NOVEL ANTIMONY-BASED HEUSLERS WITH POTENTIAL SPINTRONIC APPLICATIONS

by

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The Heusler alloys, or compounds to be precise, have become a well-known name among materials scientists, solid-state physicists and other researchers of the field. In this set of studies, we examined a ternary system, i.e. Fe-Ti-Sb using experimental methodology comprised of different microstructural and structural tests alongside theoretical evaluations. The results showed that there was a compound present in the system, Fe$_{1.5}$TiSb, which had the structural hallmarks of a Heusler, albeit with vacancies in the tetragonal positions. This meant that the compound not only was most probably ‘layered’ between half a full Heusler, but also it was paramagnetic, the compound exhibited a novel Slater-Pauling behavior.

The next system studied was Fe$_x$Co$_{1-x}$TiSb, eventually leading to observation of a novel half Heusler compound, Fe$_{0.5}$Co$_{0.5}$TiSb. The compound showed a C1$_b$ signature and no sign of any other phase were witnessed microstructurally. Magnetometry and transport measurements revealed the nature of the material to be an antiferromagnetic material with possible semiconductivity. Theoretical evaluations further validated the possibility of an antiferromagnetic coupling between iron and cobalt in this compound.

Following the discovery of the Fe$_{1.5}$TiSb, colleagues in our theory group encouraged us to look into another possible ‘layered’ Heusler, Co$_{1.5}$TiSn, based on the former compound’s prototype. The experiments not only found that the Co$_{1.5}$TiSn has all the hallmarks of a Heusler, but also magnetometry tests, especially the interesting evaluation of a Rhodes-Wohlfarth model, led to conclusion that the compound has half-metallic characteristics, found also by theory.
LIST OF ABBREVIATIONS AND SYMBOLS

A : Area

AFM : Antiferromagnetic

B$_0$ : Flux Density

BSE : Backscattered Electrons

CCD : Charged-Coupled Device

CE : Cluster Expansion

d : Interplanar Spacing

DFT : Density Functional Theory

DOS : Density of States

EBSD : Electron Back Scatter Diffraction

E$_f$ : Fermi Energy Level

$\varepsilon$ : Electromotive Force

F : Ferromagnetic

FCC : Face-Centered Cubic

FIB : Focused Ion Beam

FM : Ferromagnetic

FWHM : Full Width at Half Maximum

$\varphi$ : Magnetic Flux

ICSD : Inorganic Structure Database
L : Camera Length
λ : Wavelength
MOKE : Magneto Optic Kerr Effect
MRAM : Magnetic Random Access Memory
MTJ : Magnetic Tunnel Junction
n : Integer
n : Number of Electrons in the Minority Channel
N : Number of Experimental Data Points
NM : Non-Magnetic
ω : Angular Frequency
p_e : Effective Paramagnetic Moment
p_s : Saturation Moment
R_{exp.} : Expected R factor
R_{wp} : Weight-Profile R factor
r : Distance of the incident beam from the diffracted beam
SC : Superconductivity
SE : Secondary Electron
SEM : Scanning Electron Microscopy
STT : Spin Torque Transfer
TEM : Transmission Electron Microscopy
t : Time
θ : Bragg Angle

iv
VSM : Vibrating Sample Magnetometry

w : Weighting factor

XRD : X-Ray Diffractometer

χ : Chi factor

y : Actual Intensity
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CHAPTER 1
INTRODUCTION

The Heusler alloys, or compounds to be precise, have become a household name in the field of materials science since the process of their prototype, \( \text{Cu}_2\text{MnAl} \) by the German mining engineer, Friedrich “Fritz” Heusler in 1903. The significance of this discovery was in the fact that none of the constituting elements of this compound were magnetic at room temperature which intrigued Heusler himself.

Since that pioneering paper, more than 1000 Heusler compounds based on the first prototype have been reported in the scientific literature. The experimental and theoretical analyses manifested that these intermetallics not only are not limited to ferromagnets but a bevy of quantum ground states, or in other words major electronic properties of matter is observed in these materials. Properties such as ferromagnetism in \( \text{Cu}_2\text{MnAl} \), ferrimagnetism in \( \text{Mn}_2\text{VAl} \), antiferromagnetism in \( \text{GdPtBi} \), semiconductivity in \( \text{CoTiSb} \), superconductivity in \( \text{Pd}_2\text{YSn} \), half metallicity in \( \text{NiMnSb} \), heavy fermion behavior in \( \text{Cu}_2\text{CeIn} \), magneto-optic behavior in \( \text{PtMnSb} \), thermoelectricity in \( \text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ti}_{0.5}\text{NiSn}_{0.998}\text{Sb}_{0.002} \) and most recently the topological insulator behavior in \( \text{LuPtSb} \).

It is obvious that there is immense technological potential available based on harvesting the aforementioned material properties.
In fact, currently there are interesting technological applications such as spintronics and its relevant role in the development of magnetic random access memories (MRAM), with spin transfer torque (STT) version of it being under investigation as candidate for the next generation of nonvolatile data retention.\textsuperscript{14} Spin polarization of half metallic Heuslers has the pivotal role in realizing these fascinating technologies. Although obtaining results well suited for market-friendly devices is challenging and yet to be realized, there has been some exciting advances using Heuslers to achieve the required goals. For instance, Co\textsubscript{2}MnAl thin films are recently reported to have been applied in the magnetic tunnel junction (MTJ) with improved room temperature characteristics\textsuperscript{15}.

Another major industrial application of Heusler alloys as mentioned previously is their utilization in the energy harvesting technologies. Reduction of the greenhouse gas emissions has become a major environmental concern emphatically mentioned in international accords such as the Kyoto agreements to be reduced in order to avoid the detrimental effects of global warming.\textsuperscript{16} The current estimates indicate that at least 60 percent of the entire industrial energy generated is dissipated in form of the heat.\textsuperscript{17} As an important example in a typical commercial gasoline-fueled internal combustion engine vehicle almost 75 percent of entire fuel energy is wasted in the form of heat.\textsuperscript{18} Considerable amount of this heat can be converted back into electricity and thus harvested by using Thermoelectric devices in effect reducing fuel consumption.

Thermoelectric materials have a dimensionless efficiency figure of merit referred to as ZT, which is directly related to electronic conductivity and Seebeck coefficient while inversely related to thermal conductivity. Unfortunately, the industrial value of ZT has remained stagnant around a value of 2 which is less than the target value of 3.
Adding to that current applied thermoelectric materials are based on the traditional Bi$_2$Te$_3$ and PbTe alloys which are composed of relatively hazardous elements. The Heusler alloys do not suffer from such a drawback and might be an alternative to an environment friendly and mechanically robust thermoelectric system with acceptable efficiency.\textsuperscript{19, 20}

1.1 Chemical Bonding and Crystal Structure

After the Cu$_2$MnAl compound was synthesized by Heusler in 1903, the structure of the material remained unknown until the advent of the X-Ray made the atomic diffraction and its consequent structural analysis feasible in the latter decades of twentieth century. One of the first researchers to use the X-Ray Diffraction (XRD) method to derive the crystal structure of these compounds was J.F.T. Young, who in 1923 using a molybdenum source for the beam generation, found out that there is a face centered cubic (FCC) phase present in some of the Heusler alloys.\textsuperscript{21} In the 1930s the progress made in the quantum theory and especially Heisenberg’s treatment of ferromagnetism with respect to electronic configuration prompted Friedrich Heusler’s son, Otto Heusler, to investigate the crystal structure of the Heusler alloys.\textsuperscript{22} around the same time Bradley and Rodgers in Britain also came to conclusion that these alloys are most possibly constructed of FCC phases.\textsuperscript{23}

Since then with advances in the X-Ray diffraction and also in Neutron diffraction, the crystal structure of the original Heusler compound is well established to be indeed related to FCC structure. Its space group number is “255” or “Fm$\bar{3}$m” in Hermann-Mauguin notation or in its Strukturbericht designation, “L2$_1$”. All these three mentioned designations are used in the scientific literature.
The chemical formula of a Heusler compound is manifested as $X_2YZ$ stoichiometry, in which $X$ is a transition metal, $Y$ is a less electronegative transition metal or in some cases a lanthanide or a alkaline metal and $Z$ is the most electronegative component belonging to occasionally metalloid elements of main groups III, IV and V or boron, carbon and nitrogen group, respectively. The composition is consequently very adaptive and by permutation as many as a thousand compounds are possibly attainable.

The unit cell of the prototypical Heusler, $\text{Cu}_2\text{MnAl}$, is constructed in a way that the $X$ element (Manganese) sits on the 8c ($1/4$, $1/4$, $1/4$) Wyckoff position, $Y$ is on 4b ($1/2$, $1/2$, $1/2$) and $Z$ is located at the 4a (0,0,0). By dividing the multiplicity number of the positions by four, the atomic ratio from 8c:4b:4a turn out to be 2:1:1, which naturally corresponds to the $X_2YZ$ formula. A designation of the unit cell is shown in figure 1.1.

Figure 1.1 The unit cell of $\text{Cu}_2\text{MnAl}$, the prototype for the $X_2YZ$ Heusler Structure.
The stacking of atoms in such a structure can also be represented by assuming 8 unit cells of the BCC-arranged CsCl lattice superimposed over each other, or as it is evident from figure 1.1, with the X atoms (in this case Cu) occupying the center of each 8 CsCl-type lattice (or the tetrahedral positions) while Y and Z atoms alternatively fill in the corner of each unit cell. The octahedral positioning of Y and Z is attributed to the ionic bonding stemming from the electronegative difference between these two atoms.²

Heuslers compounds are not limited to the above-mentioned stoichiometry and structure: There is also a major subclass present under the same material category similar to the Heusler composition in which a 2:1:1 atomic ratio between X,Y and Z elements exist, the ratio between the same atoms will be 1:1:1. Therefore, they are known as “half Heuslers”. Additionally, the crystal structure of the half Heusler compounds is identical to that of the original Heusler (or Full Heuslers as they are sometimes called to be distinguished from their half Heusler counterparts), with the exception that the X element no longer fully occupies the tetrahedral positions and half of the total eight of them are empty. This way the total number of the atoms within the cell is reduced from 18 in case of full Heusler to 16 in the latter.

The prototype of such a structure is the MgAgAs compound which has the following designations: Space group 216 in the inorganic structure database (ICSD ), C1₅b in the Strukturbericht and F4̅3m in the Hermann-Mauguin system with the X element at the 4a (0,0,0), Y at 4b (1/2,1/2,1/2) and Z at 4c (1/4,1/4,1/4) position. Caution should be taken here that the electronegativity of elements will directly affect both the nature of bonding within the crystal structure and the atomic loci.² As a result, a peculiarity encountered is that the MgAsAs atomic coordinates are not prevalent among the half Heuslers with most compounds conforming to the structure of CuMgSb in which X atom fills the 4c and Y and Z at 4b and 4a respectively.²,²⁴
A representation of the CuMgSb is shown at figure 1.2. Care must be taken that as the atomic ratio of the half Heusler follows a 1:1:1 ratio, theoretically there are 6 possible permutations to put atoms in the 4a, 4b and 4c positions without compromising the 1:1:1 stoichiometry. The positioning of the atoms in each permutation will result not only a different diffraction signature but it also has a profound effect on the electronic bandstructure and the consequent properties.

![Figure 1.2 The unit cell of CuMgSb half Heusler compound.](image)

There is also another possible class of materials under the group of Heuslers which are not necessary ternary intermetallics as full and half Heuslers are, but in fact are quaternary compounds. The prototype of this subgroup is LiMgPdSn which is in fact could be considered as a permutation of space group 216 half Heusler with Li at 4b (3/4,3/4,3/4), Mg at 4b (1/2,1/2,1/2), Pd at 4c (1/4,1/4,1/4) and Sn at 4a (0,0,0). Such an atomic array can accommodate three transition metals instead of two in case of the ternary Heuslers.
The compound formulation is occasionally also shown as X̅XYZ, with X valence being higher than that of X̅, while valence of Y is lower than the other two.²⁵,²⁶ A representation of the quaternary Heusler compound prototype is shown in figure 1.3.

Figure 1.3 The Prototype of a quaternary Heusler, the LiMgPdSn unit cell.

Stacking of the constituting elements in the octahedral or tetrahedral positions alongside their relative electronegativity is crucial in the resulting ionic or covalent bonds within the material and their effect in determining the electronic behavior of the compound. There are different models proposed to explain the electronic structure of the Heusler materials.² According to a simple tight bonding model suggested by Jung for the half Heuslers, the least electronegative element, X, within the Heusler compound exchanges its valence electrons with more electronegative elements Y and Z present within the formula.²⁷ In this way charge stability is achieved with Y having a d¹⁰ configuration and Z having a s²p⁶ one, basically summing to a total of 18 valence electrons that are compensated by the electropositive X element.
As a result, the half Heuslers with a total of 18 valence electrons are stable semiconductors while a deviation from this amount to values such as 17 or 19 renders a compound to be magnetic or occasionally a different crystal as well.\(^\text{27}\)

For the full Heusler semiconductors the number of transferring valence electron changes from 18 to 24 as a similar mechanism of electrons taken from d orbitals by the partially-filled s and p ones is in effect.

### 1.2 Electronic Structure and Half Metallicity

In 1982, Van Engen and coworkers studying the PtMnSb Heusler compound in the K.H.J. Buschow’s group in Philips research laboratories observed an exceptionally high magneto-optic Kerr effect (MOKE) rotation in the material.\(^\text{28}\) At the time Buschow group was exploring a considerable number of alloys and compounds for potential magneto-optic recording applications among which were Heusler alloys which at the time were considered not to be of much technological significance ever since their discovery earlier in the century.\(^\text{29}\) The encouraging experimental data on PtMnSb prompted them to delve into the theoretical analysis of this material in order to investigate its bandstructure and subsequent magnetic behavior. Adopting a theoretical approach proposed by Kübler, de Groot and coworkers at Buschow’s group and research institute for materials in Netherlands came to conclusion that a group of half Heusler possess a peculiar electronic bandstructure which renders the material remarkably 100 percent spin polarized through a semiconducting behavior for minority spin electrons while the majority spin electrons were metallic. They heralded this new class of materials as “half metals”.\(^\text{30}\) All these pioneering breakthroughs sparked a revival of research on Heusler compounds.
An instructive schematic representation of the possible electronic bandstructure is shown at figure 1.4. (a) illustrates a normal metal with limited density of states (DOS) at Fermi level. (b) Shows a metal in which the DOS at the Fermi level is the same for spin up and spin down channels resulting in the material being spin resolved. In (c) the Fermi is located in such a manner that the DOS is not equal anymore for the two spin channels resulting in a magnetization of the material and so a ferromagnet is generated.

![Figure 1.4](image)

**Figure 1.4** (a) The Density of States (DOS) of a metal (b) a non-magnetic metal (c) a ferromagnetic material (d) half metallic ferromagnet (e) compensated half metallic ferrimagnet. Reproduced with permission from ref. 2.

The DOS in (d) shows the interesting bandstructure of a half metal in which the Fermi level \(E_F\) is located at a gap in the minority spin channel while at the majority channel there are states available. Such an electronic configuration means that the material acts as a semiconductor or insulator to the minority spin while it is conductive to the majority one, or in other words the material is “spin polarized”.

In the case of Heuslers, the minority gap occurs since there is an extensive hybridization of the $d$ orbitals of the two transition metals. The $sp$ orbitals do not play a crucial role in the generation of the minority gap as they are considerably beneath the Fermi level. A schematic of orbital contribution to bandstructure of a half metallic Heusler is also shown at figure 1.5.

![Schematic of orbital contribution to bandstructure of a half metallic Heusler](image)

**Figure 1.5** The schematic electronic bandstructure of a half metallic Heusler with the relevant orbital contributions. Reproduced with permission from ref 32.

A crucial test for determining half metallicity in the Heusler alloys is based on ruled derived by Slater and Pauling and named after them. The rule provides a simple relation between the magnetic moment of the Heusler compound and the total of number of the valence electrons. This is due to the fact that the magnetic moment is related to the number of electrons within the minority the channel:\(^2\)

$$m = N_\uparrow - 2n_\downarrow \quad (1.1)$$
With $m$ being the atomic magnetic moment, $N_v$ valence electron concentration and $n_\downarrow$ the number of electrons in the minority channel. If $s$ and $p$ electrons are considered irrelevant and only $d$ orbitals in the minority state are taken into account, there will be nearly 3 electrons in the $d$ states, resulting in the (1.1) getting simplified as $^2$:

$$m = N_v - 6 \quad (1.2)$$

In case of half Heuslers, as there are three atoms present in the compound, the total moment for the XYZ stoichiometry will become:

$$M_{\text{Half-Heusler}} = N_v - 18 \quad (1.3)$$

A similar argument can be adopted for full Heuslers. The compound has 4 atoms per unit cell so (1.2) can be rewritten as:

$$M_{\text{Full-Heusler}} = N_v - 24 \quad (1.4)$$

The Slater-Pauling behavior for some of the half metallic cobalt-based full Heuslers and also for some ferromagnetic elements and alloys are shown in the figure 1.6 $^2$

**Figure 1.6** (a) The Slater-Pauling behavior for some of the cobalt-based full Heuslers. (b) The bcc and fcc sections of the generalized Slater-Pauling diagram with respect to the behavior of some full Heuslers. Reproduced with permission from ref. 2.
It should be noted that although the Slater-Pauling rule is a necessary step in verification of half metallicity in the Heusler compounds, it is by no means a sufficient one. An essential experimental method is to detect the spin polarization of the material. There are different approaches devised to reach this goal with one of the relatively easy methods, referred to as Point Contact Andreev Reflection or PCAR, widely used to confirm the spin polarized nature of bulk or thin films. Here a superconducting electrode injects Cooper pairs into the specimen. If the specimen is half metallic, no conductivity should be detected while the presence of normal ferromagnet reflects a hole with opposite spin into the metal. This is relevant if bias voltage is less than the superconductor’s gap. Figure 1.7 is a schematic representation of PCAR method.

![PCAR schematic](image)

Figure 1.7 Schematic configuration of a PCAR setup. A superconducting (SC) electrode sends a cooper pair into a ferromagnet (F) and with respect to the bias voltage a conductivity is detected. Reproduced with permission from Ref. 33.

Some qualitative methods have also been proposed in order to confirm the half metallic character of a compound. One such a method is based on Rhodes-Wohlfarth model. Initially the model used the ratio of the effective paramagnetic moment ($p_e$) to saturation moment ($p_s$) to distinguish the Heisenberg magnets with localized electrons from weak itinerant ferromagnets. For the former the $p_e/p_s$ ratio, or Rhodes-Wohlfarth ratio, is equal to 1 while for the latter it could be much higher.
A quarter of century later after the advent of this model, some members of the same research group in the Netherlands who discovered the new materials class of half metals, observed that these materials have an unusually low Rhodes-Wohlfarth ratio not witness before, with all the values less than unity.\textsuperscript{36} The explanation that they presented was that the initial Rhodes-Wohlfarth fails to consider the large contribution of itinerant spin-polarized electrons in half metals leading to drastic reduction of the $p_{c}/p_{s}$ ratio. Therefore, with an easy magnetometry measurement from ferromagnetic to paramagnetic regime of the material it is possible to verify the half metallic behavior of the compound.

1.3 Research Objectives

Prompted by extensive theoretical calculations by W.H. Butler and coworkers on both full and half Heuslers, our objective was concentrated on evaluating which of the predicted half metallic Heuslers had not been explored sufficiently. Our efforts pinpointed the Fe-Ti-Sb system in which there were no substantial evidence in the literature as far as characterization of the material was concerned. It was also seen that the microstructural analysis of Heuslers, especially in their bulk form, was not as thoroughly performed as expected from a metallurgy/materials science standpoint. This all encouraged us to synthesize the promising compounds through arc melting and eventual heat treatment to evaluate the possibility of a single phase half metallic alloy emerging.
For our research we adopted the bulk synthesis of Heusler compounds by the arc melting method, which is the prevalent choice of process for the synthesis of these metallic materials. The next step, as it is usual with processing any novel material, was to characterize the alloys by structural and microstructural instrumental techniques available to us in materials science, such as metallography, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Electron Back Scatter Diffraction (EBSD) and Transmission Electron Microscopy (TEM). Eventually as the crucial property of these alloys, the magnetic behavior was studied by using Vibrating Sample Magnetometry (VSM).

2.1 Arc Melting and Preliminary Sample Preparation

The first step in processing the Heusler compounds in their bulk form is usually the arc melting. A compact arc melter MAM-1 system designed by Edmund Bühler GmbH™ was used for this task. A picture of the instrument is shown in figure 2.1.
Arc melting is a well-established method for processing different metallic compounds and alloys. As it can produce temperature up to 3500 °C it is also proved useful in synthesis of ceramic compounds and composites. The benefits of the technique lies in its relatively high speed of sample preparation, high homogeneity and user facility. In the case of intermetallics and specifically Heuslers, the sample preparation step consists of weighting the constituting elements in their relative atomic weight ratio with respect to the final compound formula. It is conventional to use elements at a 3N minimum purity level. For this goal a precise weighting scale with credible calibration should be used. In our case an electronic balance, A&D Weighting™ ER-182A with a precision of 0.1 milligrams was utilized.
Caution must be considered when volatile elements such as Manganese and to a lesser extent Antimony is opted for arc melting, as the relatively high vapor pressure of these materials results in the loss of matter during the arc melting and consequently in order to compensate for such loss it is customary to put an excess amount of such elements up to 5 to 10 percent of the initially calculated mass. After the elements are properly weighted, they are put in a crucible inside the arc melter chamber and the system is closed for evacuation pumping. The choice of pump is dependent on sensitivity of the target material to oxidization. In some cases such as oxides and ceramics or some electronic materials as oxygen might play a detrimental role in final properties of the material, the usage of high vacuum pump such a turbomolecular one for the arc melting is recommended. The MAM-1 instrument used for these studies uses a turbomolecular pump capable of reaching a base pressure of less than $5 \times 10^{-5}$ mbar. After such a low vacuum is reached, 5N purity Argon is first introduced into chamber before the ignition of the arc. The crucible upon which the elements are located is made out of copper to enhance better conduction and also is water cooled. A picture of MAM-1 chamber with electrode and the crucible is shown at figure 2.2. It is also recommendable to first melt an oxygen getter element such as titanium or zirconium immediately after the ignition of the arc so that any remaining oxygen within the chamber is eliminated. Then the electrode is moved over the constituting elements and by gradually increasing the arc intensity and also using the electrode handle to stir the melt a molten ‘button’ composed of elements is formed. The shape of the sample is usually an indication of how well the constituents are mixed. As mentioned before, in case of thorough mix achieved within the sample, the shape will be quite round and therefore it is called a button, while lack of miscibility manifests itself in an irregularly-shaped sample. An example of a properly mixed button and a sample with clear lack of component miscibility is shown in figure 2.3.
It is recommended that each run does not exceed a time limit of 60 seconds as continuation of the arc might instigate emission of X-ray which is hazardous to the user. Sometimes the button is cracked or the some pieces of the elements are left out during the first run of the arc melting which means that the runs should be repeated until the button is comprised of all the element shots or pieces and no constituting part is left out.

![Figure 2.2](image)

**Figure 2.2** The MAM-1 arc melter chamber with electrode and crucible positions.

After a button in which all the elements’ pieces are amassed, it is required to flip this first button to its back and at least melt the sample again for 2 more runs to ensure that macro segregation is minimized. Before the utilization of scanning electron microscopy and electron dispersive spectrometry became abundant, it was conventional to weight the finalized button and compare it to the total weight of constituting elements in order to confirm a proper mixing of elements and lack of macrosegregation. It should be noted in some cases this approach could be misleading, such as the case of Cr-Mn-Sb alloys in which although the finalized mass of the sample does not deviate from the initial weight of elements, the sample shows considerable macro segregation of chromium if cut into pieces.
So it is recommended that the arc melted samples be cut into proper pieces and their cross sections examined before any claim about the homogeneity of the alloy. In our studies we used an Allied High Tech Inc. Techcut 4™ precision low speed saw to cut the samples. If no sign of macrosegregation was seen pieces were cut for heat treatment.

![Image: Co₄CrIn sample with an irregular shape resulting from lack of miscibility of chromium. A round-shaped Fe₂TiSb signaling a satisfactory constituent miscibility.](image)

**Figure 2.3** The Co₄CrIn sample with an irregular shape resulting from lack of miscibility of chromium. A round-shaped Fe₂TiSb signaling a satisfactory constituent miscibility

Heat treatment is a crucial step in preparation of almost every metal and alloy as it is rarely the case that the as-cast sample is homogenous or exhibits satisfactory materials properties. So one of the crucial steps in metallic materials processing is homogenization heat treatment with the aim of reducing segregations, both macro and micro, to a minimum.⁴ The Heuslers usually require relatively long and high-temperature homogenization cycles as the diffusion of the atoms progresses rather slowly within these systems.⁷ So in order to apply the heat treatment cycle the samples should be detached from the atmosphere to avoid their oxidization under such extreme conditions. A conventional method is to seal the samples in quartz tubes under vacuum. The samples are sealed using an oxyhydrogen torch after being pumped with a rotary-vane pump for at least 6 hours.
Tantalum foils are also sometimes used to wrap the sample to avoid further possible reactions with ambient especially in case of reactive or volatile nature of the alloy. A picture of two sealed Heusler samples is shown in figure 2.4.

![Fig 2.4.png](image)

**Figure 2.4** Co$_2$CrGe and Fe$_2$MnGe arc melted samples sealed in quartz tubes.

Heat treatment was performed using a General Signal Lindbergh™ tube furnace of the type 55332 and also a Paragon Sentry Xpress 4.0™ box furnace. The homogenization cycle should be adopted so in case of material containing volatile elements such as manganese, antimony or bismuth the heating ramp is slow enough not to enhance the vaporization of the volatile elements resulting in pressure accumulation and the consequent cracking of the quartz tube. For this it is experimentally recommendable that the heating ramp not be adjusted faster than 9 °C per minute. The dwelling temperatures for homogenization are empirically found but according to our studies a rule of thumb would be a heat treatment at 900 °C for 3 days as a starting point.
Once again this is by no means a scientific rule but in absence of calorimetric measurements it is a valid path to be considered; and if the sample is not molten after homogenization, it can give us important data through its microstructure by showing which feature, grains or dendrites, are present and consequently the degree in which the heat treatment need to be advanced is inferred.

After the dwelling time has run its course, the sample is brought to room temperature. The cooling ramp, if slow such as in furnace cooling, can result in an equilibrium atomic structure and also single phase microstructure. But once again this is also experimentally established and is dependent on the nature of the alloy: There are reports that fast cooling such as quenching in cool water can be beneficial in some cases, rendering the material pure phase. The materials studies in our research work reached single phase structure during slow cooling ramps of as low as 2 °C per minute. Quenching on the other hand resulted in multiple phases emerging and material becoming rather an alloy instead of a compound, with latter being our goal. After the end of the cycle the quartz tubes were broken and the samples were checked for any abnormalities in shape or in form and if the sample appeared to be intact after the heat treatment, a chip was taken off using the precision saw for magnetometry studies and the rest of the sample proceeded to the next step which was metallography.

2.2 Metallography

Metallography is an indispensable technique for revealing the microstructure of metallic materials. The exposed microstructure can be further analyzed using conventional optical microscopes or by adopting electron microscopy, scanning and transmission, to elaborately study the morphology, composition and crystal structure at higher magnifications and resolutions.
The first step in preparing a metallography sample is mounting, in which the metallic sample is encapsulated in a resin-hardened plastic cylinder basically mount. The diameter of the mount depends on the mold used. Compression mounting machines have fixed diameters ranging from 1 inch to 1.5 inches. The height of the sample depends upon how much resin is applied.

Usually for microscopy and X-Ray diffraction purposes it is within a range of 0.5 to 0.75 inch to both enable proper handling of the sample during grinding and polishing process and also allow it to fit within sample requirements for microscopes and XRD instruments.\textsuperscript{5} The choice of the mounting powder or resin relies on the factors that affect mechanical properties of the sample, such as brittleness or edge retention or especially if scanning electron microscopy is considered, the conductivity of mount is essential. On the other hand, if a measurement such as electronic transport is considered, a conductive mount is not favorable so a non-conductive mount could be considered. The applied pressure and temperature and cooling time differs from mounting material to other and is provided by the commercial supplier but usually the temperature is 180 °C with a pressure of 4200 psi is sufficient. The mounting instrument used in this set of studies was a Struers LaboPress-3\textsuperscript{TM}, a picture of which is shown is at figure 2.5.

\textbf{Figure 2.5} Struers LaboPress-3\textsuperscript{TM} Hot mounting system. Reproduced from ref. 6.
The mounting powder adopted was a graphite-based conductive resin produced by Allied High Tech Products, Inc. As the diameter of the mounting system was 1.25 inches, the temperature recommended for molding was 180 °C and a pressure of 20 kN was used to get the optimum results.

After the mount is ready, the next step is grinding it so that any mount residue on sample surface is eradicated and then the surface is further grinded so that a pristine surface void of any oxide layer or such is prepared for polishing and eventually etching and revealing the microstructure of the material. The medium used for grinding are circular abrasive papers made of silicon carbide or alumina. As the former has superior abrasive performance and is relatively cheap, it is more popular among metallographers. The diameter of the papers could be different from 8 to 12 inches depending on different requirements and the accommodating size of the grinder machine. The machine used in this case was a Struers DAP-V system whose image is shown at figure 2.6

![Figure 2.6 The Struers DAP-V™ grinding and polishing system.](image-url)
The mesh size of abrasive paper is an indicator of its roughness with lower mesh sizes being rougher than the higher ones. Commercially there are different sizes available from 60 to 1200 and sometimes higher. A grinding recipe for a smoothly cut sample, such as the ones cut by precision saws, would start from a mesh size of 180, and proceed to finer papers such as 320, 600 and finally 1200. It should also be noted that for samples with rougher sectioning surfaces, for example those cut manually by a normal band saw, starting at a lower mesh size paper such as 60 might be effective in realizing an optimum surface for metallography. For our studies a set of 180, 320, 600 and 1200 SiC papers supplied by Allied High Tech products, Inc. were used.

The grinding process itself needs sufficient experience and dexterity from the part of metallographer to result in a sample with an acceptably smooth surface. This is where metallography becomes more an art than a science. A good practice is to start holding the sample mount at the outer periphery of the rotating grinding paper with a relatively low rotating speed such as 100 to 300 rpm and advancing towards the center of the paper. Water should be constantly applied during the process to wash away the grinding residue and also cool down both the sample and the paper to avoid any potential detrimental thermal effect.

The amount of manual pressure applied on the mount is another factor which should be learned through various trials and experiences. An uneven force applied on the sample will result in the loss of flatness as some edges are grinded more than the others. A skilled metallography technician usually holds the mount on a certain position for a period of approximately 2 minutes and then moves about the diameter of the sample forward towards the center of the paper, with sample rotated about 90 degrees each time to ensure that scratch lines from the previous are eliminated.
After a certain period on an abrasive paper which is usually not more than 15 minutes and with certainty that all the scratches on the sample are of the same size and all parallel to one another, the mount is then moved to the lower mesh size paper.

The next stage in metallographic sample preparation is polishing, which is evidently using an agent to polish the surface of the sample so that the roughness is minimized and a high reflectivity is obtained. The absence of the scratch marks from the grinding step and the deliverance of high metallic shine on the surface enhances the possibility of obtaining most data for the microstructure of the sample under optical or electron microscopes.

Here a polishing agent which is usually a suspension of diamond particles is applied to rotating polishing pad. The agent used could be in form of diamond paste in different mesh sizes. For rough polishing higher sizes e.g. 30 microns could be a proper starting point and then applying a paste with a lower size and a finer mesh is required. One path to be taken with respect to polishing is to adopt agents in different order-of-magnitude of sizes. This means starting from the highest available mesh size (in our case it was 40 micron Diamond water-solution and diamond paste provided by Allied High Products, Inc. and Beta Diamonds Products, Inc.) and going one order lower, 10 micron and then one 1 micron and finally the lowest possible mesh size which is usually 0.1 micron.

As it was the case with grinding the same machine can be used for polishing though here we used a polishing pad upon which the polishing agent is applied. The pad is made of soft material such a felt or nylon to retain the agent while the pad is rotating. In case a diamond paste is used a stream of paste is injected on a whole radius of the pad and then gently diluted with the tip of gloved finger. If a diamond suspension is used, the whole area of the pad can be wetted.
A metallographer might choose a rotating speed of 100 rpm to 300 rpm, with sample rotated 90 degrees and advanced towards the center as it was the case with grinding. The applied pressure on the mount and the time spent on each mesh size pad is of obvious importance to the quality of the polished sample. It is imperative after each step and before moving to lower mesh to wash the sample thoroughly to clean any residue, otherwise there might be some artifacts emerging on the surface misleading the interpretation of the microstructure. At the end it is also recommendable to use an even finer agent, such a colloidal silica in mesh sizes around 0.02 microns to minimize any possible surface roughness and to enhance the surface quality for those surface-sensitive measurements such as electron backscatter diffraction or EBSD. Care should be taken in choosing a different pad for colloidal silica to avoid damage for remainder diamond particle to the sample surface. Unlike diamond polish step which usually should take about 15 minutes, silica polish of about 5 minutes is sufficient to provide satisfactory results.

After all these steps and stages, the sample should be void of any major scratches and manifesting good reflectivity with a metallic shine. At this level a chemical agent can be applied to the surface of the sample to reveal its morphological features. This step, which is actually the final step in metallography preparations is called etching. The etchants are mixtures of aqueous acids with some chemical compounds and are diverse. The proper choice of an etchant is important with respect to the material etched. The reaction is such that the etchant attacks different morphologies with different rates, thus emerging them by enhancing a topographic surface contrast discernable under a microscope. Different etchants have different activities and so different etching rates. Sometimes finding the best etchants to reveal most features with best optical quality is itself a complicated project, but metallographers have adopted some conventional etchants during the course of the past century which can be used as a starting point.
For a thorough listing of different etchants for various alloys consult reference 7. In this case three etchants with different levels of activity was chosen for the task: Nital 3% (3 mL of Nitric acid in 100 mL alcohol) which is a low activity etchant intended traditionally for carbon steels and used in our case for sensitive alloys such as manganese rich ones and CoTiSn.

A midrange activity etchant we adopted was Marble (10 grams of CuSO$_4$, 50 mL HCl and 50 mL of water) and a higher activity one which was Adler (9 grams of CuNH$_3$Cl, 45 grams of hydrated FeCl$_2$, 150 mL of HCl and 75 mL of DI Water).

The samples can be immersed in the etchants from seconds to minutes depending on the rate of etching. After immersion the sample are washed with water for a few seconds and then with an alcohol. For sensitive samples it would be required to dry the sample immediately after the previously-mentioned steps using a dryer or a hydrogen source.

The following steps would most of time result in a high quality surface if carefully performed. The resultant sample would then be ready for optical microscopy. The system used in our case was a Zeiss Axioplan 2™ optical microscope.

### 2.3 X-Ray Diffraction Analyses

X-Ray Diffraction, or XRD as it is sometimes abbreviated, is one of the fastest and simplest methods for characterizing crystalline materials. The method is useful in determining the crystal structure of the compounds, lattice constants and also detection of impurities and present phases in general.

The impingement of a monochromatic X-Ray with a certain wavelength on a crystalline material will result in the electromagnetic ray interacting with the electron cloud of the atoms within the material and eventually scattered by them.
The scattered wave now has amplitude which is called “the atomic scattering factor” related to the number of the electrons within the atom and consequently differing from element to element. In some cases the scattered beams could be in phase in one another resulting in doubling of amplitude. This phenomenon is called ‘diffraction’.

A crucial factor in occurrence of diffraction is that the scattered waves should have a path difference related to an integer of the wavelength, $\lambda$; otherwise the scattered waves will be out of phase and so cancel out each other. Therefore, in a crystalline solid as the distance between atoms or interplanar spacing, $d$, fixed, there will an incident angle in which the scattered beams will be coherently in phase to one another giving rise to diffraction. Such a characteristic angle is called a Bragg angle, and the relationship between the beam wavelength and interplanar spacing is expressed in the general formula below, called the Bragg law:

$$n\lambda=2d\sin \theta \quad (2.1)$$

The Bragg law is the cornerstone of X-Ray diffraction analysis. $n$ is the number of beam wavelengths from different atomic plans and usually is considered to be unit value.\(^8\)\(^,\)\(^9\)

The outcome of an X-Ray diffraction analysis on a crystalline compound will be a spectrum unique to that material which shows a specific pattern composed of intensity peaks emerging at different $\theta$ angles meeting the Bragg law. Therefore every pure crystalline material has a ‘fingerprint’ of X-Ray diffraction for itself which serves as indispensible tool to detect its presence in solid system. The interplanar spacing is the main factor to this uniqueness, as it is related to the lattice constant of material and specific plans upon which the Bragg law is allowed and therefore the diffraction happens. The relationship between the different $d$ spacing in the crystal systems is shown at figure 2.7.
Figure 2.7 Interplanar spacing of different crystal systems. Reprinted with permission from Ref. 8.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Interplanar Spacing Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2+k^2+l^2}{a^2} \right) + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2(1-3\cos^2\alpha+2\cos^2\alpha)}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2h l \cos \beta}{a c} \right)$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$\frac{1}{d^2} = \frac{1}{V^2} \left( S_{11} h^2 + S_{22} k^2 + S_{23} k^2 + 2S_{12} h k + 2S_{25} k l + 2S_{13} h l \right)$</td>
</tr>
</tbody>
</table>

On the triclinic system, $V$ is the volume of a unit cell and the coefficients are given below.

- $S_{11} = h^2 c^2 \sin^2 \alpha, \quad S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma)$
- $S_{22} = a^2 c^2 \sin^2 \beta, \quad S_{23} = a^2 b c (\cos \beta \cos \gamma - \cos \alpha)$
- $S_{33} = a^2 b^2 \sin^2 \gamma, \quad S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta)$

It is also noteworthy that as the symmetry decreases from cubic to triclinic (from top to bottom in Figure 2.7) the number of the diffracted planes and therefore observed peaks in the XRD spectrum of the material also increases.

Knowing the interplanar spacing formula renders the XRD pattern a useful instrument in deriving the lattice constant of the material considering the locations of the peaks and therefore the $\theta$ values. But it should be noted that due to the interference-based nature of diffraction, not every atomic plane will diffract the incident beam. In some cases there are destructively scattered and canceling each other as a consequence and as a result in certain crystal structures only the planes meeting the Bragg conditions with a non-zero consequent structure factor are reflected and observed. The condition for this constructive interference can be calculated for different Bravais lattices and is summarized in the figure 2.8.
Figure 2.8 The planar reflections in specific Bravais lattices.
Reprinted with permission from Ref.8

The discussed conditions will be effective in making the X-Ray diffraction a facile method in deriving the crystal structure of compounds. As the X-Ray spectrum of each material is unique, its XRD pattern can be used as a fingerprint in distinguishing it from other possible candidates.

Nowadays there are computer databases and software available which can immediately scan and designate a certain XRD spectrum for possible candidates and match the pattern to the best possible compound(s). One example is the database devised by International Centre for Diffraction Data or ICDD.

If a new material is synthesized, obviously there are no reports on its XRD signature in any database, so it is customary to hypothetically assign a crystal structure for the material and then using that structure as a model, generate a related XRD pattern using simulation software.
The adopted model should be consistent with the chemical composition of the material as a first step in devising the model.

Therefore it is imperative that the atomic Wyckoff positions of the model have multiplicity ratios in line with the chemical stoichiometry of the material otherwise the model will be erroneous even if the final generated pattern matches well with the experimental data. The next crucial step is adopting the lattice constant(s) so that the generated pattern is in good agreement with the actual measurements. If the lattice constants chosen are correct, then peak positions should be located at almost exact positions seen on the experimental spectrum.

Although the lattice constant can be manually calculated from the observed pattern using the Bragg law, it is conventional to pinpoint the value to three digits after the point. For this purpose usually a fit of the hypothetical model to the experimental data is done to ensure the accuracy of lattice constant estimation. A method to achieve this objective is through fitting refinements. Most of the refinement methodology regime is based on minimizing the sum of square differences between the proposed model intensity and that of the actual data, which is also called the least square method. One such method which is also one of the most frequently applied is called the ‘Rietveld refinement’. This refinement is based on minimizing the expected calculated intensity and the actual observed intensity in the data by refining the position of atoms, the occupation levels and thermal factors. In fact thousands of intensity positions are considered for this minimization to occur. The corresponding generalized minimum formula is such:

\[ S = \sum w_i (y_i(\text{obs.}) - y_i(\text{calc.}))^2 = \text{Minimum} \]  

\( y \) is the actual intensity in many unlimited positions of \( 2\theta \), and \( w \) is called weighting factor.
Although the Rietveld refinement is performed by software, it is by no means a method which can be independently ‘done by the machine’ without any astute control from the operator. There are many factors to be refined which could themselves are quite complex and sometimes might render the refinement ambiguous and misleading if not carefully monitored.

The main refinement parameters can be categorized into three main groups: 

1. The basic experimental parameters such as profile parameters, halfwidths and asymmetries of the peaks.

2. The second group includes crystallographic parameters such as space group, and

3. The third group encompasses structural parameters such as Debye-Waller factors.

Using the approximate value for each parameter, the software attempts the refinement until after many refinement cycles a certain amount of convergence is achieved.

The success of convergence is manifested in form of goodness-of-fit parameters such as $\chi^2$ factor. A good fit usually has a $\chi^2$ in single digits and as near the value of 1 as possible. The further the factor is from 1, the more the fit becomes unreliable. At the initial stages of the fitting, this factor could emerge as large but eventually as more runs of the software are done, the number reduces to lower value with the convergence, which is indicative of the fit gradually improving. This factor itself is a function of two other weight factors, weight-profile R factor or $R_{wp}$ and expected R factor, $R_{exp}$:

$$\chi^2 = \frac{\sum w_i (y_i(obs.) - y_i(calc.))^2}{\sum w_i (y_i(calc.))^2}$$ (2.3)

The respective definition of the $R_{wp}$ is:

$$R_{wp}^2 = \sum w_i (y_i(obs.) - y_i(calc.))^2 / \sum w_i (y_i(calc.))^2$$ (2.4)

Which itself is one of the most statistically accessible indexes for showing deviation from the ideal model. The $R_{exp}$ is the highest possible attainable $R_{wp}$, and also another important statistical factor calculated and presented in the Rietveld literature.
The relevant formula is:

\[ R_{\text{exp}} = N / \sum_i w_i (y_i (\text{obs.}))^2 \]  

(2.5)

With \( N \) being the number of the experimental data points in the spectrum.

Although with advent of faster computers in 1980s the usage of Rietveld refinement software has become common practice as an effective method of evaluating the proposed crystal models to actual data, the Rietveld method is not considered to be immune to controversy among some scientific cycles. One such problem is with the fitting parameters and their considerable vulnerability to the effects of the background signal. There have been reports of auspicious R-factors achieved even without any valid crystal model.\(^{11}\) Another issue is the paradox of lengthier XRD measurement, which will lead to higher data points and higher statistical precision and consequently lower \( R_{\text{exp}} \) values. Simultaneously this situation will also increase \( R_{wp} \) value, meaning longer counting in the measurement will deteriorate the \( \chi^2 \) value and therefore will infer a bad fit and an unacceptable crystal model.\(^{47}\) These conditions have resulted in cases that fitting parameters are of low quality while there are minimal discrepancies between the proposed model and measured data and vice versa. So in order to avoid the confusion it would be recommendable to compare as many fitting parameters as possible to arrive at a conclusion regarding the validity of the fit. Also as mentioned before, it is also imperative to monitor the decrease in the fitting values during the convergence. In case the value is not decreasing at the course of refinement there might be a problem to consider. Also if the chi-square factor is disproportionately higher than 1, the systematic problems with the sample and the measuring instrumented should also be considered.\(^{11}\)
The caveats given above call for an elaborate guideline for XRD measurement and eventual Rietveld fitting: Data collection should be optimized as a first step, with the measuring instrument precisely calibrated with a standard sample.  

Also the background signal should be minimized as much as possible as it has detrimental effect on the fit: For this goal special sample holders could be adopted or the beam path could be put under vacuum or a crystal analyzer could be located between the sample and detector on the beam path. Also the size of the sample should be such that that it lies within an optimum region of 1 to 5 microns. The larger size particles might negatively affect the intensity of the peaks while the lower sizes result in peak broadening and deterioration in Full Width at Half Maximum (FWHM) values.

In fact the larger the grains, the smaller number will be diffracted by the beam, resulting in the intensity of some peaks becoming uncharacteristically higher than expected. In order to eradicate this problem it is recommendable to rotate the sample around the axis perpendicular to the surface of the sample, or the φ axis. This increases the possibility of more grains located in the beam path and therefore diffracted and is especially required when obtaining data from bulk metallic materials.

A preferred procedure of Rietveld refinement is to obtain the most accurate experimental data, devise the best possible crystal model and start the fine tuning the relevant parameters in the refinement software. It is advisable that the parameters are refined consecutively and gradually in specific steps, for example first the scaling factor should be refined for at least three cycles, then in following order atomic positions, occupancy levels, background signal, remaining parameters especially the peak distributions and finally Debye-Waller factors.
Finally it should be mentioned that Rietveld refinement is not be used as a stand-alone method to confirm the specific structure within a material.

Further diffractive characterizations such as Transmission Electron Microscopy (TEM) diffraction patterns and Electron Back Scatter Diffraction (EBSD) phase maps might be needed to approve the validity of the model and even more importantly are chemical analyses approaches to evaluate the phase model with respect to the actual composition of the material. In this set of studies we have used a Bruker D8 Discover™ system to obtain our XRD spectra. The instrument had the capability of rotating the sample around the φ axis to reduce the surface effects stemming from relatively large grains sizes and preferred orientations. The optimal time of measurement was found to be a total of 9 minutes for the entire spectrum. Also some oscillation in the X-Y plane was done to ensure the minimization of the surface effects in the measurement. The source used was cobalt.

The simulation software utilized to generate the XRD spectrum was CaRine 3.1™ which incorporated the multiplicity factors, structure factors and atomic scattering factors. The software chosen to perform the Rietveld refinement was Crystal Impact Match!™ based on the FullProf program platform.¹³

2.4. Electron Microscopy Methods

The electron microscopy methods were used in these studies to characterize the microstructure and its features. The instruments used were Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The different setup between the two systems is shown in figure 2.9.
The SEM shares similarities with a conventional confocal optical microscope in the sense that both are actually mapping instead of direct imaging. But unlike the optical microscope, the much lower electron wavelength used in the SEM will result in a considerably higher spatial resolution when the beam is focused. Therefore the SEM chamber is held under vacuum to avoid the electrons getting scattered by atmospheric gas molecules. In the SEM electrons can be focused into a small electron probe and scanned through the surface of the sample.
The sample could be simply encapsulated within an ordinary metallographic conductive mount, which in contrast to TEM makes the sample preparation an advantage in the SEM. The electron primary incident beam can interact with the sample arising two major electron phenomena: One is called backscattered electrons (BSE) which are primarily incident electrons reflected from the sample surface at angles between 90 to 180 degrees with respect to the incident beam.\textsuperscript{15,16} Another type of electrons resulting from interaction of the beam with the specimen is secondary electrons (SE) which have lower energy than BSE and therefore penetrate the sample weakly in about 3 to 10 nanometers.\textsuperscript{15} The energy of the BSE lies usually between the energy of the incident beam and 50 eV while for the SE it could be as near to zero as possible. More than 90 percent of the images reported in the scientific literature are taken in the SE mode as it is easy to collect these electrons and more importantly they can generate a topographic image of the sample surface with resolutions of up to 1 nm. The BSE has the difference of being highly dependent on the atomic number of the element with which it reacts: The higher the atomic number transpires more backscattered electrons. The BSE enables a chemical contrast of the image as a result and is a very useful tool in emerging microstructural features such as grain boundaries that might be difficult to observe under the usual SE mode.

Besides imaging, SEM is also a useful spectrometry tool for deriving the chemical composition of the morphologies seen under the microscope: The electrons can also have an entirely different interaction with specimen material than the two phenomena mentioned above. This interaction is called ‘characteristic X-Ray’ and as its name implies is an X-Ray generated from material when the incident electron beam excites an inner shell electron of the material to a higher energy orbit and the resulting vacancy is immediately filled by an electron from a higher energy shell.
The energy difference in this de-excitation process is manifested in the form of a photon which is called a X-Ray characteristic photon and its energy is related to the atomic number of element scattering the incident electron beam. There are detectors capable of producing spectra from these X-Ray photons which can differentiate the electrons either based on energy or their wavelength. In case of Energy Dispersive Spectroscopy or EDS, a dispersive semiconductor diode serves as the detector in which emission of the photon excites the electrons in the n and p semiconductors and therefore a specific current proportional to the photon energy is generated.\(^\text{16}\) The EDS has two main limitations one being the resolution limited to 150 eV and consequently there might be some cases which two peaks belonging to two different elements cannot be distinguished, and the other is elements with atomic weight lower than sodium cannot be detected as the energy excited from these elements are too low to be properly detected.\(^\text{14}\) Care should be taken so that the adopted beam current does not increase the ‘dead time’ of the detector over its ‘live time’. The dead time is the time in which the detector is not active while the live time is the time in which it is collecting the data from the sample.

EDS is an important method in quantifying the elements present in the sample based on their atomic percentage or weight percentage. Still the accuracy level of detection might not be as high as more precise methods such as electron probe microanalyzer. An acceptable limit of accuracy is 10 to 15%.\(^\text{14}\)

Although it is possible to obtain crystallographic and structural data using transmission electron microscopy, there has been a novel diffractive method incorporated within the SEM to achieve the same objectives.
The superiority of the method lies in the fact that unlike TEM which needs elaborate sample preparation techniques such as Focused Ion Beam (FIB) to prepare a very thin sample for diffraction analysis, the EBSD needs only the metallographic mount with a well prepared surface. Another advantage of TEM is that diffractive data can be taken from as many as grains and as much large areas as possible, in contrast to TEM that is limited to one to three grains as the FIB sample is usually statistically bound to limited grains sampling.

Alongside EDS, EBSD is a very effective tool for identification of phases in the microstructure. The end product of an EBSD measurement could be a phase map, showing the presence of the sought crystal structure within the SEM image in the form of a map. Also it can generate a figure of crystallographic orientations of the grains present in the microstructure which is indispensable in exposing the texture and local strain within the material. Both of these tools can be applied up in wide dimensional range of millimeters to nanometers on the sample.

The mechanism of EBSD, as it is name implies, is diffraction and therefore similar to the XRD method with the exception of diffractive source being the electron beam instead of an X-Ray one. The electron beam slowly scans the surface of the specimen and the resulting backscattered electrons are collected by charge couple device (CCD) camera which is driven close to the sample surface. The sample itself is tilted at a high angle of 60 to 80 degrees to enhance the received signal. The pattern formed from each scanned points are in fact some bands famously called ‘Kikuchi bands’ which follow the Bragg law and their intensity is complexly dependent on the structure factors of the diffracted material and therefore a unique signature of it.
The bands are sent to the computer for proper indexing and are almost immediately corroborated with the target phase to see if a match with it occurs. A Schematic of an EBSD setup is shown in figure 2.10.

**Figure 2.10** The schematic of main parts of an EBSD setup. Reprinted with permission from ref.19.

It is imperative that the sample preparation for the EBSD result in a very good surface quality Otherwise the signal received might be spurious. Usage of final polishing agent with low mesh such as colloidal silica is highly recommended. Also it is required to minimize the surface charging as much as possible. From a sampling statistics standpoint it is also preferred than the scanning step size be not more than a tenth of the average grain or feature size, so that enough data is gathered from the surface. Choosing a sampling area in which a normal distribution of microstructural features is present would be necessary as well.
TEM is a versatile approach to analyze materials at low dimensions. Here high electron beam acceleration voltages of up to 400 kV can bring about wavelengths near the atomic resolution and therefore it is possible to form a diffraction pattern from the atomic planes of a very small sampling area, e.g. precipitates, with high accuracy. As the diffractive angle of electrons is much lower than that of X-Rays, the Bragg law can be simplified as

$$rd = \lambda L \quad (2.6)$$

In which \( r \) is the distance of the incident beam from the diffracted beam on the image, \( d \) is the interplanar spacing of the material, \( \lambda \) the electron wavelength and \( L \) the camera length which is defined as the distance from the specimen to the camera or its recording film.

The formula 2.6 basically suggests that diffraction from a polycrystalline sample will result in certain \( r \) or rings with this radius emerging on specific diffracted planes, so by measuring the radii it is possible to derive the interplanar spacing and vice versa, which is an important tool in distinguishing the crystal structure of material. In case a single crystal is present, such as a single grain, the pattern will not be in shape of rings but spots each of which are reciprocal lattice equivalent of individual atomic planes.

TEM samples can be prepared using different techniques such as mechanical, chemical and vacuum techniques. In our set studies we used the focused ion beam or FIB to prepare a sample. Here using Gallium ions a very thin slice of the material is cut from the surface of the sample on what is basically an SEM instrument giving the element of accuracy in selecting the specific microstructural features for analysis. The system was a Tescan Lyra™ FIB-SEM machine. Eventually a FEI Quanta™ tool was the instrument used for TEM studies. The SEM and EBSD images and data was obtained from a JEOL 7000™ FE-SEM.
2.5. Magnetic Measurements

Magnetic behavior of materials is exposed through specific methods which are generally called magnetometry. The main two requirements for observing this behavior are firstly inducing an external magnetic field to magnetize the material, and secondly measuring and recording the produced magnetization behavior. The magnetization field can be produced through three different sources such as permanent magnets, electromagnets and solenoids.

One of the widely used techniques for measuring magnetization and hysteresis loops of magnetic materials is the famous Vibrating Sample Magnetometry or VSM as it is called. The core of the technique is based on Farday’s law electromotive force, emf or \( \varepsilon \):

\[
\varepsilon = -N\frac{d\varphi}{dt} \quad (2.7)
\]

Where \( N \) is the number of the coil turns in an area of \( A \), and the flux density in the air will be \( B_0 = \frac{\varphi}{A} \), which in the presence of pulsing field will turn the formula 1.11 into:

\[
\varepsilon = -N A \omega B_0 \sin \omega t \quad (2.8)
\]

Consequently the VSM instrument has a source of magnetic field, which could be an electromagnet or occasionally a superconductor. The sample is vibrated within the field with the help of a mechanical vibrator while a non-magnetic rod holds the sample in the field. The frequency applied is dependent on the type of the driving force used: If a loudspeaker is applied, the frequency will be approximately 100 Hz with an amplitude of 0.1mm, while a linear motor has a frequency lower than 40 Hz with amplitudes higher than 1 mm.

The mechanical oscillation of the sample will induce an alternating electromotive force in the detection coils, which itself has a direct relation to the magnetic moment of the material. The signal is sent to an amplifier which is only capable of detecting signals at the vibrating frequency.
It is therefore necessary to ensure the stability of the vibration frequency and the amplitude alongside any potential vibrations in the pickup coils as well. Figure 2.11 shows a schematic of a Quantum Design VSM system.  

![Schematic of a Quantum Design VSM system](image)

**Figure 2.11.** Schematic of a Quantum Design VSM system. Reprinted from Ref. 19.

The VSM can operate in wide range of temperatures such as from near zero Kelvin up to 1000 Kelvin, which is useful in deriving the magnetic thermal behavior of materials such as Curie temperature or Rhodes-Wohlfarth model.

The accuracy of the system is good and especially for the small amount of the material on thin films this accuracy is crucially assistive in achieving a correct reading of the moment.
For our set of studies we used a Quantum Design Dynacool™ system which has a good accuracy level of measuring moments lower than $10^{-6}$ emu and apply fields up to 9 Tesla for a temperature range of 5 to 400 Kelvin.

2.6. Theoretical Calculations

Although the theoretical calculations in this thesis were performed by our colleagues in Professor William H. Butler and Christopher Wolverton groups, it would be useful to briefly describe the methodology adopted.

For electronic bandstructure generation, a density functional theory (DFT) approach was taken using the VASP software. The software receives an input of space group, atoms, lattice constant, magnetic moment and k points and energy cutoff to minimize the energy through elaborate nonrelativistic quantum calculations to finally generate the bandstructure. The cluster expansion (CE) is an expansion of Ising model in which a binary alloy $A_xB_{1-x}$ in which many possible occupation sites or clusters are permuted for a specific property and for example the end result could be a ground-state evaluation of possible compounds being stable.

2.7 References


CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF Fe-Ti-Sb INTERMETALLIC COMPOUNDS: DISCOVERY OF A NEW SLATER-PAULING PHASE


3.1 Introduction

The ternary intermetallic Heusler compounds with compositions $X_2YZ$ (“full” Heusler) and $XYZ$ (“half” Heusler) have been a subject of great interest in spintronics owing to the fact that many of them are predicted to be “half-metallic” ferromagnets.\(^1\) The term “half-metallic” refers to the existence of a gap in the density of states at the Fermi level for one spin channel and not for the other, leading to the possibility of 100% spin polarization of the electron current. Additionally, many of these Heusler compounds have relatively high Curie temperatures, raising the possibility of high polarization at or above room temperature.\(^1\)-\(^5\)

We recently completed a first-principles study of over 500 candidate full- and half-Heusler compounds, with a view to identify unstudied materials that were predicted to be stable and half-metallic. After screening candidate materials identified by the first-principles study from an experimental point of view (e.g., toxicity, fabricability, homogeneity, possibility of decomposition into more stable binary compounds, etc.) and examining the available literature, we found a number of promising candidate material.\(^6\),\(^7\)
One of the most intriguing was Fe$_2$TiSb, which was predicted by the calculations to have a negative formation energy and to be a (near) half-metal in the L2$_1$ structure. Perhaps surprisingly, a literature survey found no reports of the magnetic and spintronic properties of this or related compounds. This made an inquiry into this metallurgical system potentially interesting, particularly as a test case for our methods of identifying new compounds. The study reported here examines the possibility of synthesizing Fe$_2$TiSb and related compounds in phase-pure form, and a consequent analysis of their structural and magnetic properties. One of the interesting insights of our study based on a combination of theory and experiment is that Fe$_2$TiSb may prefer to form as a naturally layered Heusler compound with layers of the full Heusler, Fe$_2$TiSb, alternating with layers of the half-Heusler, FeTiSb. The predicted lowest energy phase with composition Fe$_{1.5}$TiSb is a nonmagnetic semiconductor, consistent with experimental observations.

3.2 Electronic Structure of Stoichiometric Heusler Compounds Based on Fe, Ti, and Sb

3.2.1 Full Heusler

Our first-principles survey included 180 prospective full-Heusler compounds in the L2$_1$ structure (composition X$_2$YZ) and 378 prospective half-Heusler compounds in the C1$_b$ structure (composition XYZ). The full results of this study and the details on the methods and parameters of the calculations are available on a website. Among the potentially interesting systems that emerged from these studies are compounds of Fe, Ti, and Sb. Considering first the hypothetical Fe$_2$TiSb compound in the L2$_1$ structure, we found it to be stable against decomposition into its constituent elements with an energy of formation of $-0.264$ eV/atom and a lattice constant of $a = 0.604$ nm. We also found it to be stable with respect to tetragonal distortion.
The most stable magnetic configuration for this phase (considering ferromagnetic, ferrimagnetic, antiferromagnetic, and nonmagnetic configurations) is a ferrimagnetic ground state with saturation magnetization of approximately \(1.00 \, \mu_B\) per formula unit at \(T = 0\) K. The magnetization is primarily on the Fe sites (0.69 \(\mu_B\)) but with a significant opposite (\(-0.31\mu_B\)) moment on the Ti and a small (\(-0.03\mu_B\)) moment on the Sb. The quoted moments are those within spheres of radius 0.145nm centered on each atom. The value of the calculated total moment (\(\sim 1.00 \, \mu_B\)) causes one to suspect that this solution to the DFT equations is a “Slater-Pauling phase.”

We use the term “Slater-Pauling phase” to describe full and half-Heusler compounds that satisfy a generalization of the rule first enunciated by Slater and Pauling, which states that compounds based on the bcc crystal structure tend to have three electrons per atom in the minority-spin channel.\(^9\)-\(^{11,12-14}\) For the Heusler half-metals, the generalization of the Slater-Pauling rule is that there tends to be a gap in the density of states for one of the spin-channels with precisely three valence electron states per atom in the gapped channel below the gap. When there is a gap like this and when the Fermi energy falls in the gap, we will refer to the phase as a Slater-Pauling half metal. Often, there is a gap with three electrons per atom, but the Fermi energy falls just above or just below the gap. We refer to such phases as “Slater-Pauling near half-metals.” Following this terminology, our DFT calculations predict L21 \(\text{Fe}_2\text{TiSb}\) to be a Slater-Pauling near half-metal. It has a gap in the minority spin channel of 0.31 eV, as shown in figure 3.1 The Fermi energy falls just below (0.05 eV) the edge of the gap so that the number of minority electrons is calculated to be 11.99915 rather than 12.
Since the total number of electrons per formula unit is 25, there must be 13.00085 majority spin electrons yielding a moment of 1.0017 $\mu_B$ per formula unit. A moment of exactly $1.0\mu_B$ would have produced a Slater-Pauling half-metal.

![Figure 3.1](image1.png)

**Figure 3.1.** Calculated density of states for L2$_1$ Fe$_2$TiSb.

### 3.2.2 Half-Heusler

Subsequent to our survey of full-Heusler compounds, we completed a survey of the half-Heusler (C1$_b$) compounds. We found that C1$_b$ phase FeTiSb is also predicted to be stable relative to decomposition into its constituent elements and tetragonal distortions of its cell, with an energy of formation of $-0.382$ eV/atom and a lattice constant of 0.595 nm. The density of states of FeTiSb is shown in figure 3.2 the lowest-energy magnetic configuration is predicted to be a Slater Pauling near half-metal with a magnetic moment of approximately $1\mu_B$ per formula unit. FeTiSb actually has Slater-Pauling gaps in both spin channels. One, however, is quite close to the Fermi energy.
The calculated Fermi energy is 0.11 eV below the gap in the majority channel, so that only 8.9775 states are occupied rather than the nine that would have been occupied had the Fermi energy fallen in the majority gap. FeTiSb has 17 valence electrons, so subtracting the 8.9775 majority electrons yield 8.0225 minority electrons for a predicted moment per formula unit of 0.955 \( \mu_B \). This system is also predicted to be ferrimagnetic with moments of 1.3 \( \mu_B \) on the Fe and \(-0.35 \mu_B\) on the Ti. Half-Heuslers typically have larger gaps than full-Heuslers. The calculated width of the Slater-Pauling gap is 0.85 eV.

![Figure 3.2](image.png) Calculated density of states for C1\textsubscript{b} FeTiSb.

3.3 Experimental

Based on the initial theoretical findings, we attempted to synthesize bulk samples of both the full Heusler Fe\textsubscript{2}TiSb and the half-Heusler FeTiSb. Stoichiometric ratios of pure elements Fe (Alfa Aesar, 99.98%), Ti (Alfa Aesar, 99.9%), and Sb (Alfa Aesar, 99.999%) were mixed together and melted using an Edmund Buehler Mini MAM-1 compact arc melting system under an ultrahigh purity Argon (99.999%) pressure of 0.02 Pa. A 10% excess of Sb was added to the initial melt to compensate for losses in the final ingot due to its higher volatility.
A small piece of Ti was melted before all arc melting runs as an oxygen getter to avoid oxidization of the sample. Ingots were remelted at least five times to ensure the homogeneity of the material.

The samples from the arc-melter were cut and mounted for metallographic studies. A JEOL 7000™ Field emission scanning electron microscope (SEM) was used for energy-dispersive x-ray spectroscopy (EDS) analysis to ensure that the chemical composition of the as-cast ingots had not deviated from the intended target stoichiometry. Samples for heat treatment were wrapped in Ta foil and sealed under vacuum in quartz tubes to avoid oxidation. These pieces were heat treated at various temperatures (400–1100°C) and dwell times (1–15 days). From metallographic and x-ray diffraction analysis of the annealed samples, a treatment at 900 °C for 7 days and cooled in the furnace at approximately 70 degrees per hour appeared to result in the optimum L2₁ structure and granular microstructure for all cases.

The crystal structures of the annealed samples were studied using a Bruker D8 Discover™ X-Ray Diffraction (XRD) system with a monochromatic Co Kα radiation. In order to minimize surface effects, the samples were mounted and polished, and rotated around the ϕ axis during the XRD measurement. Electron backscatter diffraction (EBSD) phase mapping using the JEOL 7000™ FE-SEM system was additionally performed to affirm the structure determined from XRD. Simulated XRD patterns were obtained both by using the CARINE crystallography 4.0™ software as well as by direct calculation to account for dispersive corrections to the atomic scattering factors while the Rietveld refinement was carried out using the CRYSTAL IMPACT MATCH!™ Software based on the FULLPROF algorithm.
The magnetic properties were measured using Quantum Design Physical Property Measurement System (PPMS) Dynacool with vibrating sample magnetometry (VSM) feature. The Transmission Electron Microscopy (TEM) diffraction pattern was obtained by using a FEI Tecnai F20™ instrument.

3.4 Results and Discussion

3.4.1 Fe$_2$TiSb

All of the as-cast Fe$_2$TiSb samples heat-treated at 900 °C for soaking times of 3, 5, 7, or 9 days showed a single, mostly granular microstructure. Energy-dispersive x-ray spectroscopy showed the composition of the grains to be Fe$_{40}$Ti$_{30}$Sb$_{30}$, with an uncertainty of ~5% in the abundance of each element, and thus quite significantly different from the intended stoichiometry - in spite of the fact that the as-cast samples were essentially stoichiometric Fe$_2$TiSb. Henceforth, we will refer to this nominal composition as Fe$_{1.5}$TiSb for simplicity. Figure 3.3 shows an example of such microstructure and its relevant EDS result for a sample heat treated at 900°C for 7 days. X-ray diffraction results on these samples, discussed further below, were consistent with a L21 phase alongside a small amount of a Fe-rich precipitate phase.

![Figure 3.3](image)

**Figure 3.3** (a) The metallography image of a Fe$_2$TiSb sample heat treated at 900 °C for 7 days. The sample was etched for 30 seconds using the marble etchant. The microstructure is evidently single grain, while the voids can be attributed to a Fe-rich precipitate at the grain boundaries, which was removed by the marble etchant. (b) SEM micrograph of the same surface showing the grain structure. EDS indicated that the composition of the grains was Fe$_{40}$Ti$_{30}$Sb$_{30}$. 

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Since the stoichiometry of the grains deviated significantly from the initial as-cast composition of Fe$_2$TiSb, we hypothesized that the bulk of the material was crystallized in the form of Fe$_{1.5}$TiSb grains, while the remaining iron precipitated in the grain boundaries and disappeared at the etching stage (used to prepare the specimens for metallographic imaging). In order to test this hypothesis, we performed an EDS analysis of non-etched samples, and indeed found an overall composition of Fe$_2$TiSb, consistent with the as-cast material and indicating a loss of iron after metallographic etching. X-ray diffraction analysis of the pre-etched material also indicates the presence of peaks corresponding to an iron-rich Fe$_{0.975}$Ti$_{0.025}$ bcc solid-solution in addition to the full-Heusler L2$_1$ phase peaks originating from the Fe$_{1.5}$TiSb grains. The etched sample, on the other hand, showed only a very small (~1%–2%) presence of the iron rich phase. Figure 3.4(a) shows the XRD patterns of etched and polished samples measured with Co $K_{\alpha}$ radiation. The XRD patterns generated by either CARINE 4.0 simulations or CRYSTAL IMPACT MATCH are similar to the pattern observed. Rietveld refinement gives good agreement ($\chi^2 = 0.9$ and average $R_{\text{Bragg}} = 0.1$) between the data and the calculated pattern for the L2$_1$ structure of the dominant phase with the experimental lattice constant of 0.5967 nm. One can also clearly see small peaks corresponding to a Fe-rich phase identified as Fe$_{0.975}$Ti$_{0.025}$ (e.g., at approximately ~52°), which are much clearer in the pre-etched samples. For the pre-etched sample, we estimate from Rietveld refinement and EBSD that the Fe-rich phase constitutes about ~10% of the total, and approximately the same amount of bcc Fe for the etched samples was estimated from magnetometry.
Figure 3.4 (a) The XRD pattern measured using Co Kα radiation of the Fe2TiSb sample heat treated at 900 °C for 7 days. The pattern is consistent with an L21 structure with a lattice parameter of 0.5957 nm for the Fe$_{1.5}$TiSb grains. The stars indicate peaks attributed to a Fe-rich precipitate. (b) The lattice value is also confirmed by a Rietveld refinement analysis with good agreement with the proposed model.

The presence of all low-angle L2$_1$ peaks, i.e., (111), (200), and (220) effectively rules out the possibility of significant deviation toward a B2 or A2 disorder. If the (111) peak were missing or reduced, this would have indicated Ti-Sb mixing and generated a B2 structure, whereas a missing or reduced (200) peak would have indicated Fe-(Ti, Sb) mixing and generated the A2 (bcc) structure. In fact, the (111) and (200) superstructure peaks are somewhat higher in intensity than expected compared to the (220) fundamental peak. The higher than expected values of intensities of the superlattice peaks could be attributed to surface effects and texture or they could be indicative of the fact that the Fe$_{1.5}$TiSb grains are not stoichiometric for a L2$_1$ structure. If we presume for the moment that we do not have a preferred texture in our samples, the trend of the x-ray diffraction intensities with Fe content can be readily seen.
If we consider a Fe$_2$TiSb compound in the L$_2^1$ structure, with Fe at the 8c (1/4, 1/4, 1/4) Wyckoff positions, the structure factors for the main peaks of interest are: $^{18-20}$

\[
F_{111} = 4|f_{\text{Ti}} - f_{\text{Sb}}| \quad (3.1)
\]
\[
F_{200} = 4|f_{\text{Ti}} + f_{\text{Sb}} - 2f_{\text{Fe}}| \quad (3.2)
\]
\[
F_{220} = 4|f_{\text{Ti}} + f_{\text{Sb}} + 2f_{\text{Fe}}| \quad (3.3)
\]

Where $f_i$ is the total atomic scattering factor for element $i$. From this we can see that having less Fe than expected would reduce the (220) x-ray structure factor and increase the (200) structure factor (leaving the (111) structure factor unchanged), consistent with the XRD results. A more quantitative analysis, including the dispersive terms in the atomic scattering factors does give a 111/200 intensity ratio similar to that observed using a nominal Fe content of 1.4–1.6 rather than 2.0.$^{15,16}$ However, we stress that we cannot rule out a net preferred texture in our samples that would alter the relative XRD intensities. Indeed, this is likely the case given that the (220) peak intensity is still smaller than expected compared to the (111) and (200) peaks. Still, with the assumption that we have no preferred texture, both qualitatively and quantitatively the XRD intensities do appear to be consistent with a Fe-deficient L$_2^1$ Fe$_{1.5}$TiSb compound. In order to further substantiate the existence of the L$_2^1$ structure, an EBSD phase map was performed. The phase mapping showing the L$_2^1$ structure is shown in figure 3.5 More than 90% of the microstructure is colored red which means that the material corresponding to an L$_2^1$ phase with a lattice constant of 0.5967 nm is homogenous throughout the sample. This is further evidence that the grains are crystallizing in a cubic L$_2^1$ structure. The remaining 10% of the sample is attributed to the Fe-rich phase precipitated at the grain boundaries, which are not evident in the EBSD maps.
The fact that the dominant phase has a composition of approximately Fe$_{1.5}$TiSb rather than Fe$_2$TiSb expected for ideal L2$_1$ compound points toward possible Fe vacancies.

Figure 3.5 (a) The electron micrograph of the as-cast Fe$_2$TiSb sample heat treated at 900 °C for 7 days taken by EBSD (b) the phase color map scan shows 90% (red color) of the sample has a homogenous L2$_1$ structure with a lattice constant of 0.5967 nm.

Magnetic characterization of the as-cast Fe$_2$TiSb sample heat treated for 7 days at 900 °C shows the sample has a ferromagnetic component with a small hysteresis, which does not completely saturate for the magnetic fields of up to 7200 kA/m (9 T) at 5 K, figure 2.6(a). This behavior is suggestive of small ferromagnetic Fe-rich precipitates in a weakly paramagnetic matrix. We find the magnetization to be 27 Am$^2$/kg at the maximum applied field of 7200 kA/m, with a coercivity of 2 kA/m. The ferromagnetic component would correspond to a very low magnetization for the dominant phase, but does agree well with ~10% of the sample having approximately the same magnetization as bcc Fe (or a very Fe-rich phase). We hypothesize, therefore, that the magnetic behavior comes from a superposition of a small volume fraction (~10%) of strongly ferromagnetic Fe-rich precipitates at the Fe$_{1.5}$TiSb grain boundaries, and a large volume fraction of Fe$_{1.5}$TiSb grains that are weakly paramagnetic.
Temperature-dependent magnetization [Figure 3.6(b)], measured at an applied field of \( H = 80 \text{ kA/m} \) during heating, is relatively uniform up to 400 K, consistent with most of the Fe-rich precipitate material being strongly ferromagnetic. The exception is a small upturn in the magnetization for temperatures below 10 K, which again could originate from weakly paramagnetic \( \text{Fe}_{1.5}\text{TiSb} \).

It would be unusual for a bulk sample to exhibit such a large Curie temperature (apparently above 400 K) with such a small moment (approximately 10\% the mass magnetization of Fe). This again suggests that the observed ferromagnetic component comes not from the bulk, but from the Fe-rich (nominally \( \text{Fe}_{0.975}\text{Ti}_{0.025} \) from the observed XRD peaks) Precipitate material, from which we would expect a high Curie temperature and low coercivity. Interestingly, first-principles Calculations (discussed later on) for \( \text{Fe}_{1.5}\text{TiSb} \), close to the observed composition for the dominant phase, indicate that a nonferromagnetic ground state is indeed favored.

![Magnetization Curve](image)

**Figure 3.6** (a) Magnetization curve of a nominally \( \text{Fe}_2\text{TiSb} \) sample at 5 K shows the dominant ferromagnetic nature of the sample. The inset is the magnetization around the origin, showing the small coercive field from the Fe-rich precipitates. (b) Temperature dependent magnetization shows no sign of phase transformation or Curie temperature below 400 K. The inset is the magnetization curve at 5, 300, and 400K showing only a minor change in the magnetization from 5 to 400 K.
3.4.2 Fe$_{1.5}$TiSb

Our observations during the synthesis of Fe$_2$TiSb suggested that Fe$_{1.5}$TiSb is, in fact, a more stable phase, a result corroborated by first principles calculations discussed later. Given this, the Fe$_{1.5}$TiSb compound seemed worthy of direct synthesis. As-cast samples were prepared in the same fashion as Fe$_2$TiSb. After the Fe$_{1.5}$TiSb samples were heat treated at 900 °C for 7 days, a single grain microstructure was observed. There were no signs of precipitates.

Figure 3.7 shows optical and SEM micrographs. Energy-dispersive x-ray spectroscopy shows that the grains present in the sample have a nominal stoichiometry of Fe$_{1.44}$TiSb$_{1.12}$. Again, for simplicity, we will refer to this nominal composition as Fe$_{1.5}$TiSb, and it appears that this particular phase is metallurgically stable in a wide range of iron doping within the Fe$_{1+x}$TiSb alloy system. The XRD data, figure 3.8, indicate the presence of a phase in an L2$_1$ structure with a lattice parameter of 0.5967 nm, which is in concordance with our observations for Fe$_2$TiSb. This shows that there is a possible limit of solubility for iron at the Fe$_{1.5}$TiSb composition, which is evidently the stable phase, and additional iron will be precipitated in the grain boundaries of the dominant L2$_1$ phase.

![Figure 3.7](image)

**Figure 3.7** (a) An optical micrograph of an as-cast Fe$_{1.5}$TiSb sample heat treated at 900 °C for 7 days. The sample was etched for 30 seconds using marble etchant. The microstructure reveals single grains without the presence of any secondary phase in the grain boundaries. (b) An SEM micrograph of the same surface showing the grain structure. EDS indicated that the composition of the grains was Fe$_{1.44}$TiSb$_{1.12}$. 

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Figure 3.8 The XRD pattern measured using Co Kα radiation of the Fe$_{1.5}$TiSb compound. All peak positions can be attributed to an L21 structure with a lattice constant of 0.5967 nm.

To perform further comparison between the diffraction pattern of Fe$_2$TiSb and Fe$_{1.5}$TiSb and verify the crystal structure, selected area electron diffraction (SAED) analysis using a FEI Tecnai F-20 Transmission Electron Microscope (TEM) was performed. Results are shown in figure 3.9. The diffraction of the Fe$_2$TiSb sample showed patterns belonging to both bcc α-Fe and L2$_1$ phases, which is in accordance with our findings suggesting Fe precipitation in this compound.
Figure 3.9 (a) A SAED ring pattern of Fe$_2$TiSb sample after heat treatment at 900 °C for 7 days. Both bcc Fe and L2$_1$ patterns are visible. (b) A SAED pattern of Fe$_{1.5}$TiSb heat treated at 900 °C for 7 days. There are spots visible belonging to the assumed L2$_1$ structure, but none corresponding to bcc Fe.

The pattern is noticeably different for the Fe$_{1.5}$TiSb sample - the Fe diffraction spots are no longer present, while the L2$_1$ pattern is still clearly visible. It is notable that the pattern belonging exclusively to the L2$_1$ phase has faded, which could be attributed to the presence of Fe vacancies in the L2$_1$ lattice, which would also be consistent with Fe precipitation.

The magnetic properties of the Fe$_{1.5}$TiSb material are qualitatively similar to those of the Fe$_2$TiSb material, with a smaller amount of the Fe-rich phase (~1.5%). Magnetization versus field characteristics at $T = 5$ K, figure 3.10, again suggests paramagnetic behavior of the dominant L2$_1$ phase plus weak ferromagnetism from the small concentration of Fe-rich grains segregated at the grain boundaries. Coercivity in the low-temperature regime is approximately 2 kA/m for Fe$_2$TiSb sample, as shown in the inset of figure 3.10(a). Magnetic measurements up to 7200 kA/m for this sample shows no sign of saturation of the magnetization at $T = 5$ K, whereas at $T = 300$ and 400 K the magnetization is nearly saturated with only 100 kA/m. Figure 3.10(b) shows the temperature-dependent magnetization, measured in similar conditions as the Fe$_2$TiSb sample.
As in that case, the temperature dependence appears to be a superposition of weak paramagnetism of the dominant Fe$_{1.5}$TiSb phase and a small ferromagnetic component due to the Fe-rich segregations at the grain boundaries. The magnetization does not change significantly over the whole temperature range, aside from the upturn in temperatures below 10 K.

**Figure 3.10** (a) The magnetization of Fe$_{1.5}$TiSb shows no indication of saturation for the fields up to 7200 kA/m at $T = 5$ K, showing the paramagnetic nature of the dominant phase. The inset shows small coercivity related to Fe-rich phase precipitates. (b) Magnetization of the sample as a function of temperature measured in an applied field of $H = 80$ kA/m during heating. The inset shows the magnetization curves measured at temperatures 5, 300, and 400 K.

Due to the smaller concentration of Fe-rich precipitates in the Fe$_{1.5}$TiSb sample (estimated as ~1.5%), the maximum magnetization measured is much smaller than for the Fe$_2$TiSb sample [Figure 3.10(b) inset].

### 3.4.3 FeTiSb

Finally, the half-Heusler FeTiSb composition was expected from our theoretical survey to also have a negative energy of formation and to be a near half-metallic compound. As-cast samples of nominal composition FeTiSb were prepared and heat treated in a similar fashion to the previous samples.
Microstructural analysis on samples annealed to 900 °C for 7 days shows that the material in fact decomposes into two separate phases. One is again the iron rich Fe\(_{1.5}\)TiSb phase, but with a significant presence of a Ti-Sb rich phase.

Figure 3.11 displays optical and SEM micrographs. The composition of the Ti-Sb rich phase was found by EDS to be approximately Sb\(_{1.8}\)Ti\(_{1.5}\)Fe. While once again the dominant phase is Fe\(_{1.5}\)TiSb, in previous cases it was excess Fe, which segregated to the grain boundaries. In contrast, in this case, excess Ti and Sb have formed a new granular phase, indicating that the level of solubility of the dominant phase for Ti and Sb might be less than its solubility level for Fe. Figure 3.12 shows XRD pattern of the sample. It clearly indicates the presence of the L2\(_1\) phase again, which originates from the Fe\(_{1.5}\)TiSb grains, as well as small yet-unidentified peaks at low angles, which are presumably attributable to the Ti-Sb rich grains. The relative peak intensities in this case are probably a reflection of an induced texture in the sample.

**Figure 3.11** (a) An optical metallography image of FeTiSb exhibiting two distinct granular phases present. (b) Shows the SEM micrograph of an iron poor grain, whose composition was found to be Sb\(_{1.8}\)Ti\(_{1.5}\)Fe. (c) Shows an iron-rich grain, whose composition was found to be Fe\(_{1.5}\)TiSb.

Magnetization versus field of the FeTiSb sample, illustrated in figure 3.13, has a similar behavior to Fe\(_{1.5}\)TiSb. We again attribute the paramagnetic response to the Fe\(_{1.5}\)TiSb phase, but in this case the contribution we attribute to the precipitates is different.
Figure 3.12 The XRD pattern measured using Co-Kα radiation of the as-cast FeTiSb compound. Most peak positions can be attributed to an L21 structure while there are some yet-unidentified peaks possibly arising from the Ti-Sb rich phase.

Figure 3.13 (a) Magnetization curves for Fe₀.₅TiSb (x = 1, 1.5, 2) Specimens. (b) Temperature-dependent magnetization of these samples Measured in the applied field of $H = 80$ kA/m during the heating.
Comparing the magnetization results from Fe$_x$TiSb ($x = 1, 1.5, 2$) samples, the common presence of the stable and weakly paramagnetic Fe$_{1.5}$TiSb phase is apparent, with a varying ferromagnetic contribution of Fe-rich precipitates for Fe$_2$TiSb and Fe$_{1.5}$TiSb samples and TiSb-rich phase for the case of FeTiSb. Magnetization versus temperature (Figure 3.13) gives a similar conclusion: ferromagnetic precipitates give a slowly-varying contribution to the magnetization. In order to verify the nature of magnetization versus temperature upturn for $T < 10$ K, field-cooling (FC) and zero-field-cooling (ZFC) measurements were performed to check for the presence of superparamagnetism in the samples, which would help determine if observed paramagnetism is indeed due to the dominant Fe$_{1.5}$TiSb grains or small precipitates. The outcome, shown in figure 3.14 does not show the expected bifurcation for superparamagnetic effects for either the Fe$_2$TiSb or Fe$_{1.5}$TiSb samples. Therefore the main source of the increased magnetization for $T < 10$ K, as well as the nonsaturated magnetization versus field at low temperatures, is most likely due to weak paramagnetism of the dominant phase Fe$_{1.5}$TiSb.
Overall, one concludes at this point that regardless of the starting composition, it is the Fe$_{1.5}$TiSb phase that is most stable, and it appears to dominate after heat treatment. This phase crystallizes in the L$_{21}$ structure, albeit one with iron sites which are approximately $2/3$ to $3/4$ occupied, and seems to exhibit weak paramagnetism. Starting from a Fe-rich composition leads to segregation of excess Fe to grain boundaries of the Fe$_{1.5}$TiSb grains, while starting from an Fe-poor composition leads to a secondary Ti-Sb-rich phase appearing. The main question to be addressed from a theoretical point of view is whether the greater stability of the Fe$_{1.5}$TiSb phase compared to FeTiSb or Fe$_2$TiSb can be explained, whether its existence in a (defective) L$_{21}$ or related structure can be explained, and whether one expects it to be nonmagnetic.
3.5 Theoretical Cluster Expansion Treatment of the Fe-Ti-Sb Alloy System

The experimental work described in previous section makes clear that the lowest energy structure in the Fe-Ti-Sb system is based on the L2₁ structure. It is also clear that it is not simply a Fe₂TiSb full-Heusler compound, and specifically, it is Fe deficient. Given this experimental input, we performed a binary cluster expansion (CE) of Fe and vacancies (hereafter, a vacancy is indicated as □) on the Fe sublattice of the Fe₂TiSb L2₁ structure in an attempt to explain the predisposition of the Fe-Ti-Sb to tolerate Fe deficiency.

We calculated the formation energy Δ₃₄(H) (per mixing site) of a compound with composition Feₓ☐₂₋ₓTiSb with respect to the end members Fe₂TiSb and☐₂TiSb using:

\[ ΔH_f = \frac{1}{2}[E(\text{Fe}_x\square_2-x\text{TiSb}) - xE(\text{Fe}_2\text{TiSb}) - (2 - x)E(\square_2\text{TiSb})] \quad (3.4) \]

Where all the required energies are calculated using density functional theory (DFT). We fit a binary CE to the formation energies calculated using equation 3.4 by minimizing the sum of squares of the residuals. We generated new structures, used their formation energies in the fit, and added terms to the CE until the cross-validation (CV) score was minimized, and adding further structures resulted in overfitting. We found a well-converged CE, with a CV score of ~20 meV/mixing atom by using 66 Feₓ☐₂₋ₓTiSb structures and their formation energies in our fit (Figure 3.15). We searched for ground states by computationally scanning through >10³ structures, which corresponds to a complete enumeration of all possible Fe/☐ orderings with <20 atoms per cell.²¹ Out of this extremely large configuration space, we predict a novel, stable ground state phase with a composition Fe₁.₅TiSb, i.e., between the full-Heusler and half-Heusler compositions, belonging to the trigonal R₃m space group, and with a formation energy of −0.223 eV/mixing atom.
Figure 3.15 Energies of 66 different arrangements of Fe and □ on the Fe sublattice of Fe$_2$TiSb in the L2$_1$ structure, calculated using DFT, and those predicted by a binary cluster expansion (CE) fit to the DFT energies. The DFT convex hull is captured well by the CE, with a cross-validation error of $\sim$20 meV/mixing atom.

This structure corresponds to a layering of the L2$_1$ and C1$_b$ structures along the [111] direction of the underlying cubic lattices (see Fig. 3.16). We provide the lattice parameters and atomic coordinates of the Fe$_{1.5}$TiSb phase in Ref. [22].

We calculated the density of electronic states in the ground state $R3m$ structure and find that it is a nonmagnetic semiconductor with a Kohn-Sham gap of $\sim$0.64 eV (see figure 3.17).
Figure 3.16. Structure of the low energy $R3m$ Fe$_{1.5}$TiSb phase obtained from a cluster expansion illustrating the layering of the L2$_1$ Fe$_2$TiSb and C1$_b$ FeTiSb along the [111] direction of the underlying cubic lattices. A (111) “defect planes” formed by vacancies is highlighted. Only a part of the periodic cell is shown here for clarity. (Sb = green, Ti = blue, Fe = red, and vacancies= unfilled spheres.)

Figure 3.17. The density of electronic states of the low-energy Fe$_{1.5}$TiSb $R3m$ structure predicted by the cluster expansion. It is a nonmagnetic semiconductor with gaps in both the spin channels.
We observe that gaps open in both the spin channels and the Fermi energy is in the gap. As discussed in section 2.2, the full-Heusler Fe$_2$TiSb compound is a Slater-Pauling near half-metal with 25 electrons, a moment of $\sim 1$ Bohr magneton per formula unit ($\mu_B$/f.u.), and a gap in the *minority* spin channel (see figure 3.1). The half-Heusler FeTiSb compound is also a Slater-Pauling near half-metal with 17 electrons, a moment of $\sim 1 \mu_B$/f.u. but with a gap in the *majority* spin channel (see figure 3.2). When the full-Heusler and the half-Heusler are layered to form the Fe$_{1.5}$TiSb compound, there are three electrons per atom in each spin channel, and therefore a Slater-Pauling gap can exist in *both* spin channels. This gap in both spin channels is precisely what we observe in the Fe$_{1.5}$TiSb compound (see figure 3.17), consistent with Slater-Pauling behavior of these compounds. And this opening of gaps in both spin channels seems to contribute to the stability of the $R3m$ structure. Thus, in full agreement with experimental data, our calculations demonstrate the existence of a Fe$_{1.5}$TiSb phase, that is, (a) stable relative to Fe$_2$TiSb and FeTiSb, (b) an ordered Fe/□ arrangement based on the Heusler structure, and (c) is a nonmagnetic semiconductor.

### 3.6 Conclusion

We investigated the structural and magnetic properties of the Fe$_x$TiSb material system, including the half-Heusler FeTiSb ($x = 1$) and the full-Heusler Fe$_2$TiSb ($x = 2$) compositions as well as the intermediate Fe$_{1.5}$TiSb composition. In all cases, after heat treatment a dominant Fe$_{1.5}$TiSb phase was revealed. Heat treatment of as-cast Fe$_2$TiSb results in Fe$_{1.5}$TiSb grains with approximately 10% by volume of an Fe-rich precipitate.
The Fe-rich precipitate is the main contributor to the magnetic behavior, with the Fe$_{1.5}$TiSb phase appearing to be weakly paramagnetic. Heat treatment of as-cast FeTiSb also results in the dominant Fe$_{1.5}$TiSb phase, but with a Ti-Sb-rich precipitate of nominal composition Sb$_{1.8}$Ti$_{1.5}$Fe. The cluster expansion results show that the FeTiSb half-Heusler is unstable with respect to two-phase decomposition into Fe$_{1.5}$TiSb and a Fe-deficient phase, Fe$_{0.5}$TiSb. We note that this Fe-deficient composition is similar to the Sb$_{1.8}$Ti$_{1.5}$Fe phase found experimentally.

Future experiments are needed to clarify the structure and properties of this phase. Direct synthesis of Fe$_{1.5}$TiSb resulted in a single phase material with only $\sim 1.5\%$ precipitates, in accordance with our initial findings and suggesting that it is the dominant phase within the entire metallurgical system. Directly synthesized Fe$_{1.5}$TiSb was also observed to be weakly paramagnetic. The crystal structure of the Fe$_{1.5}$TiSb material is related to the cubic L2$_1$ structure, with Fe in the 8$c$ Wyckoff position and Ti and Sb in 4$a$ and 4$b$ positions, respectively. The main difference in contrast to the postulated full Heusler compound is the overall composition of Fe$_{1.5}$TiSb, from which we conclude that in the 16 atom L2$_1$ fcc cell there should be two Fe vacancies.

Our cluster expansion calculations revealed that Fe$_{1.5}$TiSb is a stable ground-state composition in the Fe$_x$TiSb system, and is expected to be a nonmagnetic Slater-Pauling semiconductor.

We predict the stable, zero-temperature low-energy phase to have a new, interesting structure type, with Fe□ ordering on the 8$c$ Wyckoff sites, occurring in the $R3m$ space group. The special stability of this structure appears to come from the formation of a gap at the Fermi energy for both spin channels, a mechanism which should apply to other Heusler systems.
While experimental studies are as yet unable to draw unambiguous conclusions about the positions of the Fe vacancies to confirm the predicted $R3m$ structure, the observed Fe$_{1.5}$TiSb composition coupled with the nonmagnetic behavior is consistent with the hypothesized layered structure.

From the XRD data, peaks which would distinguish between a defective L2$_1$ structure and an $R3m$ structure are predicted to be of low intensity, making unambiguous identification of the $R3m$ structure difficult. While the $R3m$ structure is predicted to be the lowest energy phase, it is also possible that kinetics on the experimental time scale are insufficient to obtain a fully ordered $R3m$ structure, and the structure experimentally observed may be a disordered state somewhere between an $R3m$ and a defective L2$_1$ structure. Further theoretical studies evaluating the free energy and configurational contribution to the entropy would help clarify the situation, as would more detailed structural characterization combined with extended heat treatment.

Concerning the nonmagnetic ground state, recall that Fe$_2$TiSb has a predicted Slater-Pauling state with a moment of +1 $\mu_B$ per formula unit, while FeTiSb has a predicted Slater-Pauling state with a moment of $-1 \mu_B$ per formula unit. The Fe$_{1.5}$TiSb material has zero moment—in fact there is no moment on any atom in the calculated phases—a bit peculiar for Fe. Locally, however, there will be fluctuations in the concentrations of the Fe vacancies, and with these will be fluctuations in the local magnetic moments. We speculate that at finite temperature, these moments are likely to average to zero, but may also be partly responsible for the upturn in magnetization at low temperature. Further theoretical work on disordered structures would help clarify the magnetic state.
3.7 References


CHAPTER 4

STRUCTURAL AND MAGNETIC PROPERTIES ANALYSES OF THE BULK Fe<sub>x</sub>Co<sub>1-x</sub>TiSb ALLOY SYSTEM: THE Fe<sub>0.5</sub>Co<sub>0.5</sub>TiSb COMPOUND AS PROTotypical HALF HEUSLER

4.1 Introduction

The Heusler alloys and compounds have become a household name in the field of materials science since the discovery of the Cu<sub>2</sub>MnSn alloy by Friedrich Heusler as a ternary compound with peculiar magnetic behavior. During the course of the past hundred years they have shown to exhibit many interesting electronic properties such as ferromagnetism, ferrimagnetism, half metallicity, superconductivity, semiconductivity, thermoelectricity and topological insulation. The technological applications of this class of intermetallics are found in diverse fields.\textsuperscript{1-5}

The so-called “half Heusler” subclass of these compounds has been considerably exploited to harvest their potential spintronic and thermoelectric capabilities. This includes a very recent report of the antiferromagnetic compound CuMnAs used as the building block of an all-antiferromagnetic memory with potentially tangible increase in speed of operation, robustness, energy efficiency and storage density which could be an instance of the importance of the antiferromagnetic spintronics.\textsuperscript{9} This subclass crystallizes in a C\textsubscript{1b} cubic structure (space group 216) and has an equiatomic ternary stoichiometry of XYZ in which X and Y are usually transition metals and Z is a metalloid element.
Following our own findings on the Co-Ti-Sb and Fe-Ti-Sb systems, we decided to exploit the quaternary amalgamation of the mentioned alloys. There were some reports in the literature indicating that the Cobalt-rich side of the Fe\textsubscript{x}Co\textsubscript{1-x}TiSb was studied for their thermoelectric capacities and results indicated that there were impurities present within the alloy microstructure especially in the Fe\textsubscript{0.5}Co\textsubscript{0.5}TiSb composition, the hypothetical half Heusler of the alloy system. This all prompted us to consider a metallurgical evaluation of the entire alloy including the iron-rich side of the system specifically in order to consider the existence of a half Heusler quaternary compound.

**4.2 Experimental**

Stoichiometric ratios of pure elements Fe (Alfa Aesar, 99.98%), Co (Alfa Aesar, 99.95%), Ti (Alfa Aesar, 99.9%) and Sb (Alfa Aesar, 99.999%) were mixed together and molten using an Edmund Buehler Mini MAM-1 compact arc melting system under an ultra-high purity Argon pressure of 0.02 Pa. A 10% excess of Antimony was added to the initial melt to compensate for the mass of the matter lost due to the volatility. A titanium oxygen getter was melted before all the runs to avoid any potential oxidization of the sample. The ingots were flipped and remelted at least 5 times to ensure the proper mixing of the all the three elements and eventual homogeneity of the material. The bulk samples were then cut and mounted for metallographic studies. A JEOL 7000 Field emission scanning electron microscope (SEM) was used for the energy-dispersive X-ray spectroscopy (EDS) to ensure the chemical composition of the as-cast ingots had not deviated from the intended target stoichiometry. The heat treatment samples were wrapped with Tantalum and were sealed under vacuum in quartz tubes in a vacuum atmosphere to avoid oxidation.
The pieces were heat treated at various temperature and dwell times out of which a cycle of treatment at 900 °C for 3 days and cooled in the furnace with an approximate rate of 90 °C per hour appeared to result in the optimum C1b structure and a homogenous microstructural stoichiometry. The crystal structure was then studied using a Bruker D8 Discover X-Ray Diffraction (XRD) system with a monochromatic cobalt Kα radiation. In order to minimize the surface and crystal orientation effects the samples were mounted, polished and rotated in the φ axis during the XRD analysis. Also electron backscatter diffraction (EBSD) phase map was performed to affirm the structure observed on the XRD pattern using the JEOL 7000 FE-SEM system. Care was taken so that the EBSD step size does not exceed the tenth of smallest microstructural feature so that no phase is left out during the scanning process. The simulated XRD patterns were obtained by using a CaRine crystallography 4.0 software and the Rietveld refinement was carried out through a Match! Software based upon FullProf algorithm. The magnetic and electric properties were measured using a Dynacool VSM and a PPMS system respectively. The Transmission Electron Microscopy (TEM) selected area electron diffraction (SAED) pattern was taken on a FEI Tecnai F-20™ system using a camera length 670 millimeters for generating the ring pattern. The TEM sample was prepared using a TESCAL Lyra3™ Focused Ion Beam (FIB) SEM system using a Gallium ion source.

4.3 Results and discussion

4.3.1 CoTiSb

All the samples heat treated at 900 °C showed a mostly granular microstructure. The EDS test showed that the composition of the grains to be CoTiSb with an uncertainty of approximately 5 % with respect to each element and therefore quite near the intended stoichiometry. Figure 4.1 shows an example of such microstructure and its relevant EDS result.
Figure 4.1 (a) The Metallography image of a CoTiSb Sample heat treated at 900 °C for 7 days. The sample was etched for 30 seconds using the marble etchant. The microstructure is evidently single grain. (b) SEM micrograph of the same surface showing the grain structure and its relevant EDS spectrum. The composition of the grains was observed to be CoTiSb.

Figure 4.2 exhibits XRD pattern of the polished and etched sample, indicative of an FCC structure. The presumed Wyckoff positions of the constituting elements is the same as the ones reported by Barth and collaborators in which Titanium was positioned at 4a (0,0,0), Antimony at 4b (1/2, ½, ½) and Cobalt at 4c (¼, ¼, ¼). There is further concordance with their findings as the calculated lattice constant from the experimental data here is 5.898 Å, which is quite similar to the reported 5.884 Å. The intensities of (111) and (200) peaks are higher relative to that of (220), which is attributed to the relatively large grain size and the consequently considerable texture effect.

Figure 4.3 shows the hysteresis loop of this compound obtained at 5 Kelvin. The material shows paramagnetic behavior with almost zero moment which is most probably originating from some negligible magnetic elements such as unreacted cobalt.
Figure 4.2 The XRD diffraction data of the CoTiSb sample heat treated at the 900 °C for 7 days. The spectrum is correlated to an C1b structure with a lattice parameter of 5.898 Å using cobalt Kα X-Ray source.

Figure 4.3 The near zero Kelvin hysteresis loop of the CoTiSb compound heat treated at 900 °C for 7 days.

The paramagnetic behavior is in line with the findings in literature that CoTiSb is semiconductor and consequently not magnetic.
4.3.2 Fe$_{0.25}$Co$_{0.75}$TiSb

The sample alloy was cast and heat treated for 7 days at 900 °C. The optical microscopy and EDS revealed that the material is comprised of large grains with a CoTiSb chemical composition and the remainder iron almost completely segregating between the mentioned grains. Figure 4.4(a) is a metallographic image showing the grain structure and the figure 4.4(b) is the EPMA relevant of the same region showing a possible segregation of iron within the grain boundaries.

The XRD pattern of the sample is shown in Figure 4.5. The signature of the CoTiSb has an overwhelming presence with some peaks attributable to the iron rich composition within the grain boundaries. This is indicative of the microstructural data with the material being composed of CoTiSb grains and iron rich intergranular segregations.

![Figure 4.4](image_url) (a) The micrograph of the Fe$_{0.25}$Co$_{0.75}$TiSb sample heat treated at 900 °C for 7 days and (b) its EPMA elemental map based on the iron element showing the grain segregation. The chemical composition of the grains matched a CoTiSb stoichiometry.
Figure 4.5 The XRD Pattern of the Fe$_{0.25}$Co$_{0.75}$TiSb heat treated for 7 days at 900 °C. Most of the peaks are related to the CoTiSb grains and the ones marked with asterisk can be attributed the iron rich phase segregated within the grain boundaries.

The magnetometry results showed that the alloy behaves still exhibits very weak magnetic moment as it was the case with the CoTiSb compound. This is in concordance with the presence of the CoTiSb as the dominant phase in the Fe$_{0.25}$Co$_{0.75}$TiSb forming a grain structure. The weakly observed magnetization is stemming from the low amounts of possible iron segregates based in the grain boundaries. The evaluation of both room temperature and 5 K magnetic behavior confirms the prevalence of a paramagnetic phase within the system. The relevant results are shown at figure 4.6.
**Figure 4.6** The magnetic behavior of the Fe\textsubscript{0.75}Co\textsubscript{0.25}TiSb alloy system at 5 Kelvin and at 300 Kelvin.

### 4.3.3 Fe\textsubscript{0.5}Co\textsubscript{0.5}TiSb

The prototypical half Heusler within the Fe\textsubscript{x}Co\textsubscript{1-x}TiSb system is a Fe\textsubscript{0.5}Co\textsubscript{0.5}TiSb alloy stoichiometry which was considered worthy of synthesis itself. After the sample was heat treated at 900 °C for 3 days a single grain microstructure was observed. There were no sign of any precipitates as it was the case with previously mentioned stoichiometries. Figure 4.7 presents the related results. The EDS analysis exhibited a consistent chemical composition on different dimensional i.e. magnification levels conforming to the overall targeted stoichiometry of approximately Fe\textsubscript{17}Co\textsubscript{17}Ti\textsubscript{32}Sb\textsubscript{32}. 
Figure 4.7 (a) The optical micrograph of a Fe$_{0.5}$Co$_{0.5}$TiSb heat treated at 900 °C for 7 days. The sample was etched for 10 seconds using the Adler etchant. The microstructure reveals single grains without the presence of any secondary phase in the grain boundaries (b) SEM micrograph of the same surface showing the grain structure and its relevant EDS composition. The grains were observed to be approximately Fe$_{17}$Co$_{17}$Ti$_{32}$Sb$_{32}$ conforming to the intended homogenous stoichiometry.

The atomic structure obtained from the XRD data indicates the presence of a C1$_b$ crystal structure signature. The calculated lattice constant is 0.5918 nm. Crystal lattice simulations were used to propose a model based on the presumed C1$_b$ lattice. In such model two atoms and two atoms of cobalt are positioned within the four possible Wyckoff locations in 4c (1/4,1/4,1/4) sites while four titanium atoms and four antimony ones are located on 4a (0,0,0) and 4b (1/2,1/2,1/2) sites respectively. This model conforms quite well to the experimental spectrum of the material as no additional peaks are observed with respect to the model and no absent peaks from the spectrum are encountered either. To quantitatively evaluate this conformity a Rietveld refinement fitting to the proposed model was also performed. The resultant fitting parameters pointed toward a good agreement between the proposed model and the real-time experimental data with an R$_{BRAGG}$ factor of only 0.1 and a reduced $\chi^2$ factor of 8.1.
The relatively higher latter fitting parameter can be attributed to some peaks having intensities somewhat different from the hypothetical XRD pattern which can be due to the fact that the grain size is substantially large in this material standing at an average of 300 µm leading to a considerable crystal orientation and texture effects resulting in the intensities not completely concordant with the theoretical values. The XRD experimental pattern and its relevant Rietveld refinement fit are shown in figure 4.8

![XRD spectrum of Fe<sub>0.5</sub>Co<sub>0.5</sub>TiSb compound](image)

**Figure 4.8** The XRD spectrum of the Fe<sub>0.5</sub>Co<sub>0.5</sub>TiSb compound. All peak positions can be attributed to a C1<sub>b</sub> structure with a lattice constant of 0.5918 nm. No ambiguous peaks were observed. The Rietveld different plot has a signature of good fit with the proposed crystal model of the hypothetical compound.

In order to verify both the presence of texture and also phase purity of material, an EBSD phase map was performed on the microstructure. Figure 4.9 shows the band contrast, phase map and the texture map of the grain structure.
As it is shown on the phase map about 90 percent of the entire microstructure on a relatively large cross section of the material (500 µm by 500 µm) has been colored red which is significant of the C1\textsubscript{b} Fe\textsubscript{0.5}Co\textsubscript{0.5}TiS with the rest of microstructure being porous. This further confirms the high purity of the material and its structural nature being a prototypical half Heusler. The inverse pole figure map also shows large grain areas having different crystal orientations which is also the reason that some of the peak intensities on the XRD pattern of the material not completely overlapping the generated pattern by the crystal simulation and the consequent higher degree of reduced $\chi^2$ factor compared to its $R_{BRAGG}$ counterpart.

![Image](image_url)

**Figure 4.9** a) The electron backscatter band contrast image of a relatively large area on the surface of the Fe\textsubscript{0.5}Co\textsubscript{0.5}TiSb sample. b) The relevant EBSD phase map scan image of the same area showing that almost the entirety of the surface corresponds to the hypothetical half-Heusler C1\textsubscript{b} phase c) The orientation map of the same location and its inverse pole figure showing the texture formation of the sample.

The case for single-phase nature of this alloy was further studied using the TEM method to gather evidence for homogeneity at very dimensions and also to verify the consistency of the assumed compound structure. Consequently, a FIB sample was taken out of a junction of three grains so that sufficient statistical data was gathered and the sampling was not limited to only one grain spot. The elemental map by EDS showed no sign of segregation among the main elements in within the sample.
Also different EDS taken from different spots on the sample indicated that the stoichiometry averaged to a Fe$_{16}$Co$_{17}$Ti$_{32}$Sb$_{32}$ which is in good agreement with the target compound composition of Fe$_{0.5}$Co$_{0.5}$TiSb. A SAED ring pattern taken from the sample is shown in figure 4.10. The ring diameters overlap quite well with the expected values for a C1$_b$ structure peaks with a lattice constant of 0.5918 nm. No other obscure spots were detected related to a possible inhomogeneity. Overall the TEM findings also conform to our previous characterizations of the Fe$_{0.5}$Co$_{0.5}$TiSb being indeed a C1$_b$ compound.

![SAED pattern](image)

**Figure 4.10** A SAED pattern of Fe$_{0.5}$Co$_{0.5}$TiSb heat treated at 900 °C for 3 days. There are spots visible belonging to the assumed C1$_b$ structure with a lattice constant of 0.5918 nm. No obscure spots were detected.

The magnetometry results of the compound showed that at many different temperatures the material had no considerable magnetic moment as shown in the isotherms of figure 4.11 (a). We also evaluated the resistance-temperature response of the material to configure the electrical properties of the compound.
The corresponding results are exhibited in figure 4.12. There were no hysteretic effects witnessed in either presence or absence of magnetic field during the measurement. (Figure 4.12(a) and 4.12(b)). As the resistance rose from 10 Kelvin below, it was suggested that a semiconducting behavior was dominant. Therefore an exponential fit for the lower temperature regime was considered and eventually applied with good mathematical juxtaposition. The finalized fit hinted to a semiconductor with a bandgap range of 0.12 meV to 0.16 meV. (Figure 4.12(c)).

At this stage the compound was considered to be a semiconductor and a paramagnet but the theory calculations by our colleagues in the Northwestern university led to a hypothetical antiferromagnetic coupling between iron and cobalt atoms resulting in a specific energy and a predicted Neel temperature at 10 Kelvin. (Section 4.4) In order to detect any Neel transition a susceptibility versus temperature measurement was done with the result manifested in figure 4.11 (b). As it seen, there is a maximum peak observed at approximately 8 Kelvin, showing an entry into an antiferromagnetic phase from this temperature upwards. This finding is in good agreement with the prediction of antiferromagnetic Neel temperature of 10 K.
Figure 4.11 (a) Moment versus temperature isotherms of the Fe$_{0.5}$Co$_{0.5}$TiSb at a range of 5 Kelvin up to the room temperature. No considerable moment is detected in the material. (b) The susceptibility versus temperature diagram of the compound. As it is seen from the inset graph, there is maximum seen at 8 Kelvin in line with a Neel antiferromagnetic behavior.

Figure 4.12 (a) The Resistance-Temperature behavior of the Fe$_{0.5}$Co$_{0.5}$TiSb compound at zero field (b) The Resistance-Temperature behavior of the Fe$_{0.5}$Co$_{0.5}$TiSb compound at 1kOe. (c) The exponential fit at the less than 10 Kelvin.

4.3.4 Fe$_{0.75}$Co$_{0.25}$TiSb

The alloy was cast by arc melting the constituting elements following the same methodology as the other compositions and a consequent heat treatment at 900 °C as it was the case with the Fe$_{0.5}$Co$_{0.5}$TiSb compound mentioned in the previous section.
In order to obtain the structural signature of alloy an XRD pattern was taken from a sample with the aim to examine the possibility of a single-phase compound emergence as it was the case with the Fe$_{0.5}$Co$_{0.5}$TiSb compound. The corresponding spectrum is illustrated in figure 4.13 which is still showing a C1$_b$ signature present with extra peaks which are not attributable to the known phases. The optical and electron microscopy results showed the evolution of a dual phase microstructure with a granular formation and a secondary intergranular phase emerging in some locations.

These observed morphologies were encountered under different heat treatment cycles and no single phase microstructure could be achieved even at higher temperatures or lengthier dwell times exhibiting the stability of these phases. The EDS analysis showed that the grain composition was somewhat deviating from the initial alloy stoichiometry related to the secondary being almost completely void of cobalt, meaning that there were diffusion of the other three constituting elements to the intergranular loci.
Interestingly the composition of the intergranular phase appeared to be approximately Sb$_{1.8}$Ti$_{1.5}$Fe which is identical to the phase we observed during the heat treatment of FeTiSb alloy. The EDS data taken from at least 13 different grains within the microstructure culminated that the grain composition could be averaged to a stoichiometry of Fe$_{0.64}$Co$_{0.25}$Ti$_{0.77}$Sb$_{0.71}$ with statistical confidence level of 95 percent, which again indicates that the grains have deviated from the starting composition, Fe$_{0.75}$Co$_{0.25}$TiSb and with iron, titanium and antimony diffusing into the grain boundaries and forming the ternary Sb$_{1.8}$Ti$_{1.5}$Fe composition with cobalt basically present within the grains only. Figures 4.14 (a) and 4.14 (b) show the optical micrograph and a corresponding SEM image of the microstructure with grains and the secondary phase respectively. It is also noteworthy the intergranular phase has the same morphology witnessed in the FeTiSb system which is somewhat lamellar.
Figure 4.14 (a) An optical micrograph of the Fe$_{0.75}$Co$_{0.25}$TiSb alloy showing grain formations and evolution of a secondary phase between them. (b) SEM image exhibiting the grains and the secondary phase found to have a stoichiometry of Sb$_{1.8}$Ti$_{1.5}$Fe through EDS.

As the XRD pattern of this alloy had a C1$_b$ signature while the stoichiometry of the grains was somewhat deviated from the C1$_b$ composition itself, we decided to perform an EBSD phase mapping on the microstructure of this alloy with the target phase being the C1$_b$ Fe$_{0.5}$Co$_{0.5}$TiSb so that we could see if the mapping process can attribute the C1$_b$ phase to the off-stoichiometric grains so that the source of the C1$_b$ signature in the XRD pattern is thus elucidated. Figure 4.15 shows the results of such an EBSD scan. Figure 4.15 (b) clearly shows a full coloring of the grains in red, signifying the presence of the target C1$_b$ there. The assigned volume fraction of the C1$_b$ stands at approximately 75 percent with the rest attributable to the ternary secondary intergranular phase, voids and porosities.
Figure 4.15 (a) Electron Backscatter band contrast image of a large section of the Fe$_{0.75}$Co$_{0.25}$TiSb alloy. (b) The phase map taken from the cross section attributes the C1$_b$ Fe$_{0.5}$Co$_{0.5}$TiSb structure to the grains (colored red). The rest of the microstructure is colored black. (c) The relevant orientation map and inverse pole figure of the cross section.

Magnetometry behavior of the material obtained from VSM measurements show a mostly paramagnetic behavior dominating with some weak contribution from possible magnetic impurities within the material. This negligible magnetic effect might arise from small magnetic phases of iron or cobalt emerging at this alloy concentration. Figure 4.16 shows the room temperature and near-absolute zero hysteresis loops.

Figure 4.16 The 5 Kelvin and 300 Kelvin hysteresis loops of the Fe$_{0.75}$Co$_{0.25}$TiSb alloy.
4.3.5 FeTiSb

Here we refer to our previous findings in the Fe-Ti-Sb system. In our initial theoretical studies, the half Heusler FeTiSb compound was expected to be a stable half metallic compound. Microstructural analysis showed that the material in fact decomposed into two separate phases. One is the iron rich Fe$_{1.5}$TiSb phase with a strong presence of a Titanium-Antimony rich phase. Figure 4.17 displays the optical micrograph and also EDS analysis of these two separate phases. The composition of the Titanium and Antimony rich phase was found out to be approximately Sb$_{1.8}$Ti$_{1.5}$Fe which was encountered in the previous section’s quaternary alloy as well. Presence of this phase can be attributed to the iron phase Fe$_{1.5}$TiSb to be the dominating phase and as the overall composition of FeTiSb is iron deficient compared to the dominant phase, unlike the case of Fe$_2$TiSb in which the excess iron precipitated on the grain boundaries in this case the excess Titanium and Antimony have formed a new granular phase indicating that the level of the solubility of the dominant phase for Titanium and Antimony might be less than its solubility level for iron.

Figure 4.18 shows the result of the XRD analysis of the sample. It shows the presence of the L2$_1$ which originate from the Fe$_{1.5}$TiSb while there are obscure peaks in the low angle which could be attributed to the titanium and antimony rich grains.
Figure 4.17 (a) An optical metallography image of FeTiSb exhibiting two distinct granular phases present. (b) The SEM image and the relevant EDS of the intergranular secondary phase being Sb$_{1.5}$Ti$_{1.5}$Fe. (c) The composition of the grains was found to be Fe$_{1.5}$TiSb.

Figure 4.18 The XRD spectrum of the FeTiSb compound. Most peak positions can be attributed to an L2$_1$ structure while there are some obscure peaks possibly arising from Titanium and Antimony rich phase.

4.4 First-Principle Calculations of Fe$_{0.5}$Co$_{0.5}$TiSb Electronic Bandstructure

Using first-principles calculations based on density functional theory (DFT), we investigate the structural order, energetics, and electronic structure of the single-phase Fe$_{0.5}$Co$_{0.5}$TiSb.
Since our experimental measurements indicate that the material assumes a C1\textsubscript{b}-type lattice, we begin by systematically investigating the energetics of various atomic configurations at the composition. We construct a cluster expansion for the energy of mixing of Fe, Co atoms on the X-site (\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)) of a XYZ C1\textsubscript{b} structure and identify the lowest-energy ordered structure. We find an overall low energy of mixing, of the order of 0.020 eV/site, indicating possible Fe-Co disorder in the material at RT or higher temperatures. Our calculations predict that the energy gain (i.e., \textit{increase in stability}) due to ferromagnetic order (FM) in the material, when compared to the non-spin polarized, non-magnetic (NM) structure is small: \(\sim0.007\) eV/atom. Nonetheless, all the atomic configurations sampled at the Fe\(_{0.5}\)Co\(_{0.5}\)TiSb composition, exhibited a near half-metallic electronic structure with the Fermi level falling at the edge of the gap in one spin channel (minor) and a finite density of states in the other spin channel (major).

Based on (a) the insignificant increase in stability due to FM order, and (b) semiconducting behavior of Fe\(_{0.5}\)Co\(_{0.5}\)TiSb in experiments, we explore other magnetic configurations, namely, different kinds of antiferromagnetic (AFM) order in the material. Of the AFM configurations sampled, we find a few (see Figure 4.19) that are almost degenerate (i.e., within 0.001-0.002 eV/atom) with the lowest energy FM configuration. This is an indication of competition between different exchange interactions, and that a more-complex AFM ordering and/or spin frustration in the lattice may be energetically more favorable than the FM ordering. Further, such energetics predict an extremely low Neel temperature if the 0 K ground state is indeed AFM. As expected, all the AFM configurations sampled show a (near) metallic electronic structure with the Fermi energy falling within the valence band but close to its maximum. This delicate electronic structure is likely to be destroyed by local off-stoichiometry, impurities, etc. due to the resulting change in the electron count.
The antiferromagnetic atomic configuration is also shown at figure 4.20. Once again the energy competition between such an antiferromagnetic phase and the potential ferromagnetic is near enough for the former to become possibly stable.

**Figure 4.19** Calculated electronic density of states (DOS) of Fe\(_{0.5}\)Co\(_{0.5}\)TiSb with (left) ferromagnetic (FM) and (right) antiferromagnetic (AFM) order. The FM configuration is a near half-metal with a finite DOS at Fermi energy \(E_F\) in only one spin channel, whereas the AFM configuration is a metal with \(E_F\) at the edge of the valence band and close to its maximum.

**Figure 4.20** Schematics showing a few possible antiferromagnetic configurations in a C1\(b\) Fe\(_{0.5}\)Co\(_{0.5}\)TiSb crystal structure. One such configuration (left) is within 0.9 meV/atom of the ferromagnetic configuration, indicating competition between different exchange interactions and possibly complex magnetic ordering in the system.
4.5 Conclusion

Our investigation into the Fe$_x$Co$_{1-x}$TiSb alloy system showed that in the cobalt-rich part of the stoichiometry the CoTiSb compound was dominating the system with iron segregating into the grain boundaries. No sign of a single-phase alloy was found in this region. Interestingly with iron content reaching the equiatomic ratio with cobalt, i.e. Fe$_{0.5}$Co$_{0.5}$TiSb, enough evidence was garnered to confirm the existence of a postulated C$_1$$_b$ half-Heusler phase when the alloy was heat treated at 900 °C for 3 days.

The further addition of iron though resulted in loss of the single-phase state, with a ternary Sb$_{1.8}$Ti$_{1.5}$Fe phase emerging and the grains becoming somewhat off-stoichiometric though still retaining a C$_1$$_b$ structure.

It is recommended that advanced structural analysis such as Mossbauer spectroscopy and neutron diffraction be performed to further analyze the disorder and atomic defect in the crystal structure of the Fe$_{0.5}$Co$_{0.5}$TiSb phase.

4.6 References


CHAPTER 5
SYNTHESIS AND CHARACTERIZATION OF Co-Ti-Sn ALLOYS:

Co_{1.5}TiSn AS A HALF METAL BASED ON THE Fe_{1.5}TiSb prototype OF LAYERED HEUSLER

5.1 Introduction

The half-metallic materials are optimal candidates for spintronic applications such as spin torque transfer random access memories.\(^1,^2,^3\) Their inherently high spin polarization and Curie temperatures are highly sought for novel magnetic recording devices. Half metallic materials have been found among the family of intermetallic compounds called Heuslers. Theoretical and experimental studies both have hint towards presence of many possible half metals within this class of intermetallics.\(^4,^5\)

Our recent findings on the Fe-Ti-Sb alloy system resulted in the possibility of the existence of an intermediate Heusler stoichiometry which neither follows the 2:1:1 full Heusler atomic ratio nor the 1:1:1 half Heusler one, but instead has the 1.5:1:1 ratio between its constituting elements and therefore can be called a ‘layered’ Heusler.\(^6\) The prototype which was Fe_{1.5}TiSb interested us in searching for the possibility of a hidden class Heuslers with this specific – and yet undiscovered – stoichiometry. Our theoretical calculations led by William H. Butler and Christopher Wolverton and their respective research groups arrived at the possibility of the Co_{1.5}TiSn being a material of interest.

Initial theoretical calculations showed that similar to Fe_{1.5}TiSb, the stacking of Cobalt vacancies in the [111] direction will result to an energetically stable material with an electronic bandstructure of a half metal as shown in figure 5.1.
Figure 5.1 Electronic Bandstructure of the Co$_{1.5}$TiSn in an R3m vacancy stacking. The Fermi level in a minority channel gap while there are majority channel states available leading to a half metallic behavior.

The cluster expansion analysis of the Co-Ti-Sn resulted not only in the Co$_{1.5}$TiSn compound being a stable ground state, but other alloys were seen to be ground states and so stable compounds such as Co$_{1.33}$TiSn, Co$_{1.67}$TiSn and CoTiSn.

Our initial literature survey showed that although that Co$_2$TiSn has been extensively studies in the past decades as a Heusler compound$^{7,8,9}$ and more recently established theoretically and experimentally as half metal by the means of ab-initio calculations and Andrew Reflectivity respectively.$^{11,12,13}$ There was only one instance related to the Co$_{1.5}$TiSn being mentioned in the scientific literature in which the named compound was confirmed to be the main phase in the CoTiSn alloy alongside some titanium and tin phases. The study was solely concentrated on neutron diffraction of the CoTiSn alloy.$^{14}$
Encouraged by the previous report on Co$_{1.5}$TiSn being stable, and also capitalizing on the fact that microstructural analyses on the bulk Co-Ti-Sn were scarce in the scientific literature, we found impetus to embark on studying this alloy system using the very same methodology we adopted in successfully characterizing the Fe-Ti-Sb alloys which led to finding of Fe$_{1.5}$TiSb as an unknown phase.

5.2 Experimental

Stoichiometric ratios of pure elements, Co (Alfa Aesar, 99.5%), Ti (Alfa Aesar, 99.9%) and Sn (Alfa Aesar, 99.99%+) were mixed together and molten using an Edmund Bühler Mini MAM-1 compact arc melting system under an ultra-high purity Argon pressure of 0.02 Pa. A titanium oxygen getter was melted before all the runs to avoid any potential oxidization of the sample. The ingots were flipped and remelted at least 5 times to ensure the proper mixing of the all the three elements and eventual homogeneity of the material. The bulk samples were then cut and mounted for metallographic studies. A JEOL 7000 Field emission scanning electron microscope (SEM) was used for the energy-dispersive x-ray spectroscopy (EDS) to ensure the chemical composition of the as-cast ingots had not deviated from the intended target stoichiometry. The heat treatment samples were wrapped with Tantalum and were sealed under vacuum in quartz tubes in a vacuum atmosphere to avoid oxidation. The pieces were heat treated in various temperature and dwell times out of which a cycle of treatment at 900 °C for 3 days and cooled in the furnace with an approximate rate of 90 °C per hour appeared to result in the optimum structure and a homogenous microstructural stoichiometry for the mainly-sought Co$_{1.5}$TiSn compound. The heat treated samples were then mounted in a conductive metallographic mount and grinded and polished with polycrystalline diamond and colloidal silica solutions. The crystal structure was then studied using a Bruker D8 Discover X-Ray Diffraction (XRD) system with a monochromatic cobalt K$_a$ radiation.
In order to minimize the surface and crystal orientation effects the samples were rotated in the $\varphi$ axis during the XRD analysis. Also, electron backscatter diffraction (EBSD) phase map was performed to affirm the structure observed on the XRD pattern using the JEOL 7000 FE-SEM system. Care was taken so that the EBSD step size does not exceed the tenth of smallest microstructural feature so that no phase is left out during the scanning process. The simulated XRD patterns were obtained by using a CaRine crystallography 4.0 software and the Rietveld refinement was carried out through a Match! Software based upon FullProf algorithm. The magnetic and electric properties were measured using a Quantum Design Dynacool$^\text{TM}$ system ranging from 5 Kelvin to 400 Kelvin.

5.3 Results and Discussion

5.3.1 Co$_{1.5}$TiSn

The alloy was arc melted using stoichiometric ratios of cobalt, titanium and tin. The workpiece was remelted several types to ensure complete mixing of the constituting elements. EDS analysis of the different sections and magnifications of the as-cast sample showed a 1.5:1:1 ratio existing between the main elements as intended.

Optimal homogenization cycle was found to be a 3-day heat treatment at 900 $^\circ$C resulting in a single grain microstructure. It should be noted that dwell times longer than 3 days and temperatures higher than 900 $^\circ$C proved to be detrimental in the sense that the impurity phases started to emerge in the microstructure under such conditions.

Optical metallography revealed a microstructure in forms of grains and no trace of a secondary phase. Only natural porosities were observed. The electron microscopy under SEM also showed the absence of any impurity other than the grains.
The EDS also confirmed that the stoichiometry of the grains has an average of Co\textsubscript{42at.\%} Ti\textsubscript{28at.\%} Sn\textsubscript{28at.\%} which is in very good agreement of the starting target composition. The microstructure micrographs are shown in figure 5.2.

![Figure 5.2](image)

**Figure 5.2** (a) The optical micrograph of a Co\textsubscript{1.5}TiSn sample homogenized at 900 °C for 3 days. The presence of grains and some gas porosities are seen. (b) The SEM image of the same sample. The selected EDS region showed a good agreement with the final Co\textsubscript{1.5}TiSn hinting the grains having the intended composition.

In order to study the crystal structure of this single-phase alloy, a lattice cell was constructed. The model for this cell was based on our assumption that similar to the Fe\textsubscript{1.5}TiSb, the Co\textsubscript{1.5}TiSn is also basically an L2\textsubscript{1} structure with two atoms missing in the 8c (1/4, ¼, ¼) position and titanium in 4b (1/2,1/2,1/2) and tin at the 4a (0,0,0) positions respectively. This meant that in the crystal simulations a 75 percent occupancy level at the 8c position should be considered, as for a 1.5:1:1 stoichiometry it is needed to reduce the multiplicity number of the 8c position from 8 to 6 in order to meet the required 6:4:4 ratio between the atomic positions multiplicity numbers.

The assessment of the presumed crystal model was done through XRD diffraction and its consequent Rietveld refinement. The obtained spectrum showed a signature of L2\textsubscript{1} lattice and no unrelated peak was observed further indicating the presence of a single-phase material as it was previously seen under the microstructure.
The Rietveld fit to the presumed crystal model resulted in good agreement with highly satisfactory fitting parameters of reduced $\chi^2$ of only 1.4 and weighted average $R_{\text{Bragg}}$ factor of 0.4.

The initially adopted Wyckoff positions were not changed after final convergence showing the validity of the model. The fitted lattice constant of the material was 6.001 Angstroms. The experimental XRD pattern and its Rietveld fit can be seen in figure 5.3.

![Figure 5.3](image)

**Figure 5.3** The experimentally observed pattern of Co$_{1.5}$TiSn, the calculated fit and the difference pattern.

The microstructural and structural data and their good agreement to the assumed model inspired us to further analyze the material through a phase map using EBSD method. The goal was to search for the target phase in the microstructure and any possible impurity present. Therefore the same atomic coordinates and lattice constant explained previously were adopted as the target phase. The material was scanned at a relatively large area size to include as many morphological and secondary phases as possible. The adopted step size of 0.3 micron was much less than the average grain size, which was 60 microns, to ensure a thorough scanning of the entire microstructure.
The obtained EBSD phase map showed an impressive 98 percent match with the microstructure. The remainder unresolved morphologies could be attributed to grain boundaries and surface effects. The respective maps are shown in figure 5.4.

**Figure 5.4** (a) The band contrast image of the Co\(_{1.5}\)TiSn alloy microstructure. An fully equiaxed cross section is observed. (b) The phase map of the same cross section. All the morphological features are colored red, which indicates a 98 percent match with the target Co\(_{1.5}\)TiSn phase structure.

Figure 5.4 (a) shows the band contrast image of the chosen microstructure cross section which shows a granular microstructure with no sign of any secondary morphology. In figure 5.4 (b) the grains are all colored red which stands for the assumed Co\(_{1.5}\)TiSn structure and thus is indicative of a homogenized single phase alloy having the L2\(_1\) structure with Cobalt vacancies in the 8c position as the initial model was adopted.

The characterization of the structure and microstructure revealed a single-phase alloy and so we decided to obtain the magnetic properties of this compound, which showed a very good agreement with our crystallographic target model. The room temperature hysteresis loop measurement showed a paramagnetic behavior as seen in figure 5.5 (a). Interestingly the near absolute zero loop obtained at 5 Kelvin not only a magnetic behavior resembling a Heusler compound with a soft magnetic hysteresis, but also the saturation moment was measured to be 0.63 \(\mu_B\)/f.u. which is interestingly quite near the predicted 0.5 \(\mu_B\)/f.u. value for the half metallic compound. (Figure 5.5 (b)).
Figure 5.5 (a) Paramagnetic behavior of Co$_{1.5}$TiSn compound at 300 Kelvin. (b) The hysteresis loop of the material at 5 Kelvin. The saturation moment stands at 0.63 μB/f.u. A comparison between both the room temperature and the near-absolute zero temperature behavior is also shown.

The results so far hinted towards a high probability that the Co$_{1.5}$TiSn is indeed a single-phase material with the predicted structure and half metallic moment. As the material showed paramagnetic behavior at room temperature, we considered to test the Rhodes-Wohlfarth model on it to see if the effective paramagnetic moment is much smaller compared to its saturation moment at near absolute zero temperatures, which has been suggested as a hallmark of half metallicity.

Rhodes-Wohlfarth was initially proposed to evaluate the nature of electronic contribution in the ferromagnetic material, if the ratio was around 1, the material behaved as a Heisenberg magnet with localized electron contribution while ratios higher than one was attributed to itinerant electrons dominance. The pioneers of the half metallicity encountered an unusually low Rhodes-Wohlfarth ratio for the established half metals which was much lower than 1.
This unprecedented behavior was attributed to drastic reduction of magnetic moment upon entry into paramagnetic moment as the density of states available was considerably reduced due to the presence of a bandgap in the half metallic material.\textsuperscript{19,20} The ratio is defined as $p_c/p_s$ with $p_s$ being the saturation moment per formula unit at zero Kelvin and $p_c$ defined as $\mu_{\text{eff}}^2 = p_c (pc+2)$. $\mu_{\text{eff}}$ being the effective paramagnetic moment, calculated from Curie-Weiss law, $C = (N\mu_{\text{eff}}^2) / 3A.k$, and $C$ being Curie-Weiss constant derived from the inverse mass susceptibility formula, $\chi^{-1} = (T-\theta)/C$. The Inverse mass susceptibility of Co$_{1.5}$TiSn compound was obtained with respect to temperature to derive the $C$ constant, which was found to be $2.437 \times 10^{-5}$ emu.Kelvin/gr.Oe. (Figure 4.6).

![Figure 5.6](image)

**Figure 5.6** (a) The inverse mass susceptibility behavior of Co$_{1.5}$TiSn with respect to temperature at 2 Tesla (b) Linear portion of the paramagnetic region of the same graph. The slope, equating to $1/C$, was found to be 41027 gr.Oe/emu.Kelvin.

Using the $C$ value, the $\mu_{\text{eff}}$ was calculated to be 0.223 $\mu_B$ and consequently $p_c$ was obtained as only 0.02 $\mu_B$. Dividing the $p_c$ by $p_s$, which is the saturation moment at 5 Kelvin, or 0.64 $\mu_B$, we found the Rhodes-Wohlfarth ratio to be 0.03 which is much lower than 1, bearing a signature of a half metallic behavior.
5.3.2 Co$_2$TiSn

Encouraged by our findings on Co$_{1.5}$TiSn compound, we decided to test our methodology further on the established half metallic compound of the Co-Ti-Sn, or Co$_2$TiSn. Another impetus for our consideration was the fact that the microstructural analysis of this compound was scantly reported giving us an ample ground for analysis.

The starting sample was prepared through arc melting of appropriate weight percentages of constituting elements. The sample was remelted at least 3 times to ensure full mixing and lack of any macrosegregation. The optimal homogenization cycle was found to be a heat treatment at 1000 °C for 7 days. It should be mentioned that the heat treatment at 900 °C rendered a dual-phase microstructure with cobalt impurities and treatment done at temperatures lower than 800 °C resulted in the inhomogeneous dendritic structure.

The microstructure of the homogenized sample is shown at figure 5.7

![Figure 5.7](image)

**Figure 5.7** (a) The optical metallography of the Co$_2$TiSn alloy heat treated at 1000 Celsius for 7 days. The microstructure is single-grain with some naturally occurring porosity. (b) The SEM image of the same cross section and EDS of a grain which exhibited a target stoichiometry of Co$_{49\text{at.\%}}$Ti$_{24\text{at.\%}}$Sn$_{24\text{at.\%}}$. 

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The figure 5.7 (a) reveals a homogenized microstructure with no sign of dendrites or intergranular phases but a fully equiaxed structure with relatively large grains beyond a 100 micron margin. The SEM also confirmed no presence of any secondary phase with EDS indicating a target composition of Co₂TiSn for the grains in figure 5.7 (b).

As the initial microstructural results hinted towards the alloy being pure phase and having the intended stoichiometry, an XRD spectrum was also obtained to evaluate the crystal structure. Once again as reported in the literature, we expected to observe a full Heusler L₂¹ signature and this was exactly seen in the data. Figure 5.8 shows the obtained pattern. All the peaks of the L₂¹ signature are seen and marked with no excess peak attributable to any possible secondary phase. The lattice constant was derived to be 6.078 Angstroms which is not far from the value reported in the literature for this material. ⁹

![Figure 5.8](image.png)

**Figure 5.8** The XRD Pattern of the Co₂TiSn using a Kα Cobalt source. All the peaks are related to the L₂¹ expected pattern.
In order to further strengthen the case for the presence of a single-phase Co$_2$TiSn alloy with no impurities and an L$_2$$_1$ full Heusler crystal structure, a phase mapping of microstructure was also performed using the Wyckoff positions of the L$_2$$_1$ prototype and a lattice constant of 6.078 Angstroms. The respective maps are shown in figure 5.9. The area was chosen large enough to cover as much as microstructural features as possible.

![Band Contrast Image and Phase Color Image](image)

**Figure 5.9** (a) Band contrast image of a Co$_2$TiSn cross sectional area with relatively large grains and some intergranular porosity. (b) The relative phase map showing almost the entirety of the microstructure colored red signifying a high match with the intended L$_2$$_1$ phase.

Figure 5.9 (a) reveals a relatively large granular structure with grain sizes at least 200 microns and beyond. The figure 5.9 (b) is the phase map taken from the same area with a 92 percent matching which indicated there is a good agreement between the microstructure and the sought phase. The remaining unresolved 8 percent can be attributed to the porosities, grain boundaries and surface noise effects.

The evidence for a pure phase material was sufficient for us to proceed to the magnetic evaluation of the Co$_2$TiSn. The material was found to be behaving magnetically at room temperature as a full hysteresis loop was obtained. The near-absolute zero hysteresis loop was obtained at 5 Kelvin.
The material was still exhibiting a hysteresis loop typical of Heuslers with no low coercivity and a soft magnetic behavior due to lack of magnetocrystalline anisotropy of the cubic Heusler structure. The saturation moment at 5 Kelvin was found to be 2.11 µB/f.u., which is in very good agreement with the expected Slater-Pauling moment of the half metallic Co$_2$TiSn. The value is quite similar as those reported previously on this compound. The relevant loops are shown in figure 5.10.

![Hysteresis Loop Diagrams](image)

**Figure 5.10** (a) The hysteresis loop of the homogenized Co$_2$TiSn at 300 Kelvin. (b) The hysteresis loop at 5 Kelvin. The saturation moment is calculated to be 2.11 µB/f.u.

As the saturation moment here was in concordance with its expected half metallic Slater-Pauling moment, it was decided to apply the Rhodes-Wohlfarth model to see if the ratio will again drop to less than 1. For this goal the inverse mass susceptibility versus temperature of the material was obtained in both cooling and heating modes from low temperatures to the high-temperature paramagnetic region of the material. Also a linear fit for the paramagnetic region was drawn whose slope equals 1/C and the related value was found 7510 gr.Oe/emu.Kelvin. The inverse mass susceptibility plot and the linear fit of its paramagnetic region is shown at figure 5.11.
Introducing the C value into the formula $C = \frac{(N\mu_{\text{eff}}^2)}{3A.K}$, the $\mu_{\text{eff}}$ will be equal to 0.55 $\mu_B$. And considering $\mu_{\text{eff}}^2 = p_c(p_c+2)$, the $p_c$ will be 0.14 $\mu_B$. As the saturation moment was 2.11 $\mu_B$, the Rhodes-Wohlfarth ratio will be 0.07, which is much less than unity and indicates a high presence of spin polarized electrons or a half metallic signature like the previous case of Co$_{1.5}$TiSn.

5.3.3 Co$_{1.75}$TiSn

The findings of the two L2$_1$-based compounds, Co$_2$TiSn and Co$_{1.5}$TiSn, with half metallic properties and also theoretical predictions by our colleagues in professor Wolverton group induced us to consider an intermediate alloy between the named compounds which obviously was the Co$_{1.75}$TiSn. The sample was arc melted based on its formula and the stoichiometric relation between constituting elements. The homogenization cycle was empirically found to be 15 days at 1000 °C. Lower dwell times and temperatures all resulted in inhomogeneous microstructures. The related optical and electron micrographs are shown in figure 5.12.
Figure 5.12 (a) Optical metallography image of the homogenized Co$_{1.75}$TiSn sample. Large grains with some porosity are seen. (b) The SEM image of the same area and an EDS taken from a grain indicate that the composition is consistent with the intended stoichiometry of Co$_{1.75}$TiSn.

The 5.12 (a) image shows a homogenized microstructure with large grains beyond a margin of 200 microns which is expected considering the high temperature and lengthy treatment cycle of heat treatment. 5.12 (b) shows a SE image and an EDS taken from a grain. The average composition was standing at Co$_{47}$ at.% Ti$_{27}$ at.% Sn$_{27}$ at.% which translates into the target stoichiometry and hints a full homogenization.

The XRD analysis of the pattern obtained from the sample still showed the same L2$_1$ signature observed for the previous cases of the Co$_{1.5}$TiSn and Co$_2$TiSn. The corresponding spectrum is shown at figure 5.13. This might be an interesting find in the sense that it infers the possibility of a solid-solution region present from the chemical range of Co$_{1.5}$TiSn to Co$_2$TiSn, as not only the microstructure is single-phase in this range but also the crystal structure remains the same within this area.

The magnetic measurements of the material showed also a mitigated saturation moment between the values of Co$_{1.5}$TiSn and Co$_2$TiSn at 5 Kelvin with a value of 1.68 $\mu_B$/f.u. Also similar to the Co$_2$TiSn the material was still behaving magnetic at room temperature. (Figure 5.14)
Figure 5.13 The XRD Spectrum of Co$_{1.75}$TiSn compound. All peaks are attributed to an L2$_1$ signature.

Figure 5.14 The hysteresis loop of the Co$_{1.75}$TiSn compound at 5 Kelvin and 300 Kelvin.

The application of the Rhodes-Wohlfarth model also bore interesting results. The slope of the paramagnetic part of the inverse mass susceptibility was found to be 8721 using which we arrived at a $\mu_{\text{eff}}$ equal to 0.424 $\mu_B$ and a consequent $p_c$ of 0.193 $\mu_B$, which if divided by saturation moment at 5 Kelvin, 1.68 $\mu_B$, will bear a Rhodes-Wohlfarth ratio of only 0.11, very similar to values witnessed for Co$_2$TiSn and Co$_{1.75}$TiSn. (Figure 5.15).
Figure 5.15  (a) Inverse mass susceptibility of Co$_{1.75}$TiSn with respect to temperature at 3 Tesla (b) The linear fit to the paramagnetic region.

As this compound is also showing a hallmark of half metallicity as far as the Rhodes-Wohlfarth model is concerned while also exhibiting a L2$_1$ signature, the interesting question here might be the possibility of a half metallic ‘region’ instead of only a compound being present in the range of Co$_{1.5}$TiSn all the way to Co$_2$TiSn.

5.3.4 CoTiSn

The CoTiSn composition has been reported to be a compound in some literature although no microstructural or structural evidence to verify such a claim has been offered. A more recent report by Nobata, Kurisu and their coworkers based mainly on neutron diffraction analyses showed that the CoTiSn alloy basically decomposes into mostly a Heusler-type Co$_{1.5}$TiSn (70 volume percent) plus some titanium and tin compounds. Here also a microstructural evaluation was lacking so it inspired us to do the same course of research we did before for this CoTiSn alloy as well especially now that no microstructural evidence was found on this system and considering that we already had synthesized a single-phase Heusler-type Co$_{1.5}$TiSn similar to the Nobata report.
So once again an alloy was formed through arc melting of main elements and the EDS of the as-cast sample proved the exact targeted ratio. Different heat treatment cycles showed that up to 900 °C and up to 15 days the material remained inhomogeneous as the microstructure were overwhelmingly dendritic.

The dendritic morphology disappeared at 1000 °C and a dwell time of 7 days giving way to a multiple phase microstructure. There were three distinct phases visible under the optical microscope: A matrix upon which other phases are embedded, a larger and brighter phase and a smaller and darker one. A metallographic optical micrograph of the microstructure is shown at figure 5.16.

![Figure 5.16](image)

**Figure 5.16** The microstructure of the CoTiSn heat treated for 7 days at 1000 °C. Three distinct morphological features can be differentiated.

The EDS analysis of the microstructure during the SEM showed that the matrix mostly has a stoichiometry of Co_{44at.%}Ti_{29at.%}Sn_{29at.%}, which can be rewritten as Co_{1.5}TiSn. The larger sized embedded phase which looked brighter under the optical microscope was found to be pure tin. The darker and smaller sized feature in the meantime showed a binary stoichiometry of Ti_{53at.%}Sn_{47at.%}. The related SEM micrographs are shown below in figure 5.17.
Figure 5.17 (a) EDS data taken from a rectangular area of the matrix. The composition conformed to \( \text{Co}_{1.5}\text{TiSn} \). (b) The embedded phase in figure (a) is measured to be \( \text{Ti}_{53}\text{at.}\%\text{Sn}_{47}\text{at.}\% \). (c) The smaller-sized features were found to be pure Sn.

The results are in good agreements with Nobata and Kurisu’s findings. According to their neutron diffraction and subsequent Rietveld analyses the CoTiSn decomposed into mostly \( \text{Co}_{1.5}\text{TiSn} \), which is exactly what we observed with this compound being the matrix of the microstructure. Also according to their report the remaining phases were Sn and \( \text{Ti}_6\text{Sn}_5 \) both of which are seen in our study with the latter phase being \( \text{Ti}_{53}\text{Sn}_{47} \) in our case.

To further analyze the structure a XRD test was done on the sample. The data resulted in a spectrum showing a \( \text{Co}_{1.5}\text{TiSn} \) signature plus some peaks which could be attributed to tin and also some to a \( \text{Ti}_6\text{Sn}_5 \) phase. The spectrum is shown at figure 5.18.
Figure 5.18 The XRD spectrum of a CoTiSn sample heat treated at 1000 °C for 7 days. The Co$_{1.5}$TiSn, Ti$_6$Sn$_5$ and Sn peaks are assigned with red, green and blue asterisks respectively.

This is in concordance with our microstructural findings as all the phases seen by microscopy are also present in the XRD pattern and once again phases marked by Nobata group using neutron diffraction is also witnessed through the X-Ray pattern.

5.3.5 Co$_{1.33}$TiSn

As initial cluster expansion prediction by our colleagues in the Wolverton group considered a possible Co$_{1.33}$TiSn ground state and a compound, measures for preparing this alloy were taken. The alloy was processed by arc melting the constituting elements and the as-cast was remelted to ensure homogeneity which was verified by the EDS of the as-cast pieces showing the target stoichiometry. The optimal homogenization cycle was found to be 7 days at 900 °C following different empirical heat treatment trials.
The metallography revealed that there were two distinct morphologies present in the system: A granular phase which comprised the most of the microstructure and a secondary phase located in-between the grains. The related images are shown in figure 5.19 (a). In order to analyze the chemical composition of these morphologies an EDS under the SEM was performed. The results pointed out that the grains which were the dominant phase as far the volume fraction was concerned were in fact having the Co$_{1.5}$TiSn, similar to the case of the multiple-phase CoTiSn alloy which also had the Co$_{1.5}$TiSn phase dominating the microstructure in the form of a matrix.

The SEM micrograph taken from the several features of the microstructure is also shown in figure 5.19 (b). The intergranular secondary phase showed a stoichiometry of Ti$_6$Sn$_5$ similar to the case of CoTiSn. In contrast to the CoTiSn system here no tangible trace of tin was seen.

Figure 5.19 (a) The optical micrograph of a Co$_{1.33}$TiSn alloy heat treated at 900 °C for 7 days. Two different phases are observable. (b) The SEM micrograph of the same sample with respective EDS of the features showing the dominant phase to be Co$_{1.5}$TiSn and the intergranular one to be Ti$_6$Sn$_5$.

The structural analysis of this alloy by XRD was also in agreement with the microstructural observations.
The obtained spectrum had a $\text{Co}_{1.5}\text{TiSn}$ signature alongside additional peaks related to the $\text{Ti}_6\text{Sn}_5$ phase. Here also no sign of the tin phase seen in the CoTiSn alloy were witnessed. The result is shown in figure 5.20

![XRD Spectrum](image)

**Figure 5.20** The XRD Spectrum obtained from a $\text{Co}_{1.33}\text{TiSn}$ Sample. The pattern shows peaks related to the $\text{Co}_{1.5}\text{TiSn}$ and $\text{Ti}_6\text{Sn}_5$ phases.

The presence of a phase besides the dominant $\text{Co}_{1.5}\text{TiSn}$ indicates that $\text{Co}_{1.33}\text{TiSn}$ is not a compound but a mixed phase like the case of the CoTiSn system. The magnetic behavior of these two alloys was studied by obtaining hysteresis loops at 5 degree Kelvin. The saturation moment of the $\text{Co}_{1.33}\text{TiSn}$ alloy was found to be 0.55 $\mu_B$/f.u. which is lower than the value seen for the $\text{Co}_{1.5}\text{TiSn}$ system.
The reason for this reduction is that the Co$_{1.33}$TiSn system has a magnetic component which is Co$_{1.5}$TiSn, that is also the dominant microstructural phase, and some non-magnetic impurities which contribute to this relative decrease in the saturation moment. The respective hysteresis loops of these two alloys are shown in figure 5.21.

![Hysteresis Loops](image)

**Figure 5.21** (a) Hysteresis loop of Co$_{1.33}$TiSn alloy at 5 Kelvin. The saturation moment was found to be 0.55 $\mu_B$/f.u. (b) Hysteresis loop of CoTiSn alloy at 5 Kelvin. The saturation moment was found to be 0.47 $\mu_B$/f.u., which is less than the amount for Co$_{1.33}$TiSn.

The CoTiSn alloy shows a lower value of the saturation moment with respect to the Co$_{1.33}$TiSn system, as in the former the volume fraction of the dominant magnetic phase which is Co$_{1.5}$TiSn is now lower as alongside the Ti$_6$Sn$_5$ secondary phase there are also tin impurities emerging in the microstructure contributing to a reduction in moment as tin is also non-magnetic.

One can summarize our findings on the magnetic behavior and the phase distribution of the Co-Ti-Sn Heusler system in the form of a graph such as the one presented in figure 5.22. It is observable that in the single-phase region, the reduction on cobalt content will lead to a tangible reduction in the compound moment as well. This can be explained in the way that the L2$_1$ lattice is quite sensitive to the presence of the magnetic cobalt atom in the tetrahedral positions and any reduction of it in the structure will result in a considerable moment decrease.
Here should be mentioned that we also synthesized a Co$_{1.62}$TiSn alloy which like its adjacent counterparts appeared to be a L2$_1$ compound with a single-phase microstructure and a Rhodes-Wohlfarth model of half metallicity, but for the sake of brevity the details of process and characterization are not mentioned.

As soon as the cobalt content goes below the Co$_{1.5}$TiSn borderline, the alloys deviate from their previous single-phase behavior and multiple phase start to emerge in the structure. Still the dominant phase was seen to be the Co$_{1.5}$TiSn, while the rest of the phases were non-magnetic therefore here the magnetic behavior almost appeared to be reaching a steady-state, with magnetic moment steadily decreasing with emergence of the non-magnetic contributors within the alloy the system.

![Graph](image)

**Figure 5.22** The magnetization and phase behavior in the Co$_x$TiSn.
It is interesting to add that the same trend witnessed in the figure 5.22 was also reported by the Pierre and coworkers. Nevertheless in the mentioned report, all the alloys of the same range in our figure 5.22 was reported to be pure-phase compounds without any microstructural or structural evidence, while our studies shows that the single-phase behavior only exists in the Co_{1.5-2}TiSn stoichiometric range and the CoTiSn decomposes into three phases almost exactly as the report by Nobata.

5.4 Conclusion

The Co-Ti-Sn alloys from their half to full Heusler equivalents were synthesized. It was seen that the Co_{1.5}TiSn was indeed a compound as predicted by our theoretical calculations with a hallmark of L2_1 structure with cobalt vacancies in the tetrahedral positions similar to our previous findings on Fe_{1.5}TiSb compound. The magnetometry measurement also was in good agreement with theory prediction of this compound being a half metal. Further magnetic analysis by Rhodes-Wohlfarth also hinted into an unusually low ratio, which also is a fingerprint of half metallicity. It was also seen that the Co_{1.5}TiSn to Co_{2}TiSn has an L2_1 signature and also microstructurally single-phase therefore raising the possibility of a solid-solution region in this chemical range. The compounds of this range also showed the unusually lower than unit Rhodes-Wohlfarth ratio which again is a hallmark of half metallicity.

The alloys with cobalt content less than the one for Co_{1.5}TiSn decomposed into a dominant magnetic phase of Co_{1.5}TiSn and intergranular Ti_{6}Sn_{5}, which also included another phase which was found to be tin in the case of CoTiSn.
This finding might open a door to the possibility of a 1.5:1:1 stoichiometry of Heusler compounds present which has been overlooked until now. The exploitation of this ‘layered’ Heuslers might be assistive in various functional electronic materials applications.

5.5 References


CHAPTER 6

CONCLUSION

Following our theorist colleagues recommendations, we obtained an extensive list of possible candidates of Heuslers with potential half metallic bandstructure. Among all of this large number of possible compounds, the Fe$_2$TiSb attracted our interest as the initial literature survey did not result in any scientific report on the experimental process of this metallic compound and also according to our density functional theory predictions this compound had a half metallic bandstructure with a relatively low moment of 1 Bohr magneton per formula unit, making it a viable candidate for spintronic explorations.

Our first processing attempts through arc melting and eventual homogenization treatments showed that at 900 °C the alloy was fully homogenized with equiaxed grains forming. The scanning electron microscopy and subsequent energy-dispersive X-Ray spectroscopy studies revealed that in fact these newly formed grains were deviating from the initial stoichiometry of the Fe$_2$TiSb, and were actually showing a Fe$_{1.5}$TiSb composition. Further analyses confirmed that this stoichiometry stood the tests and also indicated that indeed iron-rich precipitates were forming between the Fe$_{1.5}$TiSb grains, accounting for the absent iron with respect to the starting stoichiometry of Fe$_2$TiSb.

The processing of the Fe$_{1.5}$TiSb confirmed the single-phase nature of the alloy, establishing it as a possible compound. The X-Ray diffraction studies revealed a L2$_1$ structure, in line with the Heusler character of the compound.
This was also corroborated through more elaborate diffractive methods such as electron backscatter diffraction maps and transmission electron microscopy selected area diffraction. The magnetic measurement revealed a material void of any significant response with a paramagnetic behavior. Such a result inspired the possible assumption of the Fe$_{1.5}$TiSb compound being a semiconductor. This called for a theoretical treatment of such compound through DFT methodology and subsequent bandstructure derivations, which eventual revealed that indeed the consequent bandstructure is of a semiconductor.

An even more important aspect to the theory of this compound was that according to the Slater-Pauling rule, the Fe$_2$TiSb compound should have an expected moment of 1 $\mu_B$/f.u., and the hypothetical FeTiSb a value of -1 $\mu_B$/f.u. Therefore if we consider the Fe$_{1.5}$TiSb, to be “lying” intermediatively as far as the iron content is concerned between the Fe$_2$TiSb and FeTiSb hypothetical compounds, the corresponding moment which is zero, is also an average of the hypothetical 1 and -1 $\mu_B$/f.u. values as well. This is a novel finding as it indicates that the Fe$_{1.5}$TiSb is in fact ‘layered’ between its two full and half Heusler counterparts and still follows the Slater-Pauling rule. Our theorists, led by Professor Butler, consequently named this compound a newly discovered layered Slater-Pauling phase.

Further on, we tried to process the half Heusler FeTiSb compound, which during our various efforts happened to be an alloy system composed of two different phases one being the previously observed Fe$_{1.5}$TiSb alongside some Ti/Sb rich phase. The theoretical energetics studies through cluster expansion also interestingly hinted that both Fe$_{1.5}$TiSb and a Ti/Sb rich phase are also energetically stable phases, in line with our experimental observations.
The scientific significance of such conclusions lies in the possibility of a yet unexplored stoichiometry available in the Heusler family, which is intermediate between full and half stoichiometries and therefore has a 1.5:1:1 atomic ratio between the ternary X, Y and Z elements. The tetrahedral positions in such compound are in fact vacant in the sense that there are 6 atoms of the X element present. This possible subclass of Heuslers could be an interesting subject of study for both theoretical condensed matter physicists and experimental materials scientists, in order to exploit potentially novel functional materials in the family of Heusler compounds.

The next level of our research concentrated on a quaternary system: As we already had explored the Fe-Ti-Sb Heusler alloys, we decided to take a step further on and add cobalt to this system and perform research on the Fe-Co-Ti-Sb possible Heuslers. The impetus this phase of our research came from our previously mentioned findings and also lack of extensive research on this specific quaternary system with some instances hinting towards of a multiphase alloy system present alongside some reports avoiding the heat treatment of antimony-rich system altogether to bypass the possible loss of the element due to its volatility.

Our course of research was concentrated on the half Heusler section of the alloy system with adding iron as the main doping element to the ternary CoTiSb compound and gradually reaches the iron-rich FeTiSb alloy.

The study revealed that there indeed was a half Heusler compound, Fe$_{0.5}$Co$_{0.5}$TiSb, observable with an established chemical composition and a C1$_b$ signature. Various characterization techniques confirmed the homogeneity of the alloy, and the half Heusler nature of it. There were no reports of any single-phase compound in this quaternary system previously.
Magnetic analysis eventually showed an antiferromagnetic behavior which was also in line with the theoretical energetic studies showing a favorable competition for the stability of a C1b Fe0.5Co0.5TiSb compound becoming antiferromagnetic rather than ferromagnetic.

No other compound were observed in this system and there were a prevalence of the CoTiSb phase in the cobalt-rich side of the alloys and in the iron-rich side there were competition between the possible C1b and titanium/antimony phases appearing in the microstructure, the latter both observed and theoretically found to be stable in our previous research on the Fe-Ti-Sb system.

The last phase of our research was based on the Fe1.5TiSb layered Heusler we discovered before: Following this interesting finding, Professor Butler took interest in a hypothetically similar compound, Co 1.5TiSn. Initial first-principle studies by Professor Butler and our colleagues in the Northwestern University resulted that a possible layered Heusler of the named composition would attain a half metallic bandstructure with an estimated saturation moment of 0.5 µB/f.u.

Our literature survey showed the scarcity of microstructural analysis on the Co-Ti-Sn system with the Co2TiSn being more exploited as a half metallic compound. No instance of the Co1.5TiSn was found with an exception of a neutron diffraction study of the CoTiSn alloy system leading to a possible evolution of a structure with a Co1.5TiSn and tin and titanium impurities. Our experimental efforts showed that not only the Co1.5TiSn was achievable with all the structural hallmarks of a Heusler compound through extensive characterization methods like SEM, EDS, EBSD and XRD, but also low temperature moment of the compound was 0.6 µB/f.u., being in very good agreement with its half metallic value.
The subsequent metallurgical tests showed that in fact a FCC solid solution region exists between Co$\text{1.5}_{\text{TiSn}}$ up to Co$\text{2}_{\text{TiSn}}$, in which the microstructure is single-phase and a L2$_1$ signature in the structure is visible.

Below the Co$\text{1.5}_{\text{TiSn}}$ stoichiometry, the alloy system starts decomposing into regions of the dominant Co$\text{1.5}_{\text{TiSn}}$ with impurities of tin and titanium detectable under optical and electron microscopes, further corroborating the reports on the neutron diffraction of the CoTiSn alloy for the very first time with visual microscopic evidence.

Even further interesting was the test of a relatively less known criterion for half metallicity, called the Rhodes-Wolfarth model, on the Co$\text{1.5}_{\text{TiSn}}$ : The compound successfully stood the test of the model in exhibiting a half metallic signature through the comparison of its effective paramagnetic moment to its zero Kelvin saturation one. The ratio was less than one, a signature of half metals. Also this unusually low ratio was observed for all the alloys within the solid-solution region between Co$\text{1.5}_{\text{TiSn}}$ to Co$\text{2}_{\text{TiSn}}$, hinting towards the possibility of a half metallic ‘region’ instead of a singular ‘compound’ being present.

The future potential plan suggestions built on all the findings mentioned in this thesis could be more elaborated analysis of the found phases, e.g. Fe$_{1.5}$TiSb, Fe$_{0.5}$Co$_{0.5}$TiSb and Co$_{1.5}$TiSn.

Methods such as high-resolution transmission electron microscopy, neutron diffraction, Mossbauer spectroscopy and nuclear magnetic resonance could be useful in further exploring these newly found Heuslers, especially with regard to the possible detection of the location of the vacancies in the layered Heuslers and also their distribution within the crystal lattice.
Besides characterization, new processing methods could also be interesting pathways to study these materials, especially thin film deposition methods which are naturally more important in realizing viable electronic devices than the bulk synthesis. For this goal, physical deposition methods such as pulsed laser deposition (PLD) or sputtering can be useful in production of films of good quality and utilization of such films in more elaborate stacks leading to potential spintronic memory devices.

Also at the moment further theoretical calculations, especially on the energetics and cluster expansion of both Fe-Co-Ti-Sb half Heusler system and the ternary Co-Ti-Sn are under way for the eventual article publication.

Lastly, I would recommend that other quaternary systems similar to the ones we covered in this scope of research be considered for processing and characterization. Two which I personally propose are FeCoTiGe and FeCoMnSb systems, both of which have never been experimentally realized and therefore have good potential for an interesting metallurgical evaluation.
REFERENCES


