



Doctor of Philosophy

First-Principles Predictions of Magnetic Properties of Heusler Compounds: Half-metallicity, Permanent Magnetism, and Anomalous Hall Conductivity

Hoang Thu Thuy

University of Ulsan Department of Physics August 2022

First-Principles Predictions of Magnetic Properties of Heusler Compounds: Half-metallicity, Permanent Magnetism, and Anomalous Hall Conductivity

By

Hoang Thu Thuy

A DISSERTATION SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF REQUIREMENTS for the degree of

DOCTOR OF PHILOSOPY

University of Ulsan Department of Physics August 2022

First-Principles Predictions of Magnetic Properties of Heusler Compounds: Half-metallicity, Permanent Magnetism, and Anomalous Hall Conductivity

This certifies that the Ph.D dissertation of Hoang Thu Thuy is approved.

Committee Chairman Prof. Sunglae Cho

Committee Member Prof. Noejung Park

Committee Member Prof. S. H. Sonny Rhim

Committee Member Prof. Sanghoon Kim

Committee Member Prof. Soon Cheol Hong

University of Ulsan Department of Physics August 2022 Dear my beloved sister, mom, and dad:

"I would like to dedicate this dissertation to them, for their scarification, pain, and unconditional love"

Acknowledgment

First of all, I would like to express my deepest gratitude to my supervisor Prof. Soon Cheol Hong, who gave me a chance to start my research adventure. His patience, immense knowledge, strictness, and continuous guidance, made my PhD possible. I also learned from him a great attitude of working hard, being disciplined, being humble. I wish Prof. Soon Cheol Hong a new beginning with full of health, joy, and freedom.

I am also grateful to Prof. Sonny Rhim for giving me insightful comments and raising interesting questions that broadened my physics knowledge to consider things from various perspectives.

I want to extend my thanks to other University of Ulsan Professors, Prof. Sanghoon Kim, Prof. Jung Dae Kim, Prof. Young Han Shin, and so on, for giving interesting and meaningful lectures. I actually learned many new things throughout taking their classes.

During my PhD at the University of Ulsan, I also received many supports from Ms. Kim and Ms. Lee from BK and EHSRC offices. So, I sincerely appreciate their dedication to their work.

It would be remiss if I did not send my thanks to Dr. Long Dang Dinh, my supervisor when I was an undergraduate student, for encouraging me to study further.

Many thanks go to Dr. Qurat, our former group member, who inspires me to be a better researcher through her kindness in sharing knowledge, ceaselessly learning, and never giving up even when facing hardship. I want to send my warmest thanks to the Vietnamese community at the University of Ulsan and the Physic department in particular, especially for Dr. Kim Ngan Tran. I shared many good times with them. It was tough for me to survive and adapt to the abroad environment without their help. I thanks them from the bottom of my heart. I also want to thank my longtime friends Ngoc and Thao, for their understanding and support despite long distances.

Special thanks to Yananose Kunihiro for spending his busy time talking with me in Korean. Thanks to Kunihiro, I got a chance to experience more about Korean life.

Words are not enough to express how thankful I am for all my dad, mom, and sister have done, and all the love, they have given me. Nothing can be done without them. And I also want to thank my nephews Chôm Chôm and Bon Bon. Their appearance brings to my family a lot of laughs and happiness.

Finally, I want to spend my last thanks to all people who I had a chance to meet. Some people I still keep in touch with; some others, I just passed by. However, in this way or that way, teaching me many different life lessons to become a more mature, diligent, and stronger person.

"You can't ever reach perfection, but you can believe in an asymptote toward which you are ceaselessly striving." - Paul Kalanithi

"Only where there is disillusionment and depression and sorrow does happiness arise; without the despair of loss, there is no hope."- Harumi Murakami

Thank you / 감사합니다 / Cåm on

Hoàng Thu Thuỷ

Abstract

Magnetic materials encompass a broad range of materials, which are applied in a diversity of fields. For example, magnetic materials are key component of motors, power generators, and spintronic devices. Even though there is a several type of magnetic materials, due to some issues at practical level, the demand of finding new magnetic material is still in need. To identify new magnetic materials, first-principles calculations are indeed faster, safer, and resource-saving compared to experiments. Among several classes of materials, Heusler compounds stand out as potential candidates in terms of material designs with an extensive tunability which can be tailored by varying chemical substitutions and structural motifs. In this work, using density functional theory (DFT), the magnetic and electronic properties of hypothetical Heusler compounds are predicted and attention is paid to half-metallicity, permanent magnetism, and anomalous Hall effect.

This dissertation is organized as follow. In the chapter 1, we present a brief introduction of Heusler compounds. We shed light on overview of Heusler compounds such as definitions, chemical formulars, and types of Heusler compounds. Finally, we discuss the concept of half-metallicity, permanent magnetism, and anomalous Hall conductivity.

In the chapter 2, we present an overview of density functional theory (DFT) by describing the theoretical foundations, advantages, and drawbacks due to approximation in exchange-correlation functional.

The chapter 3 aims to perform a systematic density functional study on alkali-metalbased half-Heusler compounds, namely ACrZ (A = Li, Na, and K; Z = As, Sb, and P), to identify the optimal half-metal (HM) for practical applications. Unlike most HMs proposed so far, the majority of ACrZ compounds in our study exhibit a wide band gap (1.60-2.38 eV) and retain robust half-metallicity even at the surface. Furthermore, the half-metallicity is robust under severe strain, up to 10 %, their stability, robust half-metallicity at the surface and under strain, and good lattice mismatch with zinc-blende semiconductors, we propose LiCrZ and NaCrZ (Z = As and Sb) as promising compounds for practical applications to spintronics.

In the chapter 4, due to the high price and limited source of rare earth (RE) elements and heavy metals (HM), demand for finding new permanent magnets (PM) without including 4d and 5d HM or RE elements is growing fast. A large saturation magnetization $\mu_0 M_s$ and uniaxial magnetocrystalline anisotropy K_u ($K_u > 0$) are demanded as necessary conditions to be a PM. We theoretically investigate structural stability and intrinsic magnetic properties of Fe₂MnSn Heusler compound, adopting cubic, tetragonal, and hexagonal, to identify a new potential PM. The most stable phase is hexagonal, followed by inverse tetragonal, inverse cubic, and regular cubic. The large enough magnetization $\mu_0 M_s$ of 1.28 T-1.59 T is predicted, for all structure phases. The inverse tetragonal phase with an uniaxial K_u of 2.36 MJ·m³ is more desirable to be PM compared to hexagonal one with a biaxial K_u of -0.72 MJ·m³. Furthermore, inverse tetragonal phase can be stabilized by H and N interstitial doping, indicated by negative formation energies of -8.55 and -35.19 kJ·mol⁻¹. Particularly, on the one hand, H has better intrinsic magnetic properties [$\mu_0 M_s = 1.66$ T, $K_u = 1.66$ MJ·m³, (BH)_{max} = 56 MGOe, and κ = 0.93] than N [$\mu_0 M_s$ = 1.36 T, K_u = 1.07 MJ·m³, (BH)_{max} = 46 MGOe, and κ = 0.73]. On

the other, N shows a better thermal stability since even having higher formation energy than hexagonal phase by 5.03 kJ·mol⁻¹.

Recently, it was shown that anomalous Hall conductivity (AHC) can be tailored via tuning Berry curvature curvature regardless of magnetization, which may pave a new way to achieve large AHC without net magnetic moment. In the chapter 5, using the PAW and FLAPW methods implemented in VASP and Fleur codes, AHC of a ferrimagnet quaternary Heusler compounds TiZrMnAl is investigated. Among three possible structural phases, α -phase is energetically most stable, by energy differences of 0.34 eV/fu and 0.03 eV/fu compared to β and γ -phase. The local magnetic moment of Mn is antialigned with those of Ti and Zr. As a result, total magnetic moment is fully compensated (m_{tot} = 0.0 μ_B) in α - and β -phase, and nearly compensated (m_{tot} = 0.1 μ_B) in γ -phase. Interestingly, α -phase possesses a large AHC of 1470 Ω^{-1} cm⁻¹, while β - and γ -phase show moderate AHC of 200 and 100 Ω^{-1} cm⁻¹, consistently in both the PAW and FLAPW methods. The large AHC in α -phase is discussed based on the global Berry curvature over whole Brillouin zone.

Contents

Abstract	4
List of Tables	11
List of Figures	13
1 Introduction	19
1.1 Heusler compounds	19
1.1.1 Regular-Heusler compounds	20
1.1.2 Half-Heusler compounds	21
1.1.3 Inverse-Heusler compounds.	22
1.1.4 Quaternary Heusler compounds	22
1.1.5 Structural distortion in Heusler compounds	23
1.2 Half-metallicity, permanent magnetism, and anomalous	Hall
conductivity	25
1.2.1 Ferromagnetic half-metallicity	25
1.2.2 Permanent magnetism	.27
1.2.3 Anomalous Hall effects.	. 31
2 Computation method	34
2.1 Basic equations for interacting electrons and nuclei	35

2.2 Thomas-Fermi-Dirac approximation
2.3 Hohenberg-Kohn Theorems
2.4 Kohn-Sham (KS) equations
2.5 Local density approximation (LDA)
2.6 Generalized-gradient approximation (GGA)
2.7 Solutions of Kohn-Sham equations
2.7.1 Plane wave and pseudopotential
2.7.2 FLAPW
3 Robust half-metallicities of alkali-metal-based half-Heusler compounds 49
3.1 Introduction
3.2 Structural models
3.3 Computational details
3.4 Results and discussions
3.4.1 Magnetic properties
3.4.2 Band gap
3.4.3 Origin of wide band gap
3.4.4 Formation energy
3.4.5 Strain effects

3.4.6 The (001) surfaces	72
3.5 Summary	79
4 High-performance permanent magnets using inverse Heusler Fe ₂ MnSn: a	first-
principles study	80
4.1 Introduction	80
4.2 Computational details.	83
4.3 Crystal structures.	84
4.4 Results and discussions.	87
4.4.1 Fe ₂ MnSn	87
4.4.2 Hexagonal Fe ₂ MnSnX _{0.25}	91
4.4.3 Inverse tetragonal Fe ₂ MnSnX _{0.25}	92
4.5 Summary	105
5 Prediction of large anomalous Hall conductivity in a compensated ferrim	agnet
quaternary Heusler compound TiZrMnAl	106
5.1 Introduction	106
5.2 Crystal structures.	109
5.3 Computational details.	111
5.4 Results and discussions	112

5.4.1 Structural parameters and electronic properties			
5.4.2 Anomalous Hall effects			
5.5 Summary.			
6 Conclusion and outlook	122		
References	124		

List of Tables

1.1 Physical properties of some typical permanent magnets
3.1 The possible phases of half-Heusler compound XYZ and their sublattice structures52
3.2 Energy difference ΔE (meV/fu) between AFM and FM states, equilibrium lattice constant
a (Å), atom-projected magnetic moment (μ_B), total magnetic moment per formula unit (μ_B),
band gap (eV) of minority spin state E_g , and k-points of CBM and VBM of ACrZ. The asterisk
(*) indicates pseudo band gap
3.3 Center of CB Cr- t_{2g} , CB Cr- e_g , and VB As- p , and the separation ΔE (in eV) as the increases
of lattice constant $a = 5.66, 6.01, and 6.37$ Å
3.4 Interlayer spacing d_{ij} (in Å) and corrugation Δz_i for Z-term and ACr-term, respectively.
The subscript $1, 2, 3$, and c denote first, second, third layers from the surface, and the center
layer, respectively
3.5 Layer-resolved magnetic moment (in μ_B) of ACrZ (A = Li, Na; Z = As, Sb) for (001)
surface of both Z-term and ACr-term
3.6 The band gaps (in eV) of ACrZ ($A = Li$ and Na; $Z = As$ and Sb) of the Z-term (001) surface,
the bulk-like center layer, and the strained bulk
4.1 Crystal structures, space groups, and Wyckoff positions of Heusler compounds
Fe ₂ MnSn
4.2 Calculated lattice parameters (in Å), total magnetic moment per formula unit, atom-

resolved magnetic moment (in μ_B), relative energy ΔE with hexagonal phase (in eV/fu), and

magnetic anisotropy K_u (MJm⁻³) of Fe₂MnSn for regular cubic (Reg. cub), inverse cubic (Inv. 4.3 Calculated lattice parameters (in Å), the relative energy difference (in eV/fu) between interstitial doping on 4f site and 6g site (in eV/fu), total magnetic moment per formula unit (in μ_B), and magnetic anisotropy K_u (in MJm⁻³) for hexagonal Fe₂MnSnX_{0.25} with (X = H, B, C, 4.4 The relative energy difference (in eV/fu) between interstitial doping on tetrahedral site16eI, 16e-II, and octahedral 24f site with octahedral 24g site in tetragonal phase of Fe₂MnSnX_{0.25} 4.5 The associated bond length (in Å) of X with Feii, Feiv, Mniv, and Sn atom, which forms the 4.6 Calculated lattice parameters (in Å), total magnetic moment per formula unit (in μ_B), magnetic anisotropy K_u (in MJm⁻³), saturation magnetization $\mu_0 M_S$ (in T), theoretical maximum energy product (BH)_{max} (in MGOe), anisotropic field $\mu_0 H_a$ (in kOe), and magnetic 5.1 The possible phases of quaternary-Heusler compound TiZrMnAl. The positions (4a, 4b, 5.2 Location of high symmetry point W for different direction, denoted as W1, W2, W3, W4, W₅, and W₆. Their positions are described in the Cartesian coordinates in units of

List of Figures

1.1 Different types of Heusler structures. (a) Regular-Heusler, (b) Half-Heusler, (c) Inverse-
Heusler. Red, blue, and grey balls stand for X, Y, and Z elements, respectively. Yellow and red
differentiate X _A and X _B in inverse structures
1.2 Different types of distortion Heusler structures. (a) Regular tetragonal, (b) Inverse
tetragonal (c) Hexagonal. Red, blue, and grey balls stand for X, Y, and Z elements, respectively.
Yellow and red differentiate X _A and X _B in inverse structures
1.3 Schematic representation of the density of states of a half-metal compared to a metal, and
semiconductor
1.4 The hysteresis loop B (M)-H of a permanent magnet. Energy product (BH) is marked by
the yellow rectangle area
1.5 The illustration of (a) ordinary Hall effects, (b) anomalous Hall effects (AHE), (c) AHE in
collinear antiferromagnet (AFM), and (d) AHE in ferrimagnet (FiM). In Fig. 1.5(d), blue and
red arrow differentiate different magnetic sublattices in FiM
2.1 The flowchart of self-consistent calculation
2.2 The classification of first-principles calculation
3.1 (a) The C_{1b} structure of the β -phase half-Heusler ACrZ compound and (b) 14 ML slab to
simulate ACr-term and Z-term ACrZ (001) surfaces. Red, blue, and green spheres represent A,
Cr, and Z atoms, respectively. Surface, subsurface, and center layers are denoted by (S), (S-1),
and (C), respectively

3.2 Calculated total energy of half-Heusler ACrZ (A = Li, Na, and K; Z = P, As, and Sb) in α -, 3.3 Calculated total energies of half-Heusler ACrZ (A = Li, Na, and K; Z = P, As, and Sb) in 3.4 Majority and minority spin band structures of ACrZ (A = Li, Na, and K; Z = As, Sb, and 3.5 Band structures of ZB-CrP, ZB-CrAs, and ZB-CrSb in majority (gray) and minority (black) 3.6 Orbital-resolved minority spin band structure of NaCrAs and ZB-CrAs at equilibrium lattice constant of NaCrAs a = 6.37 Å. Cr- t_{2g} , Cr- e_g , and As-p orbitals are denoted in red, blue, and green, respectively. The symbol size is proportional to the weight of the orbital. The 3.7 Orbital-resolved minority spin band structure of ZB-CrAs at a = 5.66, 6.01, and 6.37 Å, in which 5.66 and 6.37 are equilibrium lattice constant of ZB-CrAs and NaCrAs. Cr- t_{2a} , Cr e_g , and As-p orbitals are denoted in red, blue, and green, respectively. The symbol size is 3.8 The band gap of ZB-CrAs as a function of lattice constant over the range between 5.66 Å 3.9 Orbital-resolved density of states of ZB-CrAs at a = 5.66, 6.01, and 6.37 Å for minority spin states. The Fermi level E_F is set to zero. Cr-t_{2g}, Cr-e_g, and As-p orbitals are denoted in

4.4 (a) Inverse tetragonal Heusler $Fe_2MnSnX_{0.25}$ with interstitial doping X (X = H, C, and N) at the most stable octahedral 24g site. Fe_i , Fe_{ii} , Fe_{iv} , Fe_v and Mn_i , Mn_{ii} denote Fe_A , Fe_B , and Mn at different sites. Changes of atom-resolved magnetic moment m_s for (b) Fe_A , (c) Fe_B , and (d) Mn atoms after introducing 6.25% concentration of X (X = H, B, C, and N). Herein, the dash lines mark the value without X.

$\Omega_{n,xy}^{z}(\mathbf{k})$ along \overline{LW} path with $n = 1,3$, and 5 (b) without SOI and with (c) SOI for α -
phase
5.7 Total Berry curvature $\Omega_{n,xy}^{z} = \sum_{n} f[\varepsilon_{n}(\mathbf{k})]\Omega_{n,xy}^{z}$ distribution over whole BZ for α -phase
(a) without SOI and (b) with SOI [001]120

Chapter 1: Introduction

The introductory chapter is divided into two parts. The first part of chapter discusses basis concepts relevant to Heusler compounds, types of Heusler compounds, their crystal structures, and our motivations of investigating this type of compounds. In the second part, half-metallicity, permanent magnetism, and anomalous Hall effects are briefly interpreted.

1. 1. Heusler compounds

Up to our knowledge, there is no absolute definition of Heusler compounds. "*Covalency*" and "*tunability*" are widely used to describe the main feature of this material's class. Heusler compounds were named after Friedrich Heusler, a German mining engineer and chemist, who was the person discovered this type of compound in 1903. The first compounds were studied are CuMnSb, Cu₂MnAl, and Cu₂MnSn, that attracted attentions since yielding ferromagnetism even consisting of no magnetic elements. Nevertheless, Mn is an antiferromagnet material, but the concept of antiferromagnetism and ferrimagnetism are still unknown until 1930-1940. Up to now, Heusler compound's family is extended to more than 1500 members, including non-magnetic, ferrimagnetic, antiferromagnetic, and ferromagnetic materials. From electronic properties perspectives, Heusler compounds can exhibits a various type of properties such as multiferroics, half-metals, superconductivities, Weyl or Dirac semimetals, topological insulators and so forth. A huge family of Heusler compounds offer a wide playground to find prospective materials for several applications.

Based on chemical formulars, Heusler compounds can be catalogized as full-Heusler compounds X_2YZ and half-Heusler XYZ [1-4]. Usually, X and Y are transitions metals (TMs) and Z is a main group *sp*-elements, and thus identified as TM-based Heusler compounds. In some cases, X or Y can be replaced by an alkali-metal, alkaline earth metal, or rare-earth element. Similarly, they can also name as alkali-metal-based Heusler compounds, alkaline-earth-metal-based Heusler compounds, and rare-earth-based Heusler compounds. Recently, it was found that Z also can be replaced by a TM, therefore is called as all-*d*-metal Heusler compounds [5].

From crystal structures point of view, Heusler compounds can have cubic, tetragonal, and hexagonal structural phases. Tetragonal and hexagonal structures are described by distorting cubic Heusler structure along with [001] and [111] direction. Next, we will go for a detail discussion on types Heusler compounds. The crystal structures of regular-Heusler, half-Heusler, inverse Heusler are presented in Fig 1.1. We start with regular-Heusler structure in section 1. 1. 1.

1.1.1 Regular-Heusler compounds

 X_2YZ regular-Heusler compounds crystalize in centrosymmetric cubic L2₁ structure with space group of Fm $\overline{3}$ m) No. 225, which consisting of four interpenetrating fcc sublattice [3]. The X, Y, and Z atom occupy the Wyckoff position 8c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4a (0, 0, 0) respectively (Fig. 1.1 (a)). In particular, the X₂ atoms locate at equivalent sites, forming a cubic primitive cell. In addition, adjacent cubes of X₂ cubic sublattice are filled alternating by Y or Z atoms.



Fig. 1.1: Different types of Heusler structures. (a) Regular-Heusler, (b) Half-Heusler, (c) Inverse-Heusler. Red, blue, and grey balls stand for X, Y, and Z elements, respectively. Yellow and red differentiate X_A and X_B in inverse structures.

1. 2. Half-Heusler compounds

XYZ half-Heusler compounds adopt a non-centrosymmetric cubic C1_b structure with the F43m space group (no. 216) [3]. XYZ half-Heusler can be obtained by removing half of the X atoms from L2₁ structure (Fig 1.1 (b)). This structure consists of three interpenetrating fcc sublattices (Fig. 1.1 (b)), each of which are occupied at 4a (0, 0, 0), 4b (1/2, 1/2, 1/2), and 4c (1/4, 1/4, 1/4) Wyckoff positions. On the other hand, half-Heusler compounds can be described as the zinc-blend (ZB) structure with the octahedral voids are filled. There are three possible atomic arrangements of half-Heusler compounds corresponding to α , β , and γ -phase. Especially, atom locates on 4a and 4c Wyckoff positions form a ZB sublattice whereas atoms occupy on 4b site fill the octahedral voids.

1. 1. 3. Inverse-Heusler compounds

The inverse Heusler compounds has the same chemical formula with regular-Heusler compounds X_2YZ but crystalize in cubic XA structure (space group F43m no. 216)[3]. The inverse Heusler structure is also can be obtained by switching one of X atom with Y or Z atom. Thus, X_2 atoms locate at non-equivalent position. In detail, X atoms are placed on 4b (1/2, 1/2, 1/2) and 4d (3/4, 3/4, 3/4) site, while Y and Z atom occupy 4c (1/4, 1/4, 1/4) and 4a (0, 0, 0) position, respectively. It is different to regular-Heusler structures that X atoms in inverse-Heusler structures do not form simple cubic lattice (Fig. 1.1 (c)).

1. 1. 4. Quaternary Heusler compounds

Quaternary Heusler compounds is described by a composition of XX'YZ. It is different to regular (inverse) Heusler structure is that one of two X atoms in X₂YZ compounds is substituted by another TM X'. Quaternary Heusler XX'YZ has co-called LiMgPdSn-type structure with space group F43m (216) [3]. It is similar to regular (inverse) Heusler structure that the structure of quaternary Heusler compounds consist of four interpenetrating cubic sublattice with 4 occupied Wyckoff positions 4a (0, 0, 0), 4c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4d (3/4, 3/4, 3/4). There are three possible atomic arrangements of quaternary Heusler compound, namely α , β , and γ -phase.

1. 1. 5. Structural distortion in Heusler compounds

Most of Heusler compounds X₂YZ crystalize in cubic structure, however, sometimes, the cubic structure is unstable under distortion, and therefore, stabilizing in tetragonal or hexagonal structure. Crystal structures of (a) regular tetragonal, (b) inverse tetragonal, and (c) hexagonal are shown in Fig. 1.2.



Fig. 1.2: Different types of distortion Heusler structures. (a) Regular tetragonal, (b) Inverse tetragonal (c) Hexagonal. Red, blue, and grey balls stand for X, Y, and Z elements, respectively. Yellow and red differentiate X_A and X_B in inverse structures.

Tetragonal Heusler compounds can be obtained by elongating or compressing (inverse) regular cubic structure along [001] direction. The tetragonal (inverse) regular unit cells shown in Fig. 1. 2(a) and (b) are rotated 45° around the *c*-axis relative to the (inverse) regular cubic structures in Fig. 1. 1(a) and (c). The regular tetragonal structure has a space group I4/mmm (No. 139). Herein, the X atoms occupy 4d (0, 1/2, 1/4), the Y atoms are placed

at 2b (0, 0, 1/2) and 2a (0, 0, 0), respectively. Inverse tetragonal has a space group of I $\overline{4}$ m2 (No. 119), it is similar to inverse cubic structure that X atoms also locate at non-equivalent positions. In detail, the first X atom sits on 2b (0, 0, 1/2), the second X atom and Y atom occupy 4d (0, 1/2, 1/4) position, and Z atom is placed at 2d (0, 0, 0) position.

It is similar to tetragonal phases that hexagonal phase also can be visualized as cubic distortion but along [111] direction. The hexagonal phase crystalizes in D019 structure with a space group P6₃/mmc (No. 194). In this structure, Fe and Mn share the same 6h (1/6, 1/3, 1/4) sites with 2/3 and 1/3 occupancy, and Z atom occupies 2c (1/3, 2/3, 1/4) sites [6-10].

1. 2. Half-metallicity, permanent magnetism, and anomalous Hall conductivity

1.2.1. Ferromagnetic half-metallicity

A systematic representation of the density of states of metals, semiconductors, and half-metals (HM) are shown in Fig. 1.3. HM is a class of material, in which one spin channel has metallic properties and the other one is semiconducting with a band gap, leading to the spin transport in only one channel [11,12]. The degree of spin-polarization (P) can be estimated as

$$P\% = \frac{N(\uparrow) - N(\downarrow)}{N(\uparrow) + N(\downarrow)} \tag{1.1}$$

where N is the density of states of at Fermi level E_F of spin \uparrow (\downarrow) channels. Therefore, 100% P is expected in HMs, which can enhance efficiency of spintronic devices, such as magnetic tunnel junctions.

One of the most important features of HM is the integral number of total magnetic moment per formula unit. This stems from total valence electron Z_v is equal to the total number of occupied electrons in the majority states $n(\uparrow)$ and minority states $n(\downarrow)$:

$$Z_V = n(\uparrow) + n(\downarrow) \tag{1.2}$$

Total magnetic moment mt can be estimated as:

$$m_t = n(\uparrow) - n(\downarrow) \tag{1.3}$$

From (1) and (2):

$$M_t = \left(n(\uparrow) + n(\downarrow)\right) - 2n(\downarrow) = Z_v - 2n(\downarrow)$$
(1.4)

The integral total magnetic moment m_t of HM is a consequence of integral total number of electrons as well as integral number of electrons for the semiconducting spin channel.



Fig. 1.3: Schematic representation of the density of states of a HM compared to a metal, and semiconductor.

1. 2. 2. Permanent magnetism

Permanent magnets (PMs) create a persistent magnetic field in free space without the continuous expenditure of electric or other forms of energy, playing a vital role in many areas of technology, such as magnetic energy converter-motors, actuators, or generators [13,14]. The hysteresis loop B(M)-H loop of a PM, that represents the relationship between induced magnetic flux density B and magnetizing force H, is shown in Fig. 1. 4 [15]. Herein, the coercivity H_c is a measure of the reversed field required to drive the magnetization to zero after being saturated, and the remanence B_r is a measure of the remaining magnetization when the driving field is dropped to zero. The negative of the H field created by the magnet on itself is defined as the demagnetizing field H_d, which depends on magnet shape. In the absence of external magnetic field, $H = H_d$, $M = M_d$, the energy product (BH) is defined as follow [16,17]:

$$\vec{H}_{d} = -D\overline{M_{r}}; \ \vec{B} = \mu_{0} \left(\overline{M_{r}} + \overline{H_{d}} \right) = \mu_{0} (1 - D) \overline{M_{r}};$$

$$(BH) = \mu_{0} D (1 - D) M_{r}^{2}$$
(1.5)

where *D* is the demagnetizing factor, which is larger than 0 and smaller than 1, i.e., 0 < D < 1, depending on the shape of the magnet. When $D = \frac{1}{2}$, (*BH*) reaches the maximum value:

$$(BH)_{max} = \frac{1}{4}\mu_0 M_S^2 \tag{1.6}$$

The maximum energy product $(BH)_{max}$ figure of merit, which evaluates the strength of magnetic flux a material generates per unit volume. $(BH)_{max}$ is equal to the biggest rectangle

described by the second quadrant of B(H) hysteresis loop (Fig. 1.4). In addition, PMs need to crystalize in a uniaxial crystal structure (tetragonal, hexagonal, or rhombohedral) to have magnetocrystalline anisotropy K_u . A good PM material requires a high saturation magnetization $\mu_0 M_s$ and a high coercive force H_c to prevent its being easily demagnetized by an external field. To attain H_c , a uniaxial K_u ($K_u > 0$), which indicates that the magnetization direction prefers to lie along the crystallographic symmetry axis [15], is demanded. Herein, $\mu_0 H_c$ can be estimated as:

$$\mu_0 H_c = \alpha \mu_0 H_a - D_{eff} M_S \tag{1.7}$$

where α is the microstructure constant and D_{eff} is an effective local demagnetizing factor. α and D_{eff} are relatively small (< 1) and can be neglected. The anisotropic field $\mu_0 H_a$ is the field that needed to saturate the magnetization in the hard-axis direction. In the context of intrinsic quantities, $\mu_0 H_a$ can be estimated as: $\mu_0 H_a = \frac{2K_u}{M_s}$. Finally, the hard parameter κ is evaluated via the ratio of anisotropy (K_u) to magnetostatic energy (BH):

$$\kappa = \left(\frac{K_u}{\mu_0 M_S^2}\right)^2 \tag{1.8}$$

 κ ($\kappa > 1$) is considered as the empirical criterion to define a PM material. However, semi-hard materials (0.5 < κ < 1) are also possible to be PM materials [16-18]. Physical properties of some typical permanent magnets are listed in table 1.1. In addition, a good PM needs a good thermal stability and high Curie temperature (T_C) are required for practical applications.



Fig. 1.4: The hysteresis loop B (M)-H of a permanent magnet. Energy product (BH) is marked by the yellow rectangle area.

	T _C (K)	$\mu_0 M_s$ (T)	(BH) _{max} (MGOe)	K_u (MJ·m ⁻³)	к
Alnico 5	1210	1.38	46.24	0.68*	0.66
BaFe ₁₂ O ₁₉	740	0.48	5.56	0.33	1.35
SmCo ₅	1020	1.08	29.03	17.2	4.30
Sm ₂ Co ₁₇	837	1.22	32.67	4.2	1.90
Nd ₂ Fe ₁₄ B	588	1.58	65.00	17.2	1.54
Sm ₂ Fe ₁₇ N ₃	749	1.55	59.00	4.20	2.13
MnBi	628	0.73	13.19	4.90	1.46
Fe ₁₆ N ₂	810	2.41	144.76	8.60	0.43

 Table 1. 1. Physical properties of some typical permanent magnets [14,15,18].

*shape anisotropy

1.2.3. Anomalous Hall effects

In a non-magnetic material sample, when an external magnetic field is applied perpendicular to an applied electric current, due to Lorentz force, the current carriers are forced to move along the curve path [Fig 1.5(a)], giving rise to a transverse electric field [19]. This is called as the ordinary Hall effect. When the sample is ferromagnet, the phenomenon is referred to as anomalous Hall effect (AHE) as presented in Fig 1. 5(b). Notably, the ordinary Hall effect requires an external magnetic field, whereas the AHE requires only a magnetization. It is different to the ordinary Hall effect that electrons in AHE are predominantly deflected in one direction, resulting in an external current which absents in non-magnetic materials. The AHE is contributed by extrinsic and intrinsic factors. Apart from extrinsic contribution from impurity, in this dissertation, we focus on intrinsic contribution. The intrinsic contribution to anomalous Hall conductivity can be given by the Kubo formula as following:

$$\sigma_{xy} = \frac{e^2}{\hbar} \sum_{n' \neq n} \int_{BZ} \frac{d^3k}{(2\pi)^3} f[\varepsilon_n(\mathbf{k})] \times \frac{2Im\left[\left\langle u_{nk} \middle| \partial_{k_x} \widehat{H}(\mathbf{k}) \middle| u_{n'k} \right\rangle \left\langle u_{n'k} \middle| \partial_{k_y} \widehat{H}(\mathbf{k}) \middle| u_{nk} \right\rangle \right]}{[\varepsilon_n(\mathbf{k}) - \varepsilon_{n'}(\mathbf{k})]^2}$$
(1.9)

Here $f[\varepsilon_n(\mathbf{k})]$ is the Fermi-Dirac distribution function, $|u_{nk}\rangle$ represents the periodic part of the *n*th Bloch state. $\varepsilon_n(\mathbf{k})$ is the eigenvalue for the *n*th eigenstates of $|u_{nk}\rangle$ at the \mathbf{k} point, and $\nabla_k \widehat{H}(\mathbf{k})/\hbar$ is the velocity operator. Since $\nabla_k \langle u_{nk} | \partial_{k_x} \widehat{H}(\mathbf{k}) | u_{n'k} \rangle = 0$ and $\nabla_k \langle u_{nk} | u_{n'k} \rangle = 0$, therefore:

$$\frac{\langle u_{nk} | \nabla_k \hat{H}(\mathbf{k}) | u_{n'k} \rangle}{\varepsilon_n(\mathbf{k}) - \varepsilon_{n'}(\mathbf{k})} = \langle \nabla_k u_{nk} | u_{n'k} \rangle$$
(1.10)

and the AHC can be rewritten as:

$$\sigma_{xy} = -\frac{e^2}{\hbar} \sum_n \int_{BZ} \frac{d^3k}{(2\pi)^3} f[\varepsilon_n(\mathbf{k})] \Omega_{n,xy}^z(\mathbf{k})$$
(1.11)

where $\Omega_{n,xy}^{z}(\mathbf{k})$ represents the z-component of Berry curvature of n-th band. The integration is taken over the Brillouin zone (BZ). The Berry curvature is defined int terms of the Berry connection $\Omega_{n,xy}^{z}(\mathbf{k}) = \nabla_{\mathbf{k}} \times A_{n}(k)$, where $A_{n}(k) = -i\langle u_{nk} | \nabla_{k} u_{nk} \rangle$ [20].

The time-reversal symmetry \hat{T} flips the sign of the Berry curvature in BZ while reversing the sign of local moment vector k:

$$\Omega_{n,xy}^{z}(\boldsymbol{k}) = -\Omega_{n,xy}^{z}(-\boldsymbol{k})$$
(1.12)

That leads to the cancellation of the Berry curvature when integrated over the full BZ. Therefore, to achieve non-vanishing AHC, materials with broken time-reversal symmetry \hat{T} are required [21,22]. However, in cases of a simple collinear antiferromagnetic materials (AFM), the AHC is vanished despite of the broken \hat{T} . A simple-minded illustration of AHE in collinear AFM and ferrimagnet (FiM) are presented in Fig. 1. 5(c) and Fig. 1. 5(d). Due to the combined symmetry operation ($\hat{T}\hat{O}$) of \hat{T} and translation symmetry \hat{O} , even though \hat{T} is broken, due to $\hat{T}\hat{O}$, the Berry curvature is still reversed its sign, causing the absence of AHE in collinear AFM. In contrast, due to two different magnetic sublattices, the combination of $\hat{T}\hat{O}$ does not reverse the sign of Berry curvature in FiM. As a result, AHE is found to survive in some non-collinear AFM or FiM. For example, collinear AFM regular Heusler compounds Ru₂MnSi has a zero AHC [4] while compensated FiM inverse Heusler compounds Ti₂MnAl has a non-negligible AHC of 300 Ω^{-1} cm⁻¹ [23].


Fig. 1.5: The illustration of (a) ordinary Hall effects, (b) anomalous Hall effects (AHE), (c) AHE in collinear antiferromagnet (AFM), and (d) AHE in ferrimagnet (FiM). In Fig. 1.5(d), blue and red arrow differentiate different magnetic sublattices in FiM.

Chapter 2: Computational method

In this chapter, we review the very basics of density functional theory (DFT), starting from Schrödinger equation for many-body system. In principle, the electronic structure of a material can be obtained by solving the time-independent Schrödinger equation. In DFT, this complicated many-body problem that involves 3N degrees of freedom for N electrons can be reduced to an effective single-particle theory by treating the ground-state density as variables not many-body wave function. The root of DFT is given by Thomas and Fermi models [24,25]. The rigorous modern form of DFT is proposed afterward by Hohenberg and Kohn (1964) [26]. Herein, the interacting problem is treated as an auxiliary independent-particle problem with all many-body effects involved in an exchange-correlation functional. Finally, by including the local density approximation (LDA), Kohn and Sham successful develop the effective singleparticle equation [27], turning DFT into practical application in 1965.

1. 1. Basic equations for interacting electrons and nuclei

Starting with a Hamiltonian for the system of electrons and nuclear [28]. Here, the Hamiltonian is equal to a sum of kinetic energy of electrons $\hat{T}_e(\mathbf{r}_i)$ (the first term), the potential energy of nuclear-electron Coulomb interaction $\hat{V}_{Ne}(\mathbf{R}_I,\mathbf{r}_i)$ (the second term), the potential energy of electron-electron Coulomb interaction $\hat{V}_{ee}(\mathbf{r}_i)$ (the third term), the kinetic energy of the nuclear $\hat{T}_N(\mathbf{R}_I)$ (the fourth term), and nuclear-nuclear Coulomb interaction $\hat{V}_{NN}(\mathbf{R}_I)$ (the last term).

$$\widehat{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 + \sum_{i,I} \frac{-Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I} \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq j} \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (2.1)$$

where electrons are denoted by lower case subscripts and nuclear, with charge Z_I and mass M_I , denoted by upper cases subscript. The eigenfunctions and eigenvalues of this Hamiltonian can be obtained by solving time-independent Schrödinger equation:

$$\widehat{H}\psi(\mathbf{R}_{I},\mathbf{r}_{i}) = E\psi(\mathbf{R}_{I},\mathbf{r}_{i})$$
(2.2)

where *E* is the eigenvalue, and $E\psi(\mathbf{R}_{I}, \mathbf{r}_{i})$ is the corresponding wave function. According to the Born-Oppenheimer approximation [29], since the mass of an electron is very light compared with the nuclear $(\frac{m_{e}}{M_{I}} \ll 1)$, then the nuclear motion is much slower than electron motion and can be fixed. Thus, the electronic wave function can be expressed as:

$$\psi(\mathbf{R}_{I}, \mathbf{r}_{i}) = \phi_{e}(\mathbf{R}_{I}, \mathbf{r}_{i})\phi_{N}(\mathbf{R})$$
(2.3)

Herein, $\phi_N(\mathbf{R})$ is a nucleus function and $\phi_e(\mathbf{R}_I, \mathbf{r}_i)$ is an electronic wavefunction depending on the position of nuclear. Assuming that the mass of nuclear is infinity, the kinetic energy of nuclear can be omitted and the nuclear-nuclear Coulomb interaction only works as an external factor. Thus, the Hamiltonian of an electronic structure can be described by:

$$\widehat{\mathbf{H}} = \widehat{T}_{e}(\mathbf{r}_{i}) + \widehat{V}_{Ne}(\mathbf{R}_{I}, \mathbf{r}_{i}) + \widehat{V}_{ee}(\mathbf{r}_{i})$$
(2.4)

Therefore, the electronic wave function $\phi_e(\mathbf{R}_I, \mathbf{r}_i)$ is solved by a set of nuclear coordinates:

$$\widehat{H}_e \phi_e(\boldsymbol{R}_I, \boldsymbol{r}_i) \{ \widehat{T}_e(\boldsymbol{r}_i) + \widehat{V}_{Ne}(\boldsymbol{R}_I, \boldsymbol{r}_i) + \widehat{V}_{ee}(\boldsymbol{r}_i) \} \phi_e(\boldsymbol{R}_I, \boldsymbol{r}_i) = E_e \phi_e(\boldsymbol{R}_I, \boldsymbol{r}_i)$$
(2.5)

Adopting Hartree atomic unit $\hbar = m_e = e = \frac{4\pi}{\epsilon_0} = 1$, equation (2.5) can be rewrite in the simplest form:

$$\left\{\sum_{i}\frac{-1}{2}\nabla_{i}^{2}-\sum_{i,I}V_{I}(|\boldsymbol{r}_{i}-\boldsymbol{R}_{I}|)+\sum_{i\neq j}\frac{1}{|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}|}\right\}\phi_{e}(\boldsymbol{R}_{I},\boldsymbol{r}_{i})=E_{e}\phi_{e}(\boldsymbol{R}_{I},\boldsymbol{r}_{i})$$
(2.6)

2.2. Thomas-Fermi-Dirac approximation

The Thomas-Fermi (TF) model is considered as modern DFT precursor since the approach describes electron density n(r) of N numbers of electrons:

$$\int d^3 \mathbf{r} \, n(\mathbf{r}) = N \tag{2.7}$$

as basic variable instead of wave function. Basic ideal of TF model is approximating kinetic energy for inhomogeneous systems as locally homogeneous [24,25]. The TF model neglects the exchange energy of electron due to the Pauli principle. Therefore, the ground-state energy $E_{TF}[n(r)]$ for electrons in an external potential is written as following:

$$E_{TF}[n] = \hat{T} + \hat{V}_{eN} + \hat{V}_{ee}$$

= $C_1 \int n(\mathbf{r})^{\frac{5}{3}} d^3\mathbf{r} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int d^3 \mathbf{r} d^3 \mathbf{r}'^{\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}$ (2.8)

where the first term is the local approximation to the kinetic energy of the ideal Fermi gas (Thomas-Fermi kinetic energy) with $C_1 = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} = 2.871$ in the atomic unit. The second

term is the classical electrostatic nuclear-electron Coulomb interaction energy (classical electrostatic Hartree energy). Finally, the last term is the potential energy due to their mutual electronic repulsion. In 1930, the exchange energy term is added by Dirac [30] as a form of local exchange with $C_2 = -\frac{3}{4}(3\pi^2)^{\frac{1}{3}}$. The equation (2.8) can be expressed as:

$$C_1 \int n(\mathbf{r})^{\frac{5}{3}} d^3\mathbf{r} + C_2 \int n(\mathbf{r})^{\frac{4}{3}} d^3\mathbf{r} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int d^3 r d^3 r'^{\frac{n(r)n(r')}{|r-r'|}}$$
(2.9)

Herein, the ground state density and energy can be obtained using the method of Lagrange multiplier by an unconstrained minimization of the functional with the Lagrange multiplier μ is the chemical potential:

$$\delta\{E_{TF}[n] - \mu(\int d^3 r n(r) - N)\}$$
(2.10)

In fact, due to lacking principal physics and chemistry quantities such as atomic shell structures and binding molecules, the kinetic energies in approximation form of Thomas-Fermi-Dirac approximation fails to descript electrons in matter for almost realistic systems. However, the appearance of Thomas-Fermi-Dirac approximation laid the foundation for using electron density as variables in DFT.

2. 3. Hohenberg-Kohn Theorems

It is different to aforementioned approaches, that only applies to a problem of electron with fixed nuclear, Hohenberg-Kohn theorems can be applied for interacting electrons moving under the influences of an external potential $V_{ext}(\mathbf{r})$ [26]. Then the Hamiltonian is given by:

$$\widehat{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 + \sum_{i} V_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.11)

where the first term and the second term indicate the kinetic and electron-electron interaction. DFT works based on two theorems as follows:

- Theorem I: For any system of interacting particles in an external potential V_{ext}(r), the potential V_{ext}(r) is determined uniquely, except for a constant, by the ground state particle density n₀(r).
- Theorem II: A universal functional for the energy E[n] in terms of the density n(r) can be defined, valid for any external potential V_{ext}(r). For any particular V_{ext}(r), the exact ground state energy of the system is the global minimum value of this functional, and the density n(r), and the density n(r) that minimizes the functional is the exact ground state density n₀(r).

In summary, according to Hohenberg-Kohn theorems, the ground state wave function $\psi_0(x_1, x_2 \dots x_3)$ is a functional of ground state electron density $n_0(r)$. Herein, the electron density is expressed as:

$$n(\mathbf{r}) = \int d_{s_1} d^3 x_2, d^3 x_3, \dots, d^3 x_n |\psi(r, s_1, x_2, \dots, x_n)|^2$$
(2.12)

The ground state energy is also a functional of density:

$$E_0 = \langle \psi_0[n_0] | \hat{H} | \psi_0[n_0] \rangle = E[n_0]$$
(2.13)

The electron density that minimizes the energy functional is the ground state density

$$E[n_0] \le E[n] \tag{2.14}$$

2. 4. Kohn-Sham (KS) equations

After the basic background of DFT is already provided, by using variational principle to derive the effective single-particle equations for the complicated many particle problems, Kohn and Sham makes DFT to be more practical. The Kohn-Sham (KS) equation reduces the interacting many-body problems into non-interacting single particle problem by adding the exchange-correlation potential $\mu_{XC}(\mathbf{r})$ [27]. The ground state energy functional from Hohenberg-Kohn expression is rewritten as:

$$E_{n}[n] = \int V(\mathbf{r})n(\mathbf{r})d^{3}\mathbf{r} + F[n]$$

= $\int V(\mathbf{r})n(\mathbf{r})d^{3}\mathbf{r} + T_{S}[n] + \frac{1}{2}\int \frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}d^{3}\mathbf{r}d^{3}\mathbf{r}' + E_{XC}[n]$ (2.15)

where $T_S[n]$ is the kinetic energy of a system of non-interacting particles with density $n(\mathbf{r})$, and $E_{XC}[n]$ is the exchange correlation energy of an interacting system with density $n(\mathbf{r})$. Following the condition $\int \delta n(\mathbf{r}) d\mathbf{r} = 0$, Kohn and Sham proved that for a given $V(\mathbf{r})$ and $\mu_{XC}(\mathbf{r})$, the calculated $n(\mathbf{r})$ of equation (2.15) is the same as the $n(\mathbf{r})$ estimated from solving the Schrödinger equation for single-particle system. The Hamiltonian equation for the auxiliary non-interacting single-particle moving in the effective potential single particle potential $V_{eff}(\mathbf{r})$ in Hartree atomic in units $\hbar = m_e = e = \frac{4\pi}{\epsilon_0} = 1$ is written as:

$$\widehat{H} = -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})$$
(2.16)

For a N non-interacting particle system, the ground state energy can be obtained by solving the Schrödinger equation for non-interacting particle as following (KS equation):

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$
(2.17)

Herein, the electron density n(r) of N the number of electrons, which is given by sums of squares of orbitals:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\Psi_i|^2$$
(2.18)

The exchange-correlation potential (or the exchange-correlation energy) is defined as:

$$\mu_{XC}(\mathbf{r}) \equiv \frac{\delta E_{XC}[n]}{\delta n(r)} \tag{2.19}$$

and the effective potential $V_{eff}(r)$ is given by:

$$V_{eff}(\mathbf{r}) = V_H(r) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{XC}(\mathbf{r})$$
(2.20)

where $V_H(r)$ is classical electrostatic Hartree energy. Since the $V_{eff}(r)$ depends on electron density n(r), the KS equation needs to be solved self-consistently.

2. 5. Local density approximation (LDA)

Solids can be simply considered as close to the limit of homogeneous electron gas immersed in a uniform positive charge background [31,32]. Thus, basic idea of local density approximation (LDA) is considering the general inhomogeneous system as locally homogeneous but interacting electron gas with a density $n(\mathbf{r})$.

The total exchange-correlation energy for spin-unpolarized system is given by:

$$E_{XC}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{XC}^{homo}(n(\mathbf{r})) d^{3}\mathbf{r}$$

= $\int drn(\mathbf{r}) [\epsilon_{X}(n(\mathbf{r})) + \epsilon_{C}(n(\mathbf{r}))]$
= $E_{X}[n(r)] + E_{C}[n(r)]$ (2.21)

And exchange-correlation potential:

$$\mu_{XC}^{LDA} = \left[\frac{d}{dn} \{ n \epsilon_{XC}^{homo}(n) \} \right]_{n=n(r)}$$
(2.22)

The energy density ϵ_{XC}^{homo} is only density dependent and can be decomposed into exchange energy density $\epsilon_X(n(\mathbf{r}))$ term and correlation energy density $\epsilon_C(n(\mathbf{r}))$ term. Correspondingly, the exchange-correlation energy functional $E_{XC}^{LDA}[n(\mathbf{r})]$ can also be treated as independent part of exchange energy functional $E_X[n(\mathbf{r})]$ and correlation energy functional $E_C[n(\mathbf{r})]$. The exchange energy density of homogeneous electron density of the homogeneous electron gas:

$$\epsilon_X(n(\mathbf{r})) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} n(\mathbf{r})^{\frac{1}{3}}$$
 (2.23)

The exchange energy functional part $E_X[n(\mathbf{r})]$ can be accurately described as [31,32]:

$$E_X[n(\mathbf{r})] = \int n(\mathbf{r}) \,\epsilon_X(n(\mathbf{r})) d\mathbf{r} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} n(\mathbf{r})^{\frac{4}{3}}$$
(2.24)

In contrast, for the correlation energy functional $E_C[n(\mathbf{r})]$ part, analytic expression only valid at low- and high-density, corresponding to infinitely weak and infinitely strong correlation limit. In the low-density limits, the correlation energy density ϵ_C is given as:

$$\epsilon_{C} = \frac{1}{2} \left(\frac{g_{0}}{r_{s}} + \frac{g_{0}}{r_{s}^{3/2}} + \cdots \right)$$
(2.25)

In the high-density limits, the correlation energy density ϵ_c is expressed as:

$$\epsilon_c = Alog(r_s) + B + r_s(Clog(r_s) + D)$$
(2.26)

Where r_s is the Wigner-Seitz radius, which can be calculated proportional to the density n:

$$r_{S} = \left(\frac{3}{4\pi n}\right)^{1/3} \tag{2.27}$$

For the spin-polarized systems, the total exchange-correlation energy is expressed as:

$$E_{XC}^{LDA}[(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}))] = \int n(\boldsymbol{r}) \epsilon_{XC}^{homo}(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})) d^{3}\boldsymbol{r}$$
(2.28)

Herein, the electron density $n = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$, and exchange-correlation potential:

$$\mu_{XC}^{LDA} = \left[\frac{\delta}{\delta n} \left\{ n \epsilon_{XC}^{homo} \left(\left(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}) \right) \right) \right\} \right]_{n_{\uparrow} = n_{\uparrow}(\boldsymbol{r}), n_{\downarrow} = n_{\downarrow}(\boldsymbol{r})}$$
(2.29)

The exact exchange correlation function is known in terms of the spin-unpolarized functional [33]:

$$E_X[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] = \frac{1}{2} (E_X[2n_{\uparrow}(\boldsymbol{r})] + E_X[2n_{\downarrow}(\boldsymbol{r})])$$
(2.30)

Fractional spin-polarization can be defined as:

$$\zeta(\mathbf{r}) = \frac{n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})}{n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})}$$
(2.31)

where $\zeta = 0$ indicates the diamagnetic spin-unpolarized systems. Correspondingly, the exchange-correlation potential in LDA is given by:

$$V_{XC}^{LDA} = \frac{\delta E^{LDA}}{\delta n(\mathbf{r})} = \epsilon_{XC}^{homo} (n(\mathbf{r})) + n(\mathbf{r}) \frac{\epsilon_{XC}^{homo} (n(\mathbf{r}))}{\delta n(\mathbf{r})}$$
(2.32)

The simple and effective LDA approximation usually reproduces quite good structure properties such as densities of states and band structures. However, the LDA approach approximates the inhomogeneous system as a local constant density $n(\mathbf{r})$, leading to several issues. For example, when the density undergoes rapid changes such as in molecules, this approximation becomes inaccurately. In addition, The LDA is not free form spurious selfinteraction in Hartree term. Therefore, the LDA potential decays asymptotically with an exponential form. However, in fact, the exchange-correlation potential must decay slowly not rapidly, that leads to the too negative binding energies and too small ionization potentials.

2. 6. Generalized-gradient approximation (GGA)

An improvement to LDA can be made by adopting the gradient of the density $\nabla n(\mathbf{r})$. The electron density is treated semi-locally, then so-called Generalized Gradient Approximation (GGA) [34-36]. The total exchange-correlation energy for spin-polarized system can be given by:

$$E_{XC}^{GGA}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] = \int f(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}), \nabla n_{\uparrow}(\boldsymbol{r}), \nabla n_{\downarrow}(\boldsymbol{r})) d^{3}\boldsymbol{r}$$
$$= \int \epsilon_{XC}^{homo}(n(\boldsymbol{r})) F_{XC}f(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}), \nabla n_{\uparrow}(\boldsymbol{r}), \nabla n_{\downarrow}(\boldsymbol{r})) d^{3}\boldsymbol{r} \quad (2.34)$$

Herein, the F_{XC} is the enhancement factor with dimensionless quantity, which can be decomposed to exchange F_X and correlation F_C part. In the limiting case:

$$f(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}), 0, 0) = n(\boldsymbol{r})\epsilon_{XC}^{homo}(n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r}))$$
(2.35)

For exchange energy part, spin-scaling relation exists:

$$E_{X}[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2} (E_{X}[2n_{\uparrow}] + E_{X}[2n_{\downarrow}])$$
(2.36)

Thus, we only need to define the spin-unpolarized cases.

LDA usually underrates the exchange energy among toms, GGA improves LDA and corrects the total energy of atoms, and then the binding energy increases. Furthermore, GGA also predicts more accurately in terms of lattice constants, bond lengths in molecules, and so forth. However, for both GGA and LDA approach does not get rid of the spurious selfinteraction, that leads to the wrong ground state for strongly correlated systems such as rareearth elements and transition metals oxides. Furthermore, the calculated band gaps are still underestimated compared to experiment values. Since there is still no precise solution, exchange-correlation energy approximation still is an active researching area.

2. 7. Solutions of Kohn-Sham equations

The schematic representation of the self-consistent loop for a solution of Kohn-Shame equation is illustrated in Fig. 2. 1.



Fig. 2.1: The flowchart of self-consistent calculation.

To solve the KS equation, for the first step, an initial electron density is evaluated from the superposition of atomic densities. Secondly, from estimated initial electron density, the effective potential $V_{eff}(\mathbf{r})$ is constructed. Next, the KS equation is solved by single particle eigenvalue and wave function, and then a new electron density is calculated. If new electron density does not meet the convergence condition, the calculations will be continuously back to the first step with a new electron density, that is generated by mixing with the calculated electron density from the previous iteration. The quantity of convergence condition is evaluated by the change of electron density, the total energy, the atomic force acting on atom, or a combination of all listed conditions, that need to be no larger than some fixed criteria. Set of self-consistent equations that will be solved simultaneously until the convergence is achieved.

The categorization of first-principles calculation according to KS equation solution is shown in Fig 2. 2. (adopted from Erich Winner classification)[37]. The DFT is employed in this dissertation is VASP (plane wave and pseudopotential) [38,39] and FLAWP [40,41]. Their physics background is briefly given below.



Fig. 2.2: The classification of first-principles calculation [40]

2. 7. 1. Plane wave and pseudopotential

The chemical bonds between atoms are formed by valence electrons while core electrons do not contribute. Therefore, once the bonding is formed, the wavefunction of valence electrons changes significantly, while core electrons have negligible effects. The core electrons are treated spherically symmetric. It is different from all-electron approach, where both core and valence electrons are taken into account, the pseudopotential scheme only considers the valence electrons and describes the valence electrons by pseudo-wavefunctions. The wavefunction function is expanded in form of linear combination of planewaves [41,42]:

$$\psi_{i,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_i, \mathbf{G}\left[\frac{1}{\sqrt{\Omega}}e^{i(\mathbf{G}+k)\mathbf{r}}\right]$$
(2.37)

2.7.2.FLAPW

FLAPW is the full-potential linearized augmented-plane-wave (LAPW) method, providing very robust and precise results [43, 44]. The basis function of LAPW is employed in FLAPW method. The plane wave is treated in term of the spheres (muffin spherical) centered at each atomic site (r < S) and the remaining interstitial region (r > S):

$$\psi_{\boldsymbol{k},\boldsymbol{G}}(\boldsymbol{r}) = \begin{cases} \exp\left((i\boldsymbol{k} + \boldsymbol{G})\boldsymbol{r}\right) & \boldsymbol{r} > S\\ \sum_{l,m} \left(a_{lm}^{\mu,\boldsymbol{G}}(\boldsymbol{k})u_{l}^{\mu}(\boldsymbol{r}) + b_{lm}^{\mu,\boldsymbol{G}}(\boldsymbol{k})\dot{u}_{l}^{\mu}(\boldsymbol{r})\right)Y_{lm}(\hat{\boldsymbol{r}}^{\mu}) & \boldsymbol{r} < S \end{cases}$$
(2.38)

However, the full-potential and change density are described without shape approximation in the interstitial region and inside the spherical muffin-tin approximation.

$$V(r) = \begin{cases} \sum_{G} G_{I}^{G} \exp(iGr) & r > S \\ \sum_{L} V_{MT}^{L}(r) Y_{L}(\hat{r}) & r < S \end{cases}$$
(2.39)

Chapter 3: Robust half-metallicities of alkali-metal-based half-Heusler compounds

This chapter is written based on T. T. Hoang et al [42]. The half-metallicities of alkali-metalsbased Heusler compounds ACrZ (A = Li, Na, and K; Z = As, Sb, and P) were studied. Our results show that it is different from most of proposed HMs so far that the present compounds have wide band gaps (1.60 – 2.38 eV). Therefore, their half-metallicities are stable against external factors, such as thermal excitation, strains, and surface/interface effects.

3.1. Introduction

Half-metals (HMs) are materials whose one spin channel behaves as semiconductor and the other behaves as metal [11,12]. The charge current in only one spin channel enhances the efficiency of spintronic devices, such as magnetic tunnel junctions [43,44]. Although HMs have been theoretically proposed in various materials, only a few have been confirmed experimentally [11]. Among the proposed HMs, Heusler compounds have attracted significant interest since their chemical composition can be altered for diverse functionalities [1,2]. Most of them also have high Curie temperature, T_C [45]. There are two types of Heusler compounds, half-Heusler and full-Heusler, conventionally denoted as XYZ and X₂YZ, respectively. Herein, we focus on the half-Heusler compound XYZ and discuss its possible practical applications to spintronics.

The first theoretically predicted HM is the half-Heusler compound NiMnSb [12], with an estimated band gap of ~0.48 eV in the minority spin channel [12,46]. A few years later, the

100% spin polarization (SP) of NiMnSb was confirmed at a low temperature (10K) [47]. However, its SP dropped significantly to nearly 50% at room temperature [48]. Subsequently, systematic density functional studies on XYZ have been performed intensively to find optimal HMs for practical applications [46,49], where X and Y are the transition elements and Z is an *sp* element. Even though some Co-based compounds are predicted to have wider band gaps than that of NiMnSb, most XYZ compounds have band gaps below 1 eV. HMs have also been predicted in certain X₂YZ compounds (X = Co, Fe, Rh, and Ru; Y = Ti, V, Cr, Mn, and Fe; Z = Al, Ga, In, Tl, Ge, Sn, and Pb) [50]. Although some Co-based compounds were successfully synthesized [51,52], they failed to achieve high SP at room temperature [53-55], except for Co₂MnSi [56]. The predicted narrow band gaps (0.2–0.5 eV) are the plausible origin of the failure [57].

The reduced SP has been attributed to thermal and surface/interface effects [11]. Thermal fluctuation may lead to spin depolarization at elevated temperatures [58-61]. At surfaces/interfaces, chemical composition, and symmetry different from bulk may also decrease SP [62-65]. Above all, materials with wide band gaps likely retain half-metallicities even under high temperatures and at surfaces/interfaces [11,66]. Most studies are dedicated to transition-metal (T)-based Heusler compounds. However, due to their relatively narrow band gaps they lose half-metallicity easily. Meanwhile, alkali-metal(A)-based Heusler compounds have been relatively overlooked, despite some meaningful theoretical works [67-73] have been done previously. Hereafter, we differentiate the A-based from the T-based compounds by denoting them as AYZ and TYZ (or T₂YZ), respectively. LiMnSi is the first predicted AYZ to exhibit half-metallicity at a lattice constant expanded by 14% [67]. Subsequently, other AYZ, such as LiCrAs [68], NaCrAs [70], NaCrP [69], KMnP [71], and NaZrZ (Z = P, As, and Sb)

[72], were predicted to be HMs. Broadly, AYZ tends to show much wider band gaps than TYZ. For example, the band gap of NaCrP is 3.21 eV [69], while that of CoCrP is 1.34 eV [49]. Furthermore, NaCrAs preserves its half-metallicity at the (001), (010), and (111) surfaces with hydrogen adsorption [73]. It is also notable that CsCrS, where a VI element is employed for Z instead of a V element of the present ACrZ, shows the wide band gap of 1.926 eV with the large magnetic moment of $5\mu_B$ [76].

Herein, we extend systematic density functional study on the half-metallicities of alkali-metal-based half-Heulser compounds, i.e., ACrZ (A = Li, Na, and K; Z = As, Sb, and P). Most investigated ACrZ show half-metallicities with wide band gaps (1.60–2.38 eV) at their equilibrium lattice constants. The band gaps originate from the sublattice zinc-blende (ZB) CrZ. An alkali element serves to expand lattice constant, widens the band gap, and provides one more valence electron to the system. Further, the robustness of half-metallicity against strain and at surface/interface is analyzed to suggest optimal HMs for real applications. Moreover, formation energy is estimated and discussed for structural stability.

3.2. Structural models

The half-Heusler and the regular full-Heusler compounds crystallize in the noncentrosymmetric cubic C1_b structure with the F $\overline{4}$ 3m (216) space group and in the centrosymmetric cubic L2₁ structure with the F \overline{m} 3m (225) space group, respectively [74]. Regular X₂YZ and α -phase XYZ are based on the rock-salt (RS) sublattice of YZ. The additional X in regular X₂YZ (α -phase XYZ) occupy (every other) body center of the RS sublattice. Unlike the regular X₂YZ, in XYZ, XY or XZ also form the RS sublattice. Three possible phases (α , β , and γ) of XYZ are listed in Table 3.1. The most stable β -phase is

presented in Fig. 3. 1(a) [67], where element Z is positioned in every other body-centered site of the RS structure of ACr. From another viewpoint, the β phase is based on the ZB structure of CrZ into which fcc A fits.

Fig. 3. 1(b) represents an asymmetric slab of 14 layers exhibiting ACr-termination (ACr-term) and Z-termination (Z-term) to simulate two nonequivalent bulk terminations. Surface, subsurface, and center layer are denoted as (S), (S-1), and (C), respectively. The vacuum spacing of 15 Å between adjacent slabs eliminates any spurious interactions. The increased number of layers changes the physical properties negligibly, including magnetic moments (< 0.002 μ_B) and interlayer distances (< 0.003 Å), implying that the 14 layers are thick enough to simulate the ACr- and Z-term surfaces.

Table 3. 1. The possible phases of half-Heusler compound XYZ and their sublattice structures^a.

Structure	Х	Y	Ζ	rock-salt	zinc-blende
α	4c	4b	4a	YZ	XY, XZ
β	4b	4a	4c	XY	YZ, XZ
γ	4a	4c	4b	XZ	XY, YZ

^a The positions (4a, 4b, and 4c) are denoted in terms of the Wyckoff notation



Figure. 3. 1: (a) The C_{1b} structure of the β -phase half-Heusler ACrZ compound and (b) 14 ML slab to simulate ACr-term and Z-term ACrZ (001) surfaces. Red, blue, and green spheres represent A, Cr, and Z atoms, respectively. Surface, subsurface, and center layers are denoted by (S), (S-1), and (C), respectively.

3. 3. Computational details

Density functional calculations are performed using Vienna Ab initio Simulation Package [38]. The generalized gradient approximation of the Perdew, Burke, and Ernzerhof [36] is used to analyze the exchange-correlation interaction within the projector augmentedwave scheme [39]. An energy cutoff of 550 eV is used for the wave function expansion. For Brillouin zone integration, the *k*-point meshes of $15 \times 15 \times 15$ and $21 \times 21 \times 1$ in the Monkhorst–Pack scheme are employed for the bulk and surface calculations, respectively. Convergence for the number of *k*-points is tested critically. In the surface calculations, interlayer distances are relaxed with the force criteria of 1×10^{-3} eV/Å.

3. 4. Results and discussions

We first estimated the structural and magnetic phases of ACrZ from total energy calculations as functions of lattice constant. The results are presented in Fig. 3. 2. and Fig. 3. 3. Table 3.2. summarizes the stable phase and energy difference between the AFM and FM states ($\Delta E = E_{AFM} - E_{FM}$). FM is more stable than AFM over a wide range of lattice constants. Structurally, ACrZ is most stable in the β -phase, except for KCrSb, which prefers the γ -phase. Even though the FM stability of a K-based compound is insensitive to the atomic number, with an increasing atomic number of Z, the FM state tends to stabilize further than the AFM state (Table 3. 2). The estimated equilibrium lattice constants in the FM states of ACrP are 5.69, 6.15, and 6.75 Å; of ACrAs are 6.00, 6.37, and 6.94 Å; and of ACrSb are 6.42, 6.78, and 7.29 Å for A = Li, Na, and K, respectively. The larger atomic numbers of A and Z result in the larger lattice constant.

Table 3. 2. Energy difference ΔE (meV/fu) between AFM and FM states, equilibrium lattice constant *a* (Å), atom-projected magnetic moment (μ_B), total magnetic moment per formula unit (μ_B), band gap (eV) of minority spin state E_g , and *k*-points of CBM and VBM of ACrZ. The asterisk (*) indicates pseudo band gap.

Compound	phase	ΔΕ	а	m _{Cr}	m_Z	m _{tot}	Eg	CBM-VBM
LiCrP	β	27	5.69	3.35	-0.15	3.51	1.99*	Х–Г
NaCrP	β	161	6.15	3.82	-0.19	4.00	2.28	X–L
KCrP	β	184	6.75	3.97	-0.25	4.00	2.38	X–X
LiCrAs	β	142	6.00	3.62	-0.12	3.98	1.90*	Х–Г
NaCrAs	β	196	6.37	3.73	-0.18	4.00	2.18	X–L
KCrAs	β	187	6.94	3.88	-0.26	4.00	2.13	Γ–Χ
LiCrSb	β	231	6.42	3.67	-0.14	4.00	1.60	Х–Г
NaCrSb	β	222	6.78	3.79	-0.20	4.00	1.88	Х–Г
KCrSb	γ	187	7.29	3.90	-0.24	4.00	2.17	X–L



Figure. 3. 2: Calculated total energy of half-Heusler ACrZ (A = Li, Na, and K; Z = P, As, and Sb) in α -, β -, and γ -phase as functions of lattice constant.



Figure. 3. 3: Calculated total energies of half-Heusler ACrZ (A = Li, Na, and K; Z = P, As, and Sb) in α -, β -, and γ -phase as functions of lattice constant *a*.

3.4.1. Magnetic properties

The magnetic moments are listed in Table 3. 2. As expected, the magnetic moment of ACrZ corresponds mainly to the transition element Cr, while the contributions from other elements are negligible. Specifically, the magnetic moment of the alkali-element A is too small to be listed in Table II. The *sp* element Z has a negatively induced magnetic moment. Notably, unlike ACrZ with a small lattice constant, the one with a large lattice constant has an integer magnetic moment (in μ_B). Since the integer magnetic moment indicates half-metallicity, the lattice constant plays a crucial role in determining the half-metallicity of ACrZ, as discussed in the following subsections.

The Slater–Pauling rules can estimate the magnetic moment of HMs [11]. The Slater– Pauling rule for HM β -ACrZ is so-called "rule of 8", expressed as $m_{tot} = (Z_t - 8) \mu_B$, where Z_t is the total number of valence electrons. By this rule, the magnetic moment of HM β -ACrZ is estimated as 4.00 μ_B , which is consistent with the observed first-principles calculations. We remind here that the magnetic moment of HM ZB-CrZ, a sublattice of β -ACrZ (Fig. 3. 1(a)), is estimated as 3.00 μ_B by the same rule [75]. Thus, presumably, the alkali-element A provides one more valence electron to the system to enhance the magnetic moment by $1\mu_B$.

3.4.2. Band gap

Fig. 3. 4. shows the band structures of ACrZ, indicating the half-metallicity character of ACrZ. Gray and black lines represent the majority and minority spin bands, respectively. The blue horizontal line indicates the Fermi level E_F set to zero. Red lines mark the conduction

band minimum (CBM) and the valence band maximum (VBM) with an arrow suggesting the band gap width. The minority spin bands have gaps at E_F , except for LiCrP and LiCrAs, while the majority bands are metallic. In other words, ACrZ are HMs, except for LiCrP and LiCrAs. The estimated energy band gaps are listed in Table II. The asterisk on the value implies a pseudo band gap located at energy other than E_F . Table II shows that the HM compound has an integer magnetic moment (in μ_B).

The investigated ACrZ have much wider band gaps (1.60-2.38 eV) than previously reported HMs, including TYZ and T₂YZ; namely, NiMnSb (~0.48 eV) [15,49], Co₂MnSi (0.41 eV), Co₂MnGe (0.21 eV) [50], CrO₂ (1.50 eV) [76], and Fe₃O₄ (0.50 eV) [77]. Most of the band gaps are indirect; CBM of ACrZ (but KCrAs) are located at the same *k*-point X, while their VBM are located at different *k*-points (Table II). Only KCrP has a direct band gap. Noteworthy, KCrSb almost has a direct band gap because of the negligible difference (~0.03 eV) between the maxima at the X and L points in the valence band of KCrSb. The external factors, such as heat, surface, and interface, may break the half-metallicity with a narrow band gap, suggesting the wide band gaps of ACrZ must be advantageous in real applications [14,69].



Figure. 3. 4: Majority (gray) and minority (black) spin band structures of ACrZ (A = Li, Na, and K; Z = As, Sb, and P) at their equilibrium lattice constants. Red lines mark CBM and VBM.



Figure. 3. 5: Band structures of ZB-CrP, ZB-CrAs, and ZB-CrSb in majority (gray) and minority (black) spin state of at their equilibrium lattice constants, 5.31, 5.66, and 6.14 Å. Red lines mark CBM and VBM.

3. 4. 3. Origin of wide band gap

Now we discuss the origin of the relatively wide band gaps of ACrZ than those of the conventional TYZ. As listed in Table II, most ACrZ stabilizes in the β phase, unlike TCrZ, which stabilizes in the α -phase [67]. This phase difference results in different band gap formation mechanisms, as discussed in detail below. ZB-TCr provides the band gap of TCrZ [78,79], while the band gap of ACrZ will be seen to originate from ZB-CrZ. Three key facts are established from Table II: (i) a large A atom corresponds to a wide band gap of ACrZ, (ii) a large Z atom indicates a narrow band gap, and (iii) only ACrZ with a lattice constant larger than 6.00 Å are HMs. Therefore, the lattice constant plays a key role in determining the half-metallicity of ACrZ. It is usually expected that a band gap formed between bonding and antibonding states is expected to narrow, as lattice constant increases. For example, a TCrZ compound, RuCrAs (a = 5.74 Å, $E_g = 0.58$ eV) [46] has a considerably smaller band gap than FeCrAs (a = 5.48 Å, $E_g = 0.96$ eV) [46,78]. However, the band gap of the present ACrZ widens with the lattice constant expansion.

The origin of the wide band gap of ACrZ may be revealed by comparing their band structure with that of the sublattice ZB-CrZ (Fig. 1(a)). ZB-CrZ itself is known to be an HM at or near its equilibrium lattice constant [80], which is evident from our calculations on band structures of ZB-CrP, ZB-CrAs, and ZB-CrSb as presented in Fig. 3. 5. Here NaCrAs and ZB-CrAs are taken as representatives of ACrZ and ZB-CrZ, respectively. Fig. 3. 6. compares the orbital-resolved minority spin band structures of NaCrAs and ZB-CrAs, employing the same lattice constant of equilibrium *a* for NaCrAs. The band structure of NaCrAs is similar to

that of ZB-CrAs. It shows clearly that the origin of the band gap formation of NaCrAs is identical to that of ZB-CrAs. The *d* orbitals of Cr are split into t_{2g} and e_g states in the tetrahedral environment, where Cr (As) is surrounded by four nearest neighbors As (Cr).



Figure. 3. 6: Orbital-resolved minority spin band structure of NaCrAs and ZB-CrAs at equilibrium lattice constant of NaCrAs a = 6.37 Å. Cr- t_{2g} , Cr- e_g , and As-p orbitals are denoted in red, blue, and green, respectively. The symbol size is proportional to the weight of the orbital. The Fermi level E_F is set to zero.



Figure. 3. 7: Orbital-resolved minority spin band structure of ZB-CrAs at a = 5.66, 6.01, and 6.37 Å, in which 5.66 and 6.37 are equilibrium lattice constant of ZB-CrAs and NaCrAs. Cr- t_{2g} , Cr- e_g , and As-p orbitals are denoted in red, blue, and green, respectively. The symbol size is proportional to the weight of the orbital. The Fermi level E_F is set to zero.

Hence, it may be enough for disclosing of the wide band gap of ACrZ to discuss the dependence of the band gap of CrAs on the lattice constant. According to the band gap formation of ZB-CrZ [75,80], the t_{2g} states of Cr form bonding and antibonding hybrid states with the p orbitals of As, while the eg states remain comparatively nonbonding. The band gap is formed by As-*p* orbital (bonding) and Cr- t_{2g} orbital (antibonding) states, as seen in Fig. 3. 6. The band gap of ZB-CrAs increases monotonically with lattice constant a, expanding it from 5.66 Å (the equilibrium lattice constant of ZB-CrAs) to 6.37 Å (the equilibrium lattice constant of NaCrAs), as shown in Fig. 3. 7, Fig. 3. 8, and Fig. 3.9. The band gap of ZB-CrAs at the equilibrium lattice constant of NaCrAs reaches to 2.33 eV which is slightly wider than the band gap (2.18 eV) of NaCrAs. The lattice constant is expanded by the element A must be a key origin of the wide band gap of ACrZ. When a reaches 6.37 Å (equilibrium lattice constant of NaCrAs) from 5.66 Å, the band gap increases from 1.85 eV to 2.33 eV, which is slightly larger than the 2.18 eV of NaCrAs. Two factors compete in determining the width of band gap. First, the covalent bonding weakens as the lattice expands, thus the band gap tends to reduce the width of the gap. Another effect of the lattice expansion is to narrow the valence and conduction bands themselves, which effectively widens the band gap, as observed in the orbital-resolved density of states ZB-CrAs at a = 5.66, 6.01, and 6.37 Å for minority spin states in Fig. 3. 9. To see the effects, the centers of the As-p VB, and $Cr-t_{2g}$ and $Cr-e_g$ CB are calculated from the orbital-decomposed DOS presented in Fig. 3. 9 and listed in Table 3. 3. As expected, separation between the centers of VB and CB decreases as the lattice increases due to weakened covalent bonding. However, separation between the edges of VB and CB increases because CB and VB narrow down as the lattice increases. The band gap widening by the narrowed bands is dominant over the band gap narrowing by the weakened covalent bonding in CrAs. Thus, the

band gap of CrAs increases as the lattice constant increases. The element A in ACrZ expands the lattice constant and provides one extra valence electron, which fills the spin-up bands but negligibly affects the spin-down band. Consequently, the band gap is widened with increased magnetic moment by 1 μ_B compared to ZB-CrZ.



Figure. 3. 8: The band gap of ZB-CrAs as a function of lattice constant over the range between 5.66 Å and 6.37 Å which are the lattice constants of ZB-CrAs and NaCrAs, respectively.



Figure. 3. 9: Orbital-resolved density of states of ZB-CrAs as the increases of lattice constant a = 5.66, 6.01, and 6.37 Å for minority spin states. The Fermi level E_F is set to zero. $\text{Cr-}t_{2g}$, $\text{Cr-}e_g$, and As-p orbitals are denoted in red, blue, and green, respectively. Note that equilibrium lattice constants of ZB-CrAs and NaCrAs are 5.66 and 6.37 Å, respectively.

Table 3. 3: Center of CB Cr- t_{2g} , CB Cr- e_g , and VB As-p, and the separation ΔE (in eV) as the increases of lattice constant a = 5.66, 6.01, and 6.37 Å.

Lattice	Center of	Center of	Center of	ΔE	ΔΕ
constant	CB Cr- <i>t</i> _{2g}	CB Cr-eg	VB As-p	Cr-t _{2g} –As-p	Cr-e _g –As-p
5.66	2.14	2.31	-2.19	4.33	4.50
6.01	2.38	2.50	-1.76	4.17	4.26
6.37	2.58	2.66	-1.39	3.97	4.05

3.4.4. Formation Energy

The structural stability estimated by formation energy is of crucial importance in practical applications. To investigate the structural stability, the formation energy of ACrZ against the decomposition into bcc A and ZB-CrZ is calculated using the following equation.

$$E_{form} = E_{ACrZ} - (E_A + E_{CrZ})$$
(3.1)

where E_{ACrZ} , E_A , and E_{CrZ} are the total energies of ACrZ, bcc A, and ZB-CrZ, respectively. The formation energy is much more conservative against decomposition into elements of A, Cr, and Z. The estimated formation energies of ACrP, ACrAs, and ACrSb (A = Li, Na, and K) are presented in Fig. 3. 10, where the role of A and Z elements are evident. The negative (positive) formation energy means that ACrZ is energetically more stable (unstable) against the composition into bcc A and ZB-CrZ. From Fig. 4, it is learnt that first, the atomic number of A plays a key role in determining the formation energy. The smallest Li and the largest K led to negative and positive formation energies, respectively. Second, the larger Z element resulted in the more negative formation energy of ACrZ. Consequently, LiCrSb and KCrP shows the most and the least stable against the decomposition into bcc A and ZB-CrZ, respectively.



Figure. 3. 10: Formation energies of ACrP, ACrAs, and ACrSb (A = Li, Na, and K). Left, middle, and right panel present ACrP, ACrAs, and ACrSb, respectively. Negative (positive) formation energy marked by red shade denotes a stable (unstable) structure.
3.4.5. Strain effects

In practical applications to spintronics, magnetic materials are usually exposed to thinfilm under strain. Furthermore, strain is also utilized to tailor the electronic and magnetic properties of materials. Thus, investigating the in-plane strain effect on the half-metallicity of ACrZ is crucial. Energy variations in CBM (E_{CBM}) and VBM (E_{VBM}) against the strain are plotted in Fig. 3. 11. The in-plane strain is given by $\eta = \frac{a-a_0}{a_0}$, where a_0 and a are equilibrium and strained ab plane lattice constants, respectively. The lattice constant c, shown in Fig. 3. 12. as c/a ratio, is optimized from total energy calculations. Fig. 3. 11. shows that the halfmetallicity of unstrained ACrZ is robust over a wide range of compressive and tensile strains, implying that HM ACrZ has a flexible advantage in forming hybrid systems with various semiconductors. Even non-HM LiCrP and LiCrAs become HM under specific tensile in-plane strain. LiCrAs also turn into HM under small tensile strain, around +2%. Thus, the proper choice of substrate can easily achieve the half-metallicity of LiCrAs.

The E_{CBM} and E_{VBM} under in-plane strain are discussed for practical device design. Fig. 3. 11. shows that E_{CBM} and E_{VBM} behave differently between the Li- and K-based compounds. The Na-based compounds show their mixed behavior. First, E_{CBM} of the Li-based compounds (i.e., LiCrP, LiCrAs, and LiCrSb) is located just below or just above E_F at $\eta = 0$, while their E_{VBM} is far below E_F. On the other hand, E_F of the K-based compounds (i.e., KCrP, KCrAs, and KCrSb) are positioned near the middle of E_{CBM} and E_{VBM}. Second, E_{CBM} and E_{VBM} of the Li-based compounds increase monotonically with η . As η increases, the E_{CBM} of LiCrP and LiCrAs shift above E_F from just below E_F, while their E_{CBM} initially far below E_F remain below E_F. Consequently, non-HM LiCrP and LiCrAs at their equilibrium turn to HM under specific tensile in-plane strain. Meanwhile, E_{CBM} and E_{VBM} behaviors of the K-based compounds are parabola-like with negative and positive curvatures, respectively. Interestingly, their E_{CBM} and E_{VBM} show maxima and minima near $\eta = 0$ to have the widest band gaps for the K-based compounds near unstrained states.



Figure. 3. 11: E_{CBM} (in red) and E_{VBM} (in blue) of the minority spin states of ACrZ (A = Li, Na, and K; Z = As, Sb, and P) as a function of in-plane strain. Fermi level E_F is set to be zero.



Figure. 3. 12: c/a ratio as a function of in-plain strain η of ACrZ (A = Li, Na, and K; Z =P, As and Sb).

3.4.6. The (001) surfaces

Practically, the magnetism and electronic structure at the surface/interface are more significant than in bulk. In real applications such as a magnetic tunnel junction, ACrZ is likely utilized in a hybrid with a semiconductor [81,82]. We considered only the surfaces of LiCrAs, LiCrSb, NaCrAs, and NaCrSb to examine the magnetism and the half-metallicity at the (001) surface and excluded other ACrZ due to their positive formation energies against the decomposition into bcc A and ZB-CrZ or non-half-metallicities.

Reasonably, InSb is a potential semiconductor for a hybrid system with LiCrAs, LiCrSb, NaCrAs, and NaCrSb since the experimental lattice constant (6.48 Å) [83] of InSb exhibits rather good mismatches of +8.00%, +1.37%, +0.93%, and -4.42%, respectively. For surface calculations, the lattice constant of InSb is considered the in-plane lattice constant.

Two different terminations are plausible for the (001) surface: Z-term and ACr-term. As shown in Fig. 3. 1(b), a 14-layer slab is used to simulate the Z- and ACr-term surface. The bulk properties shown by the center layers confirm the sufficient thickness of the slab. The interlayer spacings are fully relaxed by minimizing total energy and force. The relaxed structures are shown in Fig. 3. 13, and the numerical values of interlayer spacings and corrugations near the surfaces are presented in Table 3. 4.

At surface, constituent atoms are rearranged differently from the bulk counterpart because of broken bonding and broken translational symmetry along the surface normal. We fully relaxed the structures along the *c*-axis. In this study, the in-plane lattice constant of a potential substrate InSb is adopted. Atoms are relaxed according to the surface effect as well as the lattice mismatch between InSb and ACrZ. The Cr and Z positioned at the same plane in bulk are relaxed in different ways at the surfaces so not to be placed at the same plane. The corrugation at ACr-term is more severe than at Z-term. The severe corrugation might be from the different valence electron characters of the Cr and A elements, i.e., *d* and *s* characters. The less localized A-*s* electron prefers spilling out into a vacuum to reduce its kinetic energy, while the relatively directional character of the Cr-*d* electron prefers staying inside to minimize energy at the expense of coming from a dangling bond.

We present the evaluated magnetic moments of Cr and Z at the surface (S) and subsurface (S-1) layers in Table 3.5, with the center layers (C) listed for comparison. Due to the reduced coordination number at the surfaces, the corresponding magnetic moments of the atoms are generally enhanced compared to those in the center layers. The magnetic moments of Cr(S) at the ACr-term surfaces of LiCrAs(Sb) and NaCrAs(Sb) increased by 7.10% (7.26%) and 11.23% (7.00%), respectively, and the magnetic moments of the subsurface Cr(S-1) atoms of the Z-term surfaces reduced by 14.75% (11.02%) and 15.30% (11.59%), respectively, compared to those of the center Cr layers. The magnetic moments of Z show a similar trend, enhanced, and reduced at the surfaces and the subsurfaces, respectively, compared to those of the center Z layers.

The left and right columns in Fig. 3. 14. represent the two-dimensional minority spin bands of LiCrAs(Sb) and NaCrAs(Sb), respectively, to investigate the half-metallicity at the (001) surface. The bands originated from Z(S) and Cr(S-1) of Z-term are indicated in green and blue, and those from Cr(S) and Z(S-1) of ACr-term are shown in red and orange, respectively. Other bands are plotted in gray. Fig. 3. 14. demonstrates robust half-metallicity at Z-term but broken one at ACr-term. The severe corrugation at ACr-term shifts down the Cr(S) band crossing the Fermi level E_F . In practical devices, the ACrZ compounds can be utilized an interfacial structure with various semiconductors. For example, at an interface ACrZ with InSb, naturally InZ and CrSb bonding are expected to form at Z-term and the ACr-term, respectively. In the interfacial structures, the bulk-like half-metallicities would recover even for the broken half-metallicity at ACr-term.

Table 3. 6. lists the calculated band gaps at Z-term and the center layer. For comparison, the band gaps of the strained bulk LiCrAs (+8.00%), NaCrAs (+1.37%), LiCrSb (+0.93%), and NaCrSb (-4.42%) are also presented. The band gaps of Z-term LiCrAs, NaCrAs, LiCrSb, and NaCrSb are 1.32, 1.41, 1.10, and 1.12 eV, respectively, slightly smaller compared to the bulk-like center layers (Table 3. 6). The band gap values of the center layers are very close to that of the strained bulk ones. These findings reconfirm that the 14-layer slab is sufficiently thick to describe a bulk surface.



Figure. 3. 13: The schematic diagram of interlayer spacing d_{ij} and corrugation Δz_i for Z-term and ACr-term. The subscript 1, 2, 3, and *c* denote first, second, third layers from the surface, and the center layer, respectively.



Figure. 3. 14: Atom-resolved minority spin band structure of ACrZ (A = Li and Na; Z = As and Sb) at Z-term and ACr-term (001) surfaces. The Fermi level E_F is set to zero.

Table 3. 4: Interlayer spacing d_{ij} (in Å) and corrugation Δz_i for Z-term and ACr-term, respectively. The subscript *1*, *2*, *3*, and *c* denote first, second, third layers from the surface, and the center layer, respectively.

		LiCrAs	NaCrAs	LiCrSb	NaCrSb
Z-term	<i>d</i> ₁₂	0.62	0.98	1.27	1.44
	<i>d</i> ₂₃	1.23	1.49	1.39	1.69
	Δz_2	0.29	0.02	0.01	0.01
Center	d_c	1.29	1.48	1.43	1.62
ACr-term	<i>d</i> ₁₂	1.12	1.38	1.39	1.73
	<i>d</i> ₂₃	1.39	1.46	1.45	1.68
	Δz_1	0.77	1.34	0.44	1.07
	Δz_3	-0.40	-0.81	-0.08	-0.10

		LiCrAs	NaCrAs	LiCrSb	NaCrSb
Z-term	Z(S)	-0.27	-0.37	-0.29	-0.38
	Cr(S-1)	3.12	3.31	3.09	3.28
Center	Z(C)	-0.14	-0.18	-0.13	-0.17
	Cr(C)	3.66	3.72	3.65	3.71
ACr-term	Cr(S)	3.92	3.99	4.06	3.97
	Z(S-1)	-0.09	-0.11	-0.08	-0.13

Table 3. 5: Layer-resolved magnetic moment (in μ_B) of ACrZ (A = Li, Na; Z = As, Sb) for (001) surface of both Z-term and ACr-term.^a

^aExperimental lattice constant of InSb (6.48 Å) is employed for the two-dimensional lattice constant of the surface

Table 3. 6: The band gaps (in eV) of ACrZ (A = Li and Na; Z = As and Sb) of the Z-term (001) surface, the bulk-like center layer, and the strained bulk.^b

	LiCrAs	NaCrAs	LiCrSb	NaCrSb
Z-term	1.32	1.41	1.10	1.12
Center	1.82	2.10	1.58	1.76
Strained bulk	1.80	2.11	1.59	1.75

^b The values of the strained bulk are estimated from Fig. 3. 11

3.5. Summary

We have studied the half-metallicity of alkali-metals-based half-Heusler, i.e., ACrZ (A = Li, Na, and K; Z = P, As, and Sb), compounds. ACrZ, except for LiCrP and LiCrAs, are predicted to be HMs with wide band gaps in the range of 1.60 - 2.16 eV, which would be advantageous for their practical applications. HM ACrZ have an integer total magnetic moment $m_{tot} = 4.00 \ \mu_B$, larger than the corresponding ZB-CrZ by 1 μ_B , achieved from one more valence electron provided by the element A. Meanwhile, LiCrP and LiCrA showed magnetic moments below 4.00 μ_B , which is 3.51 and 3.99 μ_B , respectively, since their minority spin CBM is positioned just below the Fermi level E_F .

The band gap formation mechanism of ACrZ is identified to be similar to that of ZB-CrZ, i.e., the hybridization between the Cr-*d* and Z-*p* states opens the band gap. The key role of the A element is two-fold. The first is to expand the lattice constant, thereby widening band gaps, and the second is to achieve structural stability through formation energy. Furthermore, the half-metallicity is robust under severe in-plane strain and at Z-term. Overall, considering all the features discussed so far, including good lattice mismatch with ZB semiconductors, we propose LiCrZ and NaCrZ (Z = As and Sb) as promising compounds for real-life applications to spintronics.

Chapter 4: High-performance permanent magnet using inverse Heusler Fe2MnSn: a first-principles study

In this chapter, we discuss the structural stability and intrinsic magnetic properties of Fe₂MnSn Heusler compounds. Regular and inverse cubic, inverse tetragonal, and hexagonal structural phases without and with 6.25% X (X = H, B, C, and N) interstitial doping, corresponding to Fe₂MnSnX_{0.25} chemical formular, are investigated. Our results demonstrate the feasibility of stabilizing tetragonal Heusler compounds by light element interstitial doping. In particular, thermally stable inverse tetragonal Fe₂MnSnH_{0.25} [$\mu_0 M_s = 1.50$ T and $K_u = 1.66$ MJ·m⁻³] and Fe₂MnSnN_{0.25} [$\mu_0 M_s = 1.36$ T and $K_u = 1.07$ MJ·m⁻³] can be promising PMs to bridge the gap between high performance but costly PM Nd₂FeB₁₄ [$\mu_0 M_s \approx 1.57$ T, $K_u \approx 4.5$ MJ·m⁻³, and (*BH*)_{max} ≈ 56 MGOe] and widely used Alnico [$\mu_0 M_s \approx 0.48$ T, $K_u \approx 0.33$ MJ·m⁻³, and (*BH*)_{max} ≈ 5.66 MGOe] materials.

4.1.Introduction

Permanent magnets (PMs) are widely applied in a diversity of areas such as electric vehicles, wind turbines, drives, storage, and to name a few [13,14]. For high performance PMs, large energy product $(BH)_{max}$ is demanded, where the intrinsic magnetic properties of saturation magnetization $(\mu_0 M_S)$ and uniaxial magnetic anisotropy (K_u) are closely related to $(BH)_{max}$. In addition, good thermal stability, and high Curie temperature (T_C) are required to fulfill practical applications [16,17]. Since the high uniaxial K_u is associated with strong spin orbit-coupling (SOC) in 4d, 5f, or 4f orbitals whereas high $\mu_0 M_S$ and high T_C usually come

from 3*d* transition metal (TM) [15,84], the most effective approach to develop a PM is alloying of TM with 4*d* and 5*d* heavy metal (HM) or rare-earth (RE) element. Actually, Nd₂FeB₁₄ [$\mu_0 M_S \approx 1.57$ T, $K_u \approx 4.5$ MJ·m⁻³, and (BH)_{max} ≈ 56 MGOe] [85] developed more than 40 years ago is still a champion PM. However, HM and RE are expensive with limited resources. Furthermore, there is a substantial performance gap between Nd₂FeB₁₄ and other widely used RE-free PMs such as Alnico [$\mu_0 M_S \approx 1.38$ T, $K_u \approx 0.68$ MJ·m⁻³, and (BH)_{max} ≈ 46.24 MGOe] and ferrite BaFe₁₂O₁₉ [$\mu_0 M_S \approx 0.48$ T, $K_u \approx 0.33$ MJ·m⁻³, and (BH)_{max} ≈ 5.66 MGOe] [17,18,21]. Therefore, finding new RE- or HM-free alternative PMs with comparable performances becomes a long-term goal and is actively on working [13,84].

Heusler compounds X₂YZ, which can be tailored by varying chemical elements [86,87], provide an expansive playground for designing new materials. Although most Heusler compounds are cubic, so improper to be PM materials due to a very weak K_u , some of Mnbased, Ni-based, Co-based, and Fe-based compounds Mn₂YZ, Ni₂YZ, Co₂YZ, and Fe₂YZ (Y=TM and Z=*sp* element) are stable in tetragonal [88-91] or hexagonal structures [92-96]. Considerably large uniaxial K_u was also predicted in som tetragonal Heusler compounds such as Ni₂CoGa (1.30 MJ·m⁻³) [91] and Fe₂NiSn (1.09 MJ·m⁻³) [90] even without RE or HM elements. Therefore, Heusler compounds recently have emerged as promising candidates for RE-or HM-free PMs. Fe-based compounds Fe₂YZ, thanks to their large predicted total magnetic moments per formula unit (around 4–6 μ_B /fu) [88], has garnered attraction [92,97]. In experiment, Fe₂YZ are usually synthesized in cubic [10,92,97] or hexagonal structures [93-96]. Some of theoretical predicted Fe₂YZ were confirmed in experiments to have large magnetic moments, such as cubic Fe₂CoGe (5.40 μ_B /fu) [97], cubic Fe₃Ga (6.14 μ_B /fu)[10], and hexagonal Fe₂MnGe (~5.00 μ_B /fu) [94].

Fe₂MnSn was predicted to be stable in inverse tetragonal phase with desirable properties to be PM candidates such as large magnetic moment (7.34 μ_B /fu) and high uniaxial K_u of 2.20 MJ·m⁻¹ [88,89]. However, the results were not supported by experiments where Fe₂MnSn was observed to be stable in a hexagonal structure rather than the tetragonal one with magnetic moment of 5.87 μ_B /fu [94]. The K_u of the hexagonal phase has not been investigated yet despite the attractive magnetic moment of 5.87 μ_B /fu in terms of a PM material. In this work, using a first-principles method, we investigate structural stability and intrinsic magnetism of Fe₂MnSn and Fe₂MnSnX_{0.25} (X is H, B, C, and N interstitial doping), referring to the interstitial doping of the light elements as one of the most potential approaches to tailoring material properties [98-102]. For example, light interstitial doping was theoretically predicted to improve the thermal stability of SmFe₁₂ [98], or to switch biaxial K_u of LaCo₅ to uniaxial [99], or to induce tetragonal distortion of cubic phases [100-102].

Our principal findings are that (i) Fe₂MnSn is stable in the hexagonal, followed by the inverse tetragonal, the inverse cubic, and the regular cubic phase; (ii) large $\mu_0 M_S$ of 1.28–1.59 T are found, regardless of structures; (iii) inverse tetragonal with an uniaxial K_u of 2.35 MJ·m⁻¹ is more favorable to be a PM than hexagonal phase with a biaxial K_u of -0.72 MJ·m⁻¹; (iv) the inverse tetragonal phase can be stabilized by interstitial doping of light elements.

4.2. Computational detail

The structural and electronic calculations are conducted by the density-functional theory (DFT) employed in the Vienna *ab initio* simulation package (VASP) [38]. The Perdew-Burke-Ernzerhof (PBE) [34] generalized gradient approximation (GGA) is employed for the exchange-correlation interactions within the projector augmented-wave scheme[39]. Energy cutoff of 450 eV is used for the wave function expansion, and the *k*-mesh of $9 \times 9 \times 9$ and $9 \times 9 \times 7$ is adopted for the Brillouin zone integration of the cubic, tetragonal, and hexagonal structure, respectively. The lattice parameter and ionic coordinates are relaxed until the force acting on ions $< 1 \times 10^{-2}$ eV/Å.

 K_u is calculated via the total energy method $K_u = \frac{(E_a - E_c)}{v}$ within self-consistent scheme, where V, E_a , and E_c are the volume, total energies with magnetization along the a (short axis), and c axes (long axis), respectively. Positive (negative) K_u indicates uniaxial (biaxial) magnetic anisotropy. A denser k-point mesh of $17 \times 17 \times 11$ is used in the noncollinear calculations with a small Gaussian smearing parameter (0.05 eV). The convergence of calculations with respect to energy cut-off and k-point sampling are carefully checked to achieve well-converged values of K_u . The SOC term is included in a second-variational way employing scalar-relativistic calculations of the valence state [103]. To confirm the validity of K_u estimated by VASP, the K_u result is double-checked by full-potential calculations with the same optimized structures obtained from VASP, employing the Fleur code [104].

4. 3. Crystal structures

The structural phases of Heusler compounds are presented in Fig. 4. 1(a) and possible interstitial occupations in the inverse cubic and hexagonal structure are shown in Fig. 4. 1(b). Cubic Heusler compounds Fe₂MnSn can be viewed as four interpenetrating fcc sublattices, composed by Fe, Mn, and Sn elements [74]. The cubic regular phase has L21₁ structure (the space group Fm3m, No. 225), in which Fe, Mn, and Sn occupy the Wyckoff position 8c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4a (0, 0, 0). Inverse Heusler XA structure (the space group F43m, No. 216) can be visualized from L2₁ structure by switching position of one of Fe atoms with Mn or Sn atom. The non-equivalent Fe atoms in the inverse Heusler structure do not form a simple cubic lattice. In detail, Fe atoms are placed on 4b (1/2, 1/2, 1/2) and 4d (3/4, 3/4, 3/4) site, while Mn and Sn atom occupy 4c (1/4, 1/4, 1/4) and 4a (0, 0, 0) Wyckoff position.

Elongating or compressing along with [001] direction of regular (inverse) cubic structure, regular (inverse) tetragonal phase with the space group I4/mmm No. 139 (the space group I $\overline{4}$ m2, No. 119) is constructed [88,89]. The Fe atoms in the inverse tetragonal structures are also placed on (non-equivalent) equivalent sites in (inverlse) regular tetragonal structures like the cubic structures. Finally, in the hexagonal D0₁₉ structure (the space group P6₃/mmc, No. 194), the Fe and Mn atoms share the same 6h (1/6, 1/3, 1/4) sites with 2/3 and 1/3 occupancy, and the Z atoms are placed at the 2c (1/3, 2/3, 1/4) sites [92-96]. We summarize crystal structures, space groups, and Wyckoff positions of Heusler compounds Fe₂MnSn in table 4. 1.

There are four possible interstitial doping sites in inverse tetragonal structure, as shown in Fig. 4. 1(b). The grey and red octahedrons stand for 24f (0, 0, 1/4) and 24g (1/4, 1/4, 1/2) interstitial sites, while the light blue and light green tetrahedrons do 16e-I (1/4, 7/8, 7/8) and 16e-II (7/8, 5/8, 7/8) interstitial sites [100]. In the case of the hexagonal structure, on the other hand, there are two possible interstitial doping sites. One is the octahedral site 6g (1/2, 1/2, 1/4), and the other is the tetrahedral site 4f (2/3, 1/3, 1/4) [105], marked by grey and light green lines.

Table 4. 1: Crystal structures, space groups, and Wyckoff positions of Heusler compounds Fe₂MnSn, in regular and inverse cubic, regular and inverse tetragonal, and hexagonal.

Fe ₂ MnSn	Space	Fe	Mn	Sn
	group			
Regular cubic	Fm3m	8c (1/4, 1/4, 1/4)	4b (1/2, 1/2, 1/2)	4a (0, 0, 0)
Inverse cubic	F 4 3m	4b (1/2, 1/2, 1/2)	4c (1/4, 1/4, 1/4)	4a (0, 0, 0)
		4d (3/4, 3/4, 3/4)		
Regular tetragonal	I4/mmm	4d (0, 1/2, 1/4)	2b (0, 0, 1/2)	2a (0, 0, 0)
Inverse tetragonal	I4m2	2b (0, 0, 1/2)	4d (0, 1/2, 1/4)	2a (0, 0, 0)
		4d (0, 1/2, 1/4)		
Hexagonal	P6 ₃ /mmc	6h (1/6, 1/3, 1/4)	6h (1/6, 1/3, 1/4)	2c (1/3, 2/3, 1/4)



Figure. 4. 1: (a) The crystal structures of regular (L2₁), inverse (XA) cubic, and hexagonal (D019) Heusler compounds. Noteworthy, regular (inverse) tetragonal is similar to their parent cubic, except the lattice constant $a \neq c$ (b) The possible interstitial sites in inverse and hexagonal Heusler structures. Pink, blue, and grey spheres stand for Fe, Mn, and Sn atoms, respectively. Pink and yellow differentiate Fe_A and Fe_B in inverse structure.

4. 4. Results and discussions

4. 4. 1. Fe₂MnSn

Firstly, from total energy calculation, we identify the most stable phases among regular (inverse) cubic, inverse tetragonal, and hexagonal, as shows in Fig. 4. 2(a). The most energetically stable structure is the hexagonal phase, followed by the inverse tetragonal, the inverse cubic, and the regular cubic. For the hexagonal phase, being the most stable phase is in an agreement with experiments [94]. Fig. 4. 2(b) presents the energy difference between cubic and tetragonal distortion $\Delta E = E_{(c/a)} - E_{(c/a=1)}$ as a function of tetragonal distortion ratio (c/a) for regular (inverse) Fe₂MnSn. According to Fig. 4. 2(b), the $\Delta E > 0$ indicates the preference of regular cubic to tetragonal distortion. In contrast, the inverse tetragonal phase is more stable than inverse cubic by 0.07 eV/fu.

Equilibrium lattice constant, relative energy ΔE per formula unit (fu) in the reference of the hexagonal phase, total magnetic moment per fu, and saturation magnetization $\mu_0 M_S$ are summarized in Table 4. 2. Large total magnetic moments are predicted regardless of the structure. The magnetic moments are 5.98, 7.69, 7.39, and 6.73 μ_B for the regular cubic, inverse cubic, inverse tetragonal, and hexagonal structures, respectively, whose corresponding to the saturation magnetization $\mu_0 M_S$ of 1.28 T, 1.57 T, 1.52, and 1.39 T. Reminding the $\mu_0 M_S$ of some typical PMs, such as Alnico 5 (1.38 T), SmCo₅ (1.08 T), Nd₂Fe₁₄B (1.57 T), and Sm₂Fe₁₇N₃ [14,18], the $\mu_0 M_S$ of Fe₂MnSn are large enough to be high performance PMs. The large total magnetic moment mainly comes from Fe and Mn, while Sn has a negatively induced magnetic moment. The inverse cubic structure (a = 6.11 Å, m_t = 7.69 μ_B/fu) is noteworthy to have a larger magnetic moment compared to the regular one (a = 6.02 Å, m_t = 5.98 μ_B/fu), even though their lattice constants are not much different. The optimized lattice constant of the hexagonal phase (a = 5.48 Å, c = 4.35 Å) agrees well with the previous experiments (a = 5.50 Å, c = 4.39 Å) but the total magnetic moment (6.73 μ_B/fu) is somewhat larger than an experiment value (5.87 μ_B/fu)[94].

Strong magnetic anisotropy is one of key physical properties for a high performance PM. The inverse tetragonal Fe₂MnSn show a strong magnetic anisotropy. Its uniaxial magnetic anisotropy parameter K_u is as large as 2.35 MJ·m⁻³, while the most stable hexagonal phase shows a biaxial K_u of -0.72 MJ·m⁻³. In other word, the hexagonal structure is less favorable for a PM whereas the inverse tetragonal phase is very attractive due the large $\mu_0 M_S$ and K_u . Interstitial doping with light elements may be helpful in achieving a uniaxial K_u in the hexagonal phase or in enhancing thermal stability of the tetragonal phase [98-102]. In this subsection, the effect of the light element doping on the magnetic properties of Fe₂MnSn is discussed. H, B, C, and N elements are studied with 6.25% concentration, corresponding to Fe₂MnSnX_{0.25} chemical formula.



Fig. 4. 2: (a) Total energy versus volumes for regular cubic, inverse cubic, inverse tetragonal, and hexagonal phases. (b) The $\Delta E = E_{(c/a)} - E_{(c/a=1)}$ as a function of tetragonal distortion ratio (c/a) of regular (inverse) Fe₂MnSn.

Table 4. 2: Calculated lattice parameters (in Å), total magnetic moment per formula unit, atomresolved magnetic moment (in μ_B), relative energy ΔE with hexagonal phase (in eV/fu), and magnetic anisotropy K_u (MJ·m⁻³) of Fe₂MnSn for regular cubic (Reg. cub), inverse cubic (Inv. cub), inverse tetragonal (Inv. tet), and hexagonal (Hex) structural phase.^{*}

Fe ₂ MnSn	Lattice parameters	m_t	m_{Fe}	m_{Mn}	m _{Sn}	ΔΕ	$\mu_0 M_S$	K _u
Reg. cub	a = 6.02	5.98	1.78	2.55	-0.17	0.26	1.28	_
Inv. cub	a = 6.11	7.69	(Fe _A)	3.03	-0.13	0.19	1.57	_
			2.25					
			(Fe _B)					
			2.54					
Inv. tet	a = 5.64, c =7.08,	7.39	(Fe _A)	2.79	-0.17	0.12	1.52	2.35
	c/a = 1.25		2.19					2.20ª
	$(a = 5.61, c = 7.14^{a})$		(Fe _B)					
			2.45					
Hex	a = 5.48, c = 4.35,	6.73	2.17	2.62	-0.16	0	1.39	-0.72
	c/a = 0.79	5.87 ^b						
	(a = 5.50, c =							
	4.39 ^b)							

* a and b mark calculation [88] and experiment [85] results from literature

4. 4. 2. Hexagonal Fe₂MnSnX_{0.25}

Table 4. 3: Calculated lattice parameters (in Å), the relative energy difference (in eV/fu) between interstitial doping on 4f site and 6g site (in eV/fu), total magnetic moment per formula unit (in μ_B), and magnetic anisotropy K_u (in MJ·m⁻³) for hexagonal Fe₂MnSnX_{0.25} with (X = H, B, C, and N).

Fe ₂ MnSnX _{0.25}	E(4f) – E(6g)	Lattice parameters	m_t	K _u
X = H	-0.17	a = 5.47, c = 4.43, c/a = 0.81	7.18	-0.97
X = B	0.27	a = 5.46, c = 4.60, c/a = 0.84	7.24	-0.68
X = C	0.13	a = 5.52, c = 4.45, c/a = 0.80	6.77	-0.81
X = N	0.09	a = 5.54, c = 4.48, c/a = 0.81	7.16	-1.05

Table 4. 3 lists the calculated lattice parameters, relative energy difference between interstitial doping on 2d site and 6g site, total magnetic moment m_t, and magnetic anisotropy K_u after interstitial doping in cases of the hexagonal phase. The B, C, and N prefer the octahedral 6g site, while only H does the tetrahedral 2d site. The c/a ratio of Fe₂MnSnX_{0.25} are 0.81, 0.84, 0.80, and 0.81 for X = H, B, C, and N, which do not significantly deviate from the c/a = 0.80 without the doping (Table 4. 2). The interstitial doping enhances total magnetic moment m_t from 6.73 μ_B to 7.18, 7.24, 6.77 and 7.16 μ_B for X = H, B, C, and N (Table 4. 2). K_u remains negative -0.97, -0.68, -0.81, and -1.05 MJ·m⁻³ for H, B, C, N. Positive uniaxial K_u is a key factor to being a PM candidate. Thus, the possibility of the hexagonal phase can be ruled out for a PM candidate.

4. 4. 3. Inverse tetragonal Fe₂MnSnX_{0.25}

For the inverse tetragonal phase, all H, B, C, and N prefers in the octahedral site 24g (Table 4. 4.). The calculated lattice parameter, total magnetic moment, and K_u of the inverse tetragonal Fe2MnX_{0.25} are listed in table 4. 5. The relative energy between tetragonal and cubic $\Delta E = E_{(c/a)} - E_{(c/a=1)}$ as a function of tetragonal distortion ratio (c/a) of Fe₂MnSn for different volumes with and without interstitials are presented in Fig. 4. 1(a). The tetragonal Fe₂MnSn possesses a tetragonal instability [106] with c/a = 1.25 and a local minimum at c/a = 0.90. Noteworthy, the local minimum has not been observed after introducing interstitial doping. ΔE can be proportional to the martensite phase transition temperature k_BT_M [107]. X obviously improves the stability of the tetragonal phase compared to the cubic one; with X = B doing the best while X = H does the worth. Interstitial doping induces a larger c/a ratio in Fe₂MnSnX_{0.25} up to 1.33, 1.36, 1.32, and 1.39 for X = H, B, C, and N compared to 1.25 in Fe₂MnSn. The total magnetic moments of Fe₂MnSnX_{0.25} are 7.33, 6.90, 6.75, and 6.69 μ_B for X = H, B, C, and N. Clearly, the total magnetic moment of 7.39 μ_B of Fe₂MnSn (Table 4. 1) decreases significantly after doping, except for X = H, even though the c/a ratio of Fe₂MnSnH_{0.25} is not much different from other doping.

Table 4. 4: The relative energy difference (in eV/fu) between interstitial doping on tetrahedral site16-eI, 16e-II, and octahedral 24f site with octahedral 24g site in tetragonal phase of Fe₂MnSnX_{0.25} with (X = H, B, C, and N).

Fe ₂ MnSnX _{0.25}	E(16e-I) – E(24g)	E(16e-II) – E(24g)	E(16e-II) – E(24g)
X = H	0.006	0.09	0.08
X = B	0.17	0.16	0.33
X = C	0.13	0.21	0.53
X = N	0.11	0.15	0.51



Fig. 4. 3: The $\Delta E = E_{(c/a)} - E_{(c/a=1)}$ as a function of tetragonal distortion ratio c/a of Fe₂MnSn for different volumes and without X and with 6.25% concentration of X (X = H, B, C, and N). Herein, the reference energy is the energy of the compound in inverse cubic structure.



Fig. 4. 4: (a) Inverse tetragonal Heusler $Fe_2MnSnX_{0.25}$ with interstitial doping X (X = H, C, and N) at the most stable octahedral 24g site. Fe_i , Fe_{ii} , Fe_{iv} , Fe_v and Mn_i , Mn_{ii} denote Fe_A , Fe_B , and Mn at different sites. Changes of atom-resolved magnetic moment m_s for (b) Fe_A , (c) Fe_B , and (d) Mn atoms after introducing 6.25% concentration of X (X = H, B, C, and N). Herein, the dash lines mark the value without X.

Bond length	Н	В	С	Ν
X - Fe _{ii}	2.00	2.00	1.94	1.94
X - Fe _{iv}	3.59	3.55	3.48	3.49
X - Mn _{iv}	1.95	2.02	1.92	1.89
X - Sn	3.13	3.16	3.18	3.17

Table 4. 5: The associated bond length (in Å) of X with Fe_{ii}, Fe_{iv}, Mn_{iv}, and Sn atom, which forms the tetrahedron surrounding X.

The bond lengths of Fe-X and Mn-X are nonidentical, resulting in the difference in charge transfer associated with those bonds. Thereby the site positions are denoted based on the associated bond lengths of each Fe (Mn) atom with X. In detail, Fe_i and Fe_{ii} correspond to Fe_A. Fe_{iii}, Fe_{iv}, and Fe_v are analogous to Fe_B. Mn_i, and Mn_{ii} accord with Mn. Magenta, cyan, yellow, red, green, blue, and orange balls denote Fe_i, Fe_{ii}, Fe_{iii}, Fe_{iv}, Mn_i, and Mn_{ii} site as in Fig. 4. 4(a). The changes in atom-resolved magnetic moment m_s for Fe_A, Fe_B, and Mn atoms are presented in Fig. 4. 4(b), Fig. 4. 4(c), and Fig. 4. 4(d), respectively. Herein, Fe_{ii}, Fe_{iv}, Mn_{ii}, and Sn form the tetrahedron surrounding atom X, those bond lengths are listed in table 4.5. The bond lengths of Fe_{ii}, Fe_{iv}, and Mn_{ii} with X when X = H and B are larger than when X = C and N, especially for Fe_{iv}. With X = B, C, and N, the magnetic moment of Fe_B (Mn) reduces significantly from 2.45 μ_B (2.78 μ_B) to 1.83, 1.71, and 1.58 μ_B (2.48, 2.17, and 2.14 μ_B) at Fe_{iv} (Mn_{ii}) site. The magnetic moments are less altered for Fe_i, Fe_{ii}, Fe_{iv}, and Mn_i other atomic sites. In cases of X = H, the influence of interstitial doping is relatively insignificantly as the magnetic moment of each site before and after interstitial doping are comparable.

 K_u remains uniaxial but sharply decreases from 2.35 MJm⁻³ to 1.66, 1.66, 1.17, and 1.07 MJ·m⁻³ for H, B, C, and N interstitial doping, respectively. Two DFT methods VASP and Fleur, give a good accordance on K_u [Fig. 4. 5(a)]. Noteworthy, the K_u value is very close between H and B (C and N). Furthermore, H and B give larger K_u values than C and N. To elucidate the physical properties of K_u , we further estimate the atom-resolved K_u via the SOC energy difference of *a*- and *c*-axis magnetization, where $K_u \approx 1/2\Delta E_{SOC}$. Because the 50% of the SOC energy translates into the crystal-field energy and the formation of the unquenched orbital moment [108], the expectation value is twice the actual value of the total energy correction to the second order in SOC [109,110]. Here, E_{SOC} is expressed as $E_{SOC} = \langle \left(\frac{\hbar^2}{2m^2c^2}\right) \left(\frac{1}{r}\right) [dV(r)]\hat{L} \cdot \hat{S} \rangle$, where V(r) is the spherical part of the effective potential within the PAW sphere, and \hat{L} and \hat{S} are orbitals and spin operators, respectively.

Table 4. 6: Calculated lattice parameters (in Å), total magnetic moment per formula unit (in μ_B), magnetic anisotropy K_u (in MJm⁻³), saturation magnetization $\mu_0 M_S$ (in T), theoretical maximum energy product (BH)_{max} (in MGOe), anisotropic field $\mu_0 H_a$ (in kOe), and magnetic hardness parameter κ for inverse tetragonal Fe₂MnSnX_{0.25} for (X = H, B, C, and N).

Fe ₂ MnSnX _{0.25}	Lattice constant	m _t	K _u	$\mu_0 M_S$	(BH) _{max}	$\mu_0 H_a$	к
X = H	a = 5.54, c = 7.42,	7.33	1.66	1.50	56	28	0.93
	c/a = 1.34						
X = B	a = 5.55, c = 7.51,	6.90	1.66	1.39	48	30	1.08
	c/a = 1.35						
X = C	a = 5.57, c = 7.40,	6.75	1.17	1.35	45	22	0.80
	c/a = 1.33						
X = N	a = 5.50, c =7.60,	6.69	1.07	1.36	46	20	0.73
	c/a = 1.38						



Fig. 4. 5: (a) Comparison between K_u calculated by VASP and Fleur. Changes of atomresolved magnetic anisotropy K_u for (b) Fe_A, (c) Fe_B, and (d) Mn atoms after introducing 6.25% concentration of X (X = H, B, C, and N). The dash lines mark the values without X.



Fig. 4. 6: (a) Orbital-resolved PDOS of Fe_B at Fe_{iv} site after introducing 6.25% concentration of X with X = H, B, C, and N. Black arrow highlights the downward shift toward to the energy region below Fermi level E_F of d_{z^2} orbital states. (b) The changes of *d*-orbitals resolved of ΔE_{SOC} with $K_u \approx 1/2\Delta E_{SOC}$.

Fig. 4. 5. presents the changes of atom-resolved K_u for (b) Fe_A, (c) Fe_B, and (d) Mn atoms of Fe₂MnSn along with X (X = H, B, C, and N) doping. K_u tends to reduce for all sites after doping. The substantial decreases of K_u in cases of C and N interstitial doping can be attributed to the reverse sign of K_u of Fe_B atoms from positive (0.17 meV) to negative (around -0.29 meV) at Fe_{iv} sites [see Fig. 4. 5(c)]. We employ the framework of perturbation theory [111] to elucidate the origin of strong reduction of K_u for Fe_B atoms at Fe(ii) site. Herein, K_u can be expressed by the SOC interaction between occupied and unoccupied bands:

$$K_{u} \approx \xi^{2} \sum_{o,u} (2\delta_{\sigma\sigma'} - 1) \frac{\left| \left\langle o^{\sigma} | \hat{L}_{z} | u^{\sigma'} \right\rangle^{2} - \left\langle o^{\sigma} | \hat{L}_{x} | u^{\sigma'} \right\rangle^{2} \right|}{E_{u}^{\sigma'} - E_{o}^{\sigma}}$$
(4.1)

where ξ denotes the strength of spin-orbit coupling, $\hat{L}_x(\hat{L}_z)$ are the angular momentum operators, $E_o^{\sigma}(E_u^{\sigma'})$ are the energy levels of occupied (unoccupied) states with spin $\sigma(\sigma')$.

Fig. 4. 6(a) presents the change of orbital resolved PDOS of Fe_B at Fe_{iv} site after doping X. When X = B, C, and N, due to 3d - 2p hybridization, a significantly broader density of states is observed. After doping X, while the majority spin state (↑) remains fully occupied, the unoccupied states in the minority spin (↓) shift toward the energy region below Fermi level E_F The changes of *d*-orbital resolved K_u of Fe_B after doping at Fe_{iv} site are shown in Fig. 4. 6(b). Without X, the $K_u > 0$ primarily arises from the $\langle xz(\uparrow) | \hat{L}_x | z^2(\downarrow) \rangle$ matrix. With X, this positive contribution is reduced along with the downward shift to E_F of d_{z^2} states in minority spin [see Fig. 4. 6(a)], which enhances the $K_u < 0$ of $\langle xz(\downarrow) | L_x | z^2(\downarrow) \rangle$. When X = H, $K_u > 0$ from $\langle xz(\uparrow) | \hat{L}_x | z^2(\downarrow) \rangle$ is reduced. When X = B, C, and N, the $K_u < 0$ from $\langle xz(\downarrow) | L_x | z^2(\downarrow) \rangle$ becomes dominant. The influences from other *d*-orbital pairs on K_u seem to be insignificant. Meanwhile, the magnetic moment and atom-resolved K_u of atoms, which

stays far from interstitial doping X (Fe_i, Fe_{iii}, Fe_v, and Mn_i), are only marginally varied even when c/a is seriously induced after doping. Thus, the hybridization of X with its local surrounding atoms takes more role in the total magnetic moment as well as K_u .

As m_t and uniaxial K_u are known, we next determine the saturation magnetization $\mu_0 M_S$, theoretical energy product $(BH)_{max}$, anisotropic field, and hard parameter κ . The energy density product maximum $(BH)_{max}$ is figure of merit of permanent magnet material which indicates how strong magnetic flux a material generates per unit volume. The energy product $(BH) = \mu_0 D(1 - D)M_S^2$, where D is the demagnetizing factor which is larger than 0 and smaller than 1, i.e., 0 < D < 1, depending on the shape of the paramagnet magnet [17,18]. When $D = \frac{1}{2}$, (BH) reaches the maximum $(BH)_{max} = (\frac{1}{4})\mu_0 M_S^2$. The anisotropic field is theoretically estimated as $\mu_0 H_a$ (= $2K_u/M_S$), where H_a is the field needed to saturate the magnetization in the hard-axis direction. The hard parameter κ [17,18] is expressed as:

$$\kappa = \left(\frac{K_u}{\mu_0 M_S^2}\right)^{\frac{1}{2}} \tag{4.2}$$

The calculated $\mu_0 M_S$, $(BH)_{max}$, $\mu_0 H_a$, and κ of Fe₂MnSnX_{0.25} for (X = H, B, C, and N) are listed in table 4. 6. Thanks to the largest total magnetic moment, Fe₂MnSnH_{0.25} shows the largest $\mu_0 M_S = 1.50$ T, generating a large $(BH)_{max}$ of 56 (MGOe). For other cases, the $\mu_0 M_S$ values of Fe₂MnSnB_{0.25}, Fe₂MnSnC_{0.25}, and Fe₂MnSnN_{0.25} are 1.39, 1.35, and 1.36 T, giving $(BH)_{max}$ of 48, 45, and 46 (MGOe). Noteworthy, the $(BH)_{max}$ of present compounds are quite comparable with the state-of-art PM Nd₂Fe₁₄B [$(BH)_{max} = 56$ (MGOe)] [85]. Fe₂MnSnB_{0.25} exhibits the highest $\mu_0 H_a$ of 30 kOe and κ up to 1.03. For other cases, Fe₂MnSnH_{0.25}, Fe₂MnSnC_{0.25}, and Fe₂MnSnN_{0.25} show $\mu_0 H_a$ of 28, 22, and 20 kOe,

corresponding to κ of 0.93, 0.88, and 0.73. Thus, Fe₂MnSnX_{0.25} (0.5 < κ < 1) are semihard magnetic materials, except X = B (κ > 1) are hard magnetic materials. Meanwhile, Fe₂MnSnH_{0.25} and Fe₂MnSnB_{0.25} have better intrinsic magnetism than Fe₂MnSnC_{0.25} and Fe₂MnSnN_{0.25}, indicating by larger $\mu_0 M_s$, (*BH*)_{max}, $\mu_0 H_a$, and κ .

As in section 4. 4. 1, the inverse tetragonal structure is unstable. Thus, it is crucial to explore the formation energy of inverse tetragonal Fe₂MnSn, upon the addition of 6.25% X-dopants concentration. Here, the formation energy of Fe₂MnSnX_{0.25} against the decomposition into end of member compounds [112,113] is calculated using the following equation:

$$H_f = E_{Fe_2MnSnX_{0.25}} - (2E_{Fe} + E_{MnSn} + 0.25E_X)$$
(4.3)

where $E_{Fe_2MnSnX_{0.25}}$, E_{Fe} , E_{MnSn} , and E_X are the total energies of Fe₂MnSnX_{0.25}, α -Fe, hexagonal-MnSn (space group P6/mmm) [114], and X atoms at their ground-sate phases (H₂ molecule, α -rhombohedral boron, graphite, and N₂ molecule). Negative (positive) H_f indicates the stable (unstable) structure against the composition into α -Fe, MnSn, and X. The formation energy is more conservative against decomposition into elements of Fe, Mn, Sn, and X. Furthermore, in practical, Fe-Mn-Sn tends to decompose into α -Fe and binary MnSn rather than elementary phases [115]. The formation energy results are presented in Fig. 4. 7.

The H_f value of inverse tetragonal Fe₂MnSn is 9.61 kJ mol⁻¹, indicating that inverse tetragonal Fe₂MnSn is unstable against α -Fe and MnSn decomposition. $H_f > 0$ agrees well with experiments of the hexagonal structure [94]. In contrast, inverse tetragonal Fe₂MnSnH_{0.25} and Fe₂MnSnN_{0.25} are thermally stable as the H_f magnitudes become negative -8.55 and -35.19 kJ·mol⁻¹. The hexagonal phase is more energetic stable than the inverse tetragonal

phase, thus, we also calculated H_f of hexagonal Fe₂MnSnH_{0.25} and Fe₂MnSnN_{0.25}. The results show that the H_f of hexagonal Fe₂MnSnH_{0.25} and Fe₂MnSnN_{0.25} are -11.93 and -30.16 kJ·mol⁻¹, respectively. Hence, the tetragonal Fe₂MnSnN_{0.25} is even more thermaly stable by 5.03 kJ·mol⁻¹ (corresponding to 0.05 eV/atom) than hexagonal Fe₂MnSnN_{0.25}, which shows uniaxial K_u and cannot be PM candidates (Table 4. 3).



Fig. 4. 7: Enthalpy of formation energy of Fe₂MnSn inverse tetragonal structure without X and with 6.25 % concentration of X (X = H, B, C, and N). Herein, the formation energy of hexagonal structure with 6.25 % concentration of X (X = H and N) is also presented and denoted by black to distinguish with tetragonal phase marked by blue.
4.5. Summary

We have reported a first-principles study on structural stability and intrinsic magnetic properties of Fe₂MnSn Heusler compounds, using VASP and FLAWP complementarily. The most stable phase is hexagonal, followed by inverse tetragonal, inverse cubic, and regular cubic structure. The present compounds are predicted to have $\mu_0 M_s$ as large as 1.28 T -1.59 T for all structure phases. Thanks to uniaxial K_u of 2.35 MJ·m⁻³, the inverse tetragonal phase is more desirable to be RE-free PM compared to the hexagonal structure phases with uniaxial K_u of - 0.72 MJ·m⁻³. We further demonstrate the feasibility of stabilizing tetragonal phase considering light element interstitial doping X (X = H, B, C, and N) with 6.25% concentration.

In particular, 6.25% concentration of H and N can improve the thermal stability of the inverse tetragonal phase, indicated by negative formation energies H_f of -8.55 and -35.19 kJ·mol⁻¹. H has good intrinsic magnetic properties, i.e., a uniaxial K_u of 1.66 MJ·m⁻³, a theoretical energy product (BH)_{max} up to 56 MGOe, a $\mu_0 K_u$ of 28 kOe, and κ of 0.93 while N [$K_u = 1.07$ MJ·m⁻³, (BH)_{max} = 46 MGOe, $\mu_0 K_u = 22$ kOe, and $\kappa = 0.73$] has a good thermal stability since being even more thermal stable by 5.03 kJ·mol⁻¹ than hexagonal phase.

Chapter 5: Prediction of large anomalous Hall conductivity in a compensated ferrimagnet quaternary Heusler compound TiZrMnAl

In this chapter, the anomalous Hall effect in a compensated ferrimagnet quaternary Heusler compound TiZrMnAl is investigated. To do so the anomalous Hall conductivity is calculated via Kubo formular, and the results are analyzed based on the total Berry curvature over whole Brillouin zone.

5.1. Introduction

When a non-magnetic material is put in an external magnetic field, which is perpendicular to an applied electric current, the current carriers are forced to move along the curve path, giving rise to a transverse electric field [19]. This effect is called as the ordinary Hall effect. When the sample is a ferromagnet, the effect is referred to as anomalous Hall effect (AHE).

The anomalous Hall conductivity (AHC) can be measured via the total Hall resistivity [116]. The total Hall resistivity ρ_{xy} is expressed as:

$$\rho_{yx} = R_0 \mu_0 H + \rho_{yx}^{AHE} \tag{5.1}$$

where R_0 is the Hall coefficient, μ_0 is the magnetic permeability of free space, and H is the external magnetic field. While the first term is referred as the ordinary Hall effect contribution, the second term ρ_{yx}^{AHE} is the total anomalous Hall component. ρ_{yx}^{AHE} is commonly believed to scale with the spontaneous magnetization of materials [19]. Therefore, it has been long

regarded that due to spin-orbit interaction SOI, the ferromagnetic materials with non-zero magnetization generate an addition transverse voltage by anomalous velocity of carriers in AHE [117]. The origin of AHE is attributed to extrinsic and intrinsic factor. The extrinsic contributions come from scattering and side sump, while intrinsic contributions can be evaluated via the electronic band structures [19,118,119]. Hence, the AHE is believed to be zero in antiferromagnetic (AFM) or compensated ferrimagnetic (FiM) materials owing to the vanishing of net magnetic moment.

Considering only the intrinsic contribution, AHC can be calculated from linear response theory [120] (or from Kubo formula [121]) via the Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$. The Berry curvature is defined int terms of the Berry connection $\Omega_{n,xy}^{z}(\mathbf{k}) = \nabla_{\mathbf{k}} \times A_{n}(k)$, where $A_{n}(k) = -i\langle u_{nk} | \nabla_{k} u_{nk} \rangle$. AHC is proportional to the Berry curvature integration over whole Brillouin zone (BZ):

$$\Omega_{n,xy}^{z} = \sum_{n} f[\varepsilon_{n}(\boldsymbol{k})]\Omega_{n,xy}^{z}$$
(5.2)

Thus, one can tailor AHC via critically altering the Berry curvature distribution, regardless of the magnetization [4,122]. A crucial feature of Berry curvature is that it is odd under a timereversal (TR) operator \hat{T} [20,22,123,124]. Hence, a broken time-reversal system is essential to have a nonzero AHC. In most collinear AFM, although \hat{T} is broken, the AHC is forced to be zero, due to the joint of $\hat{T}\hat{O}$ symmetry operator, where \hat{O} is a space group operator.

While most studies on AHE have been done on FMs, AHE in non collinear AFMs have attracted the community[124]. Theoretical studies predicted non-negligible AHE in some non-collinear AFMs, such as Mn₃Ir (200 Ω^{-1} cm⁻¹) [22], Mn₃Pt (98 Ω^{-1} cm⁻¹), Mn₃Sn (120

 Ω^{-1} cm⁻¹) [125,126], and Mn₃Ge (330 Ω^{-1} cm⁻¹) [125-127] despite the absence of net magnetization, in which the influences of symmetry constrained by magnetization on Berry curvature was revealed. These predictions were confirmed in experiments [128-130] afterward. Recently, studies on AHE in magnetic materials without net magnetic moment have been extended to compensated FiMs. Nonzero AHC has been theoretical found in inverse Heusler compounds Ti₂MnAl (300 Ω^{-1} cm⁻¹) [23] and Mn₃Al (-320 Ω^{-1} cm⁻¹) [131].

Heusler compound is considered as a good platform for tailoring AHC via Berry curvature [4,122,132], owing to their feasible properties tuned by varying chemical elements [7,8]. Therefore, in this work, we investigate the AHE in α -phase, β -phase and γ -phase of ferrimagnet quaternary Heusler compounds TiZrMnAl. Herein, all phases have (nearly) compensated moment. Despite of the similar equilibrium lattice constant, as well as total magnetic moments, the AHC is totally different. Noteworthy, the α -phase shows a AHC as large as 1470 Ω^{-1} cm⁻¹ while β - and γ -phase only do a moderate AHC of 200 and 100 Ω^{-1} cm⁻¹. The large AHC in α -phase is explained via the total Berry curvature over the whole BZ.

5. 2. Crystal structures

Quaternary Heusler compound TiZrMnAl constitutes of face-centered cubic lattice with four occupied Wyckoff positions 4a (0, 0, 0), 4c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4d (3/4, 3/4, 3/4). Detail of atomic occupation in three possible phases are listed in table 5.1 [133]. For all phases, Al is fixed at 4d position. In α -phase, Ti, Zr, and Mn atoms occupy 4a, 4c, and 4b Wyckoff positions. In β -phase, the position of Zr and Ti atoms are interchanged, while in γ phase, the position of Zr is switched with Mn. Three possible structural phases (α , β , and γ) and their relationship are illustrated in Fig 5. 1. These phases are distinguished by their octahedral environment.

Without magnetization, crystal structure of quaternary Heusler compound has a space group of $F\bar{4}3m$ (No. 216) [76], comprising of mirror planes $M_{\pm 110}$, $M_{1\pm 10}$, and $M_{0\pm 11}$, together with the three two-fold rotations $C_{2,x}$, $C_{2,y}$, and $C_{2,z}$. In our work, we choose the magnetization along with z-axis. The choice of magnetization direction alerts the symmetry from cubic to tetragonal described by the magnetic space group I $\bar{4}m'2'$ [134], where the prime denotes TR [105,135-138]. The Mn local magnetic moment is antialigned with Ti and Zr local magnetic moments. Magnetic unit cell for α -phase, β -phase, and γ -phase in the presence of magnetic moments as presented in Fig 5. 2.



Fig. 5. 1: Crystal structures of quaternary Heusler compounds TiZrMnAl in conventional cubic unit cell with space group $F\overline{4}3m$ (No. 216) and their octahedral environments for α -phase, β -phase, and γ -phase. Blue, green, magenta, and grey balls denote Ti, Zr, Mn, and Al atoms.

Table 5.2: The possible phases of quaternary-Heusler compound TiZrMnAl. The positions (4a,4b, and 4c) are denoted in terms of the Wyckoff positions.

Structural phase	Ti	Zr	Mn	Al
α-phase	4a	4c	4b	4d
β -phase	4c	4a	4b	4d
γ-phase	4a	4b	4c	4d



Fig. 5. 2: Magnetic unit cell for α -phase, β -phase, and γ -phase in the presence of magnetic moments, denoted by arrows, along the z axis, whose magnetic space group is $I\overline{4}m'2'$.

5. 3. Computational methodology

The electronic band structures are calculated by density-functional theory (DFT) using the Vienna ab initio simulation package (VASP) [38]. The exchange-correlation interactions have been treated with the Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation (GGA) [35]. We use an energy cutoff of 450 eV for the plane-wave basis expansion and a *k*-mesh of $21 \times 21 \times 21$ within Monkhorst-Pack scheme for self-consistent calculation.

We obtain AHC via WANNIERBERRY[139] code with an interpolation-grid of $500 \times 500 \times 500$. The convergence of AHC is carefully checked with respect to the interpolation-grid. Herein, AHC is calculated using Kubo formula [19,20], as follows:

$$\Omega_{n,xy}^{z}(\boldsymbol{k}) = -\sum_{n'\neq n} \frac{2Im\left[\left\langle u_{n\boldsymbol{k}} \middle| \partial_{k_{x}} \widehat{H}(\boldsymbol{k}) \middle| u_{n'\boldsymbol{k}} \right\rangle \left\langle u_{n'\boldsymbol{k}} \middle| \partial_{k_{y}} \widehat{H}(\boldsymbol{k}) \middle| u_{n\boldsymbol{k}} \right\rangle\right]}{[\varepsilon_{n}(\boldsymbol{k}) - \varepsilon_{n'}(\boldsymbol{k})]^{2}}$$
(5.3)

and

$$\sigma_{xy} = -\frac{e^2}{\hbar} \sum_n \int_{BZ} \frac{d^3k}{(2\pi)^3} f[\varepsilon_n(\mathbf{k})] \Omega_{n,xy}^z(\mathbf{k})$$
(5.4)

where $\Omega_{n,xy}^{z}$ is the z-component of Berry curvature, $|u_{nk}\rangle$ represents the periodic part of the n-th Bloch state, $\varepsilon_{n}(\mathbf{k})$ is the eigenvalue for the nth eigenstates of $|u_{nk}\rangle$ at the **k** point, and $\nabla_{\mathbf{k}}\hat{H}(\mathbf{k})/\hbar$ is the velocity operator.

The Wannier functions is extracted from DFT calculation via the WANNIER90 package [140], with an initial guess for the orbitals as the 3*p* and 3*d* orbitals of Ti Zr, and Al; and 3*s* and 3*p* orbitals of Al. The reliability of Wannier function is verified by comparing the band structure from DFT and WANNIER90. The full-potential linearized augmented plane wave (FLAPW) method as implemented in FLEUR [104] was employed to confirm the validity of AHC calculated by VASP.

5. 4. Results and discussions

5. 4. 1. Magnetic and electronic properties

The calculated lattice constant of TiZrMnAl for each structural phase is shown in table 5. 2. According to table 5. 2, the α -phase is the most stable phase, established by a relativity energy difference of 0.34 and 0.03 eV/fu compared to β -phase and γ -phase. The equilibrium lattice constants are 6.41, 6.48, and 6.39 Å for α -, β -, and γ -phase, respectively. Meanwhile, the atom-resolved magnetic moments of Ti (1.58, 1.62, and 0.29 μ_B) is larger than those of Zr (0.80, 1.15, and 0.07 μ_B). The Mn local magnetic moment (-2.34, -2.74, and -0.59 μ_B) is antialigned with Ti and Zr local magnetic moments. The total magnetic moments are 0.00, 0.00, and 0.10 μ_B , indicating the vanishing net magnetic moment in α - and β -phase. The zero magnetic moment of TiZrMnAl satisfies the Slater-Pauling rule in quaternary Heusler materials [141] $m_t = Z_V - 18$, where Z_V is the total valence electron number per formula unit.

Table 5.1: Calculated lattice parameters a_0 (in Å), atom-resolved magnetic moment, total magnetic moment per formula unit (in μ_B), and the relativity energy difference (in eV/fu) with α -phase.

Structural phase	<i>a</i> ₀	m _{Ti}	m _{Zr}	m _{Mn}	m _{tot}	ΔE
α-phase	6.41	1.58	0.80	-2.34	0	0
β-phase	6.48	1.62	1.15	-2.74	0	0.34
γ-phase	6.39	0.29	0.07	-0.59	0.10	0.03

The electronic band structure of TiZrMnAl is shown in Fig. 5. 2. For α -phase, there is a band gap of 0.85 eV in minority spin. In majority spin, the conduction band minimum (CBM) and valence band maximum (VBM) directly get touch at Fermi level E_F along \overline{LW} symmetry line. Another the CBM touches E_F along \overline{KT} symmetry line. For β -phase, there is also a band gap of 0.26 eV in minority spin. The CBM of minority spin (along \overline{XT}) indirectly contacts with VBM of majority spin (along \overline{XK} and \overline{LW}) at E_F . The α -phase and β -phase, exhibiting a band gap in one of the spin channels and a zero band gap in the other, therefore, is called spin gapless semiconductor (SGSs) [142,143]. In SGSs, the 100% spin-polarized carriers can be excited from the valence to conduction bands with no energy cost, leading to the feasible spin transport, which is advantageous for future spintronic applications [144]. The γ -phase is metal, where the CBM and VBM in both majority spin and minority spin across E_F , this is in consistent with the nearly vanished total magnetic moment estimated in table 5.1.



Fig. 5. 3: Band structures along the high-symmetry lines of the fcc lattice of quaternary Heusler compounds TiZrMnAl for α -phase, β -phase, and γ -phase, where red (blue) denotes the majority (minority) spin.

5. 4. 2. Anomalous Hall effects

The calculated AHC values of TiZrMnAl for each structural phases (α , β , and γ) are presented in Fig. 5. 4. The results show that the α -phase possesses a large AHC of 1470 Ω^{-1} cm⁻¹ while β - and γ -phase show moderate AHC of 200 and 100 Ω^{-1} cm⁻¹. Both VASP and Fleur give consistent results. Especially, the calculated AHC in α -phase has peak at Fermi level E_F , while other energy levels (especially energy levels below E_F) are less significant. Noteworthy, the AHC of α -phase is quite comparable to that of regular Heusler compound Co₂MnAl (1800 Ω^{-1} cm⁻¹) and Rh₂MnAl (1500 Ω^{-1} cm⁻¹), which has a large total magnetic moment of 4.04 and 4.06 μ_B [132]. Furthermore, the AHC of α -phase is much larger than AHC in other discovered compensated ferrimagnetic materials Ti₂MnAl (300 Ω^{-1} cm⁻¹) [23] and Mn₃Al (-320 Ω^{-1} cm⁻¹) [131]. The tunable spin transport properties owing by SGSs, large AHC, and vanishing total magnetic moments, that makes the stable α -phase of TiZrMnAl to be a promising candidate for spintronic application.



Fig. 5. 4: AHC σ_{xy} as a function of energy of quaternary Heusler compounds TiZrMnAl for α -phase, β -phase and γ -phase. The red solid line and the blue dash line stands for the calculated AHC from VASP and Fleur.



Fig. 5. 5: Band structures and Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$. Colors represents $\langle S_{z} \rangle$ along the same path with Fig. 5. 4.

Since the AHC can be estimated via Berry curvature, for the shake of finding the physical origin of large AHC in the α -phase, we firstly discuss the details of Berry curvatures. In Fig. 5. 4, we show the total Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k}) = \sum_{n} f[\varepsilon_{n}(\mathbf{k})]\Omega_{n,xy}^{z}$ along the same high-symmetry lines at Fig 5. 3. The total Berry curvature in α -phase is dominated by the gapless band along \overline{LW} [up to 10000 (bohr²)] and significantly larger than that of β -phase (700 bohr²) and γ - phase (250 bohr²). From now on, we will focus on the gapless band along \overline{LW} in α -phase, which exhibits a gigantic Berry curvature. The Berry curvature of gapless point is general large [19,20], however, the large AHC is generally found in Heusler compounds only when the band crossing between two different spin channels. When the crossing band occurs in the same spin channel usually do not give a significant large AHC[122].



Fig. 5. 6: (a) The BZ of fcc, where red line marks the considering symmetry path. Green line indicates the mirror plane M₁₁₀. Band structures in a narrow energy window and Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$ along \overline{LW} path with n = 1,3, and 5 (b) without SOI and with (c) SOI for α -phase.

Since the total Berry curvature is dominant by the contribution of Berry curvature at the gapless band along \overline{LW} symmetry line, we consider the Berry curvature of the gapless band along \overline{LW} for different directions. Here, the position of high symmetry point L is fixed,

while the position of W is taken along different direction. Fig 5. 6(a) illustrates our considering high symmetry point W points denoted by W₁, W₂, W₃, W₄, W₅, and W₆, which forms the edge of hexagonal plane of the BZ of fcc.

Table 5.2: Location of high symmetry point W for different direction, denoted as W₁, W₂, W₃, W₄, W₅, and W₆. Their positions are described in the Cartesian coordinates in units of $(\frac{2\pi}{a}, \frac{2\pi}{a}, \frac{2\pi}{a})$.

	Position
W1	0.75 0.25 0.50
W2	0.25 0.75 0.50
W3	0.50 0.25 0.75
W_4	0.25 0.50 0.75
W5	0.75 0.50 0.25
W ₆	0.50 0.75 0.25

In Table 5.2, we list the positions of our considering high symmetry points W. Fig 5. 6 shows band structures in a narrow energy window and Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$ along \overline{WL} path (b) without SOI and with (c) SOI for α -phase. Without SOI, quaternary Heusler compounds have M₁₁₀ is one of the symmetry operations. Because W_{n+1} can be obtained by W_n (n = 1, 3, 5) via the symmetry of M₁₁₀, the gapless bands along $\overline{LW_n}$ have the opposite signs and equal values of $\Omega_{n,xy}^{z}(\mathbf{k})$ with the gapless bands along $\overline{LW_{n+1}}$ (n = 1,3, and 5) [see Fig 5. 6(b)], resulting the zero Berry curvature in total. With SOI along [001], the mirror planes, which parallel to the magnetization direction, preserve the direction of spin, thus Berry curvature does not flip its sign via M₁₁₀ mirror planes. As in Fig 5. 6(c), the positive and negative Berry curvatures do not contribute equally anymore, we observe the dominant contributions of $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$. Furthermore, the gapless band is gapped with SOI. We do not have any answer for this observation at this moment, it requires more detail symmetry analyses.

The magnetism breaks some symmetry of crystal. Therefore, to evaluate AHC qualitatively, we extend the Berry curvature to whole BZ. We show in Fig 5. 7, the total Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$ distribution over whole BZ α -phase without (a) SOI and with (b) SOI. Without SOI, the contribution of Berry curvature $\Omega_{n,xy}^{z}(\mathbf{k})$ over whole BZ is symmetric. During the integration, the equally contribution of $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$ and $\Omega_{n,xy}^{z}(\mathbf{k}) < 0$ leading to the zero $\Omega_{n,xy}^{z}(\mathbf{k})$ in total. With SOI, $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$ is dominant, giving a rise to the large AHC in α -phase.



Fig. 5. 7: Total Berry curvature $\Omega_{n,xy}^z = \sum_n f[\varepsilon_n(\mathbf{k})]\Omega_{n,xy}^z$ distribution over whole BZ for α -phase (a) without SOI and (b) with SOI [001].

5.5. Summary

In this work, using first-principles calculations, we have investigated the AHE in three structural phases of a quaternary Heusler compounds TiZrMnAl. The α -phase, in which Ti and Mn form octahedral site, is the most stable phase. The total magnetic moment is compensated in α -, β -phase, and nearly compensated γ -phase. α - phase and β -phase are spin-gapless semiconductors, in which their CBM and VBM touch at Fermi level, while γ -phase is metal. Despite of the similar equilibrium lattice constant (6.41, 6.48, and 6.39 Å for α -, β -phase, and γ -phase), as well as total magnetic moments, the AHC is totally different. The α -phase possesses a large AHC of 1470 Ω -1 cm⁻¹, while β - and γ -phase show moderate AHC of 200 and 100 Ω ⁻¹ cm⁻¹. Without SOI, the direct gapless bands along \overline{LW} have the opposite sign of Berry curvature via M₁₁₀ mirror planes, that cancel each other. As a result, the integration of $\Omega_{n,xy}^{z}(\mathbf{k})$ over the whole BZ is zero. With SOI, the symmetry becomes asymmetric, causing the governing of $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$, that gives a rise to large AHC in α -phase.

Chapter 6: Conclusions and outlooks

Inspiring by the tunable properties, we have theoretical studied structural stability, electronic, and magnetic properties of Heusler compounds, focusing on half-metallicities, permanent magnetisms, and anomalous Hall effects. In addition, their potential for practical application is also addressed.

In chapter 3, the alkali-metals-based half-Heusler ACrZ (A = Li, Na, and K; Z = P, As, and Sb) compounds are identified as potential half-metallic ferromagnets with wide band gaps (1.60 - 2.16 eV). The band gap formation mechanism of ACrZ origins from the sublattice zincblende CrZ, where the hybridization between the Cr-*d* and Z-*p* states opens the band gap. In addition, the half-metallicity is robust stable against severe in-plane strains and even at Z-term (001) surfaces. Considering their thermal stabilities and lattice mismatches with semiconductor substates, among studied compounds, LiCrZ and NaCrZ (Z = As and Sb) stands out as the most promising candidates for practical applications.

In chapter 4, we have investigated the feasibility of Fe₂MnSn Heusler compound to be rare-earth free permanent magnet. Some possible structures are adopted, namely regular and inverse cubic, inverse tetragonal, and hexagonal. Large $\mu_0 M_S$ of 1.28 T – 1.59 T are found in Fe₂MnSn regardless of structural phase. In particular, the inverse tetragonal have large uniaxial K_u of 2.35 MJ·m⁻³ but the structure is unstable. We further demonstrate that the inverse tetragonal phase can be stabilized by interstitial doping of light elements. In particular, 6.25% H and N can improve the formation energy H_F of inverse tetragonal up to -11.93 and -30.16 kJ·mol⁻¹. H has good intrinsic magnetic properties, i.e., a uniaxial K_u of 1.66 MJ·m⁻³, a theoretical energy product (BH)_{max} up to 56 MGOe, a $\mu_0 K_u$ of 28 kOe, and κ of 0.93 while N [$K_u = 1.07 \text{ MJ} \cdot \text{m}^{-3}$, (BH)_{max} = 46 MGOe, $\mu_0 K_u = 22 \text{ kOe}$, and $\kappa = 0.73$] has a good thermal stability since being even more thermal stable by 5.03 kJ·mol⁻¹ than hexagonal phase.

In chapter 5, the AHE of a ferrimagnet quaternary Heusler compounds TiZrMnAl is investigated. Three possible atomic configuration is considered. The α -phase, in which Ti and Mn form octahedral site, is the most stable phase. The total magnetic moment is compensated in α -, β -phase, and nearly compensated γ -phase. The α -phase possesses an AHC as large as 1470 Ω^{-1} cm⁻¹, while β - and γ -phase show moderate AHC of 200 and 100 Ω^{-1} cm⁻¹, despite the vanishing net magnetization. The tunable spin transport properties owing by SGSs, large AHC, and vanishing total magnetic moments, that makes the stable α -phase of TiZrMnAl to be a promising candidate for spintronic application. The gapless band along \overline{LW} of α -phase shows a gigantic Berry curvature up to [up to 1000 (bohr²)], this is significantly larger than that of β phase (700 bohr²) and γ - phase (250 bohr²). However, only the large Berry curvature at gapless band along \overline{LW} is not enough to explain for the large AHC in α -phase. By evaluating the total Berry curvature $\Omega_{n,xy}^{z} = \sum_{n} f[\varepsilon_{n}(\mathbf{k})]\Omega_{n,xy}^{z}$ over whole BZ, we found that the governing of $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$ after tuning SOI also plays a crucial role in driving a large AHC in α -phase of TiZrMnAl. To understand why $\Omega_{n,xy}^{z}(\mathbf{k}) > 0$ becomes dominant, there are more detail symmetry analyses need to be done, but we leave this work for future studies.

References

[1] T. Graf, S. S. P. Parkin, and C. Felser, IEEE Trans. Magn. 47, 367-373 (2011).

[2] A. J. Bradley and J. W. Rodgers, Proc. R. Soc. Lond. Series A 144, 340 (1934).

[3] C. Felser and A. Hirohata, *Heusler Alloys, properties, growth, applications* (Springer Series in Materials Science 222, 2016).

[4] K. Manna, Y. Sun, L. Muechler, J. Kübler, and C. Felser, Nat. Rev. Mater. 3, 244(2018).

[5] S. Sanvito, C. Oses, J. Xue, A. Tiwari, M. Zic, T. Archer, P. Tozman, M. Venkatesan,M. Coey, S. Curtarolo, Sci. Adv. 3, e1602241 (2017).

[6] D. Zhang, B. Yan, S.-C. Wu, J. Kübler, G. Kreiner, S. S. P. Parkin, and C. Felser, J.Phys. Condens. Matter 25, 206006 (2013).

[7] F. Meng, X. Liu, Q. Li, and H. Luo, J. Magn. Magn. Mater. 482, 224 (2019).

[8] S. Keshavarz, N. Naghibolashrafi, M. E. Jamer, K. Vinson, D. Mazumdar, C. L. Dennis, W. Ratcliff, J. A. Borchers, A. Gupta, and P. LeClair, J. Alloys Compd. **771**, 793 (2019).

[9] M. Kratochvílová, D. Král, M. Dušek, J. Valenta, R. H. Colman, O. Heczko, and M. Veis, J. Magn. Magn. Mater. 501, 166426 (2020).

[10] M. Kratochvílová, M. Klicpera, F. Malý, J. Valenta, M. Veis, R. H. Colman, and O. Heczko, Intermetallics 131, 107073 (2021).

[11] M. I. Katsnelson, V. Y. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Rev. Mod. Phys. 80, 315 (2008).

[12] R. A. de Groot, F. M. Mueller, P. G. v. Engen, and K. H. J. Buschow, Phys. Rev. Lett.50, 2024 (1983).

[13] R. W. McCallum, L. H. Lewis, R. Skomski, M. J. Kramer, and I. E. Anderson, Annu.Rev. Mater. Res 44, 451 (2014).

[14] J. M. D. Coey, J. M. Cadogan, and D. H. Ryan, *Nd-Fe Permanent Magnets: Their Present and Future Applications* (Elsevier Applied Science, London/New York, 1985).

[15] J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, 2010).

[16] R. Skomski and J. M. D. Coey, Scr. Mater. 112, 3 (2016).

[17] J. M. D. Coey, Scr. Mater. 67, 524 (2012).

[18] J. M. D. Coey, IEEE Trans. Magn. 47, 4671 (2011).

[19] N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, and N. P. Ong, Rev. Mod. Phys.82, 1539 (2010).

[20] D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. 82, 1959 (2010).

[21] L. Šmejkal, R. González-Hernández, T. Jungwirth, and J. Sinova, Sci. Adv. 6, eaaz8809 (2020).

[22] H. Chen, Q. Niu, and A. H. MacDonald, Physical Review Letters 112, 017205 (2014).

[23] W. Shi, L. Muechler, K. Manna, Y. Zhang, K. Koepernik, R. Car, J. van den Brink, C.Felser, and Y. Sun, Phys. Rev. B 97, 060406 (2018).

[24] L. H. Thomas, *Math. Proc. Camb. Philos. So* (Cambridge University Press, 1927), pp.542.

[25] E. Fermi, Z. Phys **48**, 73 (1928).

[26] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[27] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[28] R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, 2004).

[29] M. Born, Ann. Phys 84, 457 (1927).

[30] P. A. Dirac, *Math. Proc. Camb. Philos. Soc* (Cambridge University Press, 1930, 1930),pp. 376.

[31] R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecule* (Oxford: Oxford University Press, 1994).

[32] M. G. Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

[33] G. L. Oliver and J. P. Perdew, Phys. Rev. A, 397 (1979).

[34] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1996).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[36] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

- [37] E. Wimmer and A. J. Freeman, *Electronic Structure* 2000, Vol. 2, Series: Handbook of Surface Sciences.
- [38] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [39] P. E. Blöchl, Phy. Rev. B 50, 17953 (1994).
- [40] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B 30, 561 (1984).
- [41] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B 24, 864 (1981).
- [42] T. T. Hoang, S. H. Rhim, and S. C. Hong, Phys. Rev. Mater 6, 055001 (2022).
- [43] Y. Lu, X. W. Li, G. Q. Gong, G. Xiao, A. Gupta, P. Lecoeur, J. Z. Sun, Y. Y. Wang,
- and V. P. Dravid, Phys. Rev. B 54, R8357 (1996).

[44] E. Y. Tsymbal, O. N. Mryasov, and P. R. LeClair, J. Phys. Condens. Matter 15, R109 (2003).

[45] E. Şaşıoğlu, L. M. Sandratskii, P. Bruno, and I. Galanakis, Phys. Rev. B 72, 184415(2005).

- [46] V. I. H. J. Ma, K. Munira, Y. Xie, S. Keshavarz, D. T. Mildebrath, C. Wolverton, A.W. Ghosh, and W. H. Butler, Phys. Rev. B 95, 024411 (2017).
- [47] R. J. Soulen, J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P.
- R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Science **282**, 85 (1998).
- [48] L. Ritchie, G. Xiao, Y. Ji, T. Y. Chen, C. L. Chien, M. Zhang, J. Chen, Z. Liu, G. Wu, and X. X. Zhang, Phys. Rev. B 68, 104430 (2003).
- [49] M. Baral and A. Chakrabarti, Phys. Rev. B 99, 205136 (2019).
- [50] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B 66, 174429 (2002).
- [51] P. Webster, J. Physics. Chem. Solids **32**, 1221 (1971).
- [52] M. Jourdan, E. A. Jorge, C. Herbort, M. Kallmayer, P. Klaer, and H.-J. Elmers, Appl.Phys. Lett. 95, 172504 (2009).
- [53] S. V. Karthik, A. Rajanikanth, Y. K. Takahashi, T. Okhubo, and K. Hono, Appl. Phys.Lett. 89, 052505 (2006).
- [54] A. Rajanikanth, D. Kande, Y. K. Takahashi, and K. Hono, J. Appl. Phys. 101, 09J508 (2007).
- [55] B. Varaprasad, A. Srinivasan, Y. Takahashi, M. Hayashi, A. Rajanikanth, and K. Hono,Acta Mater. 60, 6257 (2012).
- [56] M. Jourdan, J. Minár, J. Braun, A. Kronenberg, S. Chadov, B. Balke, A. Gloskovskii,
 M. Kolbe, H. J. Elmers, G. Schönhense, H. Ebert, C. Felser, and M. Kläui, Nat. Commun. 5,
 3974 (2014).

[57] S. Ishida, S. Fujii, S. Kashiwagi, and S. Asano, Phys. Soc. Jpn. 64, 2152 (1995).

[58] L. Chioncel, E. Arrigoni, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. Lett. **96**, 137203 (2006).

[59] M. Ležaic['], P. Mavropoulos, J. Enkovaara, G. Bihlmayer, and S. Blügel, Phys. Rev.Lett. 97 026404 (2006).

[60] B. Hu, K. Moges, Y. Honda, H. Liu, T. Uemura, M. Yamamoto, J. Inoue, and M. Shirai,Phys. Rev. B 94, 094428 (2016).

[61] K. Nawa, I. Kurniawan, K. Masuda, Y. Miura, C. E. Patrick, and J. B. Staunton, Phys.Rev. B 102, 054424 (2020).

[62] G. A. de Wijs and R. A. de Groot, Phys. Rev. B 64, 020402 (2001).

[63] M. Ležaic['], P. Mavropoulos, J. Enkovaara, G. Bihlmayer, and S. Blügel, J. Phys.:Condens. Matter. 17, 3121 (2005).

[64] I. Galanakis, J. Phys.: Condens. Matter. 14, 6329 (2002).

[65] D. Steil, S. Alebrand, T. Roth, M. Krauß, T. Kubota, M. Oogane, Y. Ando, H. C.Schneider, M. Aeschli- mann, and M. Cinchetti, Phys. Rev. Lett. 105, 217202 (2010).

[66] A. Mann, J. Walowski, M. Mu'nzenberg, S. Maat, M. J. Carey, J. R. Childress, C.

Mewes, D. Ebke, V. Drewello, G. Reiss, and A. Thomas, Phys. Rev. X 2, 041008 (2012).

[67] L. Damewood, B. Busemeyer, M. Shaughnessy, C. Y. Fong, L. H. Yang, and C. Felse,Phys. Rev. B 91, 064409 (2015).

[68] R. L. Zhang, L. Damewood, Y. J. Zeng, H. Z. Xing, C. Y. Fong, L. H. Yang, R. W.Peng, and C. Felser, J. Appl. Phys. **122**, 013901 (2017).

[69] D. Hoat, M. Naseri, R. Ponce-Pérez, J. Rivas-Silva, A. Kartamyshev, and G. H. Cocoletzi, Chem. Phys **537**, 110848 (2020).

[70] M. Rostami, M. Abedi, P. Amantorkaman, and F. Kanjouri, Vacuum 175, 109278(2020).

[71] A. Dehghan and S. Davatolhagh, J. Alloy. Comp. 772, 132 (2019).

[72] M. Moradi, N. Taheri, and M. Rostami, Phys. Lett. A **382**, 3004 (2018).

[73] Lin H. Yang, R. L. Zhang, Y. J. Zeng, and C. Y. Fong, *Design of Alkali-Metal-Based Half-Heusler Alloys Having Maximum Magnetic Moments from First Principles* (CRC, Boca Raton, 2018), pp. 69-77.

[74] T. Graf, C. Felser, and S. S. P. Parkin, Prog. Solid State Chem. **39**, 1 (2011).

[75] P. M. I. Galanakis, Phys. Rev. B 67, 104417 (2003).

[76] P. Schlottmann, Phys. Rev. B 67, 174419 (2003).

[77] H. T. Jeng and G. Y. Guo, Phys. Rev. B **65**, 094429 (2002).

[78] Z. Hao, R. Liu, Y. Fan, and L. Wang, J. Alloy. Compd. 820, 153118 (2020).

[79] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B 66, 134428 (2002).

[80] J. E. Pask, L. H. Yang, C. Y. Fong, W. E. Pickett, and S. Dag, Phys. Rev. B 67, 224420(2003).

[81] R. Farshchi and M. Ramsteiner, J. Appl. Phys. 113, 191101 (2013).

[82] A. Hirohata, M. Kikuchi, N. Tezuka, K. Inomata, J. Claydon, Y. Xu, and G. van der Laan, Curr. Opin. Solid State Mater. Sci. **10**, 93 (2006).

[83] M. E. Straumanis and C. D. Kim, J. Appl. Phys. 36, 3822 (1965).

[84] A. Vishina, O. Y. Vekilova, T. Björkman, A. Bergman, H. C. Herper, and O. Eriksson,Phys. Rev. B 101, 094407 (2020).

[85] M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, and S. Hirosawa, J. Appl. Phys.57, 4094 (1985).

[86] L. Wollmann, A. K. Nayak, S. S. P. Parkin, and C. Felser, Annu. Rev. Mater. Res 47, 247 (2017).

[87] C. Felser, L. Wollmann, S. Chadov, G. H. Fecher, and S. S. P. Parkin, APL Mater. 3, 041518 (2015).

[88] S. V. Faleev, Y. Ferrante, J. Jeong, M. G. Samant, B. Jones, and S. S. P. Parkin, Phys.Rev. Appl. 7, 034022 (2017).

[89] S. V. Faleev, Y. Ferrante, J. Jeong, M. G. Samant, B. Jones, and S. S. P. Parkin, Phys.Rev. Mater. 1, 024402 (2017).

[90] Y. I. Matsushita, G. Madjarova, J. K. Dewhurst, S. Shallcross, C. Felser, S. Sharma, and E. K. U. Gross, J. Phys. D: Appl. Phys. 50, 095002 (2017).

[91] H. C. Herper, Phys. Rev. B **98**, 014411 (2018).

[92] D. Zhang, B. Yan, S.-C. Wu, J. Kübler, G. Kreiner, S. S. P. Parkin, and C. Felser, J.Phys. Condens. Matter 25, 206006 (2013).

[93] Q. Li, K. Sun, S. Liu, H. Luo, and F. Meng, Intermetallics 117, 106671 (2020).

[94] M. Kratochvílová, D. Král, M. Dušek, J. Valenta, R. H. Colman, O. Heczko, and M. Veis, J. Magn. Magn. Mater 501, 166426 (2020).

[95] F. Meng, X. Liu, Q. Li, and H. Luo, J. Magn. Magn. Mater. 482, 224 (2019).

[96] S. Keshavarz, N. Naghibolashrafi, M. E. Jamer, K. Vinson, D. Mazumdar, C. L. Dennis, W. Ratcliff, J. A. Borchers, A. Gupta, and P. LeClair, J. Alloys Compd. **771**, 793 (2019).

[97] T. Gasi, V. Ksenofontov, J. Kiss, S. Chadov, A. K. Nayak, M. Nicklas, J. Winterlik,M. Schwall, P. Klaer, P. Adler, and C. Felser, Phys. Rev. B 87, 064411 (2013).

[98] D. Odkhuu, T. Ochirkhuyag, and S. C. Hong, Phys. Rev. Appl. 13, 054076 (2020).

- [99] H. Ucar, R. Choudhary, and D. Paudyal, J. Alloys Compd. 836, 155263 (2020).
- [100] Q. Gao, I. Opahle, O. Gutfleisch, and H. Zhang, Acta Mater. 186, 355 (2020).
- [101] D. Odkhuu and S. C. Hong, Phys. Rev. Appl. 11, 054085 (2019).
- [102] I. Khan and J. Hong, J. Phys. D: Appl. Phys. 47, 415002 (2014).
- [103] D. D. Koelling and B. N. Harmon, J. Phys. C: Solid State Phys. 10, 3107 (1977).
- [104] FLEUR Project, available at: <u>http://www.flapw.de</u>.

[105] M. I. Aroyo, J. M. Perez-Mato, D. Orobengoa, E. Tasci, G. de la Flor, and A. Kirov,Bulg. Chem. Commun 43, 183 (2011).

[106] A. S. Mikhaylushkin, I. A. Abrikosov, A. B. Belonoshko, B. Johansson, and S. I. Simak, Phys. Rev. B **79**, 132106 (2009).

- [107] S. R. Barman, Aparna Chakrabarti, Sanjay Singh, S. Banik, S. Bhardwaj, P. L. Paulose,
- B. A. Chalke, A. K. Panda, A. Mitra, and A. M. Awasthi, Phys. Rev. B 78, 134406 (2008).

[108] V. Antropov, L. Ke, and D. Åberg, Solid State Commun. 194, 35 (2014).

- [109] J. Zhang, P. V. Lukashev, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. B 96, 014435(2017).
- [110] R. Skomski, A. Kashyap, and A. Enders, J. Appl. Phys. 109, 07E143 (2011).
- [111] D.-s. Wang, R. Wu, and A. J. Freeman, Phys. Rev. B 47, 14932 (1993).
- [112] S. P. Ong, L. Wang, B. Kang, and G. Ceder, Chem. Mater. 20, 1798 (2008).
- [113] S. P. Ong, A. Jain, G. Hautier, B. Kang, and G. Ceder, Electrochem. Commun. 12, 427(2010).
- [114] H.-C. Wang, S. Botti, and M. A. L. Marques, npj Computational Materials 7, 12 (2021).

[115] Y. Liu, B. Zhou, C. Wu, H. Peng, J. Wang, and X. Su, J. Phase Equilib. Diffus. 39, 280 (2018).

- [116] E. M. Pugh, N. Rostoker, and A. Schindler, Phys. Rev. 80, 688 (1950).
- [117] R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954).
- [118] S. Onoda, N. Sugimoto, and N. Nagaosa, Phys. Rev. Lett. 97, 126602 (2006).
- [119] Y. Yao, L. Kleinman, A. H. MacDonald, J. Sinova, T. Jungwirth, D.-s. Wang, E. Wang, and Q. Niu, Phys. Rev. Lett. 92, 037204 (2004).
- [120] S. Tomiyoshi and Y. Yamaguchi, J. Phys. Soc. Japan 51, 2478 (1982).
- [121] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs, Phys. Rev. Lett. 49, 405 (1982).
- [122] K. Manna, L. Muechler, T. -H. Kao, R. Stinshoff, Y. Zhang, J. Gooth, N. Kumar, G.
- Kreiner, K. Koepernik, R. Car, J. Kübler, G. H. Fecher, C. Shekhar, Y. Sun, and C. Felser, Phys. Rev. X 8, 041045 (2018).
- [123] F. D. M. Haldane, Phys. Rev. Lett. 61, 2015 (1988).
- [124] L. Šmejkal, A. H. MacDonald, J. Sinova, S. Nakatsuji, and T. Jungwirth, Nat. Rev. Mater. 7, 482 (2022).
- [125] Y. Zhang, Y. Sun, H. Yang, J. Železný, S. P. P. Parkin, C. Felser, and B. Yan, Phys.Rev. B 95, 075128 (2017).
- [126] J. Kübler and C. Felser, EPL 108, 67001 (2014).
- [127] Z. Q. Liu, H. Chen, J. M. Wang, J. H. Liu, K. Wang, Z. X. Feng, H. Yan, X. R. Wang,
- C. B. Jiang, J. M. D. Coey & A. H. MacDonald, Nat. Electron. 1, 172 (2018).
- [128] A. K. Nayak, J. E. Fischer, Y. Sun, B. Yan, J. Karel, A. C. Komarek, C. Shekhar, N.
- Kumar, W. Schnelle, J. Kübler, C. Felser, S. S. P. Parkin, Sci. Adv. 2, e1501870.
- [129] S. Nakatsuji, N. Kiyohara, and T. Higo, Nature 527, 212 (2015).

[130] H. Iwaki, M. Kimata, T. Ikebuchi, Y. Kobayashi, K. Oda, Y. Shiota, T. Ono, and T. Moriyama, Appl. Phys. Lett. 116, 022408 (2020).

[131] M. Park, G. Han, and S. H. Rhim, Phys. Rev. Research 4, 013215 (2022).

[132] J. Kübler and C. Felser, Phys. Rev. B 85, 012405 (2012).

[133] Q. Gao, I. Opahle, and H. Zhang, Phys. Rev. Materials **3**, 024410 (2019).

[134] A. P. Cracknel, J. Phys. C 2, 1425 (1969).

[135] G. Burns and A. M. Glaze, *Space Groups for Solid State Scientists* (Academic Press, New York, 2013).

[136] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids: Representation Theory for Point Groups and Space Groups* (Oxford University Press, New York, 1972).

[137] J. M. P.-M. M. I. Aroyo, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov, and H. Wondratschek, Z. Kristallogr. Cryst. Mater. 221, 15 (2006).

[138] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga,A. Kirov, and H. Wondratschek, Acta Crystallogr. A 62, 115 (2006).

[139] S. S. Tsirkin, Npj Comput. Mater. 7, 33 (2021).

[140] G. Pizzi et al., J. Phys.: Condens. Matter 32, 165902 (2020).

[141] K. Özdoğan, E. Şaşıoğlu, and I. Galanakis, J. Appl. Phys. **113**, 193903 (2013).

[142] X. L. Wang, Phys. Rev. Lett. 100, 156404 (2008).

[143] S. Ouardi, G. H. Fecher, C. Felser, and J. Kübler, Phys. Rev. Lett. 110, 100401 (2013).

[144] D. Rani, L. Bainsla, A. Alam, and K. G. Suresh, J. Appl. Phys. 128, 220902 (2020).