and Aldo H. Romero
“Searching Materials for Future Quantum Computers using HPC”
High Performance Computing (HPC) day, April 16, (2015), West Virginia University, USA. POSTER
12. **Sobhit Singh**, Irais Valencia-Jaime, A. C. Garcia-Castro, and Aldo H. Romero
“Prediction of New Crystal Structures of Bi-Sb Compounds using Minima Hopping Structural Search Method”
Annual Meeting of the Mid-Atlantic Section of the APS, October 03-05 (2014), Penn State University, USA POSTER
13. **Sobhit Singh**, M. S. Seehra, and S. Thota
“Effect of Cu doping on the magnetism of $\text{MnCo}_{2-x}\text{Cu}_x\text{O}_4$ cubic spinels”
APS March Meeting, March 03-07 (2014), Denver, USA. POSTER

14. S. Thota, K. Pisane, **Sobhit Singh**, and M. S. Seehra

“On the Cubic Phase Stability and Magnetic Properties of Cu-doped ZrO_2 ”

APS March Meeting, March 03-07 (2014), Denver, USA. POSTER

Awards and Honors Received During Ph.D.

- Recipient of the West Virginia University (WVU) Foundation Distinguished Doctoral Scholarship:
<https://enews.wvu.edu/articles/2018/03/01/eight-graduate-students-awarded-wvu-foundation-scholarships>

2018
- Recipient of the 2018 Research Trust Fund Seehra Research Award; *citation–for advancing research in physics by publishing his research in high-quality peer-reviewed physics journals*

2018
- Ovshinsky Travel Award for my talk on the “*Coexistence of topological fermions and topological bosons in special triple-point-metals*” at the APS March Meeting, LA

2018
- Received scholarship to attend the Joint International Max Planck Research Schools (IMPRS) Workshop on Condensed Matter, Quantum Technology and Quantum Materials, 03 - 07 April 2017; Max Planck Institute for the Physics of Complex Systems (MPIPKS), Dresden, Germany

2017
- Robert T. Bruhn Research Award, WVU

2017
- Awarded \$500 NSF student travel fellowship to attend and present my work at the IEEE NANO 2017 conference, Pittsburgh, USA

2017
- Received full scholarship to attend the International Summer School on Computational Materials, May 30 - June 10, 2016, Sherbrooke University, CANADA

2016

- Jefimenko Physics Fellowship at WVU; *[citation](#)– to advance research in energy and environmental sciences as well as nanotechnology and material sciences activities in the department* **2016**
- Honorable Mention Ovshinsky Travel Award for my talk on the “*Prediction of Weyl semi-metallic phase in inversion-asymmetric BiSb*” at APS March Meeting, Baltimore, USA **2016**
- Oleg D. and Valentina P. Jefimenko Physics Fellowship at WVU; *[citation](#)– to advance research in energy and environmental sciences as well as nanotechnology and material sciences activities in the department* **2015**
- Outstanding first year graduate student award (Arthur Weldon Prize) at WVU **2014**

Biographical Sketch

Sobhit Kumar Singh was born to parents Mrs. Urmila Devi and Mr. Krishna Bahadur Singh, and raised in a small town near Shravasti district of Uttar Pradesh state in India (*Shravasti is well-known for its associations with the life of Lord Buddha*). After finishing his schooling at his hometown Ikauna in 2008, he joined Lucknow Christian Degree College to pursue a Bachelor of Science (B.Sc.) degree. He was awarded Gold medal for securing highest marks in all three years of his B.Sc. degree. He was also honored with the Best Disciplined Volunteer award by the National Service Scheme, India. During 2011–2013, he attended Indian Institute of Technology Guwahati (IIT-G) to join the master’s degree (M.Sc.) program in Physics. There he was introduced to the materials research field by Prof. Subhash Thota. In the research group of Prof. Thota, Sobhit learned various experimental techniques used for the synthesis and characterization of magnetic nano-materials. In the Fall of 2013, he joined the Ph.D. program (Physics) at West Virginia University. In the first few years of his Ph.D. degree, he worked in the laboratory of Prof. Mohindar S. Seehra, where he synthesized various nanoparticles of different shapes and sizes and investigated their structural and magnetic properties.

Encouraged by Professor Seehra to get additional training in theoretical/computational physics and by his own passion to acquire a profound understanding of the materials research from both theoretical and experimental aspects, he joined the computational materials research group of Prof. Aldo H. Romero. Under the guidance of Prof. Romero, he learned advanced computational techniques and developed a wide range of skills used in materials research. After completing his Ph.D., Sobhit will be joining the condensed matter theory research group at Rutgers university in Fall 2018 as a postdoctoral fellow.

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