Electronic and Magnetic Materials From Two-dimensional Honeycomb Tin Lattices

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
Maxx Que Arguilla
Graduate Program in Chemistry

The Ohio State University
2017

Dissertation Committee:
Professor Joshua E. Goldberger, Advisor
Professor Psaras McGrier
Professor Yiying Wu
Copyrighted by

Maxx Que Arguilla

2017
Abstract

The discovery of new families of layered 2D crystals that have diverse sets of electronic, optical, and spin-orbit coupling properties, enable the realization of unique electronic and magnetic phenomena in the single-layer regime. Herein, we present the synthesis and characterization of three classes of exfoliatable and non-exfoliatable 2D-honeycomb Sn and main group-based layered materials with diverse properties ranging from topological insulators to anisotropic magnets. In Chapter 2, we present the growth and electronic, optical and Raman properties of an array of layered Zintl phases which feature flat or puckered anionic sheets of group 14 (CaSi₂, CaGe₂, EuGe₂ and BaSn₂) and group 14/15 elements (NaSnP, KSnAs and KSnSb). We show that the Raman-active modes in these phases strongly depend on the reduced mass and the in-plane bond lengths in the 2D sheets. We have also experimentally determined that CaSi₂ (6R), CaGe₂ (6R) and EuGe₂ are metallic while NaSnP, KSnAs and KSnSb are semiconducting. In addition, we have shown via DFT calculations that BaSn₂ possesses topologically-protected surface states and is a strong 3D Z₂-type topological insulator. In Chapters 3 and 4, we discuss the structural, electronic and magnetic properties and exfoliation of a family of vdW layered Zintl phases with the ASn₂As₂ (A= Na, Sr and Eu) stoichiometry which exhibit unique electronic and magnetic properties such as: anisotropic two-carrier
transport in NaSn$_2$As$_2$ and tunable anisotropic magnetism, with anti-ferromagnetic coupling out-of-plane and ferromagnetic coupling in-plane, in EuSn$_2$As$_2$/Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ ($x = 0.25, 0.50$ and $0.75$). Lastly, in Chapter 5, we have shown two routes towards the realization of $sp^3$-hybridized 2D vdW Tin phases. First, we alloy Sn into the 2D germanane (GeH) lattice via the low temperature topochemical deintercalation of CaGe$_2$.$_{2-x}$Sn$_{2x}$ in HCl to produce sheets of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ held by van der Waals forces ($x = 0, 0.04, 0.07, 0.09$). This enabled the tuning of the optoelectronic properties of GeH from a band gap of $1.59$ eV down to $1.38$ eV with just $9\%$ of Sn, which we have demonstrated through the combination of absorbance and single crystal wavelength-dependent photoconductivity measurements. Second, we impart synthetic insights on the creation of highly unstable crystalline 2D van der Waals phases with high Sn content ($\geq 50\%$). We show that the deintercalation of Sn-based layered Zintl phases (NaSnP, KSnAs and KSnSb) into 2D organic-functionalized materials is limited by an underlying electrochemical process, wherein the Zintl phase precursor reduces the alkyl halide (organic ligand source and deintercalant) via a one-electron reduction process which produces organic radicals that further amorphize the crystalline framework. By choosing the correct alkyl halide/Zintl phase pair, where the alkyl halide’s reduction process is more negative in potential than the oxidation process of the Zintl phase, we have observed evidence of formation of 2D Sn(CH$_2$CH$_3$)Pn (Pn = P, As and Sb) phases that have absorption edges from $1.3$ eV (P) down to $0.2$ eV (Sb). Overall, the creation and discovery of these classes of electronic and magnetic materials beyond graphene will
allow for the experimental demonstration and realization of novel physical phenomena, properties and applications in 2D.
Acknowledgments

Working in the multi-disciplinary field of materials chemistry, at the crossroads of chemistry, physics and materials science, has introduced me to a number of valuable academics who have generously lent a helping hand and have contributed greatly to the accomplishment of this dissertation.

First and foremost, this dissertation would not be possible without my advisor, Prof. Joshua E. Goldberger. I would like to express my deepest gratitude for introducing me into the exciting and fast-moving field of 2D materials and for trusting me and allowing me to take on relevant scientific problems on the field. In addition, I would also like to thank Prof. Goldberger for being an all-around mentor, especially for the hands-on mentorship in my formative years of graduate research in which the skills that I have acquired during those times have greatly helped me transition to an independent researcher and for allowing me (and for providing funds!) to explore several of my scientific ideas for the projects that I have worked on in the years that followed. I am truly grateful for these and for the unending guidance, support, patience and motivation during my time in the Goldberger group.

I also would like to express my sincerest gratitude to the members of my dissertation committee: Prof. Yiying Wu and Prof. Psaras McGrier for the scientific insights and for reading my dissertation.
This dissertation would also not be possible without the help of my numerous collaborators at Ohio State and beyond. I would like to thank all of the members of the IRG-2 (NSF-MRSEC) and the 2-DARE (NSF-EFRI) teams for the scientific insights and close collaboration on the various projects that I have worked on. Specifically, I would like to thank the following people who have contributed to this dissertation (in order of appearance in the manuscript): Prof. Roland Kawakami, Dr. Jyoti Katoch, Mr. Jinsong Xu and the LBNL MAESTRO Beamline team (Dr. Eli Rotenberg, Dr. Roland Koch, Dr. Chris Jozwiak, Dr. Aaron Bostwick and Dr. Søren Ulstrup) for the ARPES measurements and preliminary exfoliation of NaSn$_2$As$_2$; Prof. Wolfgang Windl and Mr. Kevin Krymowski for DFT calculations of NaSn$_2$As$_2$ and other related phases; Prof. David McComb and Ms. Amanda Hanks for HRTEM measurements of NaSn$_2$As$_2$; Prof. Jie Shan and Dr. Xiaoxiang Xi for few layer transport measurements of NaSn$_2$As$_2$; Prof. Joseph Heremans and Mr. Bin He for Seebeck measurements of NaSn$_2$As$_2$ and other related phases; and Prof. Yiying Wu and Mr. William McCulloch for the electrochemical measurements on layered Zintl phases.

I also would like to thank the current and past members of the Goldberger group for the collaborative work within the group, the awesome company and the lasting friendship. I would like to give special thanks to the mentorship of Dr. Shishi Jiang on the various syntheses and characterization techniques in the beginning of my graduate research and to Dr. Basant Chitara for imparting great knowledge on device fabrication and characterization. I would like to acknowledge Mr. Zachary Baum for DFT calculations on BaSn$_2$ and EuSn$_2$As$_2$; Mr. Nicholas Cultrara for the help on various
transport measurements; and the undergraduate students who worked with me with various projects, Mr. Alexander Cea, Mr. Dominic Ross and Mr. Alex Cardwell. A big thanks also goes to everyone in the group (past and present) who, in one way or another, have made the time that I have spent in the lab a lot more fun: Ms. Elizabeth Bianco, Ms. Sheneve Butler, Dr. Christian Büttner, Mr. Fan Fan, Dr. Arijit Ghosh, Dr. Tianyang “Tony” Li, Mr. Aaron Manos, Mr. Rick Morasse, Mr. Mike Nicholl, Mr. Michael Scudder, Mr. Chuanchuan Sun, Ms. Ashley Wallace and Dr. Daniel Weber.

To my friends from the Philippines who never let the communication and the friendship end with the distance and the community of Filipino graduate students here in the US, for the fun get-togethers that always recharged and refreshed me to go back in lab and continue doing research, thank you very much!

My journey through graduate school and science, in general, would have never been possible without the unending support and constant motivation of Dr. Herdeline Ann Ardoña. Even if we pursued our degrees far apart from each other, our shared passion towards science has made it a lot more bearable. The distance made everything a little bit more challenging, but in the end, has made our bond stronger than ever. Thank you very much for always believing in me and in what I can do since day one and for continuously inspiring me to push forward and be the best that I can be.

Last but not the least, I would like to give my utmost gratitude to my family for their never-ending support and belief in every endeavor that I pursued thus far. They may be 8,246 miles away but their love (and the video calling technology) has always made
me feel that wherever I go, I always felt that I never left home. Everything that I have
achieved since the beginning until now is because and is always dedicated to all of you.

M. Q. Arguilla

Columbus, OH 2017
Vita

March 2007 .......................................................... Saint Louis College Science High School
June 2007 to April 2011 .................................. B.S. Chemistry, University of the Philippines-Diliman
August 2012 to May 2014 ......................... Graduate Teaching Associate, Department of Chemistry, The Ohio State University
May 2014 2012 to Present ......................... Graduate Research Associate, Department of Chemistry, The Ohio State University

Publications


x


**Fields of Study**

Major Field: Chemistry
# Table of Contents

Abstract ............................................................................................................................... ii

Acknowledgements ........................................................................................................... v

Vita .................................................................................................................................. ix

List of Tables .................................................................................................................... xvii

List of Figures .................................................................................................................. xx

Chapter 1: Introduction .................................................................................................... 1

1.1 The Advent of Two Dimensional Materials ................................................................. 3

1.2 2D-Enabled Phenomena: The Search for High-Mobility Carriers, Dissipationless
    Transport and 2D Magnetism ....................................................................................... 6

1.3 Layered Zintl Phases as Modular and Multifunctional 2D Materials ....................... 14

1.4 Beyond Graphene: \(sp^3\)-Hybridized Group 14 Graphane Analogues ....................... 17

1.5 Chapter Outlines ....................................................................................................... 33

1.6 References ................................................................................................................. 34

Chapter 2: Topologically Protected States, Optical Properties and Raman-Active
    Vibrational Modes in Metallic and Semiconducting Layered Zintl Phases ............ 44

2.1 Introduction ............................................................................................................... 46

2.2 Experimental ............................................................................................................ 50

    2.2.1 Materials and Crystal Growth ........................................................................... 50

    2.2.2 Polarized Raman Spectroscopy ...................................................................... 52
Chapter 4: Topotactic Approaches Towards Tin-Containing Graphane Analogues

4.1 Introduction .................................................................................................................. 114

4.2 Experimental .............................................................................................................. 117

4.2.1 Crystal Growth ........................................................................................................ 117

4.2.2 Material Characterization ....................................................................................... 117

4.2.3 Magnetic Measurements ......................................................................................... 118

4.2.4 DFT Calculations .................................................................................................... 118

4.2.5 Bulk Electronic Transport ....................................................................................... 119

4.2.6 Mechanical and Liquid Phase Exfoliation ............................................................... 119

4.3 Results and Discussion ............................................................................................... 120

4.4 Conclusion .................................................................................................................. 141

4.5 References .................................................................................................................. 141

Chapter 5: Topotactic Approaches Towards Tin-Containing Graphane Analogues ..... 148

5.1 Introduction .................................................................................................................. 150

5.2 Experimental .............................................................................................................. 151

5.2.1 Synthesis of BaSn₂, NaSnP, KSnAs, KSnSb and CaGe₂-2xSn₂x ......................... 151

5.2.2 Synthesis of 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb) and Ge₁-xSnₓH₁-x(OH)ₓ .... 152

5.2.3 X-ray Diffraction of CaGe₂-2xSn₂x, 2D Sn(Ethyl/methyl)Pn (Pn = P, As and Sb) and Ge₁-xSnₓH₁-x(OH)ₓ ................................................................. 152
5.2.4 Fourier-Transform Infrared (FTIR) Spectroscopy of 2D Sn(Ethyl/Methyl)Pn
(Pn = P, As and Sb) and Ge_{1-x}Sn_xH_{1-x}(OH)_x .................................................. 153

5.2.5 Raman Spectroscopy of NaSnP, KSnAs, KSnSb, 2D Sn(Ethyl/Methyl)Pn
(Pn = P, As and Sb) and Ge_{1-x}Sn_xH_{1-x}(OH)_x .................................................. 153

5.2.6 Tin Percentage Determination of Ge_{1-x}Sn_xH_{1-x}(OH)_x ......................... 153

5.2.7 Absorption measurements of 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb)
and Ge_{1-x}Sn_xH_{1-x}(OH)_x .................................................................................. 153

5.2.8 X-Ray Photoelectron Spectroscopy .............................................................. 154

5.2.9 Photocurrent Measurements of GeH and Ge_{0.91}Sn_{0.09}H_{0.91}(OH)_{0.09} ........ 154

5.2.10 Cyclic Voltammetry of the Layered Zintl Phases and the Precursor Alkyl
Iodides ..................................................................................................................... 154

5.3 Results and Discussion ...................................................................................... 155

5.3.1 Band Gap Tuning of Germanane via Alloying with Sn ............................... 155

5.3.2 Synthetic Routes Towards BN-like SnPn (Pn = P, As and Sb) Graphane
Derivatives .............................................................................................................. 165

5.4 Conclusion ......................................................................................................... 174

5.5 References ........................................................................................................ 175

Chapter 6: Conclusions and Outlook ................................................................. 180

Appendix A: Supporting Figures For Chapters 2 to 5 ........................................ 183

Bibliography .......................................................................................................... 235

Chapter 1 ............................................................................................................. 235
Chapter 2 ..............................................................................................................244
Chapter 3 ..............................................................................................................251
Chapter 4 ..............................................................................................................259
Chapter 5 ..............................................................................................................264
List of Tables

Table 1.1 The bulk TRIMS (Γ_i) with the corresponding parity, δ(Γ_i), and Z_2 invariants for several topological insulators\textsuperscript{35} ..................................................................................................................10

Table 1.2 The band gaps of different sp\textsuperscript{3}-hybridized Group 14 elements in bulk and in 2D ........................................................................................................................................................................28

Table 2.1 The space groups, in-plane lattice parameters and in-plane bond lengths of the two-dimensional honeycomb Zintl phases that were investigated in this study ....56

Table 2.2 Wyckoff sites and Raman-active modes of constituent atoms in 6R-layered Zintl phases assuming a D\textsubscript{3d} point group. .................................................................................................................................58

Table 2.3 Wyckoff sites and Raman-active modes of constituent atoms in 2H-layered Zintl phases assuming a C\textsubscript{6v} point group. Modes that are in bold are not observable in the back-scattering geometry .........................................................................................................................62

Table 2.4 Wyckoff sites and Raman-active modes of constituent atoms in 1T-layered Zintl phases assuming a D\textsubscript{3d} point group .................................................................65

Table 4.1 Crystal Data and Refinement Results for EuSn\textsubscript{2}As\textsubscript{2}, using Hexagonal Axes .121

Table 4.2 Fractional atomic coordinates and isotropic displacement parameters based on the refined EuSn\textsubscript{2}As\textsubscript{2} structure .........................................................................................................................122
Table 4.3 Selected bond lengths (Å) and bond angles (°) in EuSn$_2$As$_2$...........................122

Table 5.1 Summary of the electrochemical potentials deduced from cyclic voltammetry measurements of the precursor Zintl phases and the alkyl iodide deintercalants ...170

Table A.1 Crystal Data and Refinement Results for CaSi$_2$.................................187

Table A.2 Fractional atomic coordinates and isotropic displacement parameters based on the refined CaSi$_2$ structure .................................................................188

Table A.3 Crystal Data and Refinement Results for CaGe$_2$.................................189

Table A.4 Fractional atomic coordinates and isotropic displacement parameters based on the refined CaGe$_2$ structure .................................................................190

Table A.5 Crystal Data and Refinement Results for NaSnP ...........................................192

Table A.6 Fractional atomic coordinates and isotropic displacement parameters based on the refined NaSnP structure. .................................................................193

Table A.7 Crystal Data and Le Bail Fitting results for KSnAs. ..............................194

Table A.8 Crystal Data and Le Bail Fitting results for KSnSb..............................196

Table A.9 Crystal Data and Refinement Results for EuGe$_2$.................................199

Table A.10 Fractional atomic coordinates and isotropic displacement parameters based on the refined EuGe$_2$ structure .................................................................200

Table A.11 Crystal Data and Refinement Results for BaSn$_2$.................................202

Table A.12 Fractional atomic coordinates and isotropic displacement parameters based on the refined BaSn$_2$ structure .................................................................203

Table A.13 Summary of optical transitions obtained from the Tauc-Davis-Mott models for semiconducting layered Zintl phases under study.................................204
Table A.14 TOPAS Rietveld Refinement parameters for NaSn$_2$As.................................206
Table A.15 Atomic coordinates for NaSn$_2$As$_2$ from Rietveld refinement.........................206
Table A.16 Selected bond lengths from the refined NaSn$_2$As$_2$ structure .........................207
Table A.17 Selected bond lengths based on the refined EuSn$_2$As$_2$ structure ...................219
Table A.18 TOPAS Rietveld refinement results for of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.04)............224
Table A.19 The atomic coordinates of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.04)...............................225
Table A.20 TOPAS Rietveld refinement results for of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.07)............225
Table A.21 The atomic coordinates of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.07)...............................226
Table A.22 TOPAS Rietveld refinement results for of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.09)............226
Table A.23 The atomic coordinates of CaGe$_2$-$_{2x}$Sn$_{2x}$ (x = 0.09)...............................227
List of Figures

Figure 1.1 Model of GeH. View from (a) the (100) and (b) the (001) directions. (Ge: blue and H: black) ..................................................................................................................5

Figure 1.2 The time-reversal invariant momentum (TRIM) points in common topological insulators and their respective Brillouin zones.35 .................................................................9

Figure 1.3 Surface electronic structures of (a) trivial, $\pi(\Lambda_a)\pi(\Lambda_b) = +1$, and (b) topological, $\pi(\Lambda_a)\pi(\Lambda_b) = -1$, insulators.35 .................................................................11

Figure 1.4 Instrument schematic of a nanoARPES measurement facility.41 .................13

Figure 1.5 Electron counting and octet completion in Ge-based Zintl phases that assume a (a) 2D structure in CaGe$_2$, (b) 1D structure in CaGe and (c) 0D structure in KGe..15

Figure 1.6 Schematic illustration of topotactic deintercalation of (a) CaGe$_2$ to (b) GeH (Ca: yellow, Ge: purple and H: black). Optical images of (c) CaGe$_2$ and (d) GeH crystals with select crystals on a 1 mm grid graph paper. Powder XRD of (e) CaGe$_2$ and (f) GeH.13 ..................................................................................................................19
Figure 1.7 (a) A single (111) plane of crystalline germanium, representing a single layer of GeH. The distance of the germanium atoms on a certain colored ring from the central germanium atom corresponds to the same color peak in (b). (b) PDFs of GeH and Ge. The starred peaks correspond to the interactions between germanium atoms in different layers.\textsuperscript{74} (c) Low-magnification and (d) magnified TEM micrograph of GeH platelets. Inset in (c) is the corresponding electron diffraction pattern collected down the [001] zone axis.\textsuperscript{13} ........................................20

Figure 1.8 AFM images of (a) an exfoliated single layer of GeH and (b) GeH thin film after deintercalation of a 5 nm thick CaGe\textsubscript{2} film grown via MBE on Ge(111). Inset in (a) is an optical micrograph of the single-layer flake.\textsuperscript{13,90} ........................................22

Figure 1.9 (a) Model of GeCH\textsubscript{3}. (Ge: blue, C: black and H: grey) (b) Optical images of GeCH\textsubscript{3} crystals with select crystals on 1 mm grid graph paper. (c) Single-crystal XRD pattern of GeCH\textsubscript{3} collected down the [001] zone axis. (d) Powder XRD pattern of GeH and GeCH\textsubscript{3}. The starred peaks correspond to diffraction reflections of an internal Ge standard. (e) FTIR spectra of GeH, GeCH\textsubscript{3}, Ge\textsuperscript{13}CH\textsubscript{3} and GeCD\textsubscript{3}. The intensities of the four spectra are multiplied by 0.5 from 400-900 cm\textsuperscript{-1}.\textsuperscript{14} ...........24

Figure 1.10 (a) Powder XRD pattern (b) and FTIR spectra of GeCH\textsubscript{3} (black), GeCH\textsubscript{2}CH\textsubscript{3} (blue), and GeCH\textsubscript{2}CH=CH\textsubscript{2} (red) .................................................................25

Figure 1.11 DFT simulations of the electronic band structure of (a) silicene and (b) silicane and the density orbitals at the high symmetry k-points: (A) Si-H $\sigma^*$, (B) Si-Si $\sigma^*$, (C) and (D) Si-Si $\sigma$ states. Inset in (a) is the hexagonal Brillouin zone.\textsuperscript{94} ....26
Figure 1.12 Electronic band structure of an isolated single layer of GeH calculated using HSE-06 theory including spin–orbit coupling predicting a 1.56 eV direct band gap. The hole and electron effective masses for each extrema are indicated in red.\textsuperscript{13} ....28

Figure 1.13 (a) DRA spectra of GeH compared to GeCH\textsubscript{3} and (b) Absorption and PL spectra of GeCH\textsubscript{3} with the actual PL observed in isopropyl alcohol as an inset. (c) Experimental and (d) theoretical linear-like dependence of the absorption onset of H- and organic-functionalized germanane on the in-plane Raman shift.\textsuperscript{14} ...........30

Figure 1.14 (a) FTIR spectra of GeH after exposure to air for up to 60 days highlighting the absence of any Ge-O vibrational mode. (b) XPS spectra of GeH exposed to air for up to five months, followed by 0.5 nm Ar etch. DRA spectra of (c) GeH and (d) GeCH\textsubscript{3} annealed in Ar/H\textsubscript{2} gas at various temperatures.\textsuperscript{13,14} ..................................32

Figure 2.1 Stacking motifs in layered main group Zintl phases. Top right image shows the in-plane honeycomb arrangement of a single layer of atoms looking down the c-axis. In these structures, the grey atoms represent the cations that hold the layers together while the red atoms correspond to the anions, which form the extended layered networks. For visual aesthetics, the cations are depicted as larger than anions .................................................................49

Figure 2.2 (a) Crystal structure and stacking motif of the 6R-layered Zintl phases, CaSi\textsubscript{2} and CaGe\textsubscript{2}. (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of CaSi\textsubscript{2} and CaGe\textsubscript{2}. The blue atoms represent Si and Ge while the gray atoms represent Ca........................................................................................................................................57
Figure 2.3 (a) Crystal structure of and stacking motif of 2H-layered Zintl phases NaSnP, KSnAs, and KSnSb. (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of KSnSb, KSnAs, and NaSnP. The green atoms represent a Group 15 element (P, As or Sb), the orange atoms represent Sn and the purple atoms represent the Group 1 cations (Na or K) .................................................................61

Figure 2.4 (a) Crystal structures and stacking motif of 1T layered Zintl phases in EuGe$_2$ and BaSn$_2$ (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of Zintl phases that have 1-layer per unit cell trigonal stacking motif. The magenta atoms represent Ge or Sn and the gray atoms represent the Eu$^{2+}$/Ba$^{2+}$ cation, respectively .................................................................64

Figure 2.5 Trends in the in-plane Raman mode of EuGe$_2$, CaGe$_2$ and GeH. The polarized Raman spectra of EuGe$_2$, CaGe$_2$ and GeH in the XY polarization geometry highlighting the in-plane normal modes, E$_{2g}$, E$_g$ and E$_2$, respectively. Inset is the dependence of the frequencies of these in-plane modes with the Ge-Ge bond length in the aforementioned phases .................................................................66

Figure 2.6 (a) DFT band structure of BaSn$_2$ without SOC. Highlighted in green is the band crossing along the A to H direction. Inset is the hexagonal Brillouin zone with the TRIMs highlighted in red. (b) DFT band structure of BaSn$_2$ with SOC turned on. The orbital character of the Sn 6s anti-bonding and the Sn 5$p_z$ bonding states are labeled. (c) Band contributions of the Sn 5$p_z$ and Sn 6s orbitals near the band inversion along the A to H direction. (d) DRIFTS absorbance spectra of BaSn$_2$ indicating an absorbance peak around ~0.2 eV .................................................................69
Figure 2.7 Diffuse reflectance absorbance spectra of NaSnP, KSnAs and KSnSb showing the consistent shift of the absorption edges to lower energies with decreasing electronegativities and increasing sizes of the Group 15 elements..........................73

Figure 3.1 (a) Crystal Structure of NaSn$_2$As$_2$ (Na, red; Sn, gray; As, blue). Top right: NaSn$_2$As$_2$ crystal structure down the c-axis. Bottom right: mm- to cm-size NaSn$_2$As$_2$ crystals. (b) Powder-XRD of NaSn$_2$As$_2$. Enclosed in parentheses are the rhombohedral miller indices .................................................................90

Figure 3.2 (a) Raman spectrum of NaSn$_2$As$_2$. (b) Polarized (at 0° and 90°) and unpolarized Raman spectra of NaSn$_2$As$_2$. (c) Radial plot (0° to 360°) of the A$_{1g}$/E$_{2g}$ intensity ratios at 228 cm$^{-1}$ and 182 cm$^{-1}$, respectively, from polarized Raman experiments. Blue dashed trace represents the fitted curve .........................92

Figure 3.3 XPS of NaSn$_2$As$_2$ showing the Na 1s, Sn 4d Sn 3d$^{5/2}$ and As 3d peaks. ........93

Figure 3.4 (a) Optical and AFM micrographs (Thickness: 65 nm; Scale bars correspond to 4 μm), (b) Powder XRD, (c) Raman spectra and (d) FTIR spectra of NaSn$_2$As$_2$ before and after exposure to air for 7 days .................................................................94
Figure 3.5 (a) AFM image of few-layers of NaSn$_2$As$_2$ from mechanical exfoliation with the corresponding thickness profile. (b) NaSn$_2$As$_2$ dispersions in solvents with increasing surface tension from left to right (IPA = isopropyl alcohol, DMF = dimethylformamide, NMP = N-methyl-2-pyrrolidone, CHP = N-cyclohexyl-2-pyrrolidone and DMSO = dimethyl sulfoxide). (c) Raman of drop-casted few-layer (average thickness = 4.6 nm) NaSn$_2$As$_2$ in 285 nm SiO$_2$/Si substrate. (d) AFM image of liquid-exfoliated NaSn$_2$As$_2$ with the corresponding thickness profile. (e) TEM of liquid-exfoliated few layers of NaSn$_2$As$_2$ with a representative selected area electron diffraction (SAED) pattern, scale bar is 500 nm.

Figure 3.6 Electronic Band Structure of NaSn$_2$As$_2$. (a) Overlay of the theoretical band structure with the ARPES spectrum of a cleaved NaSn$_2$As$_2$ single crystal, acquired at photon energy 127 eV and $T = 41$ K. The bands that correspond to the electron pockets are labeled as $b_{n1}$ and $b_{n2}$, while the bands that comprise the hole pockets are labeled as $b_p$. (b) Heyd-Scuseria-Ernzerhof (HSE) band structure of NaSn$_2$As$_2$ with spin-orbit coupling (SOC). (c) Density of states of the contributing orbitals in NaSn$_2$As$_2$ near the Fermi level.

Figure 3.7 (a) Temperature-dependent in-plane resistivity of bulk and exfoliated NaSn$_2$As$_2$ down to 2.1 K. Inset is an optical microscope image of the Hall bar device. The thickness of the flake is 350 nm and the width to length ratio of the channel is 1.44. (b) The magnetic field dependence of the transverse resistance of the Hall bar device at 4 different temperatures. (c) The Hall coefficient extracted from (b).
Figure 4.1 (a) The crystal structure of EuSn₂As₂ (Eu = Orange, Sn = gray and As = blue).

Top right: the structure down the c-axis showing the hexagonal ordering of the Eu²⁺ cations in-plane. Bottom right: an image of mm-sized crystal of EuSn₂As₂. (b) Powder XRD data of EuSn₂As₂ with the corresponding Miller indices in parentheses. (c) Polarized Raman spectra using 785 nm laser excitation. The scattered light is co-polarized (0°) and cross-polarized (90°) with respect to the excitation source ..............................................................................................................123

Figure 4.2 Temperature-dependent magnetic susceptibility of EuSn₂As₂ oriented at different crystal orientations with respect to the measuring magnetic field of (a) 0.01 T and (b) 3.5 T. Inset in (a) is the Curie-Weiss fit corresponding to the inverse susceptibility of the crystal with its a-axis oriented parallel to the applied field. The blue data points correspond to measurements with the a-axis parallel to the field, the red data points correspond to measurements with c-axis oriented parallel to the field and the green data points correspond to measurements with the c-axis oriented parallel to the field corrected for self-demagnetization. FC values are denoted as crosses, and ZFC values are denoted with circles, and are nearly superimposable. FC was performed using the same field strength as the measuring magnetic field..............................................................................................................126

Figure 4.3 Field-dependent magnetic susceptibility of EuSn₂As₂ at 5 K with the a/b-axis (blue), c-axis (red) and c-axis that is demagnetization-corrected (green) parallel to the applied field..............................................................................................................129
Figure 4.4 (a) Powder diffraction patterns of Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ (x = 0, 0.25, 0.50, 0.75 and 1). (b) Vegard’s law plot of the $a$- and $c$-lattice parameters of Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ (x = 0, 0.25, 0.50, 0.75 and 1). (c) Unpolarized Raman spectra of $c$-axis oriented crystals of Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ (x = 0, 0.25, 0.50, 0.75 and 1)

Figure 4.5 Temperature-dependent magnetic susceptibility of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ oriented along different crystal orientations with respect to the measuring magnetic field of (a) 0.01 T and (b) 2.5 T. Inset in (a) is the Curie-Weiss fit corresponding to the inverse susceptibility of the crystal with its $a$-axis oriented parallel to the applied field. The blue data points correspond to measurements with the $a$-axis parallel to the field and the red data points correspond to measurements with $c$-axis oriented parallel to the field. FC values are denoted as crosses, and ZFC values are denoted with circles, and are nearly superimposable. FC was performed using the same field strength as the measuring magnetic field. (c) Field-dependent magnetic susceptibility of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ at 5 K with the $a$-axis (blue) and $c$-axis (red) parallel to the applied field. (d) Zoomed in field-dependent magnetic susceptibility at 5 K plot highlighting the small coercive field of the Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ soft ferromagnet

Figure 4.6 (a) Electronic band structure of the antiferromagnetic magnetic ground state of EuSn$_2$As$_2$ highlighting its semi-metallic nature. (b) Partial density of states of the bands near the Fermi level
Figure 4.7 Temperature-dependent resistivity of EuSn$_2$As$_2$ showing its metallic behavior along the temperature range with a cusp near the magnetic ordering temperature. Top left: Characteristic micrograph of a EuSn$_2$As$_2$ crystal in a four-probe geometry. EuSn$_2$As$_2$ crystal Bottom right: high temperature resistivity which increases with increasing temperatures ............................................................. 138

Figure 4.8. (a) AFM image and height profile of few layers of EuSn$_2$As$_2$ mechanically-exfoliated onto a 285 nm SiO$_2$/Si substrate. Highlighted are the ~0.9 nm steps corresponding to a single SnAsEuAsSn layer. (b) A continuous thin flake of EuSn$_2$As$_2$ with the corresponding height profile. (c) TEM micrograph of liquid-exfoliated EuSn$_2$As$_2$ sheets. Inset is the SAED pattern indexed to a hexagonal unit cell assuming a [001] zone axis ................................................................. 140

Figure 5.1 (a) Schematic of the topochemical deintercalation of CaGe$_{2-2x}$Sn$_{2x}$ to Ge$_1$. xSn$_x$H$_{1-x}$(OH)$_x$ (Ca: yellow, Ge: blue, H: black, O: red and Sn: green). (b) a/b- and (c) c-lattice parameters of CaGe$_{2-2x}$Sn$_{2x}$ to Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$. (d) Optical image of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ crystals on a 2.5 mm grid paper. (e) Capillary mode powder XRD pattern of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ (x=0-0.09). The internal Ge standard is labeled with an asterisk ( * ) ......................................................................................... 156

Figure 5.2 (a) Transmission mode FTIR spectra of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ (x=0-0.09). (b) Raman spectrum of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ with the A$_1$ mode highlighted as an inset. Raman shifts of the (c) A$_1$ and (d) E$_2$ phonon modes of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ as a function of Sn concentration ........................................................................................................ 160
Figure 5.3 (a) Diffuse reflectance absorption spectrum of $\text{Ge}_{1-x}\text{Sn}_x\text{H}_{1-x}(\text{OH})_x$ plotted in terms of the Kubelka-Munk function, $F(R)$, and the photon energy. (b) Optical band gap of $\text{Ge}_{1-x}\text{Sn}_x\text{H}_{1-x}(\text{OH})_x$ versus the Sn concentration ........................................162

Figure 5.4 (a) Diffuse reflectance absorption measurements, (b) FTIR spectra, and XPS spectra of the (c) Ge 2$p_{3/2}$ and (d) Sn 3$d_{3/2}$ of $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$ before (red) and after 15 day exposure to air (black) and after subsequent 1 M HCl washing (green) .........................................................................................163

Figure 5.5 (a, left) Image of the actual device based on $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$ and (a, right) schematic illustration and dimensions of the photodetector (not drawn to scale). (b) Typical I-V plot of the $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$ photodetector in dark and at 600 nm illumination. (c) Photocurrent response at selected illumination wavelengths and (d) wavelength-dependent normalized photocurrent for the $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$ photodetector compared to GeH at a 3V bias voltage ....165

Figure 5.6 (a) Schematic of the topochemical deintercalation of NaSnP at -10°C using methyl iodide as a deintercalant. Bottom left: crystal model of the proposed Sn(CH$_3$)$_3$P structure where only the Sn atoms are functionalized. Bottom Right: XRD pattern of Sn(CH$_3$)$_3$P which highlights the in-plane diffraction peaks. (b) Raman spectrum of Sn(CH$_3$)$_3$P showing the in-plane (E”) and out-of-plane (A’) Raman modes. (c) FTIR spectrum of Sn(CH$_3$)$_3$P showing the presence of methyl vibrational modes and the functionalization of only the Sn atom. (d) Absorbance spectrums of Sn(CH$_3$)$_3$P featuring an extrapolated 1.4 eV absorption edge ...........168

xxix
Figure 5.7 (a) Schematic for the coin cell used for the electrochemical measurement of the oxidation potential of the layered Zintl phases. (b) Cyclic voltammogram of the three layered 1-14-15 layered Zintl phases that were deintercalated in this study. (c) cyclic voltammograms of the alkyl iodide deintercalants that were used in this study .......................................................... 170

Figure 5.8 Generalized scheme on the electrochemical matching of the oxidation potentials and reduction potentials of the precursor Zintl phases and the alkyl iodide deintercalants, respectively. Inset is the electron transfer mechanism that illustrates the pathway towards the 1e⁻ reduction of the alkyl iodide and the subsequent amorphization of the deintercalation product .......................................................... 171

Figure 5.9 Structural and optical properties of 2D Sn(CH₂CH₃)Pₙ (Pₙ = P, As an Sb) phases. (a) Representative post-reaction flakes of Sn(CH₂CH₃)Sb. (b) FTIR spectra of the Sn(CH₂CH₃)Pₙ phases highlighting the various vibrational modes of ethyl and Sn-C stretching. (c) Raman spectra comparison of the deintercalated phases Sn(CH₂CH₃)Pₙ phases with the precursor Zintl phases. (d) Diffuse reflectance absorbance measurements of the deintercalated phases highlighting the absorption onset energies the small peaks below 0.5 eV are IR-active vibrational modes of the ethyl group ........................................................................................................................................ 173

Figure A.1 Atom displacements for the out-of-plane (A₁g⁻³) and in-plane (E₉⁻¹) Raman vibrational modes of CaSi₂ ........................................................................................................................................ 184

Figure A.2 Unpolarized Raman spectra of 6R-layered Zintl phases, (a) CaSi₂, (b) CaGe₂, showing both the in-plane and out-of-plane Raman modes................................. 185
Figure A.3 Powder XRD Rietveld refinement results for CaSi$_2$ using TOPAS. The green cross marks correspond to the Bragg reflections of CaSi$_2$..........................186

Figure A.4 Powder XRD Rietveld refinement results for $\beta$-CaGe$_2$ using TOPAS. The phase fraction of Ge was refined to be 24%. The green and orange cross marks correspond to the Bragg reflections of CaGe$_2$ and Ge, respectively.......................188

Figure A.5 Logarithmic plot of the co- and cross-polarized NaSnP Raman spectra highlighting the weak Raman modes in the spectra (arrows)..........................190

Figure A.6 Unpolarized Raman spectra of 2H-layered Zintl phases, (a) NaSnP, (b) KSnAs and (c) KSnSb, showing both the in-plane and out-of-plane Raman modes ......................................................................................................................................191

Figure A.7 Powder XRD Rietveld refinement results for NaSnP using TOPAS. The phase fraction of Sn was refined to be 15.9%. The green and orange cross marks correspond to the Bragg reflections of NaSnP and Sn, respectively ..................191

Figure A.8 Powder XRD Le Bail fitting results for KSnAs using TOPAS. The green cross marks correspond to the Bragg reflections of KSnAs ..........................................................193

Figure A.9 Powder XRD Le Bail fitting results for KSnSb using TOPAS. The green cross marks correspond to the Bragg reflections of KSnSb .........................195

Figure A.10 Unpolarized Raman spectra of 1T-layered Zintl phases, (a) EuGe$_2$ and (b) BaSn$_2$, showing both the in-plane and out-of-plane Raman modes .........................197

Figure A.11 Powder XRD Rietveld refinement results for EuGe$_2$ using TOPAS. The phase fraction of Ge was refined to be 10.6%. The green and orange cross marks correspond to the Bragg reflections of EuGe$_2$ and Ge, respectively.......................198
Figure A.12 Powder XRD Rietveld refinement results for BaSn\(_2\) using TOPAS. The green cross marks correspond to the Bragg reflections of BaSn\(_2\)........................................201

Figure A.13 Kubelka-Munk diffuse reflectance spectra of metallic Zintl phases showing the broadband absorption across the visible and near-infrared range. The absorbance spectrum of KSnSb was included for reference.................................................................203

Figure A.14 Diffuse reflectance absorbance spectra of semiconducting Zintl phases fitted using the Tauc-Davis-Mott models of 3D densities of states of (a) 3D indirect allowed, (b) 3D direct allowed transitions.................................................................204

Figure A.15 Powder XRD Rietveld refinement results for NaSn\(_2\)As\(_2\) using TOPAS .....205

Figure A.16 Verification of the Sn:As stoichiometry in NaSn\(_2\)As\(_2\) measured via X-Ray Fluorescence. Red data points correspond to different mixtures of elemental Sn and As to prepare a standard calibration curve.................................................................207

Figure A.17 XPS spectra of the NaSn\(_2\)As\(_2\) crystals after exposure to 4 days in air (green) and after etching the top 1 nm (red) using a Ar\(^+\) ion etch, highlighting the a) Na 1s, b) Sn 4d, c) Sn 3d\(_{5/2}\), and d) As 3d peaks.................................................................208

Figure A.18 AFM images and height profiles of mechanically-exfoliated NaSn\(_2\)As\(_2\) onto 285 nm SiO\(_2\)/Si ...............................................................209

Figure A.19 Step height analysis of AFM micrographs taken on exfoliated NaSn\(_2\)As\(_2\) flakes with multiple step edges. Step thicknesses were obtained from averaged heights along the horizontal length of each step.................................................................210
Figure A.20 AFM thickness histogram of different step heights obtained from mechanically-exfoliated NaSn$_2$As$_2$ showing that cleaved steps always have thicknesses that were multiples of ~0.9 ± 0.2 nm

Figure A.21 UV-Vis Spectrum of NaSn$_2$As$_2$ dispersed in various solvents

Figure A.22 AFM images and height profiles of CHP-exfoliated NaSn$_2$As$_2$ flakes that were prepared via dropcasting onto 285 nm SiO$_2$/Si

Figure A.23 AFM thickness histogram of 36 different flakes that were prepared via dropcasting CHP-exfoliated NaSn$_2$As$_2$ onto 285 nm SiO$_2$/Si

Figure A.24 Representative EDX spectrum of solvent-exfoliated NaSn$_2$As$_2$

Figure A.25 HRTEM image of CHP-exfoliated NaSn$_2$As$_2$ highlighting long-range order based on the (015) lattice fringes. Inset is a fast Fourier transform of the image showing a [2-51] zone axis

Figure A.26 XPS spectra of the liquid-exfoliated NaSn$_2$As$_2$ flakes after exposure to 1 day (green) and 3 days in air (purple), highlighting the a) Na 1s, b) Sn 3d$_{5/2}$, and c) As 3d peaks

Figure A.27 Adhesion energy of NaSn$_2$As$_2$ as a function of layer separation. The data for the DFT-D2 (plain GGA) calculation are red (blue). The interlayer separation is relative to the equilibrium separation of bulk NaAs$_2$Sn$_2$

Figure A.28 ARPES spectrum of NaSn$_2$As$_2$, collected at 127 eV at 41 K

Figure A.29 HSE band structure of a single layer NaSn$_2$As$_2$ which shows that the metallic character is preserved in isolated layers

Figure A.30 Powder XRD Rietveld refinement results for EuSn$_2$As$_2$ using TOPAS
Figure A.31 X-Ray Fluorescence verification of the Eu:Sn and Sn:As stoichiometry in EuSn$_2$As$_2$. Different ratios of Eu$_2$O$_3$ and elemental Sn (Eu:Sn) and elemental Sn and As (Sn:As) were used to prepare a standard calibration curve ..............................219

Figure A.32 Field-cooled temperature-dependent magnetic susceptibility of EuSn$_2$As$_2$ with the a/b-axis (blue) and c-axis (red) parallel to the field showing the standard deviation........................................................................................................................................220

Figure A.33 Curie-Weiss fit corresponding to the ZFC inverse susceptibility of the EuSn$_2$As$_2$ crystal with its c-axis oriented parallel to the applied 0.01 T field........220

Figure A.34 Temperature-dependent magnetic susceptibility of EuSn$_2$As$_2$ with the c-axis parallel to the applied field of 5T..................................................................................................................221

Figure A.35 AFM images and height profiles of mechanically-exfoliated EuSn$_2$As$_2$ onto 285 nm SiO$_2$/Si ........................................................................................................................................222

Figure A.36 (a) The powder XRD spectra of the precursor CaGe$_{2-x}$Sn$_x$ Zintl phases (b) The zoomed-in powder XRD spectra highlighting the (100) peak (c) The full width at half maximum (FWHM) of the (100) peak versus the Sn concentration.................223

Figure A.37 (a) X-ray Fluorescence Spectrum of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$. (b) Tin content of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ from X-Ray fluorescence. Red line: linear fitting of standard sample mixtures..............................................................................................................................228

Figure A.38 The FWHM of the (100) and (002) peaks of the Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ (x = 0-0.9) XRD pattern........................................................................................................................................228

Figure A.39 The FT-IR spectrum of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ from (a) 1750 cm$^{-1}$ to 2150 cm$^{-1}$ and (b) 400 cm$^{-1}$ to 800 cm$^{-1}$.........................................................................................................................................................229
Figure A.40 $E_2$ phonon mode full with at half maximum (FWHM) of 2D Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ with various Tin content .................................................................229

Figure A.41 Ge$_{0.96}$Sn$_{0.04}$H$_{0.96}$(OH)$_{0.04}$ absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.4 meV was deduced from the 301.4 cm$^{-1}$ Raman Shift .................................................................230

Figure A.42 Ge$_{0.93}$Sn$_{0.07}$H$_{0.93}$(OH)$_{0.07}$ absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.3 meV was deduced from the 300.9 cm$^{-1}$ Raman Shift .................................................................231

Figure A.43 Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.1 meV was deduced from the 299.2 cm$^{-1}$ Raman Shift .................................................................232

Figure A.44 Absorption spectrum of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ from 1 eV (1240 nm) to 4.13 eV (300 nm) ........................................................................................................233

Figure A.45 Transmission mode absorbance spectrum of a ~3.5 ± 0.5 μm thick Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ flakes before and after exposure to ambient air and after subsequent 1 M HCl washing .................................................................233

Figure A.46 The FT-IR spectrum of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ before and after exposure to ambient air and after subsequent 1 M HCl washing in the 400-1000 cm$^{-1}$ region .234
Chapter 1 Introduction

In this introductory chapter, we present a brief overview of the state-of-the-art in terms of materials and physical, electronic and magnetic phenomena in two-dimensional (2D) materials. First, we discuss the structure and electronic properties of graphene and related phases including its broad impact towards the materials and condensed matter community. We then present several influences of 2D materials in terms of the discovery and experimental proof of long withstanding problems in condensed matter physics especially the search for dissipationless transport at room temperature and the realization of ferromagnetism in the 2D limit. Also included in this chapter is a discussion on emerging families and classes of 2D materials beyond graphene which possess unique properties wherein we focus on the structure and chemistry of the less-explored class of exfoliatable and non-exfoliatable layered Zintl phases. We also present a detailed review of the progress in the creation and synthesis of 2D \( sp^3 \)-hybridized Group 14 graphane analogues including the topochemical deintercalation chemistry from precursor layered Zintl phases, electronic and optical properties both in theory and in experiment, stability

\[1 \text{ Parts of this chapter were reproduced from Jiang, S.,* Arguilla, M. Q.,* Cultrara, N. D.,* and Goldberger, J. E. Covalently-Controlled Properties by Design in Group IV Graphane Analogues. Acc. Chem. Res., 48, 144-151, (2015). Copyright 2016 American Chemical Society.} \]
and exfoliation. Last, we highlight the topics per chapter that will be presented in this dissertation.
1.1 The Advent of Two Dimensional Materials

As a result of the widespread integration of semiconductor technology into all facets of life, the Group 14 semiconductors, silicon and germanium, are the most important and ubiquitous materials of the current era. Not only are they the workhorse materials of transistor technology, silicon and germanium are the most prevalent materials employed in photovoltaics and photodetectors, and have attracted considerable attention as thermoelectric energy generators. Still, the neverending push towards device miniaturization calls for the need to understand the nature of these materials when reduced below the nanoscale. The creation of single-atom thick layers provides an avenue for the discovery of new phenomena and properties that can potentially overcome some inherent limitations in the parent three-dimensional (3D) semiconductors. For example, the indirect nature of silicon and germanium’s band gap limits their efficiency in optoelectronics, and prevents their implementation into light emitting applications.

Graphene’s discovery has shown that it is possible to prepare single atom thick layers of a two-dimensional (2D) material, and as a consequence, numerous methods have been developed to facilitate the understanding of the unique properties that emerge in single layers. Graphene is a single layer of graphite, and is comprised of a π-bonded honeycomb lattice of carbon atoms. Graphene, with its linear dispersion at the K point and massless Dirac Fermions, has unique properties like high carrier mobilities (~200,000 cm² V⁻¹ s⁻¹), leading to the observation of the quantum hall effect at room temperature, as well as high thermal conductivity, and an exceptional mechanical strength. Nevertheless, the fact that this high mobility state only appears as a result of the linear
Fermi-Dirac dispersion of carbon’s half-filled $2p_z$ orbitals and semimetallic zero band gap, limits the ability to readily integrate graphene into current semiconductor technology, which require materials with band gaps for optimal performance. For example, the lack of a band gap prevents graphene transistors to have large ratios in current between the on and off state. Functionalization of graphene to make hydrogen-terminated graphene, or graphane, opens a sizable band gap, but dramatically decreases the carrier mobility to 10 cm$^2$ V$^{-1}$ s$^{-1}$, by bonding to the C $2p_z$ orbitals thereby eliminating the Fermi Dirac state.$^{10}$ While graphene is a fascinating and promising material, the limitations of its electronic structure has inspired researchers to explore other 2D materials beyond graphene.

An entire field of research has emerged investigating other similar 2D Van der Waals solids.$^6$ These materials allow for manual exfoliation to single and few-layers, breaking the weak interlayer interactions while maintaining the strong in-plane bonding. While there is an ever expanding class of these materials, this account will primarily focus on the Group 12 (silicon, germanium, and tin) analogues of graphane. These structures are comprised of 2D puckered honeycomb networks of sp$^3$-hybridized Group 14 atoms, and are terminated with hydrogen or other ligands (Figure 1.1).
Although they all belong to Group 14, heavier elements like Si, Ge, and Sn do not readily form $\pi$-bonds. This arises from their larger atomic size, which increases their bond distances, thereby reducing overlap between nearest neighbor $\pi$-bonding $p$ orbitals. In other words, each Si/Ge/Sn atom would preferentially bond to another ligand rather than form a $\pi$-bond with its neighbor. Since every atom in the 2D network has a covalently bound ligand, the identity of this ligand can provide a versatile synthetic handle for tuning the electronic structure and properties in these materials. For example, with the appropriate surface terminating ligand these 2D materials can feature direct band gaps,$^{11-15}$ potentially enhancing silicon’s and germanium’s performance in photovoltaics, photodetectors, light-emitting diodes, and lasers. Furthermore, these puckered honeycomb networks are structurally analogous to Si and Ge(111) surfaces, allowing the use of established surface functionalization chemistries$^{16-20}$ to modify the ligand.
1.2 2D-Enabled Phenomena: The Search for High-Mobility Carriers, Dissipationless Transport and 2D Magnetism

The rise of graphene brought with it the understanding and realization of various physical phenomena and, at the same time, opened up new avenues towards the applications of 2D materials as platforms for the demonstration of exotic phenomena that is unique to 2D. Historically, electronic materials have only been categorized into two distinct classes: insulating/semiconducting and conducting/metallic. But then, in the 1980s, the integer quantum hall (QH) phase in two-dimensional electron gas (2DEG) systems was discovered and demonstrated experimentally.\textsuperscript{21} In the QH phase, low temperatures and high magnetic fields create localized electronic states in the bulk and delocalized extended states that propagate along the edges of the material which produces quantized hall resistance corresponding to integers of $e^2/h$ along the bulk of the material and dissipation-less transport along the edges, respectively. The induced localization on the surface means that the surface of the 2DEG is gapped/insulating while the edges. This coexistence of two distinct states in one material opened up the notion of the evolution of electronic states with ‘topology’ in electronic phases.

Since the QH phenomena relies on low temperatures ~4 K to freeze-out any defects, the discovery of graphene’s extremely high mobility carriers negated the need for cooling which consequently allows for the realization of the QH effect at room temperature.\textsuperscript{22} This concept of electronic topology and the coexistence of an insulating and metallic state in materials was extended through the demonstration of the same quantization observed in quantum hall phases but without the application of strong magnetic fields, where the high magnetic fields that are required to drive the quantized
edge states is replaced by an internal field present within the atoms that constitute the phase, which is spin-orbit coupling. This new insulator phase, first demonstrated experimentally through CdTe/HgTe/CdTe quantum wells at a certain critical thickness of the HgTe layer sufficient to induce a band inversion, is now classified as two-dimensional topological insulators (2D-TI) or quantum spin hall (QSH) insulators.\textsuperscript{23,24}

In this system, the surface of the 2D material has an insulating gap that is opened through the SOC-induced lifting of the degenerate states caused by the band inversion. Along the edges, crystal symmetry is broken and SOC is suppressed. In turn, the system would try to close the gap which results to Dirac-like band crossing along the edges of the material that creates spin-up and spin-down electrons that travel in opposite directions. Along the edges of a 2D TI, the electrons can travel through a non-magnetic defect/impurity either in a clockwise direction or a counter-clockwise direction that are related by time reversal symmetry (TRS) where the spin can rotate by an angle of either $-\pi$ or $\pi$ resulting to a difference of a full $2\pi$ rotation. According to quantum mechanics, a full $2\pi$ rotation of a spin-$1/2$ particle yields a $-1$ wavefunction which means that these two paths interfere destructively.\textsuperscript{25} This means that, as long as there are these two paths that are related by TRS, the effect of a non-magnetic impurity is “cancelled” and that perfect and dissipationless transmission is achieved. Magnetic defects, on the other hand, can break TRS which, in turn, suppresses the destructive interference. In 3D systems, the bulk of the material is insulating while the TRS-protected states persist on the surface.

As a whole, these phases are called 2D or 3D topological insulators due to the coexistence of robust edge and surface states and an insulating surface and bulk in 2D and 3D, respectively.\textsuperscript{23,26-34} As promising as it is for the realization of room temperature
dissipationless transport, the minute band gap in HgTe limits its application to
temperatures at or below 30 K since room temperature excitation (~25 meV) suppresses
the insulating state and turns the conductance of the system into a trivial metallic state.
This has inspired the prediction of various 2D materials that are potential topological
phases with band gaps that are significantly larger and are theorized to be robust against
room temperature excitation.\textsuperscript{15,23,26-34} Of these phases, the –OH/halide functionalized 2D
$sp^3$-hybridized Sn systems\textsuperscript{15} will be a recurring topic in this manuscript as it has served as
one of the motivations towards the search and synthesis of tin-based 2D honeycomb
lattices.

Topological insulators (TIs) are unique phases such that these materials possess
an insulating bulk and a conducting Dirac-like surface (3D-TI)/edge (2D-TI) state with
counter-propagating spins.\textsuperscript{3} The emergence of the Dirac-like states with counter-
propagating spins is mainly due to the parity inversion (inversion of bonding and anti-
bonding molecular orbitals) which is brought about by strong SOC while the protection
from scatterers is due to the underlying symmetry in the structure. Based on the type of
symmetry that protects the Dirac-like surface/edge states from scatterers, these TIs can be
classified as $Z_2$-TIs or topological crystalline insulators (TCIs). The presence of Dirac-
like states in $Z_2$-TIs are characterized by the $Z_2$ topological invariant, $\nu_0$.\textsuperscript{28} This
topological invariant, $\nu_0$, can be calculated through equation (1):

\[
(-1)^{\nu_0} = \prod_{i=1}^{8} \delta(\Gamma_i)
\]  

(1)
where $\delta(\Gamma_i)$ is the parity invariant (+1 for a band/orbital inversion and −1 for no inversion) at the eight bulk time-reversal invariant momentum ($\Gamma_i$) points (TRIMs) (Figure 1.2).

**Figure 1.2** The time-reversal invariant momentum (TRIM) points in common topological insulators and their respective Brillouin zones.\textsuperscript{35} (Reproduced with permission from Ref. 35 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2015 by Wiley-VCH Verlag GmbH & Co. KGaA Lic. No. 4151490759145)

These TRIMS are points that can be connected in the Brillouin zone through the reciprocal lattice vector and time-reversal operation. A value of $\nu_o = 1$ signifies a non-trivial (topological) insulator while $\nu_o = 0$ corresponds to a trivial insulator. Table 1.1 shows the $\nu_o$ of some candidate TI phases. Notice that under the $Z_2$-topological invariant, $\nu_o$, only the phases that posses odd numbered band/orbital inversions that crosses the Fermi level (+1 $\delta(\Gamma_i)$) are classified as topological insulators.
Table 1.1 The bulk TRIMS ($\Gamma_i$) with the corresponding parity, $\delta(\Gamma_i)$, and $Z_2$ invariants for several topological insulators.\textsuperscript{35} (Reproduced with permission from Ref. 35 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2015 by Wiley-VCH Verlag GmbH & Co. KGaA Lic. No. 4151490759145)

<table>
<thead>
<tr>
<th>Material</th>
<th>TRIMS</th>
<th>Parity Invariant, $\delta(\Gamma_i)$</th>
<th>$Z_2$-Invariant, $\nu_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$X$</td>
<td>$-1$, $-1$, $-1$, $-1$</td>
<td>0</td>
</tr>
<tr>
<td>Sb</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$X$</td>
<td>$-1$, $-1$, 1, $-1$</td>
<td>1</td>
</tr>
<tr>
<td>Bi$_{1-x}$Sb$_x$, (0.08 &lt; x &lt; 0.22)</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$X$</td>
<td>$-1$, $-1$, 1, $-1$</td>
<td>1</td>
</tr>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$F$</td>
<td>$-1$, 1, 1, 1</td>
<td>1</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$F$</td>
<td>$-1$, 1, 1, 1</td>
<td>1</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$Se</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$F$</td>
<td>$-1$, 1, 1, 1</td>
<td>1</td>
</tr>
<tr>
<td>PbTi$_2$Te$_4$</td>
<td>1$\Gamma$, 1$\Gamma$, 3$L$, 3$F$</td>
<td>1, $-1$, 1, 1</td>
<td>1</td>
</tr>
<tr>
<td>SmB$_6$</td>
<td>1$\Gamma$, 3$X$, 3$M$, 1$R$</td>
<td>1, $-1$, 1, 1</td>
<td>1</td>
</tr>
<tr>
<td>SnTe</td>
<td>1$\Gamma$, 3$X$, 4$L$</td>
<td>$-1$, $-1$, 1</td>
<td>0</td>
</tr>
<tr>
<td>PbTe</td>
<td>1$\Gamma$, 3$X$, 4$L$</td>
<td>$-1$, $-1$, $-1$</td>
<td>0</td>
</tr>
</tbody>
</table>

To further understand the topology of these Dirac-like states and their protection against non-magnetic scatterers, this can be extended to the surface fermion parity, $\pi(\Lambda_a)$, at the surface TRIMs ($\Lambda_a$).

$$\pi(\Lambda_a) = (-1)^{n_b} \delta(\Gamma_i) \delta(\Gamma_j)$$  \hspace{1cm} (2)

where $n_b$ is the number of occupied spin-degenerate bands.\textsuperscript{36}
From equation (2), a $-1$ product of two surface fermion parities, $\pi(\Lambda_a)\pi(\Lambda_b)$, along the TRIMs (ex. $\Lambda_a$ and $\Lambda_b$) in the Brillouin zone corresponds to a TRS-protected topological state (Figure 1.3) characterized by two opposite spins propagating in opposite directions.

Figure 1.3 Surface electronic structures of (a) trivial, $\pi(\Lambda_a)\pi(\Lambda_b) = +1$, and (b) topological, $\pi(\Lambda_a)\pi(\Lambda_b) = -1$, insulators.\textsuperscript{35} (Reproduced with permission from Ref. 35 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2015 by Wiley-VCH Verlag GmbH & Co. KGaA Lic. No. 4151490759145)

TCIs, on the other hand, are typically characterized as trivial insulators under the $Z_2$ topological invariant.\textsuperscript{37} This is due to the presence of even-numbered band inversions, thus creating even-numbered Dirac-like surface states (Figure 1.3) which, under equation (1) gives a topological invariant value of $\nu_0 = 0$ (trivial insulator). Since TRS is broken in these systems, the protection of these Dirac-like surface states comes from the inherent crystal symmetry (rotation, reflection, etc.) in the material. These crystal symmetry-protected Dirac-like states, contrary to TRS-protected states, are protected, not only against non-magnetic scatterers, but also from magnetic scatterers.
One of the most powerful and widely used tool that is used to directly probe the topological protection ($Z_2$-topological invariant or the mirror Chern number) of Dirac-like surface states is angle-resolved photoemission spectroscopy (ARPES). In this technique, the single-particle electronic excitation density is measured and the distribution of electrons along the reciprocal space of the solid is deduced (Figure 1.4). This is possible due to the ejection of electrons from the surface or from the bulk to the vacuum (at a certain kinetic energy) upon the absorption of energy corresponding to the energy of the light ($h\nu$) that hits the surface of the solid. The electron density measured along the reciprocal space (k-space or momentum space) provides information on the electronic band structure of the bulk and surface of the material under study. In addition to this, the electron spin corresponding to the surface electronic space can also be determined via ARPES measurements. The spin detection is enabled by a ferromagnet-based very low energy electron diffraction (VLEED) detector. Here, the electron spin is deduced from the intensities of the diffracted beams which are dependent on the spin polarization of the primary electron beam relative to the magnetization. Recently, there have also been developments on the spatial resolution of the incident photon beam where the typical $\mu$m-range spot size was reduced down to few of tens of nanometers. In addition to the lateral resolution, this same technique can also probe very thin structures and was successful in measuring the electronic states (surface states) of single-atom-thick graphene. This miniaturization of the lateral and vertical resolution gives rise to potential measurements of the bulk and surface electronic structures of potential TI nanostructures.
Another field that was instigated through the experimental techniques that were developed for graphene is the search phases that exhibit long-range robust ferromagnetic coupling in the single-atom-thick regime. The intrinsic anisotropy in 2D magnetic materials prevents the influence of strong thermal fluctuations, theorized by the Mermin-Wagner theorem\textsuperscript{42} to be one of the possible reasons towards the suppression of long-range magnetic order in 2D, and promotes the persistence of a long-range ferromagnetic order going from the bulk down to the single layer limit. Now, due to the rediscovery of previously-known layered magnets and the air-free exfoliation of single layers of these materials, long-range intrinsic magnetism in the few-to-single-layer regime was experimentally demonstrated in CrI\textsubscript{3} and Cr\textsubscript{2}Ge\textsubscript{2}Te\textsubscript{6} via scanning magneto-optic Kerr microscopy.\textsuperscript{43,44}
1.3 Layered Zintl Phases as Modular and Multifunctional 2D Materials

Due to the explosion of the field of 2D materials, a continuous search for new classes of 2D materials which might host the next exotic phenomena or application has been going on since the discovery of room temperature quantum Hall effect in graphene. To date, there have been numerous families of 2D materials that have been created and rediscovered that ranges from the huge family of transition metal dichalcogenides to the emerging class of 2D MXenes. These 2D materials beyond graphene have also demonstrated a plethora of optoelectronic, spintronic, magnetic and even catalytic properties and applications.

One of the materials classes that haven’t received much attention in the 2D community are the layered Zintl phases. Zintl phases, in general, are typically composed of anionic 0D clusters, 1D wires or 2D sheets of main group elements that are held by alkali, alkaline earth or lanthanide cations. These phases follow the Zintl-Klemm counting rules, which assures that the main group elements have a closed shell of 8 electrons or follows the octet rule. Because of the dimensionalities of these phases can be tuned by either varying the stoichiometry of the main group element and the cation or by tuning the size ratios between the two. For example, in the first case, the dimensionalities of a Ge lattice can be tuned by varying the stoichiometric ratios of Ge and the cation that holds the Ge anions (Figure 1.5). In CaGe₂, Ge is bonded to three other Ge atoms which gives it 4 + 3 valence electrons which is then completed to an octet by the donation of 1e⁻ from the Ca²⁺ cation to each Ge atom (Figure 1.5a). Since the bond lengths of Ge in this structure is in the range of typical Ge-Ge bond lengths, the structure forms a 2D sheet. This structure is analogous to the 3D bulk structure of Ge in wherein the bonds along the
[111] direction are all replaced by Ca$^{2+}$ cations. By changing the stoichiometry to 1:1, the Ge atoms start to bond to only two other Ge atoms forming zig-zag wires which gives every Ge atom $4 + 2$ valence electrons that is supplemented to form an octet by the donation of $2e^-$ from the Ca$^{2+}$ cation (Figure 1.5b). By taking it further, through the replacement of the Ca$^{2+}$ cation with a larger Group 1 cation that has 1e- less, such as in KGe, the Ge atoms are driven apart and to bond to three other Ge atoms to form isolated [Ge$_4$]$^{-}$ tetrahedral which has a valence electron count of $4 + 3$ which is then completed to octet by the 1e$^-$ from K$^+$ (Figure 1.5c).

Figure 1.5 Electron counting and octet completion in Ge-based Zintl phases that assume a (a) 2D structure in CaGe$_2$, (b) 1D structure in CaGe and (c) 0D structure in KGe.

This structural diversity and the unprecedented control over the dimensionality of the phases have attracted much exploration and discovery of phases that obey this Zintl-Klemm rule. This has resulted to the creation of a huge library of 0D, 1D, 2D and 3D
Zintl phases each having unique properties and applications.\textsuperscript{57-65} Of these phases, the 2D/layered Zintl phases have started to gain attention in the 2D community due to the fact that these layered phases hosted main group 2D isolated sheets that are held by cations. These 2D/layered Zintl phases also hosted a huge variety of physical and electronic properties such as superconductivity in the Group 2/Group 13/Group 14 series with 1:1:1 stoichiometry\textsuperscript{66} and in CaSi\textsubscript{2}\textsuperscript{67} at high pressures; semiconducting properties in hydrogenated Group 2/Group 13/Group 14 series with 1:1:1 stoichiometry,\textsuperscript{68} anisotropic magnetism in Ln/Group 13/Group 15 series with 1:2:2 stoichiometry,\textsuperscript{59-61} and even topologically-protected phases in the Group 2/Group 14 series with 1:2 stoichiometry.\textsuperscript{69,70} Although promising as 2D/layered materials, the Zintl phases are limited by their bulk properties since most of these layered materials do not feature easy cleavage axes such as a vdW gap. However, there have been several known layered Zintl phases, the properties of which will be delved in detail on Chapters 3 and 4, that intrinsically feature a vdW gap which is imparted by a layer that does not have any cations.\textsuperscript{71,72} These phases are typically comprised of Group 1 or 2 cations coupled to Sn and As in a 1:2:2 stoichiometric ratios. These phases feature sandwiches of \~1 nm sandwiches of Sn-As-Cation-As-Sn that are held by vdW gaps which potentially allow for the exfoliation of these phases into single to few-layer Sn-As-Cation-As-Sn sandwiches. Aside from being hosts for 2D properties and a wide range of properties, the ionic bonding across the layers allows for the use of these phases as platforms for topochemical deintercalation reactions to form another class of layered vdW materials: the \textit{sp}\textsuperscript{3}-Hybridized Group 14 Graphane Analogues.\textsuperscript{13,73,74}
1.4 Beyond Graphene: \(sp^3\)-Hybridized Group 14 Graphane Analogues

Though the synthesis of polysilanes, polygermanes, and polystannanes from small molecules has been well developed,\textsuperscript{75-77} they are limited to 1D inorganic polymers and single rings. To date, there have been no synthetic routes for preparing Group 14 graphane analogues from small molecule precursors due to the lack of a mechanism for controlling growth in 2D. However, the layered Zintl phases, CaSi\(_2\), CaGe\(_2\), and BaSn\(_2\), are comprised of puckered honeycomb \([\text{Si}^\circ]_n\), \([\text{Ge}^\circ]_n\), and \([\text{Sn}^\circ]_n\) graphane-like layers held together by the Group 2 \([\text{M}^{2+}]\) cations (Figure 2a). Consequently, the preparation of Group 14 graphane analogues relies on developing soft chemical processes that can topotactically deintercalate the \(\text{M}^{2+}\) cations while maintaining the structure and covalently terminating the anionic Group 14 layers.

The topotactic deintercalation of CaSi\(_2\) using HCl can be traced back to Wöhler in the 1860’s, Kautsky in the 1920’s, and the structure and properties were partially resolved in the 1980’s and 1990’s.\textsuperscript{11,12,78-83} It was reported that siloxene (Si\(_6\)H\(_3\)(OH)\(_3\)) preferentially forms at temperatures greater than 0 °C and layered polysilane (Si\(_6\)H\(_{6-x}\)(OH)\(_{1-x}\) (x<1)) forms at -30 °C.\textsuperscript{11,12,81} These structures are silicon graphane analogues, or silicanes, with -H/-OH, and -H terminal substituents, respectively. Compared to the indirect band gap of crystalline silicon (1.1 eV), siloxene has a direct band gap at around 2.4 eV with strong photoluminescence (PL).\textsuperscript{12} Other silicon graphane analogues terminated with organic functional groups were also reported in the past decade that feature PL ranging from 2.7 to 2.9 eV.\textsuperscript{84-86} However, all these reactions rely on the topotactic deintercalation of CaSi\(_2\) in aqueous HCl, which readily produces partially OH-terminated SiH\(_3\)(OH)\(_{1-x}\) due to the significantly stronger Si-O bond (800 kJ/mol)
compared with the Si-H bond (300 kJ/mol). This ambiguity in surface functionalization convolutes efforts to correlate the effects of surface functionalization on the optoelectronic properties of these single-atom thick semiconductors. In contrast, the difference of bond strength is much smaller between Ge-O (660 kJ/mol) and Ge-H (320 kJ/mol) and furthermore, any native germanium oxide or hydroxide termination is readily dissolved in aqueous HCl, thereby producing pure germanane (GeH). Indeed it was reported by Brandt and Stutzmann that CaGe$_2$ thin films grown on germanium wafers can be topotactically deintercalated to form GeH, with little surface oxidation.$^{87}$

Recently our group has synthesized for the first time millimeter-scale crystals of GeH via the topotactic deintercalation of large CaGe$_2$ single crystals in aqueous HCl (Figure 1.6).$^{13}$ Here, Ca$^{2+}$ is removed via the formation of a soluble CaCl$_2$ species and the anionic [Ge]$_n$ layer is terminated by H atoms. The X-ray diffraction (XRD) confirms that the layered hexagonal germanium lattice is maintained, and an increase in the interlayer distance occurs (5.1 Å to 5.5 Å) upon replacing the Ca$^{2+}$ with two Ge-H bonds (Figure 1.6e,f). The large full-width half maximum of all the peaks that contain any c-axis reflections indicates that there exists a significant amount of disorder in the c-axis, which is common in layered materials. Pair distribution function (PDF) analysis collected from synchrotron measurements directly confirms the honeycomb 2D network of germanium atoms.$^{74}$ Compared with the PDF of crystalline Ge, GeH has systematic absences at 5.66 Å, 7.35 Å, and 8.95 Å (Figure 3b) that arise in 3D crystalline Ge. In Ge, these peaks correspond to Ge–Ge pairs between atoms in different (111) layers (Figure 1.7a,b). All other peaks can be indexed to the Ge–Ge pairs within a single Ge(111) plane. The interlayer disorder of GeH prevents the observation of scattering between any
interlayer Ge–Ge pairs. Furthermore, transmission electron microscopy (TEM) analysis indicates the layered morphology of GeH (Figure 1.7c,d). Finally, the most conclusive technique for determining the nature of the ligand bonded to each germanium atom is Fourier transform infrared spectroscopy (FTIR). Every vibrational mode observed in the FTIR corresponds to a Ge-H bond, with no peaks corresponding to any Ge-O vibrational mode. The identity of each mode was readily verified with deuterium labeling.13

Figure 1.6 Schematic illustration of topotactic deintercalation of (a) CaGe2 to (b) GeH (Ca: yellow, Ge: purple and H: black). Optical images of (c) CaGe2 and (d) GeH crystals with select crystals on a 1 mm grid graph paper. Powder XRD of (e) CaGe2 and (f) GeH.13
Figure 1.7 (a) A single (111) plane of crystalline germanium, representing a single layer of GeH. The distance of the germanium atoms on a certain colored ring from the central germanium atom corresponds to the same color peak in (b). (b) PDFs of GeH and Ge. The starred peaks correspond to the interactions between germanium atoms in different layers.74 (c) Low-magnification and (d) magnified TEM micrograph of GeH platelets. Inset in (c) is the corresponding electron diffraction pattern collected down the [001] zone axis.13

The synthesis of large millimeter-scale flakes of GeH enables the isolation of single- and few-layer thick sheets via mechanical exfoliation using PDMS and scotch tape (Figure 1.8a), by adapting the procedure developed by Frindt.88,89 These single-layer flakes were exfoliated onto 110 nm thick and 300 nm thick SiO$_2$/Si substrates, which provide suitable optical contrast. However, mechanical exfoliation is a labor-intensive and non-scalable process for producing single and few-layer thick materials. Additionally, the interlayer van der Waals interactions in GeH are calculated to be ~35% stronger in
GeH compared to graphene\textsuperscript{13}, which experimentally makes the preparation of large areas of single layer GeH more challenging. The ability to synthesize precise layer thicknesses of these Group 14 graphane analogues on Si and Ge substrates, would enable their seamless integration into existing semiconductor fabrication infrastructure. This can be achieved by first epitaxially growing the precursor Zintl phases onto Si and Ge substrates. The $a,b$-parameters of the precursor CaGe$_2$ Zintl phase closely match the spacing of the Ge(111) surface to less than 0.5\%. This enables the direct epitaxial growth of CaGe$_2$ thin films on Ge(111) wafers, which can be subsequently topotactically deintercalated to obtain GeH. Indeed, we have prepared 5 nm thick films of CaGe$_2$ on Ge(111) via molecular beam epitaxy (MBE), which would correspond to $\sim$10 layers.\textsuperscript{90} These co-deposited CaGe$_2$ thin films have grain sizes on the order of a few micrometers, which is the typical sizes of terrace formed due to the miscut of the Ge(111) growth substrate. Upon treatment in HCl, these thin films exhibit the same XRD and Raman profiles as those produce from single crystals of CaGe$_2$. Consequently, the combination of epitaxial growth and topotactic deintercalation represents a promising and scalable route for the preparation of precise layer films of Group 14 graphane analogues and simplifies subsequent VLSI processing.
Figure 1.8 AFM images of (a) an exfoliated single layer of GeH and (b) GeH thin film after deintercalation of a 5 nm thick CaGe$_2$ film grown via MBE on Ge(111). Inset in (a) is an optical micrograph of the single-layer flake.$^{13,90}$

The presence of a covalently bound surface ligand on every atom in these Group 14 graphane analogues opens up the possibility of tuning the properties by varying this surface ligand. There has been extensive work during the past few decades showing that every atom on Si and Ge(111) surfaces can be terminated with small organic substituents such as –CH$_3$ and –CCH.$^{16-20,91}$ In contrast to H-terminated Si/Ge(111) surfaces, which oxidize within 30 minutes of exposure to air, these organic-terminated surfaces have been shown to be resistant towards oxidation for at least 30 days.$^{19,91,92}$ Consequently, it is easy to envision 2D derivatives of these same organic functionalized surfaces.

To these ends, we have developed a one-step metathesis approach that directly converts CaGe$_2$ crystals into organic-terminated germananes by topotactically reacting it with organoiodines. For instance, we have prepared ~1 mm flakes of GeCH$_3$ (Figure 1.9a,b) by reacting CaGe$_2$ with CH$_3$I.$^{14}$ Through this reaction, Ge$^-$ anions bond to the CH$_3$ group, and the iodide reacts with Ca$^{2+}$ to form a soluble CaI$_2$ species, which is easily
separated. Single crystal and powder XRD analysis show that the hexagonal unit cell of CaGe$_2$ is retained and GeCH$_3$ has a similar 2H unit cell (two GeCH$_3$ layers per unit cell) as GeH (Figure 1.9c,d). The interlayer distance of GeCH$_3$ is increased by 3.1 Å compared to GeH, which is close to the estimated increase (~2.5 Å) based on the bond length and van der Waals radii differences of these two ligands. The methyl-termination is further confirmed by FTIR measurements (Figure 1.9e). Compared with GeH, the intense Ge-H stretching mode at 2000 cm$^{-1}$ is almost entirely gone, while a Ge-C stretching mode at 573 cm$^{-1}$ is observed. Other vibrational modes like -CH$_3$ stretching, bending and rocking modes are also detected. The identity of each mode can be further verified upon comparison with the FTIR spectra of Ge$^{13}$CH$_3$ and GeCD$_3$. 
This one-step metathesis method is a general route for prepare organic ligand terminated germananes. By substituting CH₃I with other organoiodine reagents like CH₃CH₂I and CH₂=CHCH₂I, we have prepared CH₃CH₂Ge and CH₂=CHCH₂Ge, respectively. The interlayer spacing is expected to increase by 3.5 and 6.2 Å, upon replacing -H in GeH with -CH₂CH₃ and -CH₂CH=CH₂, respectively. This is in close agreement with the increases in interlayer spacing of 3.7 and 5.8 Å observed via XRD (Figure 1.10a). In FTIR spectra, Ge-C stretching can be detected in all three spectra.
along with the near elimination of the Ge-H stretching mode. All the other vibrational modes can be assigned to the corresponding organic functional groups. The observation of H-C≡C- stretching and bending modes at 3076 and 1626 cm\(^{-1}\) further confirms the termination with -CH\(_2\)CH=CH\(_2\). The versatility of this reaction scheme enables the grafting of functional ligands with tunable polarity, reactivity, and mechanical strength for a wide variety of applications.

![Figure 1.10](image)

**Figure 1.10** (a) Powder XRD pattern (b) and FTIR spectra of GeCH\(_3\) (black), GeCH\(_2\)CH\(_3\) (blue), and GeCH\(_2\)CH=CH\(_2\) (red).

The rich surface functionalization chemistry allows these Group 14 graphane analogues to be highly tunable electronic and optoelectronic building blocks for next generation devices. By substituting the main group element and varying the surface ligand, one can tune the electronic structure of these materials to produce unique properties that do not exist in the parent 3D semiconductor structure. To understand how the presence of a surface ligand influences the electronic structure of these 2D graphane analogues, here we describe density functional theory (DFT) simulations illustrating the difference between silicene and silicane as a model system.\(^{93,94}\)
Silicene is a 2D material comprised of a honeycomb arrangement of Si atoms in which every Si shares three $\sigma$ and one $\pi$ bond with the three neighboring Si atoms.\textsuperscript{94,95} Similar to graphene, this structure exhibits Fermi-Dirac behavior at the K point on account of the half-filled $3p_z$ orbitals (Figure 1.11a). Adding hydrogen as a surface terminating ligand to silicene produces silicane (SiH) through the formation of a covalent bond with the Si $3p_z$ orbital.\textsuperscript{94-96} This bonding and anti-bonding interactions splits the Dirac cone at the K point thus opening a sizeable band gap (Figure 8b). The electronic band structure of silicane calculated at the the HSE-06\textsuperscript{97,98} level predicts it to have an indirect band gap of 2.94 eV from $\Gamma$ to M and a direct band gap of 3.14 eV at $\Gamma$.\textsuperscript{94} The conduction band valley at $\Gamma$ is comprised of Si-H $\sigma^*$ states, the conduction band minimum (CBM) at M corresponds to Si-Si $\sigma^*$ states, whereas the valence band maximum (VBM) corresponds to Si-Si $\sigma$ states (Figure 1.11b).

\textbf{Figure 1.11} DFT simulations of the electronic band structure of (a) silicene and (b) silicane and the density orbitals at the high symmetry k-points: (A) Si-H $\sigma^*$, (B) Si-Si $\sigma^*$, (C) and (D) Si-Si $\sigma$ states. Inset in (a) is the hexagonal Brillouin zone.\textsuperscript{94}
The band structure of GeH and SnH are closely related to SiH. However, in the case of GeH, the CBM occurs at $\Gamma$ and not M, leading to a 1.56 eV direct band gap with an effective electron mass of $m_{e,\Gamma^*} = 0.09$ (Figure 1.12). This is consistent with the observed absorption onset at 1.59 eV and with the observation of PL in GeH at 1.56 eV at low temperature. The direct band gap of GeH is in sharp contrast to the 0.67 eV indirect band gap of crystalline germanium. In crystalline germanium, the CBM occur in the four equivalent valleys at the L $<111>$ point, which has a much higher effective mass ($m_{e,L^*} = 1.64$) than the conduction band valleys at $\Gamma$ ($m_{e,\Gamma^*} = 0.041$). However, since GeH can be thought of as hydrogen-terminated isolated (111) sheets of germanium, we are effectively eliminating the L wavevector in the Ge Brillouin zone, resulting in a material that has a direct gap and a considerably higher electron mobility. Electron mobility is inversely proportional to effective mass. We calculated from first-principles the phonon-limited electronic mobility for an isolated single layer of GeH obtaining a room temperature mobility of $\sim 18,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This 5× increase in electron mobility from bulk Ge (3,900 cm$^2$ V$^{-1}$ s$^{-1}$) is consistent with the reduced electron effective mass in GeH. These Group 14 graphane analogues also feature significantly larger band gaps compared to the parent 3D material (Table 1.2).

The 2D sp$^3$-hybridized Sn is predicted to be a topological insulator when terminated by electronegative groups such as -OH and various halides, yet remains as a trivial insulator when terminated by smaller less electronegative ligands such as -H. This topological phase emerges when the Sn 5$s$ $\sigma^*$ bands drop below the 4$p_x$ and 4$p_y$ VBM, which are split on account of the large spin-orbit coupling in Sn. Consequently, 2D tin is predicted to exhibit the quantum spin Hall effect.
Figure 1.12 Electronic band structure of an isolated single layer of GeH calculated using HSE-06 theory including spin–orbit coupling predicting a 1.56 eV direct band gap. The hole and electron effective masses for each extrema are indicated in red.\textsuperscript{13}

Table 1.2 The band gaps of different $sp^3$-hybridized Group 14 elements in bulk and in 2D.

<table>
<thead>
<tr>
<th>Element</th>
<th>3D $sp^3$ (eV)</th>
<th>2D $sp^3$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5.48 (indirect)$^{100}$</td>
<td>3.5* (-H, direct)$^{101}$</td>
</tr>
<tr>
<td>Si</td>
<td>1.12 (indirect)$^{102}$</td>
<td>2.4 (-OH/-H, direct)$^{11}$; 2.94* (-H, indirect)$^{94}$</td>
</tr>
<tr>
<td>Ge</td>
<td>0.67 (indirect)$^{99}$</td>
<td>1.59 (-H, direct)$^{13}$; 1.71 (-CH$_3$, direct)$^{14}$</td>
</tr>
<tr>
<td>Sn</td>
<td>0 (α-Sn); 0.05 (β-, direct)$^{103}$</td>
<td>~0.30* (-H-halides, direct)$^{15}$</td>
</tr>
</tbody>
</table>

*Theoretical

Aside from alloying the main group element, another route that can be used to tune the properties of these materials is through the variation of the surface ligand. Because the CBM at $\Gamma$ corresponds to the Group 14-ligand $\sigma^*$ antibond, this energy level
can be raised or lowered depending on the electronegativity of the surface terminating ligand. Since the ligand also influences the geometry of the entire lattice, this also leads to change in the bond lengths and bond angles in the 2D network, significantly affecting the rest of the band structure. Therefore, substituting one ligand for another will affect the entire electronic band structure, and can significantly change the observed band gap and direct/indirect nature. A systematic experimental study comparing the electronic and optical properties of uniformly functionalized 2D Group 14 graphane analogues is needed to foster a deeper understanding of the influence of surface ligands on the electronic structure of these materials.

Experimentally, we have demonstrated that the band gap of GeH can be increased by 0.1 eV (Figure 1.13a) by replacing the -H with -CH$_3$. Furthermore, very intense band edge PL is observed in GeCH$_3$ (Figure 1.13b) with a quantum yield of 0.2%. In contrast to other layered materials like MoS$_2$, this PL is independent of layer thickness, thus obviating the need for large area single layers for practical devices. The change in PL indicates that optical properties of these 2D Group 14 graphane analogues can potentially be improved with different ligand terminations. In addition to these three organic functional groups previously described in this chapter, a library of organic ligands have also been recently grafted to the germanane 2D lattice which enabled the tuning of the optical gap of germanane. By comparing the Raman modes, which is an excellent indicator of changes in Ge-Ge bond lengths, with the absorption onsets that were obtained from absorbance measurements, it was observed bulky and electron-withdrawing ligands stretch the 2D Ge framework which consequently shift the optical band gaps to lower energies. On the other hand, the inverse was observed for smaller and
electron-donating ligands (**Figure 1.13c,d**). In summary, the combination of alloying and covalent functionalization provides an unprecedented level of control over electronic structure in a 2D crystal, creating a versatile platform for electronic and optoelectronic applications.

**Figure 1.13** (a) DRA spectra of GeH compared to GeCH<sub>3</sub> and (b) Absorption and PL spectra of GeCH<sub>3</sub> with the actual PL observed in isopropyl alcohol as an inset. (c) Experimental and (d) theoretical linear-like dependence of the absorption onset of H- and organic-functionalized germanane on the in-plane Raman shift. ⑪
The potential utility of these Group 14 graphane analogues for any functional device strongly hinges on their air and temperature stability. It has been established that silicon-based 2D systems such as SiH readily oxidize upon exposure to air.\textsuperscript{85,86} GeH, however, shows a remarkable resistance to oxidation.\textsuperscript{13} The lack of oxidation in the bulk material is observed in FTIR measurements (Figure 1.14a) after air exposure to up to 60 days where the absence of different GeO\textsubscript{x} vibrational modes\textsuperscript{105} from 800 to 1000 cm\textsuperscript{-1} indicate that the bulk of GeH is unchanged. On the other hand, X-Ray Photoelectron Spectroscopy (XPS) (Figure 1.14b) is the most sensitive technique in determining the presence of oxidation on the surface. After five months of exposure to air, a Ge\textsuperscript{2+/3+} shoulder emerges at 1219.3 eV (29.7\% Ge\textsuperscript{2+/3+}) indicating surface oxidation is prevalent. After Ar ion etching the top 0.5 nm (\textapprox 1 layer), the Ge\textsuperscript{2+/3+} peak almost completely disappears with 10.1\% Ge\textsuperscript{2+/3+} remaining.\textsuperscript{13} Together, the XPS and FTIR suggest that GeH is resilient towards oxidation and only the surface layer slowly oxidizes.

The thermal stability of these 2D materials strongly depend on the identity of the surface terminating ligand. We observed that in GeH, the emergence of thermal-induced amorphization begins at 75 °C.\textsuperscript{13} We have observed that measurements focused on changes in properties are the most sensitive methods for detecting amorphization, compared to bulk structural analyses like XRD and Raman spectroscopy. The absorption of the new and emerging amorphous germanium species lower than the 2D germanane band gap is more readily observable than the gradual disappearance of a crystalline phase in XRD or Raman. Upon annealing at 75 °C and above, there is an increasing red shift in the absorption onset, consistent with the formation of amorphous GeH, and at higher
temperatures, amorphous Ge (Figure 1.14c).\textsuperscript{13} This amorphization process was further confirmed with temperature dependent PDF measurements.\textsuperscript{74} In contrast, GeCH\textsubscript{3} starts to amorphize at a significantly higher annealing temperature, at around 250 °C (Figure 1.14d).\textsuperscript{14} In summary, the oxidation resistance of germanane and the improvement in thermal stability by methyl termination makes these materials attractive candidates for next generation devices, and can be potentially robust enough to withstand the demands for fabrication and operation.

![Figure 1.14](image.png)

**Figure 1.14** (a) FTIR spectra of GeH after exposure to air for up to 60 days highlighting the absence of any Ge-O vibrational mode. (b) XPS spectra of GeH exposed to air for up to five months, followed by 0.5 nm Ar etch. DRA spectra of (c) GeH and (d) GeCH\textsubscript{3} annealed in Ar/H\textsubscript{2} gas at various temperatures.\textsuperscript{13,14}
1.5 Chapter Outlines

Succeeding this introduction chapter is Chapter 2, which delves into the structural and electronic properties of a number of layered Zintl phases which feature sheets of anionic Group 14 and Group 15 elements. Aside from serving as precursors for topochemical deintercalation into 2D $sp^3$-hybridized vdW systems, these phases on their own possess unique electronic properties ranging from semiconductors, metals and even being topological insulators. Lastly, the factors influencing the Raman-active modes such as the symmetry, stacking and bond lengths are also discussed.

Chapter 3 introduces a model phase, NaSn$_2$As$_2$, in the new class of exfoliatable A Sn$_2$As$_2$ (A = monovalent or divalent cation) Zintl phases. In this chapter, we present structural properties, air-stability and different routes towards exfoliation is presented. In addition, the theoretical and experimental electronic band structure as well as bulk and few-layer transport measurements are also discussed in this chapter.

Chapter 4 focuses on the demonstration of the flexibility of the ASn$_2$As$_2$ phase to accommodate various cations in the structure. This chapter will focus on the creation and anisotropic magnetic properties, of EuSn$_2$As$_2$, the first magnetic Zintl phase in the ASn$_2$As$_2$ materials class. The electronic properties and exfoliation studies of this EuSn$_2$As$_2$ phase is then discussed. The possibility of alloying Eu$^{2+}$ with a non-magnetic cation, Na$^+$, is also presented, which includes its consequences on the bulk magnetic properties of the material.

Chapter 5 presents two approaches in the creation of Sn-containing graphane analogues. First, the alloying of Sn into the GeH lattice to tune the band gap of GeH is
discussed. The detailed characterization and experimental proof of the inclusion of Sn into the GeH lattice is included in the first section. Second, insights on the chemical routes towards creating crystalline 2D $sp^3$-hybridized vdW systems which contains $\geq$50% of Sn in the lattice is discussed.

Lastly, Chapter 6 summarizes the key points and conclusions in this manuscript including the outlook towards the future directions of the classes of materials presented in this dissertation.

1.6 References


(71) Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets Isostructural to Grey Arsenic - Synthesis and Crystal-Structure of NaSn$_2$As$_2$, Na$_0.3$Ca$_0.7$Sn$_2$As$_2$, Na$_0.4$Sr$_0.6$Sn$_2$As$_2$, Na$_0.8$Ba$_0.2$Sn$_2$As$_2$, and K$_0.3$Sr$_0.7$Sn$_2$As$_2$. *Z. Anorg. Allg. Chem.* **1995**, *621*, 576-582.


42

Chapter 2: Topologically Protected States, Optical Properties and Raman-Active Vibrational Modes in Metallic and Semiconducting Layered Zintl Phases

In this chapter, we present a detailed investigation of the in-plane and cross-plane phonon modes of various layered Zintl phases that contain honeycomb sheets of flat or puckered Group 14 or 15 elements. We have grown crystals of CaGe$_2$, BaSn$_2$, EuGe$_2$, CaSi$_2$, NaSnP, KSnAs, and KSnSb, in which we highlight the first pure synthesis of BaSn$_2$. Through polarized Raman spectroscopy, we assign the phonon modes of these layered Zintl phases to either in-plane (E$_2$/E$_{2g}$/E$_g$) or out-of-plane (A$_1$/A$_{1g}$) lattice vibrations. We show, in general, the dependence of the Raman frequencies on the reduced mass and bond lengths of the constituent elements in the 2D sheets. Moreover, we also probe the electronic structure of Sn-based layered Zintl phases. We demonstrate via density functional theory (DFT) and $Z_2$-parity invariant calculations that BaSn$_2$ is a strong 3D topological insulator with surface states that are protected by time reversal.

$^2$Parts of this chapter were reproduced from Aruguilla, M. Q., Cultrara, N. D., Scudder, M. R., Jiang, S., Ross, R. D. and Goldberger, J. E. Optical Properties and Raman-Active Phonon Modes in Two-Dimensional Honeycomb Zintl Phases. *J. Mater. Chem. C*, 2017, Accepted Manuscript (DOI: 10.1039/C7TC01907F) with permission from the Royal Society of Chemistry.
symmetry. We also experimentally show the existence of a sizeable optical band gap of 0.90 eV in NaSnP, 0.62 eV in KSnAs, and 0.52 eV in KSnSb. Overall, this chapter establishes a new class of topological insulators and semiconducting layered materials, and identifies the relative influence of stacking sequence and atomic structure on the various normal Raman modes of layered honeycomb Zintl phases.
2.1 Introduction

Recently, there has been an immense interest in the chemistry and physics of two-dimensional (2D) and layered materials\textsuperscript{1-6} including the elemental 2D systems,\textsuperscript{7,8} transition metal oxides and dichalcogenides,\textsuperscript{4,9,10} Group 13/14/15 chalcogenides\textsuperscript{11} and Group 14 (Si/Ge/Sn) graphane analogues.\textsuperscript{12-18} The Group 14 graphanes, such as germanane, are direct band gap semiconductors whose electronic structures can be tuned via changing the identity of the surface functional ligand.\textsuperscript{19} Furthermore many of these graphane analogues have been predicted to be topological phases.\textsuperscript{20} The syntheses of these phases rely on the topotactic deintercalation of layered intermetallic precursors that are comprised of the same honeycomb framework of atoms, such as CaGe\textsubscript{2}.\textsuperscript{21-29} In these layered phases, atomically flat or puckered anionic layers of Group 13-15 elements are sandwiched by and charge-balanced by Group 1, 2 or lanthanide cations. These layered honeycomb Zintl phases themselves can exhibit interesting properties and can be superconductors,\textsuperscript{30} 3D Dirac semimetals\textsuperscript{31} and anisotropic magnets.\textsuperscript{22,26,32-36} As more and more interest turns towards these layered precursor phases, it is prudent to fully investigate the crystal and electronic structure and properties of these materials.

For example, it has been predicted via density functional theory (DFT) that NaSnP, KSnAs and KSnSb are semiconducting with band gaps ranging from 0.1 eV to 1 eV.\textsuperscript{28-30} Since the discovery of these phases more than 20 years ago, the only experimental report on the band gap of these phases is the extrapolated gap from thermopower measurements of KSnSb, which is subject to the device
geometry, contact material and temperature stability.\textsuperscript{37} To date, there has not been any spectroscopic evidence, which is the most reliable method for determining the existence of a band gap in a material,\textsuperscript{38-40} of an optical gap on these phases.

The recent years have also seen a great influx, both in theory and in experiment,\textsuperscript{41-50} of new and re-discovered classes of solid state phases that featured topologically-protected edge and surface states in 2D and 3D, respectively. These discoveries have led, not only in the demonstration of novel physical phenomena, but it has also posed an alternative avenue towards the realization of dissipationless transport at room temperature. In the case of CdTe/HgTe/CdTe quantum wells,\textsuperscript{49,50} the only experimentally demonstrated 2D Topological insulator or quantum spin Hall insulator (QSHI) to date, at a certain thickness of the HgTe layer, quantized conductance, corresponding to dissipationless and topologically protected transport along the edges of HgTe, have only been observed at 30 K.

To achieve room temperature QSH effect, the spin-orbit coupling (SOC) induced gap opening should be significantly larger than room temperature thermal excitation (\textasciitilde 25 meV). In order to address this, a huge amount of theoretical 2D phases with significantly larger SOC-induced gaps have been proposed.\textsuperscript{42,43,46,47,51,52} Of these phases, the most compelling prediction, due to the availability of a known synthetic precursor,\textsuperscript{53} is on the possible realization of QSH effect on hexagonal 2D $sp^3$-hybridized Sn sheets with every Sn atom functionalized by either a –OH group or a halide (F, Cl, Br or I).\textsuperscript{52} Although chemical routes towards the creation of van der Waals 2D Sn-(OH/X) sheets have not been realized yet, several forms of 2D honeycomb lattices with various levels
of stability have been shown to exist and have been characterized.\textsuperscript{53,54} Among these phases, BaSn\textsubscript{2}, a layered Zintl phase consisting of anionic sheets of Sn atoms, [Sn\textsuperscript{−}], that are held by a Ba\textsuperscript{2+} cations is stable at ambient temperatures and pressures and can be grown by typical solid state melt synthesis.\textsuperscript{53} BaSn\textsubscript{2} also possesses the correct electron count for a semiconductor but the longer bond lengths compared to α-Sn suggests that there is a possibility of band inversion at certain crystal momentum points that might lead to topologically-protected states. This, and the reported difficulty in the growth of pure BaSn\textsubscript{2},\textsuperscript{53,55} demand a detailed study of both the electronic band structure and synthesis of pure BaSn\textsubscript{2}.

Raman spectroscopy has also become one of the most prevalent techniques for characterizing the structure, stacking sequence and layer thicknesses of layered 2D materials.\textsuperscript{28,56-61} These layered honeycomb Zintl phases can have a wide variety of stacking sequences depending on the size of the cations that hold these layers,\textsuperscript{22,62} annealing\textsuperscript{27,28} and application of high pressures.\textsuperscript{63} Typically, these stacking motifs range from 6-layers per Rhombohedral unit cell (6R) to 2-layers per Hexagonal unit cell (2H) to 1-layer per Trigonal or Hexagonal unit cell (1T or 1H) (Figure 2.1). The stacking motif in these layered structures can also influence the electronic properties of these materials. For example, CaSi\textsubscript{2}, which is metallic in a (6R) structure, becomes superconducting after high pressure transformation into the 1T phase.\textsuperscript{65} Moreover, it has recently also been shown that 6R-CaSi\textsubscript{2} transforms to a three-layer per unit cell structure (3R, space group) via annealing at high temperatures, which can be distinguished via Raman spectroscopy.\textsuperscript{27,28} This
shows the importance of Raman spectroscopy in the determination of the structure and stacking motif of layered Zintl phases.

**Figure 2.1** Stacking motifs in layered main group Zintl phases. Top right image shows the in-plane honeycomb arrangement of a single layer of atoms looking down the *c*-axis. In these structures, the grey atoms represent the cations that hold the layers together while the red atoms correspond to the anions, which form the extended layered networks. For visual aesthetics, the cations are depicted as larger than anions.
2.2 Experimental

2.2.1 Materials and Crystal Growth

Crystals of CaSi$_2$ were purchased from Materion (99% purity). Flat, hexagonal flakes of CaSi$_2$ were confirmed to be pure with a 6R stacking motif via Rietveld refinement of the XRD pattern. CaGe$_2$ crystals were synthesized by melting stoichiometric amounts of Ca (Acros, 99 %) and Ge (Acros, 99.999 %) with a small excess of Ca (1.05:2) in a quartz tube at 950°C and slowly cooling to room temperature. A small amount of residual Ge was observed in the powder diffraction of CaGe$_2$. BaSn$_2$ was synthesized following methods reported in literature. EuGe$_2$ was grown following methods reported in literature. Briefly, Eu (Alfa Aesar, 99.9%) and Ge was loaded in an alumina crucible with a 1:2 stoichiometry and heated at 1050°C for 72 hours and was slowly cooled to room temperature. Similar to previous reports, a residual amount of Ge was observed from the XRD measurements. NaSnP was grown by melting at 700°C elemental Na (Sigma Aldrich, 99.9 %), Sn (STREM, 99.8 %) and P (Sigma Aldrich, 99.99 %) following a 1:1:1 stoichiometry in a quartz tube followed by slow cooling to room temperature. A small amount of residual Sn was detected in the powder diffraction of NaSnP. KSnAs and KSnSb were synthesized by adding stoichiometric amounts of As (STREM, 99 %) and Sb (STREM, 99.5%), respectively, to KSn and were heated to 550°C (As) and 530°C (Sb) for 12 hours and cooled slowly to room temperature. The precursor KSn phase, on the other hand, was grown by heating elemental K (Sigma Aldrich, 99 %) and Sn in 1:1 stoichiometry to 280°C followed by cooling to room temperature. GeH was synthesized following the methods reported in literature.
Briefly, the large crystals of the precursor CaGe$_2$ Zintl phase were deintercalated using concentrated HCl$_{\text{(aq)}}$ for 8 days at -40°C. The samples were washed with methanol and were dried under vacuum at room temperature for several hours. All sample preparations other than the deintercalation of CaGe$_2$ were performed in an inert Ar-filled glovebox and all of the reaction tubes were sealed at pressures lower than 60 mTorr. Na, K, Ca and Ba were all stripped off of the oxide layer prior to use. The crystal structure and purity of all of the phases were confirmed by performing Rietveld refinement (Bruker TOPAS software package) on powder X-Ray diffraction patterns obtained either via flat plate powder X-Ray diffraction (XRD) measurements on a Bruker D8 diffractometer (sealed Cu X-Ray tube: 40 kV and 40 mA) or capillary mode in the case of BaSn$_2$, due to its extreme air sensitivity. For other air-sensitive phases such as KSnAs and KSnSb, XRD measurements were collected in a Rigaku Miniflex II diffractometer using a thin protection layer of amorphous Kapton tape whose background was subtracted in the Le Bail fitting of the diffractograms. Because of the anisotropic nature of these layered materials, the preferred orientation of these layered phases along the [0 0 1] direction was corrected in the refinement process. Among these phases, BaSn$_2$ is extremely air sensitive and can start to tarnish within 15 minutes of exposure in an Ar-filled glovebox with <0.5 ppm O$_2$/H$_2$O. BaSn$_2$ is only stable for extended periods of time when kept in a tube that is sealed under <20 mTorr. KSnAs and KSnSb are stable inside the same glovebox environment, but oxidize rapidly in ambient air. NaSnP oxidizes after a couple of hours exposure to air. Crystals of EuGe$_2$ and CaGe$_2$ show signs of surface oxidation/tarnishing after one day in air. CaSi$_2$ is the most stable, with no visible signs of
oxidation even after a couple of days, likely due to the presence of a robust surface oxide.

2.2.2 Polarized Raman Spectroscopy

Room temperature back-scattering Raman spectroscopy on \( c \)-axis oriented crystals, which were performed on a Renishaw Invia Raman spectrometer equipped with a Pike Technologies KRS-5 polarizer and a charge-coupled device (CCD) detector using a 633 nm laser illumination source. In these measurements, the scattered light is polarized either parallel (0°, \(-Z(XX)Z \) geometry) or perpendicular (90°, \(-Z(XY)Z \) geometry) with respect to the polarization of the laser source. For air-sensitive samples, Raman measurements were performed on a custom-built sample holder with fused quartz windows that are sealed together by a rubber o-ring. The Raman shifts were calibrated using a Si standard. The \( c \)-axis orientation was identified from large domains of flat facets on platelet-like crystals using optical microscopy. In these measurements, good signal-to-noise spectra were obtained for all samples using a laser power density of around 1.6 x 10^2 W/cm^2 and 50 s of exposure time.

2.2.3 Electronic Band Structure Calculations of BaSn\(_2\)

To evaluate the electronic structure of BaSn\(_2\), we calculated the electronic band structure with density functional theory (DFT) based on the modified Becke-Johnson (mBJ) exchange potential\(^{64}\) as implemented via Wien2K in the presence and absence of SOC\(^{65}\). The orbital contribution of specific bands at special points in the Brillouin Zone was determined by calculating their respective population matrices. To calculate the \( Z_2 \)-parity invariant, we used the method proposed by Kane and Fu\(^{66}\) for inversion-symmetry
space groups wherein we calculated the parity eigenvalues of the Bloch wave function of the spin-degenerate valence bands at the 3D time reversal invariant momentum (TRIM) points.

2.2.4 Absorbance Measurements

Kubelka-Munk (KM) diffuse Reflectance absorbance (DRA) measurements in the visible range (>1 eV) were performed using a Perkin-Elmer Lambda 950 UV/vis spectrophotometer fitted with an integrating sphere. The samples were diluted using MgO (Merck) and were measured using an air-free sample holder with a quartz window. The background (MgO + quartz) absorbance were subtracted to obtain the final absorbance spectra of the Zintl phases. On the other hand, for the infrared regime (<1 eV), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were performed on KBr-dispersed Zintl phases using a Perkin-Elmer Frontier Dual-Range (Far infrared/Mid-infrared) spectrometer with an integrating sphere inside a glovebox under N₂-atmosphere.

2.3 Results and discussion

Of the various layered Zintl phases, both CaSi₂ and CaGe₂ have historically been the most well-studied due to the air-stability and ease of growth of these phases. The most thermodynamically favoured polymorph of these two phases presents in a 6R, R-3m space group where, following the Zintl-Klemm concept, the puckered and anionic honeycomb sheets of either [Si]⁻ or [Ge]⁻ ions are held together by Ca²⁺ cations (Figure 2.2a). In order to analyse the various normal modes in these Zintl phases (and all of the succeeding analyses), we adopt the methodology proposed by Rousseau et al.⁶⁷ in the determination of the Raman
scattering tensors for the D\textsubscript{3d} point group. This corresponds to the symmetry at the \( \Gamma \) point of the R-3m space group of CaSi\textsubscript{2} and CaGe\textsubscript{2}. For both CaSi\textsubscript{2} and CaGe\textsubscript{2}, the Raman scattering tensors are as follows:

\[
A_{1g} = \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b \\
\end{pmatrix}
\]

\[
E_{g}(1) = \begin{pmatrix}
c & 0 & 0 \\
0 & -c & d \\
0 & d & 0 \\
\end{pmatrix}
\]

\[
E_{g}(2) = \begin{pmatrix}
0 & -c & -d \\
-c & 0 & 0 \\
-d & 0 & 0 \\
\end{pmatrix}
\]

By using these tensors, the intensity, \( I \), of the \( A_{1g} \) and \( E_{g} \) (which is doubly degenerate in the xy-plane, hence \( E_{g}(1) \) and \( E_{g}(2) \)) modes can be calculated using polarization-dependent Raman scattering intensity equation given by equation (1):

\[
I \sim \sum_{j} |e_{s} R_{tj} e_{l}|^2
\]

(1)

where \( R_{tj} \) corresponds to the \( j^{th} \) Raman tensor, \( e_{s} \) corresponds to the polarization vector of the scattered photons while \( e_{l} \) corresponds to the polarization vector of the incoming photons. In the back-scattering geometry, co-polarized measurements (XX) has the same polarization vector for the scattered and incoming photons, \( e_{s} = e_{l} = (1, 0, 0) \).

Using these vectors in equation (1) results to an intensity proportional to \( a^2 \) for the \( A_{1g} \) mode, an intensity proportional to \( c^2 \) for the \( E_{g}(1) \) mode and an intensity proportional to 0.
for the $E_g(2)$ mode. With these intensities, both the $A_{1g}$ and $E_g$ modes are expected to appear in the XX polarization geometry. On the other hand, for cross-polarized measurements (XY), the polarization vector for the scattered photons correspond to $e_s = (0, 1, 0)$ while the polarization vector for the incoming photons correspond to $e_i = (1, 0, 0)$. Using these vectors in conjunction with Eq. (1), the intensity of the $A_{1g}$ becomes 0, while the intensities of the $E_g(1)$ and $E_g(2)$ modes becomes 0 and $c^2$, respectively. This results to the disappearance of the $A_{1g}$ mode/s and the persistence of the $E_g$ modes in the XY polarization geometry. Through this technique, we can use polarized Raman spectroscopy in the co- and cross-polarized geometries to experimentally assign the symmetry of the observed Raman modes in layered Zintl phases.

By using these polarization selection rules and combining it with the expected Raman-active modes derived from the irreducible representations of CaSi$_2$ and CaGe$_2$ in equation (2):

$$\Gamma_R = A_{1g} (Ca) + E_g (Ca) + 2A_{1g} (Si/Ge) + 2E_g (Si/Ge)$$  \hspace{1cm} (1)

we assign the six experimental Raman peaks (Figure 2b) observed for both phases to three pairs of $A_{1g}$ and $E_g$ modes which correspond to the three unique atoms (Ca, Si/Ge (1) and Si/Ge (2)) occupying the 6c Wyckoff site. The details of the symmetry elements, site occupation and Raman-active modes are summarized in Table 2.2. In CaSi$_2$, we assign the three $A_{1g}$ modes to: 384 cm$^{-1}$ ($A_{1g}^1$), 340 cm$^{-1}$ ($A_{1g}^2$) and 201 cm$^{-1}$ ($A_{1g}^3$) while the three $E_g$ modes are assigned to: 420 cm$^{-1}$ ($E_g^1$), 410 cm$^{-1}$ ($E_g^2$) and 130 cm$^{-1}$ ($E_g^3$) (Figure 2.2b). The atomic displacements associated with these vibrational modes are
shown in Figure A.1. These values and their corresponding symmetries are in agreement with the reported values for 6R-CaSi$_2$\cite{28}. In the case of CaGe$_2$, we assign the three A$_{1g}$ modes to: 297 cm$^{-1}$, 194 cm$^{-1}$ and 136 cm$^{-1}$ while the three E$_g$ modes are assigned to: 240 cm$^{-1}$, 234 cm$^{-1}$ and 125 cm$^{-1}$ (Figure 2.2b). In layered rhombohedral or hexagonal materials, the E$_g$ modes correspond to in-plane lattice vibrations while the A$_{1g}$ modes correspond to out-of-plane lattice vibrations.\cite{12,59,60,68,69} These Raman modes are all observable in unpolarized Raman measurements on the same samples (Figure A.2). In these two phases, going to a heavier main group element shifts both the in-plane and out-of-plane Raman vibrational modes to significantly lower frequencies, which is expected considering the inverse dependence of the Raman mode frequency with reduced mass and the longer Ge-Ge bond lengths (Table 2.1) compared to the Si-Si bond lengths (Table 2.1) deduced from the Rietveld refinement of the powder pattern of CaSi$_2$ (Figure A.3; Table A.1-2) and CaGe$_2$ (Figure A.4; Table A.3-4).

Table 2.1 The space groups, in-plane lattice parameters and in-plane bond lengths of the two-dimensional honeycomb Zintl phases that were investigated in this study.
**Figure 2.2** (a) Crystal structure and stacking motif of the 6R-layered Zintl phases, CaSi$_2$ and CaGe$_2$. (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of CaSi$_2$ and CaGe$_2$. The blue atoms represent Si and Ge while the gray atoms represent Ca.
Table 2.2 Wyckoff sites and Raman-active modes of constituent atoms in 6R-layered Zintl phases assuming a D$_{3d}$ point group.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>Site Symmetry</th>
<th>Raman-Active Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>6c</td>
<td>C$_{3v}$</td>
<td>A$<em>{1g}$ + E$</em>{g}$</td>
</tr>
<tr>
<td>Si or Ge (1)</td>
<td>6c</td>
<td>C$_{3v}$</td>
<td>A$<em>{1g}$ + E$</em>{g}$</td>
</tr>
<tr>
<td>Si or Ge (2)</td>
<td>6c</td>
<td>C$_{3v}$</td>
<td>A$<em>{1g}$ + E$</em>{g}$</td>
</tr>
</tbody>
</table>

Next, we studied the polarization Raman spectra of NaSnP, KSnAs, and KSnSb. In these phases the honeycomb frameworks alternated between Sn and a Group 15 element (P, As, Sb) in a BN-like fashion (Figure 2.3a). In order to make these materials have the same electron count as CaSi$_2$, the anionic Sn-P/As/Sb layers are held together with a Group 1 element (Na or K) and crystallize into 2H structures. In contrast to the inversion-symmetric CaSi$_6$/Ge$_6$ octahedra in CaSi$_2$ and CaGe$_2$, these 1-14-15 structures form non-centrosymmetric octahedra around the cation due to the Group 14 and Group 15 elements occupying opposite sides of the layers. The Raman active-modes deduced for these 2H phases are in equation (3):

$$\Gamma_R = A_1 (\text{Na or K}) + E_2 (\text{Na or K}) + E_1 (\text{Na or K}) + A_1 (\text{Sn}) + E_2 (\text{Sn})$$
$$+ E_1 (\text{Sn}) + A_1 (\text{P, As or Sb}) + E_2 (\text{P, As or Sb}) + E_1 (\text{P, As or Sb})$$

(3)

Selection rules dictate that only the $A_1$ and $E_2$ modes are observable in the back-scattering geometry, and not the $E_1$ mode. The out-of-plane modes ($A_1$) are only
observable via Raman measurements in the XX polarization geometry while the in-plane modes (E\textsubscript{2}) are observable for both geometries. The details of the symmetry elements, site occupation and Raman-active modes are summarized in Table 2.3. Using these, we assign symmetries to the Raman modes observed from XX- and XY-polarized Raman spectra. In NaSnP, we assign the three expected out-of-plane A\textsubscript{1} modes to 317 cm\textsuperscript{-1}, 191 cm\textsuperscript{-1} and 119 cm\textsuperscript{-1} while the three expected in-plane E\textsubscript{2} modes can be assigned to 363 cm\textsuperscript{-1}, 322 cm\textsuperscript{-1} and 269 cm\textsuperscript{-1} (Figure 2.3b). To highlight the less-intense peaks, the logarithm of the Raman intensities of the NaSnP (XX) and (XY) spectra were plotted versus the Raman shift (Figure A.5). In the case of KSnAs and KSnSb, we only observe two Raman-active modes each corresponding to an out-of-plane plane A\textsubscript{1} mode at 212 cm\textsuperscript{-1} for KSnAs and at 172 cm\textsuperscript{-1} for KSnSb and to an in-plane E\textsubscript{2} mode at 187 cm\textsuperscript{-1} for KSnAs and at 158 cm\textsuperscript{-1} for KSnSb (Figure 2.3b). The absent 2 E\textsubscript{2} modes in KSnAs and KSnSb likely have intensities that are too weak to be observed. Both the in-plane and out-of-plane Raman modes are observable in the unpolarized Raman spectra of NaSnP, KSnAs and KSnSb (Figure A.6). The absent 2A\textsubscript{1} Raman modes for KSnAs and KSnSb likely occur below 100 cm\textsuperscript{-1}, which is the instrumental limit. The shift to lower frequencies of the Raman modes from NaSnP to KSnAs to KSnSb is due to the increasing reduced mass and bond length of Sn-P/As/Sb (Table 2.1) obtained from the Rietveld refinement of NaSnP (Figure A.7, Table A.5,A.6) and deduced from reported literature structures\textsuperscript{24} of the extremely air-sensitive KSnAs (Figure A.8, Table A.7) and KSnSb (Figure A.9, Table A.8)
phases whose lattice parameters from the Le Bail fitted diffractograms agree well with reported values. 24
**Figure 2.3** (a) Crystal structure of and stacking motif of 2H-layered Zintl phases NaSnP, KSnAs, and KSnSb. (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of KSnSb, KSnAs, and NaSnP. The green atoms represent a Group 15 element (P, As or Sb), the orange atoms represent Sn and the purple atoms represent the Group 1 cations (Na or K).
Table 2.3 Wyckoff sites and Raman-active modes of constituent atoms in 2H-layered Zintl phases assuming a C\textsubscript{6v} point group. Modes that are in bold are not observable in the back-scattering geometry.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>Site Symmetry</th>
<th>Raman-Active Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na or K</td>
<td>2b</td>
<td>C\textsubscript{3v}</td>
<td>A\textsubscript{1} + E\textsubscript{2} + E\textsubscript{1}</td>
</tr>
<tr>
<td>Sn</td>
<td>2a</td>
<td>C\textsubscript{3v}</td>
<td>A\textsubscript{1} + E\textsubscript{2} + E\textsubscript{1}</td>
</tr>
<tr>
<td>P or As or Sb</td>
<td>2b</td>
<td>C\textsubscript{3v}</td>
<td>A\textsubscript{1} + E\textsubscript{2} + E\textsubscript{1}</td>
</tr>
</tbody>
</table>

BaSn\textsubscript{2} and EuGe\textsubscript{2} crystallize into a 1-layer unit cell structure. (Figure 2.4a). These two structures have puckered arrangement of Ge/Sn atoms forming extended sheets in a 1T stacking motif. The details of the symmetry elements, site occupation and Raman-active modes are summarized in Table 2.4. Using these symmetry and structural information and combining it to the Rosseau’s method in normal mode determination, the Raman-active modes deduced from the irreducible representation are listed in equation (4):

\[
\Gamma_\text{R} \text{EuGe}_2/\text{BaSn}_2 = A\textsubscript{1g} (\text{Ge or Sn}) + E\textsubscript{2g} (\text{Ge or Sn}) \quad (4)
\]

Again, due to the back-scattering geometry of the measurement, the E\textsubscript{1g} mode is not observable. The in-plane A\textsubscript{1g} modes are only allowed in the XX-polarization geometry while the E\textsubscript{g} modes are observable in both the XX- and XY-geometries. From the co-and cross-polarized Raman spectra of EuGe\textsubscript{2}, and BaSn\textsubscript{2}, we assign
the 200 cm$^{-1}$ and 142 cm$^{-1}$ frequencies to the out-of-plane A$_{1g}$ modes and the 226 cm$^{-1}$ and 160 cm$^{-1}$ Raman shifts to the in-plane E$_g$ modes, respectively. Both of these modes are observable in the unpolarized Raman spectra of EuGe$_2$ and BaSn$_2$ (Figure A.10). Similar to the previous layered Zintl phases, the shift to lower frequencies of the in-plane and out-of-plane Raman modes is consistent with increasing reduced mass and longer bond lengths going from Ge to Sn which was obtained from the refined structures from the powder XRD of EuGe$_2$ (Figure A.11, Table A.9,A.10) and BaSn$_2$ (Figure A.12, Table A.11,A.12).
Figure 2.4 (a) Crystal structures and stacking motif of 1T layered Zintl phases in EuGe$_2$ and BaSn$_2$ (b) Polarized Raman spectra in the XX (blue) and XY (red) polarization geometry of Zintl phases that have 1-layer per unit cell trigonal stacking motif. The magenta atoms represent Ge or Sn and the gray atoms represent the Eu$^{2+}$/Ba$^{2+}$ cation, respectively.
Table 2.4 Wyckoff sites and Raman-active modes of constituent atoms in 1T-layered Zintl phases assuming a $D_{3d}$ point group.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>Site Symmetry</th>
<th>Raman-Active Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu/Ba</td>
<td>1a</td>
<td>$D_{3d}$</td>
<td>--</td>
</tr>
<tr>
<td>Ge/Sn</td>
<td>2d</td>
<td>$C_{3v}$</td>
<td>$A_{1g} + E_{2g}$</td>
</tr>
</tbody>
</table>

Aside from the influence of the reduced mass of the constituent atoms to the frequencies of the Raman-active modes, another factor that greatly affects these frequencies is the bond length between the atoms that sit on Wyckoff sites that possess Raman-active modes. To probe the dependence of the in-plane Raman modes to the bond length of the constituent atoms in the honeycomb 2D sheets, we compare the XY-polarized Raman spectra of EuGe$_2$, CaGe$_2$, GeH, three phases in which the frameworks that are comprised purely of Ge atoms (Figure 2.5). GeH, a 2D sheet of honeycomb Ge atoms terminated by hydrogen atoms, has been shown, both experimentally using Raman spectroscopy and theoretically via ab initio density functional calculations of the phonon modes at the $\Gamma$-point of the relaxed structure using the Perdew-Burke-Ernzerhof (PBE) functionals as implemented in VASP,$^{12}$ to have two Raman modes: an in-plane ($E_2$) mode corresponding to 302 cm$^{-1}$ and an out-of-plane ($A_1$) mode corresponding to 228 cm$^{-1}$. In contrast to the highly crystalline melt-grown Zintl phases, GeH, which is synthesized by topochimically deintercalating CaGe$_2$ using HCl, has significantly broader Raman peaks. We attribute this broadness in the Raman modes to defects, that are likely
Ge vacancies. It has also been recently shown via pair distribution function that, in these 2D GeH sheets, the Ge atoms are separated by a 2.435(28) Å bond length.\footnote{14} From the cross-polarized Raman spectra, the in-plane Raman modes shift lower in frequency, from GeH to CaGe$_2$ to EuGe$_2$. This shift to decreasing frequencies is coincident with an increasing Ge-Ge bond length going from 2.44 Å in GeH to 2.5021(17) Å and 2.5072(15) Å in CaGe$_2$ and up to 2.5772(3) Å in EuGe$_2$ (Figure 2.5, inset).

\textbf{Figure 2.5} Trends in the in-plane Raman mode of EuGe$_2$, CaGe$_2$ and GeH. The polarized Raman spectra of EuGe$_2$, CaGe$_2$ and GeH in the XY polarization geometry highlighting the in-plane normal modes, $E_{2g}$, $E_g$ and $E_2$, respectively. Inset is the dependence of the frequencies of these in-plane modes with the Ge-Ge bond length in the aforementioned phases.

Due to the recent resurgence of Zintl phases as opto-electronic, electronic and thermoelectric materials, we also probed the optical absorption properties of
the layered Zintl phases presented in this study. From previously reported theoretical DFT calculations, it has been shown that CaSi$_2$, CaGe$_2$, EuGe$_2$ and BaSn$_2$ are all metallic or semi-metallic in nature.\textsuperscript{22,55,70,71} Of these phases, only CaSi$_2$ and EuGe$_2$ have been experimentally proven to be metallic using angle-resolved photoemission spectroscopy in CaSi$_2$\textsuperscript{72} and temperature-dependent transport in EuGe$_2$.\textsuperscript{22} By using DRIFTS and DRA spectroscopy, we observe minimal broadband absorption and no significant absorption edges from the visible to Infrared range in CaSi$_2$, CaGe$_2$ and EuGe$_2$ (Figure A.13). This further confirms the previous assignment of a metallic character in CaSi$_2$ and EuGe$_2$ and shows, for the first time experimentally, that CaGe$_2$ is also metallic.

By moving down the periodic table, to Sn in BaSn$_2$, the longer bond lengths and stronger spin-orbit coupling (SOC) start to play a more important role in influencing the electronic structure of the layered Zintl phase. In BaSn$_2$, the longer Sn-Sn bond length (2.92 Å in-plane; 5.16 Å out-of-plane) compared to α-Sn (2.8 Å) contributes to the weaker orbital overlap especially in the out-of-plane direction. Based on DFT calculations (Figure 2.6a), the destabilization of the Sn 5$p_z$ bonding orbital near the Fermi level induces a band crossing between the Sn 5$p_z$ bonding orbital and the Sn 6$s$ anti-bonding orbital which consequently results to linear-like band dispersions (indicative of high mobility carriers) that cross at the Fermi level. Due to this band inversion of opposite parity bands (+ parity for bonding and – parity for anti-bonding) at a time-reversal invariant momentum (TRIM) point (A point) in the Brillouin zone, we look into the effect of spin-orbit coupling to the electronic band structure of BaSn$_2$ to probe the possibility of
topologically-protected states in the structure (Figure 2.6b). By including SOC in the DFT calculation of the electronic band structure of BaSn_2, the degeneracy along the band crossing at the Fermi level is lifted and a ~0.2 eV band gap is opened turning the semi-metallic state without SOC to an insulating state with SOC. We also further confirm that the band inversion between the bonding Sn 5p_z orbital and the anti-bonding Sn 6s persists after considering SOC in the calculations (Figure 2.6c). Indeed, the band inversion at the A TRIM point and the lifting of the degeneracy of the inverted bands point towards the possibility of topologically-protected states in the electronic structure of BaSn_2. In addition, the DRIFTS spectra of BaSn_2 shows an intense absorbance at around 0.2 eV, which closely matches the predicted SOC-induced gap of around 0.21 eV and demonstrates the existence of bulk insulating states.
Figure 2.6 (a) DFT band structure of BaSn$_2$ without SOC. Highlighted in green is the band crossing along the A to H direction. Inset is the hexagonal Brillouin zone with the TRIMs highlighted in red. (b) DFT band structure of BaSn$_2$ with SOC turned on. The orbital character of the Sn 6$s$ anti-bonding and the Sn 5$p_z$ bonding states are labeled. (c) Band contributions of the Sn 5$p_z$ and Sn 6$s$ orbitals near the band inversion along the A to H direction. (d) DRIFTS absorbance spectra of BaSn$_2$ indicating an absorbance peak around $\sim$0.2 eV.
Because of the inversion-symmetric space group of BaSn$_2$, we can adopt the method by Kane and Fu,$^{66}$ to prove whether or not the band inversion at the A point is a topologically-protected state. Based on this method, the $Z_2$-parity invariant, which is the determinant of a topologically-protected state, is calculated using the following equation:

$$(-1)^{\nu_0} = \prod_{i=1}^{\Gamma_i} \delta(\Gamma_i)$$  

(5)

where $\delta(\Gamma_i)$ is the product of the parities of the valence bands at each TRIM point and $\nu_0$ corresponds to the $Z_2$-parity invariant. A $\nu_0 = 1$ assures that the band inversion is a topologically protected non-trivial state while $\nu_0 = 0$ indicates that the inversion is a trivial, non-time reversal symmetry protected state. From our parity analysis of the valence bands bands at the TRIMs, we obtained a $Z_2$-parity invariant of 1 which indicates that, since the band inversion occurs at the A point, BaSn$_2$ has topologically-protected surface states and that it is a strong 3D topological insulator. Several other groups have also reported similar results around the time that we finished these calculations.$^{55,70}$

The introduction of ionic character within each honeycomb plane via the inclusion of a significantly more electronegative Group 15 element (P, As or Sb) to the Group 14 element, in this case, Sn, leads to an opening of a sizeable band gap in the 1-14-15 phases.$^{37,73-75}$ An analogous example occurs in hexagonal BN, which has a ~5.9 eV band gap$^{76,77}$ compared to the metallic nature of graphite, due to the large electronegativity difference between B and N. As semiconductors, these 1-14-15 phases have been reported to have room temperature resistivities ranging from ~4 x 10$^2$ $\Omega\text{m}$ in NaSnP$^{78}$ down to ~1.5 x 10$^{-2}$ $\Omega\text{m}$ in KSnSb.$^{37}$ The
lower resistivities in KSnSb have been partially attributed to the low effective mass of carriers in KSnSb \textsuperscript{79} \((m_h^* = 0.25; m_e^* = 0.04)\), leading to high carrier mobilities. These effective masses are comparable to GaAs \textsuperscript{80}. Based on previously reported DFT calculations, an indirect gap of \(\sim 1.05\) eV was assigned to bulk NaSnP \textsuperscript{73} using Heyd-Scuseria-Ernzerhof exchange-correlation functionals, which can be quite close to experimentally observed values, while indirect band gaps of \(\sim 0.1\) eV was calculated for both KSnAs and KSnSb, using PBE level theory, which typically underestimates the band gap by 30-50\%. \textsuperscript{74,75} In addition, a gap of \(\sim 0.33\) eV was extrapolated from transport and Seebeck measurements for KSnSb. \textsuperscript{37,73} Still, optical absorption measurements are the most direct and accurate method for determining the band gap and the direct or indirect nature of the transition. To probe and confirm the semiconducting nature of this material, we performed a combination of visible (DRA) and Infrared (DRIFTS) absorbance measurements on NaSnP, KSnAs and KSnSb (Figure 2.7). From these spectra, we observe absorption onsets of 0.51 eV, 0.65 eV and 0.91 eV for NaSnP, KSnAs and KSnSb, respectively. To accurately deduce the band gap from the optical absorption spectra, we modeled the absorbance spectra following the various Tauc-Davis-Mott expressions for the various optical transitions that can possibly occur in these layered Zintl phases. Because of the cross-plane ionic bonding that holds these 2D layers together and the predicted indirect nature of the band gap, we assigned the band gaps of these materials using the expression for 3D indirect allowed transition. In this model, the absorbance is proportional to \((\hbar \omega - E_{g'} \pm E_p)^2\), where \(\hbar \omega\) is the photon energy, \(E_{g'}\) is the indirect energy gap and \(E_p\) is the phonon
energy of the major $E_2$ mode. By plotting $(KM \text{ Absorbance} \times \hbar \omega)^{1/2}$ vs. $\hbar \omega$, we determined the value of the band gap by extrapolating the linear region near the absorption onset to the abscissa (Figure A.14a). The 3D indirect gaps for NaSnP, KSnAs and KSnSb were found to be $0.95 \pm 0.033$ eV, $0.65 \pm 0.023$ eV and $0.54 \pm 0.020$ eV, respectively. Similarly, the energy of the 3D direct allowed transitions can be derived by, plotting $(KM \text{ Absorbance} \times \hbar \omega)^2$ vs. $\hbar \omega$ (Figure A.14b). The values of the direct gap of these materials were determined to be $1.28$ eV, $0.97$ eV and $0.80$ eV for NaSnP, KSnAs and KSnSb, respectively, which, as expected for an indirect band gap material, are larger than the indirect gap. (Table A.13). The shift of these gaps towards higher energies with increasing electronegativity differences between Sn and the Group 15 element from Sb to As to P is consistent to the increasing localization of the lone pairs (which contributes to the valence band) to the more electronegative atom, resulting to the lowering of the valence band and the subsequent opening of a larger gap.\textsuperscript{74}
Figure 2.7 Diffuse reflectance absorbance spectra of NaSnP, KSnAs and KSnSb showing the consistent shift of the absorption edges to lower energies with decreasing electronegativities and increasing sizes of the Group 15 elements.

2.4 Conclusions

Overall, we have presented in this chapter the in-plane and out-of-plane vibrational modes in layered Zintl phases consisting of flat or puckered honeycomb sheets of Group 14 and 15 elements. We have shown that the frequency of the Raman modes of the three different stacking motifs (6R, 2H and 1T) for these layered Zintl phases strongly depends on the reduced mass and the bond lengths (Tt-Tt and Tt-Pn) of the elements that comprise the 2D sheets. With respect to the electronic structure of the layered Zintl phases in this study, we have also shown, via optical absorption measurements, that CaSi$_2$, CaGe$_2$ and EuGe$_2$ are metallic and have broadband absorption. We have also demonstrated via the
combination of DFT measurements and $Z_2$-parity invariant analysis that BaSn$_2$ is a strong 3D topological insulator. Lastly, we have experimentally shown that NaSnP, KSnAs and KSnSb are semiconducting with indirect band gaps that ranged from 0.95 eV in NaSnP down to 0.54 eV in KSnSb. This enables the use of these 2D layered Zintl phases for optoelectronic and electronic applications and as platforms for the realization of unique physical phenomena in 2D. Since Raman spectroscopy is one of the most powerful methods for identifying and probing the layer thickness of 2D materials, this study also establishes the vibrational properties for this emerging class of Group 14/15 layered Zintl phases.

2.5 References


(76) Cassabois, G.; Valvin, P.; Gil, B. Hexagonal Boron Nitride is an Indirect Bandgap Semiconductor. *Nat. Photon.* 2016, 10, 262-266.


Chapter 3 Stability, Exfoliation and Anisotropic Electronic Properties of 

NaSn$_2$As$_2$—an Exfoliatable Layered Zintl Phase

In this chapter, we show that layered vdW Zintl phases can be readily exfoliated using both mechanical and liquid-phase processes, using NaSn$_2$As$_2$ as a model system. We also rigorously characterize the vibrational and electronic properties and air stability of NaSn$_2$As$_2$ crystals. We evaluate the bulk Raman spectrum and identify the peak symmetries of the modes via polarized Raman spectroscopy. We show that NaSn$_2$As$_2$ is resistant towards oxidation, with surface oxidization occurring in ambient conditions over a couple of days. Finally, using a combination of angle-resolved photoemission spectroscopy (ARPES), density functional theory (DFT), and bulk and layer-dependent transport, we show that this material is an excellent 2D semimetal, with anisotropic two carrier transport and resistivities on the order of $10^{-6}$ $\Omega$ m, both in bulk and when exfoliated to few layers.

3.1 Introduction

Over the past few years there have been numerous exciting physical phenomena that have been both discovered and theoretically predicted to occur in single and few-layer thick van der Waals (vdW) materials. The initial discoveries of Dirac physics in graphene,\textsuperscript{2,3,8} and thickness-dependent tunability of band gaps in transition metal dichalcogenides (TMDs)\textsuperscript{6,9-12} have led to an explosion of exotic phenomena in single-layer and few-layer materials such as the valley Hall effect,\textsuperscript{13-15} magnetic proximity effects,\textsuperscript{16-19} and topological insulator phases.\textsuperscript{1,20,21} The existence of such a plethora of new phenomena in ultrathin layers stems from their sensitivity to doping,\textsuperscript{22-27} local chemical environments,\textsuperscript{28,29} electrical gating,\textsuperscript{6} as well as the elimination of inversion symmetry to access spin-based phenomena.\textsuperscript{13,30,31} Consequently, there is considerable interest in these materials for applications ranging from opto/spin/electronics\textsuperscript{13,17,32-38} to transparent conductors\textsuperscript{24,39,40} to sensing\textsuperscript{41-44} to catalysis.\textsuperscript{45-47}

To date most of these reports have focused on graphenes,\textsuperscript{2,16,17,21-24,41} Group 14 graphene and graphane analogues,\textsuperscript{48-51} transition metal MXenes,\textsuperscript{52-54} and TMDs.\textsuperscript{6,9,13,14,34,35,42,43,55-58} A much less explored class of potential vdW materials are the layered Zintl phases.\textsuperscript{59-65} Layered Zintl phases are typically comprised of layers of Group 1 or Group 2 cations that are ionically bonded to layers of $p$-block elements that form a covalently bonded extended lattice. One potential advantage of building two dimensional (2D) materials from main group elements compared to transition metals, is the higher conductivities and mobilities that can be accessed as a result of the conduction and valence bands being comprised of $p$-orbitals, which have much broader band dispersion.
than $d$-orbitals. Second, many of these materials are shown to be metals, semiconductors, and even superconductors (i.e. BaGaSn). There have also been numerous predictions of exotic physics, such as topological nodal-line characters in AT$_2$ phases (A = Ca, Sr and Ba, Tt = Si, Ge and Sn) and 3D-Dirac states in SrSn$_2$As$_2$. Also, the large spin-orbit coupling inherent to the heavy atoms in the framework of these materials can give rise to various spintronic phenomena, especially when combined with perpendicular electric fields that can be maximized upon exfoliation. Furthermore, they have been investigated as hydrogen storage materials such as in the layered polyanionic hydrides (i.e. SrAl$_2$ → SrAl$_2$H$_2$). Finally, extensive work by our lab has shown that layered Zintl phases can be readily transformed into hydrogen- and organic-functionalized graphane materials. Being able to create exfoliatable Zintl phase derivatives will enable future studies on the layer dependence of these electronic, topological, and spintronic properties and may lead to exciting phenomena.

There are numerous examples of layered Zintl phases that have weak bonding between the layers, which can enable their exfoliation. These Zintl phases have the general formula of AT$_2$Pn$_2$ (A = Group 1 or 2, Tt = Group 14 tetrel element and Pn = Group 15 pnictogen element), of which there have been reported at least 7 different phases and alloys. These materials consist of the Group 1 or 2 element being sandwiched between two layers of honeycomb networks of puckered alternating BN-like TtPn layers. Due to the greater electronegativity, the pnictogens are tilted to be in close proximity to the Group 1 or 2 element, and the Tt atom is oriented towards the Tt atoms in an adjacent layer (Figure 3.1a). From electron-counting arguments, there is weak-to-
no covalent bonding between Tt atoms in neighboring TtPnPnPnTt layers. In NaSn$_2$As$_2$, each As atom, which is in close proximity to the Na atom, has 3 covalent bonds and formally 8 electrons, while each Sn atom has 3 covalent bonds and thus 7.5 electrons. In SrSn$_2$As$_2$, each Sn atom would formally have 8 electrons. Therefore, the weak bonding between the Sn atoms in these phases could enable these materials to be readily exfoliated. To date, there have been little to no experimental studies about the vibrational and electronic behavior of these materials, their air-sensitivity, and especially on their potential for exfoliation.

3.2 Experimental

3.2.1 Crystal Growth

Bulk crystals of NaSn$_2$As$_2$ were grown via a quartz tube melt synthesis under a ~50 mTorr pressure with 1:2:2 Na:Sn:As loading. The tubes were heated to 750°C for 3 to 5 hours, cooled to room temperature for 40 to 60 hours followed by a 50-hour annealing at 400°C. The preparation and handling of all the reagents were done in an Ar-filled glovebox. Sodium metal cubes (Na, Sigma Aldrich, 99.9%) were used after the oxide layer was stripped off via mechanical cleavage. Tin (Sn, STREM Chemicals, 99.8%) and arsenic (As, STREM Chemicals, 99%) were purchased and used without further purification. Note that since As is toxic, extreme caution should be observed when handling this compound.
3.2.2 Material Characterization

The crystal structure and phase purity of the as-grown crystals were identified via flat plane X-Ray diffraction measurements done on a Bruker D8 powder X-Ray diffractometer (sealed Cu X-Ray tube: 40 kV and 50 mA). The Raman scattering spectra were collected using a Renishaw InVia Raman equipped with a Pike Technologies KRS-5 polarizer and a charge-coupled device detector. The Raman spectra were collected using a 633 nm laser as an illumination source. Fourier-Transform Infrared measurements were performed using a Perkin-Elmer Frontier Dual-Range Far-IR/Mid-IR spectrometer. The stoichiometric elemental ratio was confirmed via X-Ray fluorescence analysis using an Olympus DELTA handheld X-Ray fluorimeter calibrated with Sn and As standards of varying ratios. The X-ray photoelectron spectra of the samples were taken using a Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromated Al X-ray source. Energy calibration was performed using the C 1s peak.

3.2.3 Bulk and Surface Air Stability

NaSn₂As₂ powders and flakes exfoliated onto 285 nm SiO₂/Si substrates were exposed to ambient air for different durations. The resulting powders/flakes were analyzed for signs of oxidation via atomic force microscopy using a Bruker AXS Dimension Icon Atomic Force Microscope, FTIR and Raman spectroscopy, XRD and XPS.

3.2.4 Mechanical Exfoliation

The NaSn₂As₂ crystal was exfoliated onto 300 nm or 285 nm SiO₂/Si substrates. The substrates were cleaned by sonication for 5 minutes each in acetone and isopropyl alcohol. The NaSn₂As₂ crystals were micro-mechanically cleaved using a silicone-free
tape until the tape had uniform coverage of thin NaSn$_2$As$_2$ flakes. This tape is then pressed facing down on the cleaned wafers to obtain thin exfoliated flakes on the substrate.

3.2.5 Liquid-Phase Exfoliation

Ground samples of NaSn$_2$As$_2$ (5 mg/mL) were sonicated for 4 hours using various solvents: IPA, acetone, 1,4-dioxane, dimethylformamide, N-methyl-2-pyrrolidone, N-cyclohexyl-2-pyrrolidone and dimethyl sulfoxide. To separate the non-dispersed flakes, the dispersions were centrifuged at 1000 rpm for 90 minutes. The supernatant was collected and a part of it was further centrifuged at 3000 rpm for another 90 minutes. To determine the best solvent for exfoliation, absorbance measurements of the dispersion were taken on a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer. For AFM, Transmission Electron Microscopy measurements and high-resolution transmission electron microscopy (HRTEM), dispersions in CHP were drop-casted onto 285 nm SiO$_2$/Si substrates and 200 mesh lacy carbon Cu grids. The substrates and grids were dried for 4 to 12 h under vacuum at ambient temperature. To remove any residual CHP, the substrates for AFM were further rinsed (3x) with IPA. The Selected Area Electron Diffraction and EDX spectroscopy were performed in an FEI/Philips CM-200T and CM-12T TEM for phase identification. HRTEM was performed using an FEI Image-Corrected Titan3 G2 60-300 S/TEM at 300 keV. All solvent and sample transfers, decantation and sample preparation were done in an Ar-filled glovebox. The samples, on the other hand, were kept in Ar-filled sealed vials during the sonication and centrifugation steps.
3.2.6 Electronic Structure: ARPES and DFT Calculations

The ARPES measurements were performed in the micro-ARPES chamber of the MAESTRO beamline at the Advanced Light Source. The chamber is equipped with a Scienta R4000 hemispherical electron energy analyzer. We successfully obtained ARPES spectra on high quality NaSn$_2$As$_2$ single crystals, which were cleaved in-situ. The measurements were done with photon energy $h\nu = 127$ eV, with an overall energy resolution of about 30 meV. The sample was cooled down to 41 K with liquid helium, and the base pressure in the chamber during the measurements was better than $2 \times 10^{-11}$ Torr. The electronic band structure was calculated with density functional theory based on a Heyd-Scuseria-Ernzerhof hybrid functional method using the Vienna Ab-initio Simulation Package (VASP).\textsuperscript{33-38} Due to the rhombohedral nature of the NaSn$_2$As$_2$ unit cell, we expanded the unit cell to a hexagonal cell, which contains three times the number of atoms as the rhombohedral unit cell. The mixing parameter, $\alpha$, was set to 0.25 in these calculations. To further accommodate the exchange effects, we included spin orbit coupling (SOC) in our calculations.

3.2.7 Bulk and Few-layer Electronic Transport

Two-probe temperature-dependent resistivity measurements were performed on a NaSn$_2$As$_2$ single crystal with pressed indium contacts using a Quantum Design 14 T Physical Properties Measurement System (PPMS) from 2 K to 300 K. For few-layer devices, NaSn$_2$As$_2$ flakes were mechanically exfoliated from bulk crystals onto SiO$_2$/Si substrates using Scotch tape. Their thickness was determined by AFM measurements. Flat flakes with good geometry were chosen to make Hall bar devices by depositing Ti/Au electrodes using standard electron beam lithography and evaporation techniques.
The longitudinal and transverse resistance values were also measured in a PPMS down to 2 K, with the excitation current limited to 10 μA. To account for magnetoresistance and longitudinal-transverse coupling, we anti-symmetrized the transverse resistance $R_t$ under opposite magnetic field directions to obtain the Hall resistance $R_{xy}$ (H).

### 3.3 Results and Discussion

NaSn$_2$As$_2$ crystallizes in a rhombohedral R-3m unit cell characterized by three centrosymmetric anionic bilayers of Sn and As held by six-coordinated Na cations (Figure 3.1a). These bilayers (SnAsNaAsSn) are bound by vdW forces with an approximate 3.3 Å gap between the Sn atoms of adjacent bilayers (Figure 3.1a). This vdW gap that exists between the bilayers allows for the possible exfoliation of NaSn$_2$As$_2$ down to SnAsNaAsSn bilayers, which from the crystal structure corresponds to ~9.2 Å per bilayer. Bulk crystals of NaSn$_2$As$_2$ were grown via a tube melt synthesis of elemental precursors of Na, Sn and As with a 1:2:2 stoichiometric loading. The resulting mm- to cm-sized crystals exhibit a metallic luster and a $c$-axis faceting (Figure 3.1a, bottom right). X-ray diffraction (XRD) measurements on NaSn$_2$As$_2$ powders followed by Rietveld refinement (Figure A.15, Tables A.14-16) reveal that the as-grown crystals are phase pure with an $a$-lattice parameter of 3.99998(10) Å and a $c$-lattice parameter of 27.5619(13) Å, consistent with previous reports (Figure 3.1b).$^{59}$ We also confirm the 1:1 stoichiometry between the Sn and As atoms via X-Ray Fluorescence (XRF) measurements (Figure A.16).
Figure 3.1 (a) Crystal Structure of NaSn$_2$As$_2$ (Na, red; Sn, gray; As, blue). Top right: NaSn$_2$As$_2$ crystal structure down the c-axis. Bottom right: mm- to cm-size NaSn$_2$As$_2$ crystals. (b) Powder-XRD of NaSn$_2$As$_2$. Enclosed in parentheses are the rhombohedral miller indices.

The Raman spectrum of bulk NaSn$_2$As$_2$ shows three peaks having narrow full-width-at-half-maximum (FWHM). These Raman stretches occur at $\sim$182 cm$^{-1}$, $\sim$206 cm$^{-1}$ and $\sim$228 cm$^{-1}$ with FWHM of 5 cm$^{-1}$, 3 cm$^{-1}$, and 6 cm$^{-1}$, respectively (Figure 3.2a). In the R-3m space group ($D_{3d}$ point group), these Raman modes can correspond to either $A_{1g}$ or $E_g$ symmetry. According to group theory, there should be 15 total vibrational
branches at the Γ point in the Brillouin zone, of which only 6 are Raman active \((2 \text{E}_g + 2 \text{A}_{1g})\). To determine the symmetry of each Raman mode, we performed polarized \((0^\circ \text{ to } 360^\circ)\) backscattered Raman measurements along the crystalline \(c\)-axis (Figure 3.2b,c).

According to the selection rules for this space group, both the \(\text{A}_{1g}\) and \(\text{E}_g\) modes should appear in the co-polarized \(-Z(XX)Z\) geometry, while only the \(\text{E}_g\) mode is allowed in cross-polarized \(-Z(XY)Z\) geometry. There is very little difference in the relative intensity of these Raman modes in the co-polarized vs. non-polarized configurations. However, in the cross-polarized geometry, the peak centered at \(\sim228 \text{ cm}^{-1}\) disappears, and the peak centered at \(\sim206 \text{ cm}^{-1}\) significantly decreases in intensity relative to the \(\sim182 \text{ cm}^{-1}\) peak. The complete disappearance of the peak centered at 228 cm\(^{-1}\) indicates that it is an \(\text{A}_{1g}\) mode. The decrease in the intensity of the Raman mode at 206 cm\(^{-1}\) suggests that it is comprised of at least an \(\text{A}_{1g}\) and an \(\text{E}_g\) Raman modes that are close in energy. Finally, the lack of polarization dependence in the 182 cm\(^{-1}\) mode suggests that it is of \(\text{E}_g\) origin.
Figure 3.2 (a) Raman spectrum of NaSn$_2$As$_2$. (b) Polarized (at $0^\circ$ and $90^\circ$) and unpolarized Raman spectra of NaSn$_2$As$_2$. (c) Radial plot ($0^\circ$ to $360^\circ$) of the $A_{1g}/E_{2g}$ intensity ratios at 228 cm$^{-1}$ and 182 cm$^{-1}$, respectively, from polarized Raman experiments. Blue dashed trace represents the fitted curve.

X-ray photoelectron spectroscopy (XPS) measurements on bulk flakes are also indicative of anionic [SnAs]$^-$ layers (Figure 3.3). From the binding energy of the Na $1s$ peak (1071 eV), it can be deduced that the Na is cationic in nature with its energy close to a Na$^+$ binding energy. Additionally, Sn is anionic based on the binding energy of the Sn $3d_{5/2}$ peak (484 eV) which is significantly lower than the Sn$^0$ $3d_{5/2}$ binding energy (485.2
Comparing the As $3d_{5/2}$ peak binding energy (39.8 eV) of NaSn$_2$As$_2$ to As $3d_{5/2}$ peaks of GaAs (41.1 eV) and As (42.0 eV) reference standards indicated a more anionic As species than in GaAs (Figure 3.3d). All together, these oxidation states indicate an anionic 2D [SnAs]$^-$ lattice which is charge-balanced by Na$^+$.

![Figure 3.3 XPS of NaSn$_2$As$_2$ showing the Na 1s, Sn 4d Sn 3d$_{5/2}$ and As 3d peaks.](image)

The air stability of these crystals was first studied by exposing ground powders and mechanically exfoliated flakes (~50-100 nm) in ambient air for 7 days. From atomic force microscopy (AFM) measurements, there is minimal change in surface roughness of the flakes following air exposure from 0.39 nm to 0.46 nm (Figure 3.4a). XRD measurements on the air-exposed samples show no new oxidized phases nor significant broadening of the diffraction peaks (Figure 3.4b). From the Raman analyses of ~100 nm flakes, there were no new vibrational modes or features (which might indicate oxidation) and no significant increase in the FWHM of the peaks corresponding to the lattice vibrational modes before and after 1 week of air exposure (Figure 3.4c). No asymmetric
vibrational modes corresponding to either Sn-O (500-700 cm\(^{-1}\))\(^{76,77}\) or As-O (700-900 cm\(^{-1}\))\(^{78}\) bond formation were observed from Fourier-transform infrared (FTIR) measurements of pristine and air-exposed powders (Figure 3.4d). XPS measurements show the oxidation of the Sn and As atoms on surface of NaSn\(_2\)As\(_2\) after one week of exposure through the appearance of a shoulder centered around 485.7 eV (accounting for 26.5% and indicative of the presence of a Sn\(^{4+}\) 3d\(_{5/2}\) peak) and around 42.8 eV (accounting for 11.5% and indicative of the presence of a As\(^{3+}\) 3d\(_{5/2}\) peak), respectively (Figure A.17). These peaks disappear after Ar ion etching the top 1 nm (~1 bilayer), calibrated for SiO\(_2\). These measurements suggest that the bulk of NaSn\(_2\)As\(_2\) is air stable with only the top surface bilayer oxidizing over time.

**Figure 3.4** (a) Optical and AFM micrographs (Thickness: 65 nm; Scale bars correspond to 4 \(\mu\)m), (b) Powder XRD, (c) Raman spectra and (d) FTIR spectra of NaSn\(_2\)As\(_2\) before and after exposure to air for 7 days.
To demonstrate the possibility of exfoliating NaSn$_2$As$_2$ into few- to single-bilayers, bulk single crystals were exfoliated onto 285 nm SiO$_2$/Si substrates via mechanical exfoliation using Scotch™ tape. From this technique, thin layers with thicknesses down to 3.6 nm, which corresponds to approximately four SnAsNaAsSn bilayers, or 4/3 of a NaSn$_2$As$_2$ unit cell ($c$ lattice parameter = 27.56 Å), were observed (Figure 3.5a, A.18). Mechanical exfoliation produced numerous few-layer flakes with multiple steps (Figure A.19), with step thicknesses that were multiples of $\sim$0.9 ± 0.2 nm (Figure A.20). The fact that these step heights only varied by this multiple, show that the cleavage occurs either between the Sn⋯Sn planes or the Na⋯As planes, but not both. To determine which plane will more likely cleave upon exfoliation, we calculated the adhesion energies by determining the difference in overall energy between the bulk structure and both NaAsSnSnAs layers and SnAsNaAsSn separated by 10 Å vacuum, using the DFT-D2 method by Grimme$^{79}$ which includes both chemical interactions from a generalized gradient approximation (GGA) and a dispersive term which describes van der Waals interactions. The adhesion energy between neighboring Sn-Sn layers was calculated to be 1.45 J/m$^2$, and 1.75 J/m$^2$ between neighboring Na⋯As layers. This validates the assignment of NaSn$_2$As$_2$ exfoliating into SnAsNaAsSn layers. Future scanning tunneling microscopy measurements would provide further verification of the surface termination of these exfoliated flakes.

Aside from mechanical exfoliation, layered 2D materials can also be exfoliated through liquid-phase exfoliation when sonicated using a suitable solvent. Here, NaSn$_2$As$_2$ powders were dispersed in various solvents from isopropyl alcohol (low surface tension)...
to dimethyl sulfoxide (high surface tension) using sonication (Figure 3.5b). From these solvents, absorbance measurements revealed that the dispersion in N-cyclohexyl-2-pyrrolidone (CHP) yielded the highest resulting concentration of the supernatant after centrifugation (Figure A.21). The Raman spectra show that the exfoliated flakes still maintain the lattice vibrational modes, which indicates that the structure is still intact after exfoliation (Figure 3.5c). The thicknesses of the dispersed NaSn$_2$As$_2$ layers were analyzed by taking AFM micrographs of the drop-casted suspension onto 285 nm SiO$_2$/Si substrates (Figure 3.5d, A.22). The thicknesses of these dropcast flakes ranged from 1 to 9 nm, corresponding to 1 to 9 SnAsNaAsSn bilayers. Additionally, the lengths and widths of these dropcast flakes ranged from 200-500 nm. The average thickness from a histogram of 36 different flakes was 4.6 nm (Figure A.23). To further probe the structure and morphology of the liquid-exfoliated NaSn$_2$As$_2$ flakes, we performed transmission electron microscopy (TEM) on filtered NaSn$_2$As$_2$ dispersions on lacy carbon grids. In these measurements, we were able to observe bright-field TEM micrographs with thin sheets of NaSn$_2$As$_2$ that have less contrast than the 10 nm lacey carbon grid, and with lengths and widths on the order of ~100 nm (Figure 3.5e). A typical electron diffraction pattern from one of these NaSn$_2$As$_2$ flakes can be indexed to a simple hexagonal unit cell with $a = b = 4.02$ Å, assuming a [001] zone axis. This is in close agreement with the X-ray crystal structure. Further confirming the NaSn$_2$As$_2$ composition, the energy-dispersive X-ray spectrum (EDX) has strong Na, Sn, and As signal (Figure A.24). Additionally, crystalline domain sizes that are greater than 50 nm have been observed in high-resolution transmission electron microscopy (HRTEM) (Figure A.25). XPS measurements show that oxidation of these very thin, solution-exfoliated samples, occurs
much more readily, even after a day of air exposure (Figure A.26). Whether oxidation occurs due to the reduced layer thickness, lateral size, or via sonication-induced defects is subject to future studies. Still, similar to almost all other 2D van der Waals materials, encapsulation methods and surface functionalization will be required in order to achieve long-term air stability from these solution-exfoliated few-layer samples.\textsuperscript{80-83}

As discussed previously, formal electron counting would suggest that NaSn\textsubscript{2}As\textsubscript{2} would have 0.5 bonds between neighboring Sn-Sn atoms. In order to determine the exact nature of this Sn···Sn interaction, we calculated the energy of the NaSn\textsubscript{2}As\textsubscript{2} bulk hexagonal cell, which contains three SnAsNaAsSn layers, as a function of interlayer spacing up to 10 Å separation. Two calculations were performed: One with the DFT-D2 method by Grimme\textsuperscript{79} that combines GGA with van der Waals interactions, and the other with straight GGA, which has been shown for the case of graphite to include no van der Waals interactions.\textsuperscript{84} The results are shown in Figure A.27. While the binding energy between the layers without van der Waals forces is 0.88 J/m\textsuperscript{2}, inclusion of van der Waals forces adds 0.57 J/m\textsuperscript{2} for a total of 1.45 J/m\textsuperscript{2}. These values are larger than the adhesion energy of other 2D van der Waals materials, which typically range from 0.2-0.6 J/m\textsuperscript{2}.\textsuperscript{83,85,86} Still, the van der Waals interaction makes up 40\% of the interaction energy and thus has nearly equal strength to the orbital interaction between the Sn layers. This significant van der Waals component further justifies the classification of this material as a van der Waals Zintl phase.
Figure 3.5 (a) AFM image of few-layers of NaSn$_2$As$_2$ from mechanical exfoliation with the corresponding thickness profile. (b) NaSn$_2$As$_2$ dispersions in solvents with increasing surface tension from left to right (IPA = isopropyl alcohol, DMF = dimethylformamide, NMP = N-methyl-2-pyrrolidone, CHP = N-cyclohexyl-2-pyrrolidone and DMSO = dimethyl sulfoxide). (c) Raman of drop-casted few-layer (average thickness = 4.6 nm) NaSn$_2$As$_2$ in 285 nm SiO$_2$/Si substrate. (d) AFM image of liquid-exfoliated NaSn$_2$As$_2$ with the corresponding thickness profile. (e) TEM of liquid-exfoliated few layers of NaSn$_2$As$_2$ with a representative selected area electron diffraction (SAED) pattern, scale bar is 500 nm.
ARPES measurements were collected to elucidate the electronic structure of NaSn$_2$As$_2$ *(Figure 3.6a, A.28)*, and compared to high-level DFT calculations with SOC *(Figure 3b)*. We show data at photon energy 127 eV, but variation of the photon energy showed little or no change in the observed bands near $E_F$ (apart from intensity due to optical matrix element variation), indicating a quasi-2D character. There is excellent agreement between experiment and theory where the only discrepancy is a shallow electron pocket observed around $\Gamma$ observed by ARPES, which was predicted to be unoccupied in the DFT calculation. The atomic and orbital contributions of each band were calculated and are shown in Figure 6c. The bands localized at -1 eV close to $\Gamma$ point correspond to filled As $p$-bands. The partially unfilled band that the Fermi level cuts through primarily consists of Sn-$s$ and Sn-$p$ character, with some As-$p$ contributions. The greater filling of the As bands compared to the Sn bands is consistent with the greater electronegativity of As.
Figure 3.6 Electronic Band Structure of NaSn$_2$As$_2$. (a) Overlay of the theoretical band structure with the ARPES spectrum of a cleaved NaSn$_2$As$_2$ single crystal, acquired at photon energy 127 eV and T = 41 K. The bands that correspond to the electron pockets are labeled as b$_{n1}$ and b$_{n2}$, while the bands that comprise the hole pockets are labeled as b$_p$. (b) Heyd-Scuseria-Ernzerhof (HSE) band structure of NaSn$_2$As$_2$ with spin-orbit coupling (SOC). (c) Density of states of the contributing orbitals in NaSn$_2$As$_2$ near the Fermi level.
Two-probe temperature-dependent resistivity measurements were performed on NaSn$_2$As$_2$ single crystals to further elucidate the electronic structure. At room temperature the in-plane resistivity of a representative NaSn$_2$As$_2$ flake was determined to be 2.9 $\mu\Omega\cdot$m, which is highly conducting. The resistivity decreases with decreasing temperatures, which is consistent with metallic behavior as a consequence of phonon-mediated carrier scattering at higher temperatures (Figure 3.7a). Longitudinal and transverse resistivity measurements have also been performed on an exfoliated flake (thickness $t = 350$ nm) patterned into a Hall bar device. The room temperature in-plane resistivity is 1.7 $\mu\Omega\cdot$m, which is comparable with that in the bulk. The temperature dependent longitudinal resistivity again reveals the metallic nature of NaSn$_2$As$_2$, with a similar residual resistivity ratio as observed in the bulk. The transverse resistivity was measured under magnetic fields applied perpendicularly to the basal plane at 2.1, 100, 200, and 300 K. The Hall coefficient is positive over this temperature range, suggesting p-type conduction, although it approaches zero at room temperature.

The low-temperature p-type character, and the observed compensation at room temperature is consistent with the band structure measured by ARPES and calculated by DFT. To understand the nature of the charge carriers, we refer to the ARPES measurement (Figure 3.6a). Here, a p-type band, $b_p$, crosses the $E_f$. Also, a small central electron pocket is observed at $\Gamma$, labeled as $b_{n1}$ and, just below $E_f$, another band ($b_{n2}$) forms a closed electron pocket ~0.75 eV deep centered on the M point. At low temperatures, these bands do not contribute carriers due to the low intersection at $E_f$, predicting a predominantly hole (p-type) carrier density. Thermal smearing of the Fermi level at RT excites carriers into the electron-like pocket around the M-point, dramatically
increasing the ratio of n-type to p-type carriers. A detailed discussion of this phenomenon (temperature-dependent carrier type) is beyond the scope of this manuscript and will be elaborated upon by temperature-dependent ARPES and anisotropic thermopower measurements in a subsequent study. Explorations of the layer dependence of this temperature-dependent multiband transport can potentially lead to interesting phenomena and DFT simulations of the electronic structure of an SnAsNaAsSn layer isolated by 10 Å vacuum predicts that the metallic behavior of a single layer is retained (Figure A.29).
Figure 3.7 (a) Temperature-dependent in-plane resistivity of bulk and exfoliated NaSn$_2$As$_2$ down to 2.1 K. Inset is an optical microscope image of the Hall bar device. The thickness of the flake is 350 nm and the width to length ratio of the channel is 1.44. (b) The magnetic field dependence of the transverse resistance of the Hall bar device at 4 different temperatures. (c) The Hall coefficient extracted from (b).
3.4 Conclusion

In summary, we have demonstrated that layered vdW Zintl phases such as NaSn$_2$As$_2$ can be exfoliated into single- and few-layer (SnAsNaAsSn) sheets. From theory, ARPES and electronic transport, these bulk crystals are metallic in nature, but the unique band features allow for varying degrees of two-carrier conduction at various temperatures. At low temperatures p-type carriers dominate, but at higher temperatures n-type conduction channels become accessible. This work opens up the future exploration of layer-dependent phenomena of NaSn$_2$As$_2$ and other numerous materials in this family of high spin-orbit coupling vdW Zintl phases for applications ranging from transparent conductors to spintronics.

3.5 References


(59) Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets Isostructural to Grey Arsenic - Synthesis and Crystal-Structure of NaSn$_2$As$_2$, Na$_{0.3}$Sr$_{0.7}$Sn$_2$As$_2$, Na$_{0.4}$Sr$_{0.6}$Sn$_2$As$_2$, Na$_{0.6}$Ba$_{0.4}$Sn$_2$As$_2$, and K$_{0.3}$Sr$_{0.7}$Sn$_2$As$_2$. Z. Anorg. Allg. Chem. 1995, 621, 576-582.

(60) Eisenmann, B.; Klein, J. Zintl-Phases with Layer Anions - Preparation and Crystal-Structures of the Isotypic Compounds SrSn$_2$As$_2$ and Sr$_{0.87}$Ba$_{0.13}$Sn$_2$As$_2$ and a Single-Crystal Structure Determination of KSnSb. Z. Anorg. Allg. Chem. 1991, 598, 93-102.


Chapter 4 Exfoliatable Magnetic Layered Zintl Phases Based on the ASn$_2$As$_2$
Structure (A = Na and Eu)

In this chapter, we report the synthesis, structure, and magnetic and electronic properties of EuSn$_2$As$_2$, which is the first exfoliatable magnetic Zintl-Klemm phase. The bulk magnetic properties show that the Eu$^{2+}$ spins are ferromagnetically coupled within each layer, and is either canted or antiferromagnetically coupled to neighboring layers, with the magnetic moments oriented along the in-plane $a/b$-crystallographic axis. Using density functional theory (DFT) and temperature-dependent transport measurements, we show that EuSn$_2$As$_2$ is semi-metallic. We also demonstrate that this layered Zintl phase can be mechanically exfoliated into few-layers with steps corresponding to a single SnAsEuAsSn sheet. Lastly, we show that the alloying of Na to the EuSn$_2$As$_2$ lattice to form Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ (x = 0.75, 0.50 and 0.25) obeys the Vegard’s law and that the magnetic coupling of the Eu$^{2+}$ 4f$^7$ spins in these alloys is persistent even with alloying with Na, down to 25% Eu (Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$). This study opens up the possibility of creating new exfoliatable magnetic materials based on

---

$^4$ Parts of this chapter were reproduced from Arguilla, M. Q., Cultrara, N. D., Baum, Z. J., Jiang, S., Ross, R. D. and Goldberger, J. E. EuSn$_2$As$_2$: An Exfoliatable Magnetic Layered Zintl Phase. Inorg. Chem. Front. 2017, 4, 378-386 with permission from the Chinese Chemical Society (CCS), Peking University (PKU), and the Royal Society of Chemistry.
layered Zintl phases whose magnetic properties can provide insights on the understanding of the magnetic phenomena in 2D.
4.1 Introduction

Over the past couple of years, there have been significant research efforts devoted towards the synthesis, processing, and applications of single and few-layer thick 2D materials that have been exfoliated from layered crystal structures held together by van der Waals (vdW) forces. Additionally, there have been a lot of exciting studies showing that when different 2D materials are vertically stacked into heterostructures, new phenomena can emerge due to the coupling of the electronic structure and their magnetic properties. For instance, the coupling of a ferromagnetic material with a topological insulator can give rise to a quantum anomalous Hall effect. Additionally, modern magnetoresistance devices are typically constructed from layers of magnetic materials that are separated by a tunneling barrier. Despite the plethora of exfoliatable vdW materials, only a small handful are constructed from atoms with localized magnetic moments with spins that are ferromagnetically coupled within each plane. Such systems include GdI\(_2\), CrI\(_3\), CrSiTe\(_3\), CrGeTe\(_3\), and Mn-doped MoS\(_2\). Each of these materials exhibit varying degrees of air-stability, bulk magnetic transition temperatures, ease of exfoliation, and very little is known experimentally about how the magnetic properties change when exfoliated to single layers. Consequently, there is a strong need for the discovery of new families of exfoliatable 2D magnetic materials.

In this chapter, we sought the creation of magnetic materials out of vdW intermetallics that obey the Zintl-Klemm concept. Zintl phases are defined as semiconducting phases consisting of complete charge transfer from a highly...
electropositive element such as a Group 1, 2 or rare earth element, to a main group element, generally from Group 13 to 15 to satisfy the octet. These materials feature well-defined architectures whose dimensionality is often dictated by the electron count and stoichiometry, allowing for the facile creation of isoelectronic and isostructural derivatives. On the other hand, there are also intermetallic phases that follow the Zintl-Klemm electron counting rules and are typically metals, semimetals, or narrow band gap semiconductors. When electropositive elements having localized spins such as lanthanides are incorporated into the intermetallic Zintl-Klemm phase, typically the large distances between these magnetic elements and the metallic behavior gives rise to mechanisms for magnetic coupling beyond direct exchange, double exchange or superexchange. Very often, magnetic coupling occurs via Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, where coupling between localized spins arises from interactions through conduction electrons. Consequently, constructing a magnetic exfoliatable vdW Zintl-Klemm phase could give rise to different layer-dependent magnetic phenomena than the transition-metal superexchange-based 2D magnetic materials that have been evaluated thus far.

Presented in this chapter is the creation of an exfoliatable magnetic material out of Zintl-Klemm phases with the general formula of ATt₂Pn₂ (A = monovalent or divalent cation, Tt = Group 14 tetrel element, Pn = Group 15 pnictogen element) (Figure 1a). These materials are comprised of honeycomb networks of puckered alternating BN-like TtPn layers that sandwich octahedrally coordinated monovalent or divalent cations. Recently, we have demonstrated that one
such member, NaSn$_2$As$_2$,\textsuperscript{6} can be readily exfoliated into layers of SnAsNaAsSn. Almost half of the adhesion energy between neighboring SnAsNaAsSn layers is due to vdW forces, however, since NaSn$_2$As$_2$ has formally 7.5 electrons per Sn atom, there is an additional covalent component to the interlayer adhesion energy. Replacing Na$^+$ with a magnetic divalent cation such as Eu$^{2+}$ would eliminate the covalent interaction between layers, potentially improving the ease of exfoliation, while introducing magnetic interactions into the systems. There have been several reports on layered magnetic Eu-based Zintl phases including EuMgSi,\textsuperscript{48} EuGaTt (Tt = Si, Ge, Sn),\textsuperscript{49} EuIn$_2$P$_2$,\textsuperscript{44} and EuIn$_2$As$_2$.\textsuperscript{43} Both the EuIn$_2$P$_2$ and EuIn$_2$As$_2$ phases are structurally similar to ATt$_2$Pn$_2$, but the Group 14 tetrel element is replaced by In, a Group 13 triel element.\textsuperscript{43,44} In contrast to ATt$_2$Pn$_2$, these phases feature strong covalent In-In bonding between neighboring InPnEuPnIn layers in order to satisfy the octet rule. The Eu$^{2+}$ 4$f^7$ moments in these layered Zintl phases are ferromagnetically coupled to their neighbors within each plane, and antiferromagnetically coupled to the Eu$^{2+}$ atoms in adjacent layers. The ferromagnetic ordering temperature (T$_c$) is 16 and 24 K for EuIn$_2$As$_2$ and EuIn$_2$P$_2$, respectively.
4.2 Experimental

4.2.1 Crystal Growth

EuSn$_2$As$_2$ crystals were synthesized via melting stoichiometric amounts of Eu:Sn:As (1:2:2) in an alumina crucible enclosed in a quartz tube jacket under 50 mTorr pressures. For Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ ($x = 0.75$, 0.50 and 0.25) alloys, the ratios between Eu and Na were varied but the overall stoichiometry between the cations, Sn and As was still maintained to be 1:2:2. The tubes were heated to 850°C for 12 hours and were slowly cooled to room temperature from 60-100 hours. All the sample preparation was performed in an Ar environment. Europium rods (Eu, Alfa Aesar, 99.9%) and Sodium cubes (Na, Sigma Aldrich, 99.9%) were used after the oxide layer was stripped-off via mechanical cleavage. Tin (Sn, STREM Chemicals, 99.8%) and arsenic (As, STREM Chemicals, 99%) were purchased and used without further purification. Note that the toxicity of As must always be considered in handling this compound.

4.2.2 Material Characterization

The crystal structure and purity of the as-grown crystals were obtained via flat plane powder X-Ray diffraction (XRD) measurements done on a Bruker D8 powder X-Ray diffractometer (sealed Cu X-Ray tube: 40 kV and 50 mA). The structure was refined using the TOPAS Rietveld refinement software. The polarized Raman spectra at 785 nm laser illumination were collected using a Renishaw InVia Raman equipped with a Pike Technologies KRS-5 polarizer and a charge-coupled device (CCD) detector following a back-scattering geometry where the scattered light is polarized parallel ($0^\circ$) and perpendicular ($90^\circ$) with respect to the excitation source. The stoichiometric ratio of Sn and As were determined via X-Ray fluorescence (XRF) measurements done on an
Olympus DELTA X-Ray fluorometer calibrated using varied ratios of Sn and Eu₂O₃ (Sn:Eu) and Sn and As (Sn:As) standards.

4.2.3 Magnetic Measurements

Magnetic susceptibility measurements on EuSn₂As₂ crystals were obtained using a Quantum Design MPMS XL superconducting quantum interference device (SQUID). Flat crystals (1-2 mg) with c-axis faceting were oriented either parallel or perpendicular with respect to the applied magnetic field. The zero field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities were collected as a function of temperature using field strengths of 0.01 T and 3.5 T. For both orientations, the magnetization as a function of field strength was also measured from -6 T to 6 T at 5 K. No diamagnetic or paramagnetic corrections were performed in the determination of the magnetic moment.

4.2.4 DFT Calculations

The AFM ground state electronic band structure of EuSn₂As₂ was calculated with DFT. First, the experimentally derived unit cell was relaxed using spin-polarized full-potential linear augmented plane wave density functional theory with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional⁵⁰⁻⁵² as implemented via Wien2K.⁵³ To assess the magnetic ground states, spin-polarized calculations were performed in the P-3ml supergroup, with both ferromagnetic and antiferromagnetic interlayer Eu²⁺–Eu²⁺ interactions considered. All non-Eu atoms were treated as nonmagnetic. This supergroup transposes rhombohedral axes to hexagonal axes, and contains three times the number of atoms. It is used for ease of comprehension and comparison of band structure to other hexagonal layered 2D materials. To model an antiferromagnetic configuration with equal numbers of spin up and spin down Eu atoms, a 1x1x2 supercell of this
structure was necessary, and used for all calculations. The orbital contribution of specific bands at special points in the Brillouin Zone was determined by calculating their respective population matrices.

4.2.5 Bulk Electronic Transport

Temperature-dependent resistivity of EuSn$_2$As$_2$ single crystals were collected via four-probe transport measurements using a Quantum Design 14 T Physical Properties Measurement System (PPMS) from 4 K to 300 K.

4.2.6 Mechanical and Liquid Phase Exfoliation

Using silicone-free tape, micro-mechanically exfoliated crystals of EuSn$_2$As$_2$ were pressed onto freshly plasma-cleaned 285 nm SiO$_2$/Si substrates. The residual adhesive on the thin flakes were cleaned using isopropyl alcohol (IPA) and blow-dried in N$_2$. The thicknesses of these flakes were determined via atomic force microscopy (AFM) using a Bruker AXS Dimension Icon Atomic Force Microscope. Ground powders of EuSn$_2$As$_2$ were also dispersed and exfoliated in $N$-cyclohexyl-2-pyrrolidone (CHP) via sonication for 2 h using a Branson 3510 bath sonicator at 40kHz. The resulting dispersion was centrifuged at 3000 rpm for 90 minutes to separate the exfoliated few-layer flakes from non-exfoliated flakes. For transmission electron microscopy (TEM) and selected area electron diffraction (SAED), the dispersion was drop-casted onto a 200 mesh lacey carbon grid, which was subsequently dried for 12 h. TEM imaging and SAED were performed using an FEI/Philips CM-200T at 200 keV.
4.3 Results and Discussion

Crystals of EuSn$_2$As$_2$ were grown from the melt (Figure 4.1a, bottom right). EuSn$_2$As$_2$ crystallizes into platelet-like morphologies having lengths and widths of 3-5 mm and thicknesses of 1-3 mm. To elucidate the crystal structure, these crystals were ground into powders for subsequent Rietveld analysis. Refinements show that of all the possible closely related space groups, the $R$-3$m$ space group gives the best fit (Figure A.30). The occupancies of each of the elements were varied to check for the possibility of Sn substitution into the Eu site and As vacancies. From these refinements, the full occupancy gave the best fit. This is consistent with a 1.0:2.0:2.0 stoichiometric ratio between the Eu, Sn and As atoms as measured via XRF analysis (Figure A.31). EuSn$_2$As$_2$ has an $a$-lattice parameter of 4.2071(5) Å and a $c$-lattice parameter of 26.463(3) Å (Figure 4.1b, Table 4.1-4.3, A.17). The crystal structure of EuSn$_2$As$_2$ was found to belong to the same structure type as NaSn$_2$As$_2$ and SrSn$_2$As$_2$. It is comprised of six layers of covalently-bonded Sn and As atoms in a puckered, honeycomb arrangement. These [SnAs]$^-$ layers arrange such that the Sn atoms in one layer are oriented towards the Sn atoms in the adjacent layer (Figure 4.1a). The As atoms in neighboring [SnAs]$^-$ layers sandwich a hexagonal layer of Eu$^{2+}$ cations, such that the Eu$^{2+}$ cations are in an octahedral coordination environment. In this structure, the interatomic distance between two Sn···Sn atoms in neighboring [SnAs]$^-$ layers corresponds to 3.33 Å and is larger than the typical Sn···Sn bond length of ~3.1 Å. This increased separation of Sn···Sn planes is indicative of vdW bonding.

EuSn$_2$As$_2$ is expected to exhibit six Raman-active modes, $2E_g + 2A_{1g}$, based on the selection rules for an $R$-3$m$ space group which corresponds to a D$_{3d}$ point group. By
performing polarized Raman spectroscopy (Figure 4.1c), we have observed three of the six possible modes (E\textsubscript{g} + A\textsubscript{1g}) and have shown the dependence of the Raman modes on the polarization of the backscattered light. For a D\textsubscript{3d} point group in a backscattering geometry, the A\textsubscript{1g} mode is enhanced while the E\textsubscript{g} mode is suppressed when the backscattered light is co-polarized with the excitation source. On the other hand, the opposite is observed for cross-polarized backscattering measurements. With these, we have assigned the Raman peaks at 161 cm\textsuperscript{-1} and 194 cm\textsuperscript{-1} to E\textsubscript{g} and A\textsubscript{1g}, respectively. For comparison, the E\textsubscript{g}, E\textsubscript{g} + A\textsubscript{1g}, A\textsubscript{1g} modes exist in NaSn\textsubscript{2}As\textsubscript{2}, at 182 cm\textsuperscript{-1}, 206 cm\textsuperscript{-1}, and 228 cm\textsuperscript{-1}, respectively.\textsuperscript{6} The fact that these Raman modes occur at lower energies in EuSn\textsubscript{2}As\textsubscript{2} is consistent with the heavier Eu\textsuperscript{2+} cation in between the layers and the larger Sn-As bond distances. It is possible that the other E\textsubscript{g} and A\textsubscript{1g} modes in EuSn\textsubscript{2}As\textsubscript{2} either occurs below 100 cm\textsuperscript{-1} or are overlapped with the observed peak at 161 cm\textsuperscript{-1}.

\begin{table}[h]
\centering
\caption{Crystal Data and Refinement Results for EuSn\textsubscript{2}As\textsubscript{2}, using Hexagonal Axes}
\begin{tabular}{ll}
\hline
EuSn\textsubscript{2}As\textsubscript{2} & Cu K\textsubscript{α1} \\
FW = 539.23 & \\textlambda = 1.5406 Å \\
Rhombohedral & 2\theta = 10 - 90 \\
R-3m (No. 166) & T = 298 K \\
a/b = 4.2071(5) Å & \\
c = 26.463(3) Å & \\
a/\beta = 90° & \\
y = 120° & \\
V = 405.63(12) Å\textsuperscript{3} & \\
R_p/R_{wp} = 3.83/4.88 (%) & \\
\hline
\end{tabular}
\end{table}

\*\(R_p = \Sigma |I_{io}| - |I_{ic}|/\Sigma |I_{io}|; R_{wp} = [\Sigma w_i(I_{io} - I_{ic})^2/\Sigma w_i(I_{io})^2]^{1/2}\), where \(w = 1/(\sigma I_{io}^2)\) and \(I_i\) is the intensity of the \(i\)th observation.
**Table 4.2** Fractional atomic coordinates and isotropic displacement parameters based on the refined EuSn$_2$As$_2$ structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{\text{iso}}$(Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.007(3)</td>
</tr>
<tr>
<td>Sn</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.20963(13)</td>
<td>0.013(4)</td>
</tr>
<tr>
<td>As</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.40624(2)</td>
<td>0.006(2)</td>
</tr>
</tbody>
</table>

**Table 4.3** Selected bond lengths (Å) and bond angles (°) in EuSn$_2$As$_2$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu–As</td>
<td>3.1019(4)</td>
<td>Sn–As</td>
<td>2.7761(3)</td>
</tr>
<tr>
<td>As–Eu–As</td>
<td>180.0 $trans$</td>
<td>As–Sn–As</td>
<td>98.53(2)</td>
</tr>
<tr>
<td>As–Eu–As</td>
<td>85.40(13) and 94.60(13) $cis$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.1 (a) The crystal structure of EuSn$_2$As$_2$ (Eu = Orange, Sn = gray and As = blue). Top right: the structure down the c-axis showing the hexagonal ordering of the Eu$^{2+}$ cations in-plane. Bottom right: an image of mm-sized crystal of EuSn$_2$As$_2$. (b) Powder XRD data of EuSn$_2$As$_2$ with the corresponding Miller indices in parentheses. (c) Polarized Raman spectra using 785 nm laser excitation. The scattered light is co-polarized ($0^\circ$) and cross-polarized ($90^\circ$) with respect to the excitation source.
To probe the magnetic ordering of the Eu$^{2+}$ 4f$^7$ spins, we performed temperature-dependent magnetic susceptibility measurements on EuSn$_2$As$_2$ crystals along different crystal orientations (in-plane and out-of-plane) with respect to the applied magnetic field (Figure 4.2), and FC and ZFC. At all field strengths measured, the FC and ZFC data are nearly superimposable. At a measuring field strength of 0.01 T (Figure 4.2a), the magnetic susceptibilities along both crystal orientations gradually increase with lower temperatures, until reaching their maxima at $\sim$24 K. This is indicative of antiferromagnetic ordering of the Eu$^{2+}$ spins in the structure or, because the susceptibility does not go to zero at temperatures approaching 0 K, the canting of the magnetic moment in each layer is also possible. Below the transition temperatures the two curves are nearly superimposable with differences that are within one-to-two standard deviations in the susceptibility values (Figure A.32). However, a Curie-Weiss fit of the magnetic susceptibility data when the field is oriented along the in-plane direction produced a Weiss constant of +24.3 K, indicative of predominantly ferromagnetic behavior (Figure 4.2a, inset). Additionally, a Curie constant of 7.81 emu K/mol was obtained and is equivalent to an effective spin-only magnetic moment of 7.90(4) $\mu_B$ per formula unit, which is in close agreement to the theoretical value of a free Eu$^{2+}$ cation (7.94 $\mu_B$). As is expected with a half-filled f$^7$ electron configuration, there is no orbital angular momentum contribution to the magnetic moment. The Curie-Weiss fit of the magnetic susceptibility data when the field is oriented along the cross-plane direction also was indicative of ferromagnetic behavior, giving a similar Curie constant of 7.85 $\mu_B$ and a Weiss constant of 24.6 K (Figure A.33). To minimize the effects of any short range
ordering of the spins close to the transition temperature, only data above 50 K were fit to the Curie-Weiss law. The fact that the Curie-Weiss law indicates a dominant ferromagnetic interaction whereas the low-field susceptibility shows antiferromagnetic ordering with possible canting indicates that there are competing Eu$^{2+}$ magnetic interactions. In order to account for the demagnetizing factor in the layered EuSn$_2$As$_2$ phase, we also corrected for the applied external field using equation (1):

\[
H_i = H_e - NM
\]

(1)

where \(H_i\) is the intrinsic field, \(H_e\) is the applied external field, \(N\) is the shape factor (which is equal to 4\(\pi\) for a sheet that is perpendicular to \(H_e\)) and \(M\) is the measured magnetization. Applying the self-demagnetization correction factor leads to a significant difference between the two crystalline orientations across all temperature values.

At a higher measuring field strength of 3.5 T (Figure 4.2b), the magnetic susceptibility behavior is different when the field is oriented along different crystal orientations. The crystal with the \(a/b\)-axis oriented parallel to the field increases at temperatures below 24 K, which is indicative of ferromagnetic ordering behavior. In contrast, the crystal with the \(c\)-axis oriented parallel to the field still approaches a maximum value near the transition temperature, indicative of antiferromagnetic ordering with possible canting. The fact that the magnetic susceptibility behavior is different along the in-plane and cross-plane crystal orientations indicates that there are competing magnetic interactions between the Eu$^{2+}$ spins along the in-plane and cross-plane directions.
Figure 4.2 Temperature-dependent magnetic susceptibility of EuSn$_2$As$_2$ oriented at different crystal orientations with respect to the measuring magnetic field of (a) 0.01 T and (b) 3.5 T. Inset in (a) is the Curie-Weiss fit corresponding to the inverse susceptibility of the crystal with its $a$-axis oriented parallel to the applied field. The blue data points correspond to measurements with the $a$-axis parallel to the field, the red data points correspond to measurements with $c$-axis oriented parallel to the field and the green data points correspond to measurements with the $c$-axis oriented parallel to the field corrected for self-demagnetization. FC values are denoted as crosses, and ZFC values are denoted with circles, and are nearly superimposable. FC was performed using the same field strength as the measuring magnetic field.
In EuSn$_2$As$_2$, the two significant Eu$^{2+}$\textendash\textendashEu$^{2+}$ interactions are the interlayer
Eu$^{2+}$\textendash\textendashEu$^{2+}$ interactions, having an interatomic distance of 9.15 Å and the much closer
nearest neighbor intralayer Eu$^{2+}$\textendash\textendashEu$^{2+}$ interactions, having an interatomic distance of
4.21 Å. The closer Eu$^{2+}$\textendash\textendashEu$^{2+}$ distance within the layer indicates a more dominant
intralayer ferromagnetic coupling. This dominant intralayer ferromagnetic coupling is
consistent with the Weiss constant being positive across all fields and crystal orientations.
Furthermore, the superposition and non-divergence of the ZFC and FC curves for both
the crystal orientations, and across both field strengths, indicate that there is no spin-
frustration, which is only expected when the Eu$^{2+}$ cations are antiferromagnetically
coupled in-plane.

It is important to point out that applying a demagnetization correction can
significantly influence the assignment in the easy axis of magnetization. When the
correction is not applied, the susceptibility is highest whenever the applied field is
parallel to the $a/b$-plane. In this uncorrected data, this would signify that the Eu$^{2+}$ spins
are likely oriented perpendicular to the $c$-axis, thus suggesting that the $a/b$-direction is the
easy axis of the magnetization for the ferromagnetic coupling of Eu$^{2+}$ spins. Indeed, very
similar behavior has been observed before in the structurally similar EuIn$_2$As$_2$ and
EuIn$_2$P$_2$. In these systems, it was similarly proposed that the Eu$^{2+}$ cations are coupled
ferromagnetically within the layer and each ferromagnetic layer of Eu$^{2+}$ cations is either
antiferromagnetically coupled to the Eu$^{2+}$ spins or canted in adjacent layer. However,
when the demagnetization correction is applied, the susceptibility is larger whenever the
applied field is parallel to the \( c \)-axis. This suggests that with the demagnetization correction, the \( c \)-axis becomes the easy axis.

Magnetization versus field curves (Figure 4.3) show that the magnetization begins to saturate at \( \sim 4.4 \) T when the \( c \)-axis is oriented parallel to the field without the demagnetization correction, where as it begins to saturate at \( \sim 2.8 \) T with the demagnetization correction. On the other hand a saturation field of \( 3.3 \) T is observed when the \( a/b \)-axis is oriented parallel to the field. From these curves, a saturation magnetization of \( 7.24(6) \) \( \mu_B \) was extrapolated for both crystal orientations. These values are close to the saturation magnetization expected for a single \( \text{Eu}^{2+} \) spin (\( M_{\text{sat}} = 7.0 \) \( \mu_B \)), and other \( \text{Eu}^{2+} \) containing magnetic materials such as \( \text{EuGa}_2\text{P}_2 \), \( \text{EuSnP} \), \( \text{EuIn}_2\text{P}_2 \), and \( \text{EuIn}_2\text{As}_2 \). When the magnetic susceptibility is measured with the \( c \)-axis oriented parallel to the field, at \( 5T \), or above the saturation field, the susceptibility versus temperature curve becomes continuous at lower temperatures, indicative of a ferromagnetic behaviour (Figure A.34).

Taken together, the orientation dependent magnetic susceptibility and magnetization vs. field plots are indicative of a magnetic structure in which the \( \text{Eu}^{2+} \) spins are ferromagnetically coupled in-plane, with antiferromagnetic coupling or a possible canting of the magnetic moments between neighboring layers. However, elucidating the actual easy axis, or spin orientation, is complicated by the platelet crystal morphology combined with the intrinsic anisotropy of the crystal structure. Applying a demagnetization correction changes the assignment of the easy axis of magnetization in \( \text{EuSn}_2\text{As}_2 \). It is important to point out that upon measuring 3-4 \( \text{EuSn}_2\text{As}_2 \) crystals, we consistently observe this change of the apparent easy axis with and without the
demagnetization correction. While most other analysis of other platelet-like crystals, including EuIn$_2$P$_2$, EuIn$_2$As$_2$, CrSiTe$_3$, CrGeTe$_3$, do not adapt this demagnetization factor in consideration of the easy axis, there is much larger difference in the uncorrected magnetization field measurements when measuring in-plane vs. cross-plane susceptibilities. Neutron diffraction experiments will be required to fully resolve the magnetic superstructure and spin orientation, which is beyond the scope of this paper. This spin orientation will be important for various spin-related applications including proximity-induced quantum anomalous Hall phenomena.

**Figure 4.3** Field-dependent magnetic susceptibility of EuSn$_2$As$_2$ at 5 K with the $a/b$-axis (blue), $c$-axis (red) and $c$-axis that is demagnetization-corrected (green) parallel to the applied field.

In order to probe the persistence of the magnetic ordering of the Eu$^{2+}$ $4f^7$ spins in the ASn$_2$As$_2$ structure, we alloyed various amounts of Na into the EuSn$_2$As$_2$ lattice to form Eu$_{1-x}$Na$_x$Sn$_2$As$_2$ ($x = 0.75, 0.50$ and $0.25$). In the powder diffraction patterns of
these alloys, there were no significant changes in the full-width-at-half-maximum of the diffraction peaks with the incorporation of Na, which is indicative of homogeneity in the cation site (Figure 4.4a). We observe a consistent decrease and a uniform increase in the a-lattice parameter and the c-lattice parameter, respectively, with increasing Na incorporation into the EuSn$_2$As$_2$ lattice. Furthermore, plotting these lattice parameters with the percentage of Na incorporation also yields a linear plot for both crystallographic orientations suggesting that the alloying process is consistent with Vegard’s law (Figure 4.4b). This also suggests that there is a complete and stoichiometric incorporation of Na into the EuSn$_2$As$_2$ lattice. In addition, Raman spectroscopy also revealed the shift of the in-plane ($E_g$) modes to higher wavenumbers with increasing Na incorporation, further proving the inclusion of Na into the lattice (Figure 4.4c). Since these modes are only dependent on the Sn and As atoms which both occupy the 6c Wyckoff site, we attribute the shift of the Raman modes to higher frequencies with the increasing spring constant, $k$, with decreasing Sn-As bond lengths and a-lattice parameters.
The homogeneous substitution of Na with Eu allows for the measurement of the magnetic properties of these alloyed systems. In order to show the persistence of the magnetic coupling of the Eu\(^{2+}\) 4f\(^7\) spins, we probed the DC Field ZFC/FC low field (0.01 T) and high field (2.5 T) temperature-dependent magnetic susceptibilities for when the field is oriented parallel to either the c-axis or the a/b-axis of Eu\(_{0.25}\)Na\(_{0.75}\)Sn\(_2\)As\(_2\), as this phase is the most magnetically dilute in the series of alloys. From low-field measurements, for both crystal orientations, we observe an almost continuous curve with a very slight discontinuity in the magnetic susceptibility curve only for when the field is parallel to the a-axis. This slight discontinuity indicates a slight canting of the magnetic moments along the in-plane direction in contrast to the out-of-plane direction where all the spins are perfectly ferromagnetically coupled (Figure 4.5a). In these curves, the absence of any hysteresis in the FC/ZFC curves suggests that there is no spin frustration.

**Figure 4.4** (a) Powder diffraction patterns of Eu\(_{1-x}\)Na\(_x\)Sn\(_2\)As\(_2\) (x = 0, 0.25, 0.50, 0.75 and 1). (b) Vegard’s law plot of the a- and c-lattice parameters of Eu\(_{1-x}\)Na\(_x\)Sn\(_2\)As\(_2\) (x = 0, 0.25, 0.50, 0.75 and 1). (c) Unpolarized Raman spectra of c-axis oriented crystals of Eu\(_{1-x}\)Na\(_x\)Sn\(_2\)As\(_2\) (x = 0, 0.25, 0.50, 0.75 and 1).
in the system. At higher fields (2.5 T), there is little or no anisotropy in the in-plane and out-of-plane susceptibilities in Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ (Figure 4.5b). To probe the overall nature of the magnetic ordering in Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$, we perform Curie-Weiss fitting of the low field magnetic susceptibility versus temperature curve at temperatures above 50 K to avoid any short-range interactions in the system (Figure 4.5a, inset). From the Curie-Weiss fitting, we extract a Curie constant of ~7.6 emu K/mol which converts to an effective spin-only magnetic moment of ~7.80 $\mu_B$ per formula unit and is consistent with a free Eu$^{2+}$ spin. On the other hand, a positive Weiss constant of was also extrapolated from the fit indicating that overall, there is ferromagnetic coupling in the Eu$^{2+}$ spins in the structure. In addition, magnetization versus field curves at 5 K were also measured for both crystal orientations of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ (Figure 4.5c). From the field-dependent curves, a soft ferromagnetic curve with a coercive field of ~20 Oe (Figure 4.5d) and saturates at ~1.5 T was observed for both cases where the field is oriented parallel to either the c-axis or the a/b-axis of the crystal. From both orientations, a saturation magnetization close to the theoretical saturation magnetization for a single Eu$^{2+}$ spin (M$_{sat}$ = 7.0 $\mu_B$) was observed. Again, similar to the temperature-dependent susceptibilities, there is little or no anisotropy in the in-plane and out-of-plane orientations of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$. Overall, these magnetic data shows that even with the dilution of a non-magnetic cation, the magnetic ordering of the Eu$^{2+}$ still persists down to 25% Eu content in the lattice.
Figure 4.5 Temperature-dependent magnetic susceptibility of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ oriented along different crystal orientations with respect to the measuring magnetic field of (a) 0.01 T and (b) 2.5 T. Inset in (a) is the Curie-Weiss fit corresponding to the inverse susceptibility of the crystal with its $a$-axis oriented parallel to the applied field. The blue data points correspond to measurements with the $a$-axis parallel to the field and the red data points correspond to measurements with $c$-axis oriented parallel to the field. FC values are denoted as crosses, and ZFC values are denoted with circles, and are nearly superimposable. FC was performed using the same field strength as the measuring magnetic field. (c) Field-dependent magnetic susceptibility of Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ at 5 K with the $a$-axis (blue) and $c$-axis (red) parallel to the applied field. (d) Zoomed in field-dependent magnetic susceptibility at 5 K plot highlighting the small coercive field of the Eu$_{0.25}$Na$_{0.75}$Sn$_2$As$_2$ soft ferromagnet.
DFT calculations of the ground state of EuSn$_2$As$_2$ further confirmed an antiferromagnetic structure and also predicted a semi-metallic band structure (Figure 4.6). First, we calculated the total energy of a 1x1x2 hexagonal supercell of EuSn$_2$As$_2$, considering both ferromagnetic and antiferromagnetic interlayer spin configurations of the Eu atoms. The total energy for the antiferromagnetic spin configuration was lower than the ferromagnetic spin configuration by 14.16 eV in the 1x1x2 hexagonal supercell (7.08 eV/hexagonal unit cell). The electronic band structure of the antiferromagnetic supercell for the bands near the Fermi level is shown in Figure 4a. The Fermi level partially cuts through a series of bands that are almost completely filled around the Γ/A points, and a series of bands that are almost completely empty near the M/L points. Together, the p-type nature of the bands at the Γ/A points and the n-type nature of the bands at M/L signify a semimetallic electronic structure. Additionally, the partial density of states plot was calculated from -10 eV to 2 eV to determine the orbital contributions of each of the major bands (Figure 4.6b). The bands from -9 to -4.5 are bonding states that are mostly Sn/As s-orbital in character. The bands that span from -4.5 eV to the $E_F$ level are mainly Sn/As p-orbital in character. The greater filling of the As p bands over the Sn p bands in this energy region is a consequence of the greater electronegativity of As. The flat bands at -0.3 eV correspond to electrons localized in Eu 4f orbitals. The antibonding orbitals directly above $E_F$ are Sn/As p-orbital in character. Finally, the orbital contributions of specific Brillouin zone points near the Fermi level was calculated. The band at Γ, that is within 0.05 eV above $E_F$ is predominantly comprised of 30% As s, 18% Sn s, and 40% Sn p orbitals. Also, the conduction band minimum at M is predominantly
comprised of 25% As p, 10% Sn s, 15% Sn p, and 21% Eu d orbitals. The partial Eu d character of this mostly empty band is indicative of the low-lying d states that can exist in mono- and divalent lanthanides.36
Figure 4.6 (a) Electronic band structure of the antiferromagnetic magnetic ground state of EuSn$_2$As$_2$ highlighting its semi-metallic nature. (b) Partial density of states of the bands near the Fermi level.

To confirm the semi-metallic behavior, we performed four-probe temperature dependent transport measurements along the $a/b$-plane of a single crystal (Figure 4.7). At room temperature, the resistivity is found to be $7.3 \times 10^{-6}$ Ω m. At temperatures higher than ~30 K (Figure 4.7, inset), a continuous increase in resistivity with increasing...
temperature is observed, and is indicative of phonon-mediated scattering that occurs at higher temperatures. Both observations are consistent with metallic behavior above the ordering temperature. However when the temperature is lowered from 30 K to 24 K, the resistivity increases slightly by a net change of 1.2%. Similar to other magnetic systems, a local maximum in resistivity was observed at the magnetic ordering temperature. This increase in resistivity near the transition is likely due to spin scattering of delocalized conduction electrons by the localized Eu$^{2+}$ magnetic moments beginning to order, reminiscent of a Kondo-type behavior. In contrast to the covalently-bonded layers in the antiferromagnets EuIn$_2$P$_2$ and EuIn$_2$As$_2$ whose resistivity increases by 25-65% near the transition temperature, there is a smaller change in resistivity near the transition temperature in EuSn$_2$As$_2$. This is likely due to the weaker interlayer Eu$^{2+}$ antiferromagnetic interactions as a consequence of the vdW gap between the layers. For comparison, some Eu$^{2+}$-containing layered intermetallics such as EuIn$_2$P$_2$, and EuIn$_2$As$_2$ show appreciable magnetoresistance at or below the transition temperature, however others such as EuMgSi show no magnetoresistance. Magnetoresistance is typically defined as:

$$ MR = \left(\frac{\rho(H) - \rho(0)}{\rho(0)}\right) \times 100\% $$

where $\rho(0)$ is the resistivity at zero applied field and $\rho(H)$ is the resistivity at an applied field of H. EuSn$_2$As$_2$ shows little-to-no magnetoresistance (MR < 5%) near the transition temperature when these crystals were measured with fields up to 7T and oriented in the cross-plane direction. Finally, below the magnetic ordering temperature, a steeper slope in the resistivity is observed on account of the significantly reduced carrier scattering by the ordered and localized spins. In total, the semimetallic electronic structure, the
presence of relatively flat, non-interacting Eu$^{2+}$ 4f$^7$ localized bands in the valence band, and the large distance between interlayer Eu$^{2+}$$\cdots$Eu$^{2+}$ spins together indicate that coupling of spins both in the in-plane and out-of-plane directions in EuSn$_2$As$_2$ occur via an indirect exchange mechanism, that is likely an RKKY mechanism.

\[\text{Figure 4.7} \] Temperature-dependent resistivity of EuSn$_2$As$_2$ showing its metallic behavior along the temperature range with a cusp near the magnetic ordering temperature. Top left: Characteristic micrograph of a EuSn$_2$As$_2$ crystal in a four-probe geometry. EuSn$_2$As$_2$ crystal Bottom right: high temperature resistivity which increases with increasing temperatures.

Finally, in contrast to other layered Eu$^{2+}$-containing Zintl phases, there exists a vDW gap in between the Sn$\cdots$Sn planes in EuSn$_2$As$_2$. This allows for the exfoliation of a SnAsEuAsSn sheet, which contains a single layer of Eu cations. Indeed, we previously determined that NaSn$_2$As$_2$ can be readily exfoliated between the Sn$\cdots$Sn planes.$^6$ To
demonstrate that EuSn\(_2\)As\(_2\) can be thinned down to few layers, we performed micro-mechanical exfoliation of EuSn\(_2\)As\(_2\) crystals using Scotch tape (Figure 4.8). These exfoliated layers on tape were pressed and transferred onto 285 nm SiO\(_2\)/Si substrates. From this method, thin few-layer flakes (3.5 nm to 18 nm) of EuSn\(_2\)As\(_2\) with lengths and widths of 1-2 microns were obtained. These flakes typically feature step sizes of \(\sim 0.9 \pm 0.1\) nm that correspond to a single SnAsEuAsSn layer (Figure 4.8a, A.35). On the other hand, a continuous flake with a thickness of 5.4 nm, corresponding to 6 SnAsEuAsSn layers, can also be obtained (Figure 4.8b). This shows that it is possible to obtain flakes of EuSn\(_2\)As\(_2\) with various thicknesses, which is vital towards future studies of layer-dependent magnetism. To further probe that exfoliation of EuSn\(_2\)As\(_2\), produces highly crystalline materials, we performed TEM imaging on drop-casted dispersions of EuSn\(_2\)As\(_2\) in CHP. Bright-field micrographs of few-layer EuSn\(_2\)As\(_2\) layers with lengths and widths of \(\sim 500\) nm and which also have significantly less contrast as compared to the 10 nm lacey carbon grid were observed under the TEM (Figure 4.8c). The SAED pattern (Figure 4.8c, inset) can be indexed to a hexagonal unit cell assuming a [001] zone axis with an a/b-lattice parameter of \(\sim 4.2\) Å, which matches the refined EuSn\(_2\)As\(_2\) structure and confirms the identity of the exfoliated EuSn\(_2\)As\(_2\) flakes. This shows that the crystallinity is retained in few-layer samples even upon exfoliation.
Figure 4.6. (a) AFM image and height profile of few layers of EuSn$_2$As$_2$ mechanically-exfoliated onto a 285 nm SiO$_2$/Si substrate. Highlighted are the ~0.9 nm steps corresponding to a single SnAsEuAsSn layer. (b) A continuous thin flake of EuSn$_2$As$_2$ with the corresponding height profile. (c) TEM micrograph of liquid-exfoliated EuSn$_2$As$_2$ sheets. Inset is the SAED pattern indexed to a hexagonal unit cell assuming a [001] zone axis.
4.4 Conclusions

In summary, we have synthesized EuSn$_2$As$_2$, which is the first exfoliatable, magnetic Zintl phase. We show that these crystals possess anisotropic magnetism, in which the Eu$^{2+}$ 4f$^7$ spins have ferromagnetic coupling within each layer, and are either canted or have antiferromagnetic coupling between each layer, with a magnetic ordering transition of around 24 K. We also show, by alloying Na into the EuSn$_2$As$_2$ lattice, that the ferromagnetic ordering of the Eu$^{2+}$ spins persists even at high substitution by a non-magnetic Na$^+$ cation into the Eu$^{2+}$ site. This possibility of alloying a non-magnetic cation also allows for the fine tuning of the magnetic anisotropy and Curie temperatures in the EuSn$_2$As$_2$ phase. From both theory and transport measurements, we also show that EuSn$_2$As$_2$ is semi-metallic and possesses a slight change in resistivity near the ordering temperature. Finally, we demonstrate that these layered EuSn$_2$As$_2$ crystals can be micro-mechanically exfoliated into few layer sheets. This work opens up the use of exfoliatable magnetic Zintl phases as platforms for the demonstration of exotic magnetic phenomena in 2D and as building blocks for next-generation spintronic devices.

4.5 References


(43) Goforth, A. M.; Klavins, P.; Fettinger, J. C.; Kauzlarich, S. M. Magnetic
Properties and Negative Colossal Magnetoresistance of the Rare Earth Zintl Phase
EuIn$_2$As$_2$. Inorg. Chem. 2008, 47, 11048-11056.

(44) Jiang, J.; Kauzlarich, S. M. Colossal Magnetoresistance in a Rare Earth

(45) Payne, A. C.; Sprauve, A. E.; Holm, A. P.; Olmstead, M. M.; Kauzlarich,
S. M.; Klavins, P. EuSnP: A Novel Antiferromagnet with Two-Dimensional, Corrugated

(46) Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets
Isostructural to Grey Arsenic: Synthesis and Crystal Structure of NaSn$_2$As$_2$, Na$_{0.3}$Ca$_{0.7}$
Sn$_2$As$_2$, Na$_{0.4}$Sr$_{0.6}$Sn$_2$As$_2$, Na$_{0.6}$Ba$_{0.4}$Sn$_2$As$_2$, and K$_{0.3}$Sr$_{0.7}$Sn$_2$As$_2$. Z. Anorg. Allg. Chem.
1995, 621, 576-582.

(47) Eisenmann, B.; Klein, J. Zintl Phases with Layer Anions: Preparation and
Crystal Structures of the Isotypic Compounds SrSn$_2$As$_2$ and Sr$_{0.87}$Ba$_{0.13}$Sn$_2$As$_2$ and a
102.

Svitlyk, V.; Cuervo-Reyes, E.; Slabon, A.; Nesper, R.; Schellenberg, I.; Pottgen, R.
Complex Physical Properties of EuMgSi – a Complementary Study by Neutron Powder

(49) You, T. S.; Grin, Y.; Miller, G. J. Planar Versus Puckered Nets in the

(50) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient

(51) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of
45, 13244-13249.

(52) Perdew, J. P.; Yue, W. Accurate and Simple Density Functional for the

(53) Blaha, P.; Schwarz, K.; Madsen, G.; Kvasnicka, D.; Luitz, J. Wien2k, an
Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties;


Chapter 5: Topotactic Approaches Towards Tin-Containing Graphane Analogues

In this chapter, we show two routes towards the realization of strong spin-orbit coupling in Group 14 graphane analogues. First, we demonstrate the creation of 2D Ge$_1$-$_x$Sn$_x$H$_{1-x}$(OH)$_x$ ($x = 0-0.09$) graphane analogues, in multilayered vdW crystals. This represents the maximum quantity of tin that could be incorporated in the starting CaGe$_2$-$_2x$Sn$_{2x}$ Zintl phase as a homogeneously distributed alloy. After deintercalation in aqueous HCl, we show that Sn is terminated with –OH, while the Ge remains terminated with –H. The band gap of the resulting 2D material systematically shifts from 1.58 eV in germanane (GeH) down to 1.38 eV with 9% tin. This change in band gap enables photodetection at energies between 1.38-1.58 eV for the 9% tin sample. These germanium/tin graphane alloys start oxidizing after exposure to air, as evidenced by the shift in the absorption spectrum and XPS. Second, we provide insights on the creation of organic-functionalized Sn-based graphane analogues with higher Sn percentages (≥50%). The deintercalation of the layered Zintl phases based on Sn/Group 15 elements (P, As, Sb) is limited by the electrochemical matching between the precursor Zintl phase and the

---

organic halide deintercalant. Because of the propensity of the organic halides to be reduced, the oxidation potentials of the highly electron-rich precursor Zintl phases should be matched with the reduction potentials of the organic halide deintercalants to avoid the formation of alkyl free radicals that further amorphizes the deintercalated structures. Taken together, this work shows that the topotactic deintercalation of Zintl phase precursors is a viable route for creating not only band-gap tunable germanium/tin graphane alloys but also 2D $sp^3$-hybridized phases that feature small band gaps, contain elements with strong spin-orbit coupling strength and have the potential to be topologically-protected phases.
5.1 Introduction

Layered two-dimensional (2D) materials have shown considerable potential as novel building blocks for semiconductor device applications including next generation electronics,1-5 photodetectors,6,7 solar cells,5,9 light emitting diodes,10 and photocatalysts.11-13 To these ends, the Group 14 graphane analogues, in which every atom exists in a ligand-terminated puckered hexagonal honeycomb geometry, have attracted recent interest as 2D materials whose properties can be tuned via covalent chemistry of the surface-ligand.14-18 For example, depending on the nature of the surface functionalization, the 2D silicanes feature band gaps ranging from 2.5-3.1 eV,19-23 the germananes have ~1.6-1.8 eV gaps.14,16,18 Furthermore, recent theoretical calculations have predicted the 2D stannananes to be quantum spin hall topological insulators with 0.3-0.4 eV gaps.24,25 Despite these exciting predictions there have been no experimental reports of any tin-containing graphane analogues. It is unclear if many of the proposed ligand terminations on tin in a 2D honeycomb lattice are even chemically stable. Indeed, previous studies on 2D silicane/germanane alloys have shown that silicon has a strong chemical preference for hydroxide termination, whereas germanium is preferentially terminated by hydrogen.26 The creation of 2D sp3-hybridized tin lattices, germanium/tin graphane alloys and Sn/Group 15 (P, As, Sb) BN-like phases held by van der Waals forces (vdW) would allow a better understanding of how the electronic structure, optical properties, and the degree of spin orbit coupling can be tuned to realize enhanced optoelectronic properties and novel topological phenomena.
The chemical route to prepare these Group 14 graphane analogues relies on the topotactic deintercalation of alloys of precursor layered Zintl phases. For example, we have previous established that CaGe$_2$ can be topochemical transformed in acidic solutions to produce hydrogen-terminated germanane (GeH). The preparation of these 2D sp$^3$-hybridized tin lattices, germanium/tin graphane alloys and Sn/Group 15 (P, As, Sb) BN-like phases alloyed 2D Group 14 graphanes requires the synthesis of layered pure Sn-based, Ge/Sn alloyed and SnP/SnAs/SnSb-based Zintl phases, respectively. In literature, there are several known phases that feature 2D anionic sheets of either pure Sn or SnP/SnAs/SnSb. On the other hand, there are a couple reports of the synthesis of CaGe$_2$-$2x$Sn$_{2x}$ ($x=0.2-0.5$) however, these Zintl phases often have a nonhomogeneous alloy distribution. Furthermore, no such study on the topochemical deintercalation of these materials has been performed.

5.2 Experimental

5.2.1 Synthesis of BaSn$_2$, NaSnP, KSnAs, KSnSb and CaGe$_2$-$2x$Sn$_{2x}$

In a typical reaction, Ca, Ge and Sn were loaded in stoichiometric amounts into a quartz tube and evacuated on a Schlenk line to milliTorr pressures. The quartz tube was sealed under vacuum using a hydrogen-oxygen torch, annealed at 950 to 1050 °C for 16 to 20 hours, and cooled to room temperature over 1 to 5 days. The preparation and handling of all reagents were all done in an Ar-filled glovebox. Germanium (Ge, 99.999%, Acros), calcium (Ca, 99%, Acros) and tin (Sn, STREM Chemicals 99.8%) were purchased and used without further purification. The detailed procedures for the
growth of BaSn$_2$, NaSnP, KSnAs and KSnSb have been described in Section 2.2.1 of this manuscript.

5.2.2 Synthesis of 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb) and Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$

CaGe$_{2-2x}$Sn$_{2x}$ crystals were stirred in concentrated HCl$_{aq}$ for 5 to 14 days at -40 °C. To purify the Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ samples, the resulting product was washed with Milli-Q H$_2$O followed by distilled acetonitrile. Samples were dried at room temperature on a Schlenk line and kept in an Ar-filled glovebox. For the organic-terminated 2D Sn/Group 15 phases, crystals of NaSnP, KSnAs and KSnSb were stirred in a solution of the alkyl halide deintercalant (in 1:1 stoichiometric ration with the precursor Zintl phase) and dry acetonitrile for 1 to 14 days. The reaction solutions were kept in an air-free rubber o-ring sealed round bottom flask that is purged with Ar. Various reaction temperatures ranging from room temperature down to -40°C were employed for these reactions.

5.2.3 X-ray Diffraction of CaGe$_{2-2x}$Sn$_{2x}$, 2D Sn(Ethyl/methyl)Pn (Pn = P, As and Sb) and Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$

Flat Plane and Capillary mode X-ray diffraction patterns of the samples (germanium was added as an internal standard) were collected on a Bruker D8 powder X-ray diffractometer (Sealed Cu X-ray tube: 40 kV and 50mA). The lattice parameters of the Zintl phases were obtained through Rietveld Analysis of the lab data.
5.2.4 Fourier-Transform Infrared (FTIR) Spectroscopy of 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb) and Ge\textsubscript{1-x}Sn\textsubscript{x}H\textsubscript{1-x}(OH)\textsubscript{x}

Mid-IR (400-4000 cm\textsuperscript{-1}) transmittance spectra of KBr-dispersed samples were collected on a Perkin-Elmer Frontier Dual-Range FIR/Mid-IR spectrometer that was loaded in an Ar-filled glovebox.

5.2.5 Raman Spectroscopy of NaSnP, KSnAs, KSnSb, 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb) and Ge\textsubscript{1-x}Sn\textsubscript{x}H\textsubscript{1-x}(OH)\textsubscript{x}

Raman scattering spectra were collected using a Renishaw InVia Raman equipped with a CCD detector. The Raman spectra were collected using a 633/785 nm near-IR diode laser as illumination source.

5.2.6 Tin Percentage Determination of Ge\textsubscript{1-x}Sn\textsubscript{x}H\textsubscript{1-x}(OH)\textsubscript{x}

The various tin content in Ge\textsubscript{1-x}Sn\textsubscript{x}H\textsubscript{1-x}(OH)\textsubscript{x} were obtained through X-ray fluorescence measurements using a DELTA hand-held X-ray fluorescence analyzer. Germanium and tin powder mixtures with 0%, 1%, 2.5%, 5%, 7.5% and 10% tin were used as calibration standards. The air sensitivity of the Zintl phase precluded the XRF measurements and the determination of the Sn percentage of the Zintl phase precursors.

5.2.7 Absorption measurements of 2D Sn(Ethyl/Methyl)Pn (Pn = P, As and Sb) and Ge\textsubscript{1-x}Sn\textsubscript{x}H\textsubscript{1-x}(OH)\textsubscript{x}

All absorption measurements were collected using a Perkin Elmer Lambda 950 UV/Vis NIR spectrophotometer. Band gap determination was performed using diffuse reflectance absorbance setup that utilizes an integrating sphere. For the oxidation studies, to confirm the changes occurred throughout the bulk of the sample, transmission measurements were performed on ~3μm-thick samples exfoliated onto
Polydimethylsiloxane, in addition to diffuse reflectance measurements. The thickness of the exfoliated flakes was calibrated using a KLA-Tencor Alpha-Step profilometer. For the MIR regime, ($400$-$4000$ cm$^{-1}$) diffuse reflectance spectra of KBr-dispersed samples were collected on a Perkin-Elmer Frontier Dual-Range FIR/Mid-IR spectrometer that is equipped with a diffuse reflectance mount with an integrating sphere and is loaded in an Ar-filled glovebox.

### 5.2.8 X-Ray Photoelectron Spectroscopy

The X-Ray Photoelectron spectra of the samples were taken using a Kratos Axis Ultra X-Ray Photoelectron Spectrometer with a monochromated (Al) X-ray source. Energy calibration was performed using the C 1s peak.

### 5.2.9 Photocurrent Measurements of GeH and Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$

Gold (20 nm) and Silver (100 nm) contacts were deposited onto the bulk flakes via E-beam evaporation through a shadow mask. The wavelength-dependent photocurrent response at 3V was measured using a Keithley 6340 Sub-femtoamp meter and a variable wavelength tungsten filament light source equipped with a monochromator (PV Measurements). The intensity of the light source was calibrated using a Silicon photodiode.

### 5.2.10 Cyclic Voltammetry of the Layered Zintl Phases and the Precursor Alkyl Iodides

To measure the cyclic voltammograms of the air- and moisture-sensitive layered Zintl phases, coin cells made from a paste of carbon black and the target Zintl phase using polytetrafluoroethylene as a binder. These pastes were sandwiched between a potassium metal anode and a Ni mesh cathode as a current collector.
the cyclic voltammograms of the alkyl iodides were measured using a standard 3-electrode set-up using a glassy carbon as a working electrode, a carbon counter electrode and an Ag+/Ag reference electrode (0.55 V) under an inert Ar atmosphere. All cyclic voltammetry measurements were performed on a Gamry Reference 600 potentiostat. Solutions of KPF₆ in propylene carbonate/ethylene carbonate (PC/EC) were used as electrolyte solutions for all electrochemical measurements.

5.3 Results and Discussion

5.3.1 Band Gap Tuning of Germanane via Alloying with Sn

The preparation of the 2D germanium/tin graphane alloys was accomplished by the topotactic deintercalation of CaGe₂₋₂ₓSn₂ₓ (x =0, 0.04, 0.07, 0.09) (Figure 5.1a). First, crystals of CaGe₂₋₂ₓSn₂ₓ (Figure 5.1a) were synthesized by sealing stoichiometric amounts of Ca, Ge and Sn inside a quartz tube, annealing to 950-1050 °C, and cooling over a period of 3-5 days. The resulting CaGe₂₋₂ₓSn₂ₓ crystals formed two-layer hexagonal P6₃mc unit cells similar to α-CaGe₂³³ where the c-axis corresponds to the out-of-plane direction while the a/b-axes correspond to the in-plane lattice directions, as determined via X-ray diffraction (XRD) (Figure A.36a). A systematic increase in both the a/b- (in-plane) and the c-lattice (out-of-plane) parameters both confirm the incorporation of Sn in the Zintl phase (Figure 5.1b,c). In addition, the narrow Full Width Half Maximum (FWHM) of the (100) peak (Figure A.36b) around a 2-Theta value of 0.1° highlights the homogeneous distribution of tin in the lattice. The crystal structure of these samples was confirmed via Rietveld analysis (Table A.18-23). Rather than
homogeneously distributing onto both germanium 2a and 2b sites, Rietveld analysis gave a much better fit when Sn preferentially occupied the Germanium 2b position only, similar to what was reported for the case of CaSn$_{0.5}$Ge$_{1.5}$. The only other phase was residual tin impurity, which is subsequently removed during the HCl deintercalation step. Rietveld analysis suggested a ~4-5% phase fraction of tin impurity for all Zintl alloys. After extensive optimization of the synthetic parameters, the maximum amount of tin that could be incorporated into the starting Zintl phase while maintaining this homogeneous distribution was 9%.

**Figure 5.1** (a) Schematic of the topochemical deintercalation of CaGe$_{2-2x}$Sn$_{2x}$ to Ge$_{1-x}$Sn$_{x}$H$_{1-x}$(OH)$_{x}$ (Ca: yellow, Ge: blue, H: black, O: red and Sn: green). (b) a/b- and (c) c-lattice parameters of CaGe$_{2-2x}$Sn$_{2x}$ to Ge$_{1-x}$Sn$_{x}$H$_{1-x}$(OH)$_{x}$. (d) Optical image of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ crystals on a 2.5 mm grid paper. (e) Capillary mode powder XRD pattern of Ge$_{1-x}$Sn$_{x}$H$_{1-x}$(OH)$_{x}$ (x=0-0.09). The internal Ge standard is labeled with an asterisk (*).
These CaGe$_{2-2x}$Sn$_{2x}$ crystals were converted into 2D Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ (x=0-0.09) by the topotactic deintercalation in aqueous HCl at -40 °C for 5-14 days (Figure 5.1a). In this process, the Ca$^{2+}$ ions in between the layers are removed via the formation of a water-soluble CaCl$_2$ species while the Ge atoms are terminated by H$^+$ from HCl and the Sn atoms are terminated by OH$^-$ from water. After HCl treatment, the product was filtered and washed with water to remove residual CaCl$_2$, and then acetonitrile, and subsequently dried under vacuum. The resulting platelet-shaped crystallites were 2-3 mm in length and width, and 10-100 µm in thickness (Figure 5.1d). Calibrated X-ray Fluorescence measurements of these crystals confirm the Ge:Sn ratio (Figure A.37).

XRD of these platelets confirmed the transformation into a 2D Ge$_{1-x}$Sn$_x$ analog (Figure 5.1e). Similar to GeH, the diffraction can be fit to a 2H unit cell where there are two Ge$_{1-x}$Sn$_x$ layers per hexagonal c-axis unit cell d-spacing. In this unit cell, the a/b-axis corresponds to the in-plane direction, parallel to the 2D germanium/tin layer while the c-axis corresponds to the out-of-plane direction. The position of the (002) peak and the (100) peaks were determined from an XRD pattern using an internal germanium standard. Compared to the original CaGe$_{2-2x}$Sn$_{2x}$ unit cell parameters, the a/b-direction is slightly contracted (Figure 5.1b) and the c-direction is significantly expanded in 2D Ge$_{1-x}$Sn$_x$ (Figure 5.1c). Furthermore, there is a significant increase in the FWHM of the (002) and the (100) peaks after the deintercalation process, with values close to what was observed in GeH (Figure A.38). Also, after deintercalation there is an increase in all the unit cell parameters with increasing Sn, suggesting that Sn remains in the lattice. The observed ~0.1 Å contraction in the a/b-direction is consistent with the change observed for going from CaGe$_2$ to GeH. However, the 1.2 Å c-axis expansion is much larger than
the ~0.4 Å increase that is observed when replacing a Ca$^{2+}$ in CaGe$_2$ with 2 Ge-H bonds between each layer.$^{14}$ This suggests the presence of –OH termination of the Sn substituents which contributes to the larger interlayer c-axis spacing.

To further elucidate the identity of the surface terminating ligand, transmission-mode FTIR measurements were performed (Figure 5.2a). Upon tin incorporation, a broad O–H stretching mode at ~3450 cm$^{-1}$ as well as a broad, intense Sn–O stretching mode centered at ~560 cm$^{-1}$ are observed.$^{34,35}$ Sn-H stretching modes centered at ~1700-1900 cm$^{-1}$ were not observed at any concentration of Sn.$^{36-41}$ Additionally, in all samples, extremely strong Ge–H stretching modes centered at ~2000 cm$^{-1}$, weaker wagging modes that occur at 570 cm$^{-1}$, 507 cm$^{-1}$, and 475 cm$^{-1}$, and weak vibrational modes at 770 and 825 cm$^{-1}$, consistent with bond-bending Ge–H$_2$ from nearest neighbor Ge atoms at the edges of the crystalline sheets are observed.$^{14}$ We do not observe any broad intense, Ge–O–Ge or Ge–O vibrational modes that should occur between 800 and 1000 cm$^{-1}$.

Furthermore, there is a consistent red shift in the Ge–H stretching frequency and the major Ge–H wagging mode upon increasing Sn incorporation (Figure A.39). For example, at a maximum of 9% Sn, the Ge–H stretching frequency decreases from 2002 cm$^{-1}$ to 1988 cm$^{-1}$ and the major Ge–H wagging mode decreases from 482 cm$^{-1}$ to 470 cm$^{-1}$. This is consistent with previously reported shifts observed in alloyed Sn/Ge:H thin films.$^{42}$ Here, it has been established that the lower electronegativity of neighboring Sn atoms as compared to Ge reduces the Ge-H vibrational frequency. Taken together, after deintercalation in HCl, the Sn atoms are terminated with –OH groups, and the Ge atoms remain terminated with –H.
Raman spectroscopy further confirms the alloy formation of the 2D network. Previous measurements showed that GeH exhibits $E_2$ Ge-Ge Raman active modes at 302 cm$^{-1}$, and an $A_1$ out-of-plane Raman active mode at 228 cm$^{-1}$, which were assigned by the close agreement with $ab$ initio calculations.$^6$ With increasing tin, there is an increasing shift in both Raman modes to lower energies, and at 9% tin, the $E_2$, and $A_1$ mode shift to 299 cm$^{-1}$ and 221 cm$^{-1}$, respectively (Figure 5.2b). Furthermore, the FWHM of the $E_2$ vibration also increases with increasing tin concentration (Figure A.40). This broadening in the FWHM and the decrease in vibrational phonon energy with increasing tin are also observed in 3D tin/germanium alloys, which occur due to the increasing average Ge-(Ge/Sn) bond length, as well as the increasing disorder in the effective mass distribution, respectively.$^{42-45}$
Figure 5.2 (a) Transmission mode FTIR spectra of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ (x=0-0.09). (b) Raman spectrum of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ with the A$_1$ mode highlighted as an inset. Raman shifts of the (c) A$_1$ and (d) E$_2$ phonon modes of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ as a function of Sn concentration.
To determine the influence of Sn-OH substitutions on the optical band gap of GeH, we performed diffuse reflectance absorption measurements (DRA) on powders (Figure 5.3a). The silver-black materials have a broad absorption over all visible wavelengths, and there is a systematic decrease in the absorption band edge with increasing tin concentration (Figure 5.3b, A.44). The linear fitting of the absorption edges of these materials results to a general decrease in the band edge from 1.59 eV for GeH down to the following band gap energies at different Sn concentrations: 1.52 ± 0.01 eV at 4%, 1.45 ± 0.01 eV at 7% and 1.38 ± 0.02 eV at 9% Sn. This shift in band gap shows a similar trend to 3D germanium/tin alloys where a decrease in band gap with increasing tin percentage is also observed.46,47 An attempt to determine whether these materials are direct band gap materials was performed by fitting the Kubelka-Munk absorbance assuming direct-allowed, direct-forbidden, indirect-allowed and indirect-forbidden gaps using the Tauc/Davis-Mott models of 2D and 3D densities of states (Figure A.41-43).48,49 For the 2D DOS model, a direct allowed band gap is characterized by a discontinuity in the absorbance resulting from the step function of the absorbance $A(\hbar\omega)$ at photon energy $\hbar\omega$. On the other hand, an indirect allowed band gap is characterized by an absorbance function proportional to $\hbar\omega - E_g' \pm E_p$ where $E_g'$ is the energy of the indirect band gap and $E_p$ is energy of the corresponding phonon mode. However, it has been experimentally established that Tauc/Davis Mott approximations very often do not definitely determine the direct or indirect nature for materials with 2D densities of states.48,49 The determination of a band gap character of these materials (direct/indirect) is further complicated in these materials by the presence of defects or disorder in the lattice, which is evident from the broad Urbach edge at the absorption tail.
Figure 5.3 (a) Diffuse reflectance absorption spectrum of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ plotted in terms of the Kubelka-Munk function, F(R), and the photon energy. (b) Optical band gap of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ versus the Sn concentration.

The air stability of these alloys was probed via a 15-day air exposure of a representative Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ sample. After exposure to air, the absorption onset of the material decreases by ~0.2 eV (Figure 5.4a). This occurs in both diffuse reflectance (Figure 5.4a) and transmission (Figure A.45) experiments, suggesting that the sample is changing uniformly. A sharp vibrational feature around 847 cm$^{-1}$ and a broad vibrational feature around 900 cm$^{-1}$ also emerged in the FTIR spectrum (Figure 5.4b). These vibrational modes correspond to Ge-O vibrations, that have been observed in amorphous GeO$_x$. No other changes were observed in the FTIR spectrum (Figure A.46). X-ray photoelectron spectroscopy (XPS) (Figure 5.4c) also confirmed the oxidation of germanium through the appearance of a shoulder centered around 1219 eV which is indicative of the presence of Ge$^{2+/3+}$ 2p$_{3/2}$ peak. A new shoulder centered around 487 eV, corresponding to a Sn$^{4+}$ 3d$_{5/2}$ peak, was observed after 15 days of exposure which indicates that tin on the surface is also oxidized (Figure 5.4d). Since no new peaks
were observed in the XRD after exposure to air, this suggests that the flakes are partially transforming to an amorphous GeO$_x$/SnO$_x$ phase.

**Figure 5.4** (a) Diffuse reflectance absorption measurements, (b) FTIR spectra, and XPS spectra of the (c) Ge 2p$_{3/2}$ and (d) Sn 3d$_{5/2}$ of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ before (red) and after 15 day exposure to air (black) and after subsequent 1 M HCl washing (green).

This amorphous GeO$_x$/SnO$_x$ layer can be readily removed via an HCl rinse. We rinsed these 15-day samples in 1 M HCl for 30 minutes, washed with acetonitrile and dried under vacuum. After washing, the absorption onset reverted back to 1.38 eV (**Figure 5.4a**) and the vibrational modes at 847 cm$^{-1}$ and 900 cm$^{-1}$ corresponding to GeO$_x$ disappeared in the FTIR spectrum (**Figure 5.4b**). Additionally, the XPS spectrum only showed Ge$^{1+}$ 2p$_{3/2}$ peak (**Figure 5.4c**) and majority of the intense Sn$^{4+}$ 3d$_{5/2}$ peak also disappeared (**Figure 5.4d**). Previous studies have established that GeO$_x$ can be washed with HCl forming a soluble GeCl$_4$ species, creating a Ge vacancy and terminating the
neighboring Ge atoms with hydrogen.\textsuperscript{50} While there have been considerably fewer studies with tin, these results show that a similar surface cleaning mechanism likely occurs with the removal of amorphous SnO\textsubscript{x}.

As has been established in 3D germanium/tin alloys, photoconductivity measurements are a powerful method to probe the effect of tin substitution on the optoelectronic properties of semiconductor materials.\textsuperscript{51-53} We performed two-probe photoconductivity measurements on single crystals of GeH and \( \text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}\text{(OH)}_{0.09} \). 100 nm Ag/20 nm Au contacts were deposited via an e-beam evaporator using a 25 \( \mu \text{m} \) shadow mask (\textit{Figure 5.5a}). These non-extrinsically doped crystals exhibit linear current vs. voltage characteristics, indicative of ohmic contacts, with resistances in the 10 G\( \Omega \) range (\textit{Figure 5.5b}). A significant photoconductive response is observed in the pure GeH device when exciting with above band gap light, and occurs rapidly with photoresponse rise times <1s (\textit{Figure 5.5c}). The wavelength dependent photocurrent response has an onset of 1.5 eV, and a maximum at 2.0 eV. Upon Sn incorporation, both the onset and the maximum are shifted to 1.36 eV and 1.88 eV, respectively, which parallels the change in the absorption spectrum (\textit{Figure 5.5d}), and proves that tin alloying is a viable route towards lowering the band gap in these 2D materials.
Figure 5.5 (a, left) Image of the actual device based on Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ and (a, right) schematic illustration and dimensions of the photodetector (not drawn to scale). (b) Typical I-V plot of the Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ photodetector in dark and at 600 nm illumination. (c) Photocurrent response at selected illumination wavelengths and (d) wavelength-dependent normalized photocurrent for the Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ photodetector compared to GeH at a 3V bias voltage.

5.3.2 Synthetic Routes Towards BN-like SnPn (Pn = P, As and Sb) Graphane Derivatives

The prediction of the possible realization of quantum spin Hall effect in $sp^3$-hybridized 2D Sn systems$^{24,25}$ has motivated the search for chemical routes towards the synthesis of these phases. As discussed in the previous section, the limited alloying of Sn into the CaGe$_2$ lattice necessitates the use of different precursor Zintl phases to enable the growth of 2D graphane analogues with Sn $\geq$50% of the lattice from topochemical
deintercalation. For the creation of a pure 2D Sn system via topochemical deintercalation, the only known layered Zintl phase precursor is BaSn$_2$. However, there are several known Zintl phase precursors that feature single atom thick honeycomb networks of Sn and a pnictogen atom in an alternating honeycomb framework separated by a Group 1 cation, including NaSnP, KSnAs and KSnSb. In order to create a pure 2D Sn system, we have subjected BaSn$_2$ towards numerous deintercalation reactions using HCl (both in aqueous and organic solvents) and various organic alkyl halides (C1 to C6, iodides, bromides and chlorides) in dry acetonitrile at various temperatures and in inert Ar enviroments. However, all of these attempts resulted in amorphous phases post-deintercalation. One possible reason for the amorphization is the extreme air-sensitivity of BaSn$_2$, which oxidizes and amorphizes within a couple of minutes in a glovebox environment even with <0.5 ppm O$_2$ and H$_2$O. Another possible reason is the weak Sn-Sn bonding within the anionic sheet which arises due to the lack of iconicity in the sheets and significantly longer Sn-Sn bond lengths compared to $\alpha$-Sn.

To mitigate the possible amorphization due to the lack of in-plane bonding ionicity, we explored the deintercalation of 1-14-15 phases which are comprised of sheets of Sn coupled with a Group 15 element such as P, As or Sb in a 1:1 stoichiometry and are arranged in a BN-like fashion. Because of the air and moisture sensitivity of these phases, we only attempted the deintercalation reactions in dry acetonitrile using alkyl halides as deintercalants. By reacting NaSnP with methyl iodide at -10°C, crystalline deintercalation products were obtained (Figure 5.6a) which featured sharp in-plane diffraction peaks that correspond to a 3.80 Å $a$-lattice parameter which is slightly contracted as compared to the precursor NaSnP Zintl phase (3.88 Å). Two Raman-active modes were also observed
which we assign as in-plane (E”) and out-of-plane (A’) modes (Figure 5.6b). From FTIR measurements (Figure 5.6c), we observe methyl functionalization only on the Sn atoms but not on the P atoms. This suggests that the contraction in the in-plane direction is possibly due to the rippling of the sheets due to the absence of a methyl group on one side of the sheet. Lastly, a 1.4 eV absorption edge was observed from the absorption spectra of Sn(CH$_3$)P (Figure 5.6d) which is significantly larger compared to the precursor NaSnP which has a band gap of 0.94 eV. The deintercalation of NaSnP to Sn(CH$_3$)P does not only allow for the creation of 2D $sp^3$-hybridized vdW systems but also provides an avenue towards the tuning of the electronic properties of its bulk counterparts.
Figure 5.6 (a) Schematic of the topochemical deintercalation of NaSnP at -10°C using methyl iodide as a deintercalant. Bottom left: crystal model of the proposed Sn(CH$_3$)$_3$P structure where only the Sn atoms are functionalized. Bottom Right: XRD pattern of Sn(CH$_3$)$_3$P which highlights the in-plane diffraction peaks. (b) Raman spectrum of Sn(CH$_3$)$_3$P showing the in-plane (E'') and out-of-plane (A') Raman modes. (c) FTIR spectrum of Sn(CH$_3$)$_3$P showing the presence of methyl vibrational modes and the functionalization of only the Sn atom. (d) Absorbance spectrums of Sn(CH$_3$)$_3$P featuring an extrapolated 1.4 eV absorption edge.

In order to create 2D $sp^3$-hybridized vdW systems that have strong SOC for the possible realization of topologically protected, we sought to apply the deintercalation route that we used to prepare Sn(CH$_3$)$_3$P to from NaSnP, to the 1-14-15 layered Zintl phases that have heavier Group 15 elements such as As and Sb. However, numerous attempts on the deintercalation of KSnAs and KSnSb using methyl iodide at various
temperatures have always resulted on a white to yellow powdery amorphous product in a bright orange solution which was confirmed to be I$_2$ in the acetonitrile solution. With only the precursor Zintl phase and the methyl iodide deintercalant present in the reaction, the only possible route towards the formation of an I$_2$ species is through an underlying electrochemical process that occurs between the Zintl phase and methyl iodide and which forms highly-reactive organic free radicals that can amorphize the structure.

In order to probe this underlying electrochemical reduction of the alkyl halide deintercalant, we measured cyclic voltammograms of coin cell assemblies (Figure 5.7a) made from the layered Zintl phases in propylene carbonate (PC)/ethylene carbonate (EC) with KPF$_6$ as electrolyte. From these voltammograms (Figure 5.7b), we observe anodic peaks for the three layered Zintl phases which we assign to the 1$e^-$ oxidation of the lattice. No cathodic peaks were observed on either of the three Zintl phases which might indicate that the lattices amorphize after the 1$e^-$ reduction process. A consistent shift to more positive oxidation potentials were also observed going from the less electronegative Group 15 element in KSnSb to the most in NaSnP (Table 5.1). On the other hand, the reduction potentials of several alkyl iodides going from methyl to butyl were also probed via cyclic voltammetry in PC/EC solutions with KPF$_6$ as electrolyte (Figure 5.7c). As expected, these electrochemical measurements revealed that methyl iodide has the greatest propensity for being reduced while butyl iodide, which had the most negative potential is the hardest to reduce (Table 5.1).
Figure 5.7 (a) Schematic for the coin cell used for the electrochemical measurement of the oxidation potential of the layered Zintl phases. (b) Cyclic voltammogram of the three layered 1-14-15 layered Zintl phases that were deintercalated in this study. (c) cyclic voltammograms of the alkyl iodide deintercalants that were used in this study.

Table 5.1 Summary of the electrochemical potentials deduced from cyclic voltammetry measurements of the precursor Zintl phases and the alkyl iodide deintercalants.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{Ox}}$ (V) vs. SHE</th>
<th>$E_{\text{Red}}$ (V) vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSnP</td>
<td>-0.70</td>
<td>--</td>
</tr>
<tr>
<td>KSnAs</td>
<td>-1.00</td>
<td>--</td>
</tr>
<tr>
<td>KSnSb</td>
<td>-1.15</td>
<td>--</td>
</tr>
<tr>
<td>Methyl Iodide</td>
<td>--</td>
<td>-0.88</td>
</tr>
<tr>
<td>Ethyl Iodide</td>
<td>--</td>
<td>-1.44</td>
</tr>
<tr>
<td>Propyl Iodide</td>
<td>--</td>
<td>-1.60</td>
</tr>
<tr>
<td>Butyl Iodide</td>
<td>--</td>
<td>-1.85</td>
</tr>
</tbody>
</table>

From matching the electrochemical oxidation potentials of the Zintl phase and the one-electron reduction potentials of the alkyl iodides, we can device a generalized scheme towards avoiding the underlying amorphization process and creating crystalline 2D $sp^3$-hybridized Sn(alkyl)Pn (Pn = P, As and Sb) vdW phases (Figure 5.8). First, amorphization of the 2D framework occurs when it is thermodynamically favorable for
the Zintl phase to reduce the organohalide precursor to form the radical alkyl group. These radicals will amorphize the honeycomb Sn-Pn framework. By matching the oxidation potential of a specific Zintl phase precursor with a corresponding alkyl iodide that has a more negative reduction potential, the one-electron transfer process from the Zintl phase to the alkyl iodide is unflavored. This suppression organic free radicals limits amorphization, enables the topotactic metathesis reaction to proceed, resulting in crystalline 2D Sn-Pn frameworks.

**Figure 5.8** Generalized scheme on the electrochemical matching of the oxidation potentials and reduction potentials of the precursor Zintl phases and the alkyl iodide deintercalants, respectively. Inset is the electron transfer mechanism that illustrates the pathway towards the $1e^-$ reduction of the alkyl iodide and the subsequent amorphization of the deintercalation product.
Using the generalized scheme presented in Figure 5.8, ethyl iodide, which has a significantly more negative reduction potential than the oxidation potentials of NaSnP, KSnAs and KSnSb was used for the room temperature topochemical deintercalation of these layered Zintl phases. There was no evidence for I₂ formation, indicating that the one-electron radical pathway did not exist. From this, post-reaction, mm-sized flakes were obtained (Figure 5.9a) Similar to Sn(CH₃)P, FTIR analyses of the deintercalated products reveal that only the Sn atoms are functionalized with an ethyl group (Figure 5.9b). Note that all of the peaks can be assigned to ethyl vibrational modes and to a Sn-C stretching mode. Raman spectroscopy on these resulting products, on the other hand, shows that the two Raman modes that we attribute to the in-plane and out-of-plane modes are shifted to lower wavenumbers as compared to their corresponding precursor Zintl phase, which again are indicative of an elongation of the in-plane bond lengths in the deintercalated phases compared to the Zintl phase precursors (Figure 5.9c). The broadness of the Raman modes of the deintercalated phases is indicative of some degree of disorder in the structure, which is also evident in the lack of crystalline peaks in the diffraction pattern of the deintercalated phases. This suggests that there is an additional route towards the amorphization of the deintercalated phases, beyond the radical-induced amorphization process. The most likely cause for this is the temperature instability of the resulting deintercalated phases even at room temperature. For instance, in GeH, the onset of temperature-induced amorphization observed to occur around 50°C, which is significantly lower than the melting point of 3D Ge.¹⁴,¹⁶,¹⁸ Last, even though the deintercalated phases did not show any crystalline peak in the diffraction patterns, the absorbance measurements still featured absorption edges for all the three phases which
consistently shift to lower energies going from the phase that contained most electronegative and smallest Group 15 element (Sn(CH$_2$CH$_3$)P) to the least electronegative and largerst Group 15 element (Sn(CH$_2$CH$_3$Sb)) (Figure 5.9d). This decrease in the apparent gap with larger Group 15 elements is consistent with the weaker orbital overlap in of the in-plane bonding orbitals (valence band) which are destabilized and go higher in energy closer to the anti-bonding orbitals (conduction band).

**Figure 5.9** Structural and optical properties of 2D Sn(CH$_2$CH$_3$)Pn (Pn = P, As an Sb) phases. (a) Representative post-reaction flakes of Sn(CH$_2$CH$_3$)Sb. (b) FTIR spectra of the Sn(CH$_2$CH$_3$)Pn phases highlighting the various vibrational modes of ethyl and Sn-C stretching. (c) Raman spectra comparison of the deintercalated phases Sn(CH$_2$CH$_3$)Pn phases with the precursor Zintl phases. (d) Diffuse reflectance absorbance measurements of the deintercalated phases highlighting the absorption onset energies the small peaks below 0.5 eV are IR-active vibrational modes of the ethyl group.
5.4 Conclusion

In summary, we have demonstrated for the first time that Sn can be incorporated onto the 2D germanane framework, thus allowing control over the optoelectronic properties and phonon modes, similar to alloying in three-dimensional semiconductors. In the 2D lattice, tin is bound by a hydroxide ligand, whereas the germanium remains terminated to hydrogen, as occurs in the non-alloyed GeH lattice. The maximum amount of tin incorporation on the 2D framework is determined by the maximum stoichiometry of tin that can be incorporated into the precursor Zintl phase, in contrast to the 3D alloyed semiconductors, which are often limited by their intrinsic thermodynamic instability. These alloys also oxidize upon exposure to air but can be reverted back to their non-oxidized state via an HCl washing process. In addition, we also presented insights on the deintercalation of Sn-based layered Zintl phases (NaSnP, KSnAs and KSnSb) into 2D organic-functionalized materials. These reactions are limited by an underlying electrochemical process, wherein a one-electron reduction of the alkyl halide produces organic radicals that amorphize the Sn framework. By reacting the alkyl halide and Zintl phase pair, in which the alkyl halide’s reduction potential is more negative than the oxidation process of the Zintl phase, enables the formation of crystalline, two-dimensional organic-terminated Sn(organic)Pn phases. The 2D Sn(CH2CH3)Pn (Pn = P, As and Sb) phases have absorption edges ranging from 1.3 eV (P) down to 0.2 eV (Sb). Thus, Sn-containing graphane are promising materials for next generation device building blocks, and materials exhibiting novel physical phenomena.
5.5 References


(32) Xu, Z., University of Houston, 1999.


Chapter 6: Conclusions and Outlook

Herein, we have presented three distinct classes of exfoliatable and non-exfoliatable layered materials that possessed a wide range of electronic and magnetic properties. The efforts in both experiments and theoretical predictions that went to this dissertation have shed light on the realization, through the different classes of materials that were explored in this study, of the properties and potential of Tin and other heavier main group elements in 2D. Specifically, we have experimentally demonstrated the electronic properties of bulk layered Zintl phases and have determined that CaSi$_2$, CaGe$_2$ and EuGe$_2$ are metallic while the Zintl phases with more significant in-plane bonding iconicity (NaSnP, KSnAs and KSnSb) are semiconducting. We have also shown that the major contributing factor in the Raman-active modes in these layered Zintl phases are the in-plane bond lengths and reduced masses of the elements that sit on Raman-Active Wyckoff sites. By using NaSn$_2$As$_2$ as a model system, we have demonstrated the potential of the relatively less explored class of AT$_2$Pn$_2$ Zintl phases as readily exfoliatable 2D materials with distinct physical properties. In addition, the creation of a magnetic analogue of the ASn$_2$As$_2$ phase did not only demonstrate the flexibility of this class of Zintl phases to accommodate various cations within the layers but also enabled the discovery of a new exfoliatable 2D magnet that has anisotropic Eu$^{2+}$ spin coupling wherein the spins are coupled ferromagnetically in-plane and antiferromagnetically out-
of-plane. In terms of the $sp^3$-hybridized van der Waals phases, we showed that the controlled inclusion of Sn in the 2D GeH lattice allows for a synthetic control towards the effective tuning of the band gap in these van der Waals phases phases. Lastly, we have presented insights on the topochemical deintercalation chemistry of 2D Sn $sp^3$-hybridized van der Waals phases wherein one of the major factors that drives the creation of these materials is the precise matching of the reduction potential of the organic halide deintercalant with the oxidation potential of the precursor layered Zintl phase.

As Feynman once said, when talking about nanotechnology and miniaturization in condensed matter, “there’s plenty of room at the bottom”. In these 2D phases, especially in the discovery of new topologically-protected phases, there is still plenty of room at the bottom (of the periodic table) for 2D main group materials that have strong spin-orbit coupling—one of the main factors that drives phases to have topologically-protected states. The flexibility of the layered Zintl phases in accommodating a diverse set of elements and whose electron counts, according to Zintl counting rules, already yield narrow gap semiconductors allow for the discovery of new phases that have heavy main group elements such as In, Pb, Bi and Te or heavier transition metals while still maintaining fully-filled (semiconducting) valence bands. As for 2D magnets, of the known exfoliatable 2D magnets, EuSn$_2$As$_2$ is the only phase that is coupled ferromagnetically in-plane and antiferromagnetically out-of-plane. The study of the magnetic properties of this phase in the single layer to few layer regime, which is currently limited by the available probes for magnetic properties in 2D, offers the possibility of controlling the dominant magnetic interactions layer-by-layer.
Overall, the classes of 2D layered materials presented in this study opens up the doors for the discovery of new members of these families of phases. Furthermore, the deeper understanding of the synthesis, structure and properties of these emerging classes of 2D layered materials based on a Sn in a honeycomb lattice alone, has enabled the realization of new topological phases, semiconductors, anisotropic two-carrier metals and anisotropic magnets. This unprecedented potential of these phases as platforms for various properties and novel physical phenomena allows for the use of these phases as components and building blocks for next-generation electronic, thermoelectric and spintronic devices and applications.
Appendix A: Supporting Figures For Chapters 2 to 5
Figure A.1 Atom displacements for the out-of-plane ($A_{1g}^{1-3}$) and in-plane ($E_g^{1-3}$) Raman vibrational modes of CaSi$_2$. 

Chapter 2: Topologically Protected States, Optical Properties and Raman-Active Vibrational Modes in Metallic and Semiconducting Layered Zintl Phases
Figure A.2 Unpolarized Raman spectra of 6R-layered Zintl phases, (a) CaSi$_2$, (b) CaGe$_2$, showing both the in-plane and out-of-plane Raman modes.
Figure A.3 Powder XRD Rietveld refinement results for CaSi$_2$ using TOPAS. The green cross marks correspond to the Bragg reflections of CaSi$_2$. 
Table A.1 Crystal Data and Refinement Results for CaSi$_2$

<table>
<thead>
<tr>
<th></th>
<th>CaSi$_2$</th>
<th>Cu K$_{\alpha_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>radiation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R-3m$ (No. 166)</td>
<td>$\lambda = 1.5406$</td>
<td>$\AA$</td>
</tr>
<tr>
<td>$a/b = 3.855(8)$</td>
<td>$2\theta = 10$</td>
<td>$90$</td>
</tr>
<tr>
<td>$c = 30.65(6)$</td>
<td>$T = 298$ K</td>
<td></td>
</tr>
<tr>
<td>$\alpha/\beta = 90^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V = 394.6(2)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.87/5.99(%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A.2 Fractional atomic coordinates and isotropic displacement parameters based on the refined CaSi$_2$ structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.080(11)</td>
<td>0.75(2)</td>
</tr>
<tr>
<td>Si</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.346(14)</td>
<td>0.99(2)</td>
</tr>
<tr>
<td>Si</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.181(15)</td>
<td>0.99(2)</td>
</tr>
</tbody>
</table>

Figure A.4 Powder XRD Rietveld refinement results for $\beta$-CaGe$_2$ using TOPAS. The phase fraction of Ge was refined to be 24%. The green and orange cross marks correspond to the Bragg reflections of CaGe$_2$ and Ge, respectively.
Table A.3 Crystal Data and Refinement Results for CaGe$_2$

<table>
<thead>
<tr>
<th></th>
<th>CaGe$_2$</th>
<th>Cu $K_{a1}$ radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$-3$m$ (No. 166)</td>
<td>$\lambda = 1.5406$ Å</td>
<td></td>
</tr>
<tr>
<td>$a/b = 3.985(2)$</td>
<td>$2\theta = 10 - 70$</td>
<td></td>
</tr>
<tr>
<td>$c = 30.63(2)$</td>
<td>$T = 298$ K</td>
<td></td>
</tr>
<tr>
<td>$\alpha/\beta = 90^o$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^o$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V = 421.2(5)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp}$</td>
<td></td>
<td>$2.64/4.13$ (%)</td>
</tr>
</tbody>
</table>
Table A.4 Fractional atomic coordinates and isotropic displacement parameters based on the refined CaGe$_2$ structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B$_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.083(1)</td>
<td>0.72(8)</td>
</tr>
<tr>
<td>Ge</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.1827(0)</td>
<td>0.38(7)</td>
</tr>
<tr>
<td>Ge</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.3496(6)</td>
<td>0.38(7)</td>
</tr>
</tbody>
</table>

Figure A.5 Logarithmic plot of the co- and cross-polarized NaSnP Raman spectra highlighting the weak Raman modes in the spectra (arrows).
Figure A.6 Unpolarized Raman spectra of 2H-layered Zintl phases, (a) NaSnP, (b) KSnAs and (c) KSnSb, showing both the in-plane and out-of-plane Raman modes.

Figure A.7 Powder XRD Rietveld refinement results for NaSnP using TOPAS. The phase fraction of Sn was refined to be 15.9 %. The green and orange cross marks correspond to the Bragg reflections of NaSnP and Sn, respectively.
Table A.5 Crystal Data and Refinement Results for NaSnP.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSnP</td>
<td>Cu K$\alpha$1</td>
</tr>
<tr>
<td>radiation</td>
<td></td>
</tr>
<tr>
<td>$P6_3mc$ (No. 186)</td>
<td>$\lambda = 1.5406$ Å</td>
</tr>
<tr>
<td>$a/b = 3.882(12)$</td>
<td>$2\theta = 10 - 90$</td>
</tr>
<tr>
<td>$c = 11.68(3)$</td>
<td>$T = 298$ K</td>
</tr>
<tr>
<td>$\alpha/\beta = 90^o$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^o$</td>
<td></td>
</tr>
<tr>
<td>$V = 152.4(11)$</td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
</tr>
<tr>
<td>$3.54/4.74(%)$</td>
<td></td>
</tr>
</tbody>
</table>
Table A.6 Fractional atomic coordinates and isotropic displacement parameters based on the refined NaSnP structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2b</td>
<td>1/3</td>
<td>2/3</td>
<td>0.281(11)</td>
<td>1.3(3)</td>
</tr>
<tr>
<td>P</td>
<td>2a</td>
<td>1/3</td>
<td>2/3</td>
<td>0.614(11)</td>
<td>0.92(3)</td>
</tr>
<tr>
<td>Sn</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.080(4)</td>
</tr>
</tbody>
</table>

Figure A.8 Powder XRD Le Bail fitting results for KSnAs using TOPAS. The green cross marks correspond to the Bragg reflections of KSnAs.
Table A.7 Crystal Data and Le Bail Fitting results for KSnAs.

<table>
<thead>
<tr>
<th>KSnAs</th>
<th>Cu $K_{\alpha_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>radiation</td>
<td></td>
</tr>
<tr>
<td>$P6_{3}mc$ (No. 186)</td>
<td>$\lambda = 1.5406$ Å</td>
</tr>
<tr>
<td>a/b = 4.100(3)</td>
<td>$2\theta = 10 - 60$</td>
</tr>
<tr>
<td>c = 12.824(1)</td>
<td>$T = 298$ K</td>
</tr>
<tr>
<td>$\alpha/\beta = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>$V = 186.74(1)$</td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
</tr>
<tr>
<td>5.01/6.57(%)</td>
<td></td>
</tr>
</tbody>
</table>
Figure A.9 Powder XRD Le Bail fitting results for KSnSb using TOPAS. The green cross marks correspond to the Bragg reflections of KSnSb.
Table A.8 Crystal Data and Le Bail Fitting results for KSnSb.

<table>
<thead>
<tr>
<th>KSnSb</th>
<th>Cu $K_{\alpha}$ radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P6_3mc$ (No. 186)</td>
<td>$\lambda = 1.5406 \ \AA$</td>
</tr>
<tr>
<td>$a/b = 4.352(6)$</td>
<td>$2\theta = 10 - 70$</td>
</tr>
<tr>
<td>$c = 13.14(2)$</td>
<td>$T = 298 \text{ K}$</td>
</tr>
<tr>
<td>$\alpha/\beta = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>$V = 215.7(6)$</td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
</tr>
<tr>
<td>$7.14/9.54(%)$</td>
<td></td>
</tr>
</tbody>
</table>
Figure A.10 Unpolarized Raman spectra of 1T-layered Zintl phases, (a) EuGe$_2$ and (b) BaSn$_2$, showing both the in-plane and out-of-plane Raman modes.
Figure A.11 Powder XRD Rietveld refinement results for EuGe$_2$ using TOPAS. The phase fraction of Ge was refined to be 10.6%. The green and orange cross marks correspond to the Bragg reflections of EuGe$_2$ and Ge, respectively.
Table A.9 Crystal Data and Refinement Results for EuGe$_2$.

<table>
<thead>
<tr>
<th>EuGe$_2$</th>
<th>Cu $K_{\alpha 1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>radiation</td>
<td></td>
</tr>
<tr>
<td>$P-3m1$ (No. 164)</td>
<td>$\lambda = 1.5406$ Å</td>
</tr>
<tr>
<td>$a/b = 4.102(3)$</td>
<td>$2\theta = 10 - 90$</td>
</tr>
<tr>
<td>$c = 4.999(4)$</td>
<td>$T = 298$ K</td>
</tr>
<tr>
<td>$\alpha/\beta = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>$V = 72.84(1)$</td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
</tr>
<tr>
<td>$3.86/5.51$%</td>
<td></td>
</tr>
</tbody>
</table>
Table A.10 Fractional atomic coordinates and isotropic displacement parameters based on the refined EuGe$_2$ structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B$_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.040(3)</td>
</tr>
<tr>
<td>Ge</td>
<td>2d</td>
<td>1/3</td>
<td>2/3</td>
<td>0.398(7)</td>
<td>0.39(3)</td>
</tr>
</tbody>
</table>
Figure A.12 Powder XRD Rietveld refinement results for BaSn$_2$ using TOPAS. The green cross marks correspond to the Bragg reflections of BaSn$_2$. 
Table A.11 Crystal Data and Refinement Results for BaSn₂.

<table>
<thead>
<tr>
<th>BaSn₂</th>
<th>Cu $K_{\alpha 1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>radiation</td>
<td></td>
</tr>
<tr>
<td>$P-3m1$ (No. 164)</td>
<td>$\lambda = 1.5406$ Å</td>
</tr>
<tr>
<td>$a/b = 4.660(2)$</td>
<td>$2\theta = 15 - 70$</td>
</tr>
<tr>
<td>$c = 5.539(3)$</td>
<td>$T = 298$ K</td>
</tr>
<tr>
<td>$\alpha/\beta = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>$\gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>$V = 104.2(1)$</td>
<td></td>
</tr>
<tr>
<td>$R_p/R_{wp} =$</td>
<td></td>
</tr>
<tr>
<td>4.60/6.34(%)</td>
<td></td>
</tr>
</tbody>
</table>
**Table A.12** Fractional atomic coordinates and isotropic displacement parameters based on the refined BaSn$_2$ structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.072(3)</td>
</tr>
<tr>
<td>Sn</td>
<td>2d</td>
<td>1/3</td>
<td>2/3</td>
<td>0.398(5)</td>
<td>0.083(3)</td>
</tr>
</tbody>
</table>

**Figure A.13** Kubelka-Munk diffuse reflectance spectra of metallic Zintl phases showing the broadband absorption across the visible and near-infrared range. The absorbance spectrum of KSnSb was included for reference.
Figure A.14 Diffuse reflectance absorbance spectra of semiconducting Zintl phases fitted using the Tauc-Davis-Mott models of 3D densities of states of (a) 3D indirect allowed, (b) 3D direct allowed transitions.

Table A.13 Summary of optical transitions obtained from the Tauc-Davis-Mott models for semiconducting layered Zintl phases under study.

<table>
<thead>
<tr>
<th>Phase</th>
<th>3D Direct Allowed (eV)</th>
<th>3D Indirect Allowed (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\hbar\omega-E_g)^2)</td>
<td>((\hbar\omega-E_g' + E_p)^{1/2})</td>
</tr>
<tr>
<td>NaSnP</td>
<td>1.28</td>
<td>0.95 ± 0.033</td>
</tr>
<tr>
<td>KSnAs</td>
<td>0.97</td>
<td>0.65 ± 0.023</td>
</tr>
<tr>
<td>KSnSb</td>
<td>0.80</td>
<td>0.54 ± 0.020</td>
</tr>
</tbody>
</table>
Chapter 3: Stability, Exfoliation and Anisotropic Electronic Properties of 
NaSn$_2$As$_2$—an Exfoliatable Layered Zintl Phase

**Figure A.15** Powder XRD Rietveld refinement results for NaSn$_2$As$_2$ using TOPAS.
Table A.14 TOPAS Rietveld Refinement parameters for NaSn₂As₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>NaSn₂As₂</td>
</tr>
<tr>
<td>Fw</td>
<td>410.253</td>
</tr>
<tr>
<td>Space Group</td>
<td>R-3m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.99998(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>27.5619(13)</td>
</tr>
<tr>
<td>Cell Volume (Å³)</td>
<td>381.91(2)</td>
</tr>
<tr>
<td>T (K)</td>
<td>295</td>
</tr>
<tr>
<td>Pattern Range (θ)</td>
<td>5-70</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>R_wp (%)</td>
<td>4.44</td>
</tr>
<tr>
<td>R_p (%)</td>
<td>3.19</td>
</tr>
</tbody>
</table>

Table A.15 Atomic coordinates for NaSn₂As₂ from Rietveld refinement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>B_eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>0</td>
<td>0</td>
<td>0.2095(7)</td>
<td>1</td>
<td>0.72(5)</td>
</tr>
<tr>
<td>As</td>
<td>0</td>
<td>0</td>
<td>0.4069(1)</td>
<td>1</td>
<td>0.34(7)</td>
</tr>
<tr>
<td>Na</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.41(4)</td>
</tr>
</tbody>
</table>
Table A.16 Selected bond lengths from the refined NaSn$_2$As$_2$ structure.

<table>
<thead>
<tr>
<th></th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-Sn</td>
<td>3.30</td>
</tr>
<tr>
<td>Na-As</td>
<td>3.07</td>
</tr>
<tr>
<td>Sn-As</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Figure A.16 Verification of the Sn:As stoichiometry in NaSn$_2$As$_2$ measured via X-Ray Fluorescence. Red data points correspond to different mixtures of elemental Sn and As to prepare a standard calibration curve.
Figure A.17 XPS spectra of the NaSn$_2$As$_2$ crystals after exposure to 4 days in air (green) and after etching the top 1 nm (red) using a Ar$^+$ ion etch, highlighting the a) Na 1s, b) Sn 4d, c) Sn 3d$_{5/2}$, and d) As 3d peaks.
Figure A.18 AFM images and height profiles of mechanically-exfoliated NaSn$_2$As$_2$ onto 285 nm SiO$_2$/Si.
Figure A.19 Step height analysis of AFM micrographs taken on exfoliated NaSn$_2$As$_2$ flakes with multiple step edges. Step thicknesses were obtained from averaged heights along the horizontal length of each step.
Figure A.20 AFM thickness histogram of different step heights obtained from mechanically-exfoliated NaSn$_2$As$_2$ showing that cleaved steps always have thicknesses that were multiples of $\sim 0.9 \pm 0.2$ nm.
Figure A.21 UV-Vis Spectrum of NaSn$_2$As$_2$ dispersed in various solvents.
Figure A.22 AFM images and height profiles of CHP-exfoliated NaSn\textsubscript{2}As\textsubscript{2} flakes that were prepared via dropcasting onto 285 nm SiO\textsubscript{2}/Si.
Figure A.23 AFM thickness histogram of 36 different flakes that were prepared via dropcasting CHP-exfoliated NaSn$_2$As$_2$ onto 285 nm SiO$_2$/Si.
Figure A.24 Representative EDX spectrum of solvent-exfoliated NaSn$_2$As$_2$.

Figure A.25 HRTEM image of CHP-exfoliated NaSn$_2$As$_2$ highlighting long-range order based on the (015) lattice fringes. Inset is a fast Fourier transform of the image showing a [2-51] zone axis.
**Figure A.26** XPS spectra of the liquid-exfoliated NaSn\textsubscript{2}As\textsubscript{2} flakes after exposure to 1 day (green) and 3 days in air (purple), highlighting the a) Na 1\textit{s}, b) Sn 3d\textsubscript{5/2}, and c) As 3d peaks.

**Figure A.27** Adhesion energy of NaSn\textsubscript{2}As\textsubscript{2} as a function of layer separation. The data for the DFT-D2 (plain GGA) calculation are red (blue). The interlayer separation is relative to the equilibrium separation of bulk NaAs\textsubscript{2}Sn\textsubscript{2}.
Figure A.28 ARPES spectrum of NaSn$_2$As$_2$, collected at 127 eV at 41 K.

Figure A.29 HSE band structure of a single layer NaSn$_2$As$_2$ which shows that the metallic character is preserved in isolated layers.
Chapter 4: Exfoliatable Magnetic Layered Zintl Phases Based on the \( \text{A}\text{Sn}_2\text{As}_2 \) Structure (A = Na and Eu)

**Figure A.30** Powder XRD Rietveld refinement results for \( \text{EuSn}_2\text{As}_2 \) using TOPAS.
Table A.17 Selected bond lengths based on the refined EuSn$_2$As$_2$ structure.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-As (3x)</td>
<td>2.7761(3)</td>
</tr>
<tr>
<td>Eu-As (6x)</td>
<td>3.1019(4)</td>
</tr>
</tbody>
</table>

Figure A.31 X-Ray Fluorescence verification of the Eu:Sn and Sn:As stoichiometry in EuSn$_2$As$_2$. Different ratios of Eu$_2$O$_3$ and elemental Sn (Eu:Sn) and elemental Sn and As (Sn:As) were used to prepare a standard calibration curve.
Figure A.32 Field-cooled temperature-dependent magnetic susceptibility of EuSn$_2$As$_2$ with the $a/b$-axis (blue) and $c$-axis (red) parallel to the field showing the standard deviation.

Figure A.33 Curie-Weiss fit corresponding to the ZFC inverse susceptibility of the EuSn$_2$As$_2$ crystal with its $c$-axis oriented parallel to the applied 0.01 T field.
Figure A.34 Temperature-dependent magnetic susceptibility of EuSn$_2$As$_2$ with the c-axis parallel to the applied field of 5T.
Figure A.35 AFM images and height profiles of mechanically-exfoliated EuSn$_2$As$_2$ onto 285 nm SiO$_2$/Si.
Figure A.36  (a) The powder XRD spectra of the precursor CaGe$_{2-2x}$Sn$_{2x}$ Zintl phases (b) The zoomed-in powder XRD spectra highlighting the (100) peak (c) The full width at half maximum (FWHM) of the (100) peak versus the Sn concentration.
Table A.18 TOPAS Rietveld refinement results for of CaGe$_{2-2x}$Sn$_{2x}$ (x = 0.04)

<table>
<thead>
<tr>
<th>Property</th>
<th>CaGe$<em>{1.92}$Sn$</em>{0.08}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>CaGe$<em>{1.92}$Sn$</em>{0.08}$</td>
</tr>
<tr>
<td>$F_w$</td>
<td>189.04</td>
</tr>
<tr>
<td>Space Group</td>
<td>P6$_{3}$mc</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.00920(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>10.2495(1)</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>142.677(4)</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>295</td>
</tr>
<tr>
<td>Pattern Range (2θ, °)</td>
<td>10-70</td>
</tr>
<tr>
<td>$λ$ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.1525</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.1023</td>
</tr>
</tbody>
</table>

CaGe$_{1.92}$Sn$_{0.08}$ = 94.91

Phase Fraction (%)             | Sn = 5.09

224
Table A.19 The atomic coordinates of CaGe$_{2-x}$Sn$_x$ ($x = 0.04$)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>B$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1/3</td>
<td>2/3</td>
<td>0.2917(6)</td>
<td>1</td>
<td>0.31(2)</td>
</tr>
<tr>
<td>Ge1</td>
<td>1/3</td>
<td>2/3</td>
<td>0.6074(3)</td>
<td>1</td>
<td>0.88(9)</td>
</tr>
<tr>
<td>Ge2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.92</td>
<td>0.38(6)</td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.08</td>
<td>0.38(6)</td>
</tr>
</tbody>
</table>

Table A.20 TOPAS Rietveld refinement results for of CaGe$_{2-x}$Sn$_x$ ($x = 0.07$)

<table>
<thead>
<tr>
<th></th>
<th>CaGe$<em>{1.86}$Sn$</em>{0.14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>CaGe$<em>{1.86}$Sn$</em>{0.14}$</td>
</tr>
<tr>
<td>$F_w$</td>
<td>191.81</td>
</tr>
<tr>
<td>Space Group</td>
<td>P6$_3$mc</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.0155(7)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>10.2530(2)</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>143.173(6)</td>
</tr>
<tr>
<td>T (K)</td>
<td>295</td>
</tr>
<tr>
<td>Pattern Range (2θ, °)</td>
<td>10-70</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.1575</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.1214</td>
</tr>
<tr>
<td>Phase Fraction (%)</td>
<td>CaGe$<em>{1.86}$Sn$</em>{0.14}$ = 95.76</td>
</tr>
<tr>
<td></td>
<td>Sn = 4.24</td>
</tr>
</tbody>
</table>
Table A.21 The atomic coordinates of CaGe$_{2z}$Sn$_{2x}$ ($x = 0.07$)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1/3</td>
<td>2/3</td>
<td>0.2959(5)</td>
<td>1</td>
<td>0.12(3)</td>
</tr>
<tr>
<td>Ge1</td>
<td>1/3</td>
<td>2/3</td>
<td>0.6082(3)</td>
<td>1</td>
<td>0.73(6)</td>
</tr>
<tr>
<td>Ge2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.86</td>
<td>0.30(5)</td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.14</td>
<td>0.30(5)</td>
</tr>
</tbody>
</table>

Table A.22 TOPAS Rietveld refinement results for of CaGe$_{2z}$Sn$_{2x}$ ($x = 0.09$)

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>CaGe$<em>{1.82}$Sn$</em>{0.18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_W$</td>
<td>193.65</td>
</tr>
<tr>
<td>Space Group</td>
<td>P6$_3$mc</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.02160(8)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>10.2550(2)</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>143.637(6)</td>
</tr>
<tr>
<td>T (K)</td>
<td>295</td>
</tr>
<tr>
<td>Pattern Range (2Ω, °)</td>
<td>10-70</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.1456</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.1035</td>
</tr>
<tr>
<td>CaGe$<em>{1.82}$Sn$</em>{0.18}$ = 95.15</td>
<td></td>
</tr>
<tr>
<td>Phase Fraction (%)</td>
<td>Sn = 4.85</td>
</tr>
</tbody>
</table>

226
Table A.23 The atomic coordinates of CaGe_{2-2x}Sn_{2x} (x = 0.09)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>B_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1/3</td>
<td>2/3</td>
<td>0.298(7)</td>
<td>1</td>
<td>0.61(2)</td>
</tr>
<tr>
<td>Ge1</td>
<td>1/3</td>
<td>2/3</td>
<td>0.608(5)</td>
<td>1</td>
<td>0.25(9)</td>
</tr>
<tr>
<td>Ge2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.82</td>
<td>0.78(9)</td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.18</td>
<td>0.78(9)</td>
</tr>
</tbody>
</table>
Figure A.37 (a) X-ray Fluorescence Spectrum of $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}\text{(OH)}_{0.09}$. (b) Tin content of $\text{Ge}_{1-x}\text{Sn}_x\text{H}_{1-x}\text{(OH)}_x$ from X-Ray fluorescence. Red line: linear fitting of standard sample mixtures.

Figure A.38 The FWHM of the (100) and (002) peaks of the $\text{Ge}_{1-x}\text{Sn}_x\text{H}_{1-x}\text{(OH)}_x$ ($x = 0$-$0.9$) XRD pattern.
Figure A.39 The FT-IR spectrum of Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ from (a) 1750 cm$^{-1}$ to 2150 cm$^{-1}$ and (b) 400 cm$^{-1}$ to 800 cm$^{-1}$.

Figure A.40 E$_2$ phonon mode full with at half maximum (FWHM) of 2D Ge$_{1-x}$Sn$_x$H$_{1-x}$(OH)$_x$ with various Tin content.
Figure A.41 \( \text{Ge}_{0.96}\text{Sn}_{0.04}\text{H}_{0.96}(\text{OH})_{0.04} \) absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.4 meV was deduced from the 301.4 cm\(^{-1}\) Raman Shift.
Figure A.42 Ge$_{0.93}$Sn$_{0.07}$H$_{0.93}$(OH)$_{0.07}$ absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.3 meV was deduced from the 300.9 cm$^{-1}$ Raman Shift.
Figure A.43 Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ absorption spectrum fitting to the Tauc/Davis-Mott models of 2D and 3D densities of states where a phonon vibration of 37.1 meV was deduced from the 299.2 cm$^{-1}$ Raman Shift.
Figure A.44 Absorption spectrum of Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ from 1 eV (1240 nm) to 4.13 eV (300 nm).

Figure A.45 Transmission mode absorbance spectrum of a $\sim$3.5 ± 0.5 µm thick Ge$_{0.91}$Sn$_{0.09}$H$_{0.91}$(OH)$_{0.09}$ flakes before and after exposure to ambient air and after subsequent 1 M HCl washing.
Figure A.46 The FT-IR spectrum of $\text{Ge}_{0.91}\text{Sn}_{0.09}\text{H}_{0.91}(\text{OH})_{0.09}$ before and after exposure to ambient air and after subsequent 1 M HCl washing in the 400-1000 cm$^{-1}$ region.
Bibliography

Chapter 1


(67) McWhan, D. B.; Compton, V. B.; Silverma, M. S.; Soulen, J. R. Crystal Structure and Superconductivity of a High-Pressure Phase of CaSi₂. *J. Less Common Met.* 1967, 12, 75-&.


(71) Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets Isostructural to Grey Arsenic - Synthesis and Crystal-Structure of NaSn2As2, Na0.3Ca0.7Sn2As2, Na0.4Sr0.6Sn2As2, Na0.6Ba0.4Sn2As2, and K0.3Sr0.7Sn2As2. Z. Anorg. Allg. Chem. 1995, 621, 576-582.


(104) Jiang, S. S.; Kryinowski, K.; Asel, T.; Arguilla, M. Q.; Cultrara, N. D.; Yanchenko, E.; Yang, X.; Brillson, L. J.; Windl, W.; Goldberger, J. E. Tailoring the


Chapter 2


(8) Ryder, C. R.; Wood, J. D.; Wells, S. A.; Yang, Y.; Jariwala, D.; Marks, T. J.; Schatz, G. C.; Hersam, M. C. Covalent Functionalization and Passivation of


Chapter 3


(59) Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets Isostructural to Grey Arsenic - Synthesis and Crystal-Structure of NaSn$_2$As$_2$, Na$_{0.5}$Sr$_{0.5}$Sn$_2$As$_2$, Na$_{0.5}$Sr$_{0.5}$Sn$_2$As$_2$, Na$_{0.6}$Ba$_{0.4}$Sn$_2$As$_2$, and K$_{0.5}$Sr$_{0.5}$Sn$_2$As$_2$. *Z. Anorg. Allg. Chem.* 1995, 621, 576-582.


Chapter 4


(46)  Asbrand, M.; Eisenmann, B.; Klein, J. Arsenidostannates with SnAs Nets Isostructural to Grey Arsenic: Synthesis and Crystal Structure of NaSn$_2$As$_2$, Na$_{0.3}$Ca$_{0.7}$Sn$_2$As$_2$, Na$_{0.4}$Sr$_{0.6}$Sn$_2$As$_2$, Na$_{0.6}$Ba$_{0.4}$Sn$_2$As$_2$, and K$_{0.3}$Sr$_{0.7}$Sn$_2$As$_2$. *Z. Anorg. Allg. Chem.* **1995**, *621*, 576-582.


**Chapter 5**


(29) Eisenmann, B.; Klein, J. Zintl-Phases with Layer Anions - Preparation and Crystal Structures of the Isotypic Compounds SrSn₂As₂ and Sr₀.₈₇Ba₀.₁₃Sn₃As₂ and a


(32) Xu, Z., University of Houston, 1999.


