Crystallography and Magnetism of Magnetocalorically Important Ni-Mn-X Based Heusler Alloys

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CRYSTALLOGRAPHY AND MAGNETISM OF MAGNETOCALORICALLY
IMPORTANT Ni-Mn-X BASED HEUSLER ALLOYS

by

Amila S. B. Madilgama

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
Physics
Western Michigan University
December 2016

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Ni-Mn-X Heusler alloys, demonstrating strong coupling between crystalline structure and magnetic state, were studied. They undergo field-induced, first-order transformations from a low symmetry martensite to a high-symmetry austenitic phase around room temperature. The substantial difference between the entropies of the two phases results in a large adiabatic temperature change, called “Giant Magnetocaloric Effect (GMCE)”. Consequently, these alloys are promising refrigerants for near-room temperature cooling systems. This magnetic cooling is an energy-efficient and eco-friendly technology.

Crystalline structures and magnetic states of these alloys, which determine their magnetocaloric performances, highly depend on their composition. To examine new paths to optimize their magnetocaloric performances, this research is focused on the crystalline and magnetic behavior of a series of alloys under various experimental conditions (one Ni-Mn-In, three Ni-Mn-In-Co and two Ni-Mn-Ga). Additionally, phase transformation temperatures, co-existing phases, site occupancies, the effects of a magnetic field on the phase transformation temperature and hysteresis were also studied.

Their chemical compositions were determined by the RBS and EDS techniques. Rietveld refinements of diffraction data, reveals austenitic structure of all these alloys is cubic $L2_1 (Fm\bar{3}m)$ and upon cooling, they transform into monoclinic martensitic phases ($P 1 2/m 1$ space group). Martensitic phase, except for Ni-Mn-Ga, is a mixture of two modulated monoclinic phases: either...
$5M \text{ & } 7M \text{ or } 6M \text{ & } 8M$. Ni-Mn-Ga alloys undergo inter-martensitic phase transformations from 7M modulated monoclinic phase to a non-modulated $L1_0$ tetragonal phase, upon cooling.

Magnetic nature was determined by thermomagnetic, AC-susceptibility, and neutron diffraction. The austenitic phase of the Ni-Mn-In and Ni-Mn-In-Co alloys is ferromagnetic due to strong ferromagnetic interactions between $Mn(4a$-sites) and $Mn(4b$-sites). In the Ni-Mn-In-Co alloys, the interactions between Co atoms enhance the ferromagnetism of the austenite. The Ni-Mn-Ga alloys in the current study are paramagnetic in the austenitic phase and they order ferromagnetically in their martensitic phase. Magnetic interactions in the martensitic phase become complex with the variation of interatomic distances between magnetic atoms due to the modulations of the martensitic phase. Consequently, different magnetic natures, ferromagnetic, antiferromagnetic, and spin-glass-like are present in the martensitic phase.

Both magnetic field and temperature drive the martensitic transformation. The hystereses associated with magnetic transformations are significantly higher than those of the crystalline transformations, and are approximately proportional to the square of the magnetic field. The hystereses associated with crystalline phase transformation have a minimum at a certain field. Because of the difference between the two transformations they merge only upon heating and under a certain magnetic field.

In all studied martensitic transformations (i.e. upon cooling) the lattice entropy decreases. However, the effect is larger when the austenite’s magnetic nature has higher entropy than the martensite does. Therefore, a magneto-structural transformation from antiferromagnetic martensite to cubic ferromagnetic austenite produces a large GMCE. However, it is vital to consider the thermal hysteresis losses associated with both phase transformations when calculating the GMCE.
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ACKNOWLEDGMENTS

Firstly, I would like to express my sincere gratitude to my Ph.D. dissertation advisor Prof. Pnina Ari-Gur for the continuous support in this study in numerous ways, for her patience, motivation, and immense knowledge. Her guidance and advice helped me not only in this research work and writing of this thesis, but also to cultivate great research ethics in myself. I could not have imagined having a better advisor and mentor for my Ph.D. study.

Besides my advisor, I would like to thank the rest of my thesis committee: Prof. Clement Burns, Prof. Arthur McGurn, and Dr. Yang Ren, for their insightful comments and encouragement. I would especially like to express my gratitude for the support and guidance of Dr. Yang Ren in the synchrotron diffraction experiment carried out at Argonne National Laboratory and analyzing of the diffraction data.

Furthermore, I express my gratitude to Dr. Victor Koledov and his research group at Kotelnikov Institute of Radio-engineering and Electronics of the Russian Academy of Sciences, Moscow, Russia, for their support and collaboration throughout this research. I would like to express my gratitude to Dr. Stuart Calder for his support in the neutron diffraction measurements carried out at Oak Ridge National Laboratory. Also, I would like to express my gratitude to Dr. Donald W. Brown for his support in the neutron diffraction measurements carried out at Los Alamos National Laboratory. Moreover, I would like to express my gratitude to Prof. Israel Felner and Dr. M. I. Tsindlekht for conducting the magnetic measurements of the \textit{Ni-Mn-In} sample at Racah Institute of Physics, The Hebrew University, Jerusalem, Israel. Also, I would like to thank
Acknowledgements–Continued

Dr. Yanglin Ge for conducting the EDS analysis on the Ni-Mn-Ga samples at Aalto University, Finland (previously Helsinki University of Technology). Likewise, my sincere thanks go to Dr. Ashgar Kayani and Dr. Amila Dissanayake for their support and guidance throughout the Rutherford Backscattering Spectrometry experiments carried out at Western Michigan University. Also, I would like to thank Mr. Michael Morris for his support by conducting the synchrotron diffraction measurements on the In-1 alloy.

I would like to express my gratitude to the following institutes for their financial support. This work is supported by Award No. RUP1-7028-MO-11 of the US Civilian Research & Development Foundation (CRDF) and by the National Science Foundation under Cooperative Agreement No. OISE-9531011. Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357. Research at Oak Ridge National Laboratory was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, and the US Department of Energy.

I thank the graduate college of Western Michigan University for providing financial support for my studies here at Western as well as numerous financial supports given to conduct and present my research work at several national and international scientific conferences. Also, I would like to thank Dr. Kirk Korista and other faculty members for their guidance and support during my study in the department of physics at WMU. Also, I would like to thank all the staff members in the department of physics for their support.

Last but not the least, I express my sincere gratitude to my family as well as all my friends for supporting me spiritually throughout my studies and my life in general.

Amila S. B. Madiligama
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CHAPTER 1

INTRODUCTION

The research work described in this dissertation is dedicated to the investigation of the crystallography and magnetic behavior of a series of Ni-Mn-X based Heusler alloys that have shown promising potential for use as refrigerants for room temperature magnetic cooling systems [1, 2]. The cooling capability of these alloys is based on the Magnetocaloric Effect (MCE). Additionally, these alloys with similar compositions exhibit several technologically important phenomena such as magnetic shape memory [3] and magnetic super-elasticity [4]. The technological importance of these alloys will be discussed in detail in the following chapters.

The temperature of almost any material can be changed by a change of the external field (such as electric, magnetic or mechanical field) applied to it; the phenomenon is called the caloric effect [5]. Caloric effect is described or quantified by the change in entropy or change in temperature, when the external field is modified isothermally or adiabatically, respectively [5]. There are several different emerging technologies based on caloric effects; depending on the external stimuli used; magnetic field, electric field, pressure and stress, they are magnetocaloric-, electrocaloric-, barocaloric-, and elastocaloric- effects. They have been studied for use in potential cooling alternatives. Among them, magnetic cooling technology, based on the magnetocaloric effect, has shown the greatest promise as an alternative commercial cooling technology to fluid-compression technology [6]. In a magnetic material (para-, ferro-, or antiferromagnetic), the direction of the magnetic moments of individual atoms is strongly affected by applying a magnetic
field. Therefore, a magnetic field is one of the most convenient thermodynamic variables that can be used to manipulate the entropy and temperature of a magnetic material. The change in the entropy of a magnetic material upon a change of the applied magnetic field to it isothermally is called MCE. In an adiabatic process, when the applied magnetic field to a magnetic material is changed, the change in the material’s temperature is also known as MCE. In magnetic cooling systems, an alternating magnetic field is utilized to cool/heat a ferromagnetic material (refrigerant) via MCE [7].

The history of the magnetic cooling concept runs to the late 19\textsuperscript{th} century. In 1881, MCE was discovered in iron by Warburg [8]. Then in 1918 this effect was explained by Weiss and Pichard as a change in the magnetic entropy of a magnetic material upon changing the applied field [9]. Later, a method of cooling by magnetic refrigeration was proposed to the application of low temperature physics by Debye [10] and Giauque [11], and this method was experimentally verified by Giauque and MacDougall in 1933 [12]. In this experiment, using liquid helium as heat removing substance they could reach 0.25 K. This technique is referred to as “the method of cooling via adiabatic demagnetization of magnetic salts” (using a cerium magnesium nitrate, for example) and is now a standard laboratory cooling technique to attain ultra-low temperatures [13]. However, this technique cannot be employed in commercial cooling applications due to its limitations, which are cooling power output and working temperature range [14].

The invention of the first room temperature proof of concept magnetic refrigerator was announced on February 20, 1997 by Ames Laboratory Scientists V. K. Pecharsky and K. A. Gschneidner et al. This discovery stimulated theoretical and experimental studies to find the materials which exhibit a giant magnetocaloric effect. This first room temperature magnetic refrigerator was based on $Gd$ spheres as a refrigerant, and had a cooling power of 600 W in a
magnetic field of 5 T. A schematic diagram of an advanced version of the first magnetic refrigerator by Ames Laboratory/Astronautics Corporation is shown in Figure 1 [8].

Thermodynamic modeling suggests, that the magnetic cooling could be over 25% more efficient than the best existing fluid-compression technology [15]. This higher efficiency may be achieved by replacing the less efficient mechanical process (compression and expansion of a fluid) in a fluid-compression cycle by a more efficient process (magnetization and demagnetization of a ferromagnetic material) in the magnetic cooling method [7]. This is because the magnetization and demagnetization processes of a magnetic material are much faster compared to the changing the pressure of a gas. The fluids which are utilized in the conventional cooling machines, such as chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) contribute to the global warming and depletion of the Earth’s ozone layer. On the other hand, solid state magnetocaloric materials leave a smaller ecological footprint compared to adverse fluids used in the fluid-compression technology. Therefore, magnetic cooling technology is a promising alternative to the Eco adverse, and less efficient fluid-compression cooling technology.

Figure 1: Schematic diagram of the rotary magnetic refrigerator by the Ames Laboratory/Astronautics Corporation of America (2001). A permeant magnet produces a maximum field of 140 kOe around the magnetocaloric wheel filled with Gd spheres. Machine operates at a frequency between 1 and 4 Hz near room temperature with a maximum temperature span of 20 °C by delivering maximum cooling power of 95 W (adapted from [8]).
Cooling systems based on magnetocaloric materials, which work under relatively high magnetic fields (~5 T), are very expensive and economically non-feasible because cryomagnets are used to produce these large magnetic fields. Therefore, the development of magnetic cooling as commercial cooling technology is highly dependent on the availability of solid state magnetic materials which exhibit large entropy change (cooling effect) under a moderate magnetic field (~2 T) produced by permanent magnets. There have been both theoretical and experimental studies conducted on various magnetic materials, investigating their suitability as for the task. Magnetic materials which undergo magneto-structural transitions (i.e. a simultaneous magnetic and crystallographic phase transformations) which are first-order phase transformations, generally demonstrate a large magnetocaloric effect. In these first-order phase transformations a sharp change in the crystalline structure is observed in the transition point. The observed entropy change in these magneto-structural transformations is higher than that of pure magnetic phase transformations (which are second order phase transformations) because of the large entropy contribution from the crystallographic phase transformation [16, 17]. This observed entropy change in first-order phase transformations in the magnetic materials is defined as Giant Magnetocaloric Effect (GMCE).

In 1996, V. K. Pecharsky and K. A. Gschneidner discovered the first magnetic material demonstrating a Giant Magnetocaloric Effect (GMCE), $Gd_5(Si_2Ge_2)$ [17]. The measured MCE of this alloy (~18.5 J Kg$^{-1}$K$^{-1}$) was about twice as large as that of pure Gd. Succeeding this discovery, $Mn-Fe-As$ compounds (under ~2 T) [18], La(Fe$_x$Si$_{12x}$)$_{13}$ compounds (under ~2 T) [19], and $LaFe_{11.83}Si_{1.17}$ alloy (under ~3 T) [20] were found to exhibit significantly higher GMCE. After 2000, $Ni-Mn-X$ based Heusler alloys gained considerable attention as new magnetocaloric materials because of their first-order martensitc transformations in the vicinity of room
temperature. These alloys exhibit both magnetic shape memory effect [3] and a large inverse magnetocaloric effect [21, 22] (these effects will be discussed in detail in chapter 2). The highest reported value of MCE of a Heusler alloy so far, $\Delta S_M = - 86 \text{Jkg}^{-1}\text{K}^{-1}$ in a field of 5 T, is demonstrated by single crystals of $\text{Ni}_{33}\text{Mn}_{20}\text{Ga}_{25}$ [23]. Nevertheless, the complexity and high cost associated with the fabrication process of single crystals as well as the required higher magnetic field are drawbacks to adopt these alloys for practical cooling applications. In 2014, the second highest value of MCE of the Heusler alloys, $\Delta S_M = - 30.0 \text{Jkg}^{-1}\text{K}^{-1}$ (under 5 T), was reported in $\text{Ni}_{52}\text{Mn}_{26}\text{Ga}_{22}$ ribbons [24]. Many magnetic materials in the Heusler family demonstrate the inverse MCE. Among them, Heusler alloys based on $\text{Ni-Mn-In}$ [25], $\text{Ni-Mn-Sb}$ [26, 27], and $\text{Ni-Mn-Sn}$ [28] exhibit a giant magnetocaloric effect. This makes them highly promising materials as refrigerants in magnetic cooling systems. A more detailed description of the near room-temperature magnetocaloric materials and recent developments in magnetocaloric materials can be found in the works presented by V. Franco et al. [29] and K. A. Gschneidner et al. [8].

A characteristic value of MCE (adiabatic temperature change) for an applied field difference of 2 T, for several of the most studied magnetocaloric materials, at either their pure magnetic transition temperature or merged magneto-structural transition temperature, is given in Figure 2 [30]. Pure magnetic transitions (second-order phase transitions) are represented by a hatched pattern while magneto-structural coupling transitions are represented by solid colors. The summarized data illustrate that the highest values of MCE are achieved when there is a first-order phase transformation. This suggests that the survey for new magnetocaloric materials needs to be focused on the materials which undergo a first-order phase transformation near room temperature.
The compound $Fe_{0.49}Rh_{0.51}$ exhibits the highest adiabatic temperature change under $2T$, but unfortunately it could not be employed for cooling applications around room temperature, as its phase transition temperature is significantly higher (Figure 2).

![Diagram showing magnetocaloric effect for various materials](image)

**Figure 2:** A characteristic value of MCE (adiabatic temperature change) for the applied field difference of $2T$, for several of the most studied magnetocaloric materials at either their pure magnetic transition (second-order) temperature, represented by hatched pattern, or merged magneto-structural transition (first-order) temperature, represented by solid colors [30].

*Ni-Mn-In* based alloys and compounds based on rare earth elements such as lanthanum and gadolinium (i.e. $La(Fe,Si)_{13}H_{0.5-1.5}$ and $Gd_5Si_{1.98-2.09}Ge_{1.91-2.02}$) exhibit relatively high GMCE compared to other materials. As shown in Figure 2, depending on the composition, rare earth compounds based on *La* and *Ni-Mn-In* Heusler alloys exhibit large magnetocaloric effect in a broad range of temperatures approximately from 240 K to 320 K. On the other hand, *Ga* based compounds exhibit large magnetocaloric effect in a relatively short range of temperatures approximately from 290 K to 310 K. However, as their names suggest, compounds based on rare
earth elements are relatively expensive and hence not economically feasible. On the other hand, constituent elements of $Ni-Mn-X$ based alloys are abundant and relatively low cost [31], and their fabrication process is relatively easy [30]. These make them inexpensive materials compared to other materials that exhibit a large magnetocaloric effect. Additionally, these alloys are ecofriendly because their constituent elements are non-toxic. Specifically, good oxidation resistance and high strength are some of the added advantages of $Ni-Mn-In$ based Heusler alloys as magnetic refrigerants [30].

Martensitic transformation temperature (which determines the operation temperature range of a refrigerant) of the $Ni-Mn-In$ alloys can be tuned by controlling the concentration of the substituted cobalt [32]. This enables an easy control of the working temperature range of these alloys as refrigerants. Therefore, the $Ni-Mn-In$ based alloys are considered as excellent candidates for this application.

$Ni-Mn-X$ based alloys exist in two phases; the higher temperature phase which is more symmetric is called austenite while the lower temperature phase is martensite and has lower symmetry compared to the austenite (the crystallography and magnetism behavior of these alloys will be discussed in details in the chapter 2). Magnetic field-induced phase transformation produces a large enough entropy change to consider them as good magnetocaloric materials. The highly symmetric cubic crystalline structure of the austenitic phase makes it simple to determine the crystallographic information such as lattice parameter, interatomic distances, and site occupancies. Consequently, that makes it less complex to determine the austenitic magnetic behavior and in turn it is well reported [33, 34]. On the other hand, crystalline structures of the martensitic phase are very complex and highly dependent on the composition. The available information of the low symmetry, complex martensitic phases is not sufficient to fully quantify
the giant magnetocaloric effect demonstrated by these alloys. This creates an obstacle to the optimization of the magnetocaloric performances of existing alloys as well as to cast new alloys with favorable compositions to achieve higher magnetocaloric performances. Thus, the main goal of this research work was to determine the crystalline structures and magnetic behavior of the martensitic phases of these Ni-Mn-In, Ni-Mn-Ga and Ni-Mn-In-Co Heusler alloys.

In this dissertation, a detailed characterization of a series of six Ni-Mn-X based alloys with different compositions and constituent atoms is presented. The series includes one Ni-Mn-In alloy, three Ni-Mn-In-Co alloys, and two Ni-Mn-Ga alloys. Some of these alloys were selected for the characterization as they have demonstrated a significant magnetocaloric performances [1, 2], while others were selected because similar composition (alloys) were reported to have several multifunctional properties [35]. The study was focused on the crystalline structures, magnetic states, phase transformation temperatures, co-existing phases, and site occupancies of the constituent atoms of these alloys in both austenitic and martensitic phases. The effects of an applied magnetic field on the structures, magnetic behavior, and phase transformations of some of these alloys also studied. In the first part of the thesis, the theoretical background of MCE, GMCE and then chemical and physical properties of some Ni-Mn-X based alloys, which demonstrate a significant interest as magnetocaloric materials, will be summarized. This discussion also elaborates on the crystallography, magnetism, phase transformations, and site occupancies of those alloys.

In the next section, which is the experimental description, characterization techniques which were used to analyze these alloys will be discussed in detail. The following material characterization techniques were used; neutron, synchrotron, and X-ray diffraction, Rutherford Backscattering Spectrometry, and thermomagnetic measurements. In thermomagnetic
measurements, magnetization of the alloys as a was measured as a function of both the temperature and the applied magnetic field. A comprehensive description will be given in this section of the importance of each characterization technique, the instruments and facilities used to collect the data, experimental procedures, data analysis methods and software.

In the subsequent section, the experimental findings, the results of the analysis of all six alloys (i.e. one Ni-Mn-In, three Ni-Mn-In-Co and two Ni-Mn-Ga alloys) will be presented. In this section, the crystalline structures of all the alloys in each phase in a broad temperature range including the vicinity of phase transformation temperature will be discussed. Also the magnetic behavior (magnetic order/disorder) in both austenitic and martensitic phases and the relationship between the site occupancies and inter-atomic distance of magnetic atoms to the magnetism in each phase will be discussed. In addition, the effects of applied magnetic fields on the phase transformation temperature and the effects of substitution of Co in Ni-Mn-In alloys on their physical and chemical properties will be discussed.

In the final sections of the dissertation, discussion, conclusions, and future studies, the significance of each experimental finding will be discussed emphasizing how to utilize these experimental discoveries to optimize the magnetocaloric performances of the existing alloys and how to choose new compositions to achieve favorable magnetocaloric performances. Finally, I will discuss the directions towards which the future studies should be carried out.
2.1 Definition of the magnetocaloric effect and its various types

MCE is an intrinsic property of all magnetic materials and is identified as the thermal response of a magnetic material upon changing the applied magnetic field [36]. The applied magnetic field can be changed in two distinct ways; adiabatically or isothermally. When the applied magnetic field is changed isothermally from a magnetic field, $H_1$, to a magnetic field, $H_2$, the resulting total entropy change in the material ($\Delta S_T = S_{T_2} - S_{T_1}$) is measured and the MCE is quantified as isothermal entropy change. On the other hand, in an adiabatic change in the applied magnetic field, the resulting temperature change is measured and the MCE is quantified as adiabatic temperature change, $\Delta T_A = T_2 - T_1$. Both isothermal entropy change and adiabatic temperature change are considered as magnetocaloric potentials or characteristic values of the MCE. Depending on the thermal response of a magnetic material, MCE can be classified into two groups; direct MCE and inverse MCE [37]. In the following section, both direct and inverse effects will be discussed briefly.

2.1.1 Direct Magnetocaloric Effect

Direct MCE is observed in both paramagnetic ($PM$) and ferromagnetic ($FM$) states of the magnetic materials. In $PM$, MCE has its maximal value at a temperature near absolute zero where the thermal energy is not sufficient to randomize the magnetic spin orientations and magnetic spins
start to align parallel each other. On the other hand, in the \textit{FM} state, the effect has its maximum just below the Curie temperature. At this temperature, the individual spins are arranged parallel to each other spontaneously and result in a large magnetization. In a magnetic material, unpaired electrons in the magnetic atoms in the crystalline lattice create a net magnetic moment.

To understand the physics behind the MCE, let us separate a paramagnetic magnetocaloric material into two subsystems, a magnetic subsystem which consists of all the magnetic moments of the magnetic atoms and a crystalline lattice that contains all the atoms in the system. Before applying a magnetic field, spins are randomly oriented and lattice vibrations are at moderate or very low level (Figure 3-a). When a magnetic field is applied to these magnetic materials, the magnetic moments of the individual atoms align with the applied field. This results in a decrease in the magnetic entropy contribution due to the ordering of the magnetic moments. To compensate for the decrease of the entropy contribution of magnetic moments of the individual atoms in an adiabatic process, the rest of the contributions to the total entropy go up. Crystalline lattice starts to vibrate in higher amplitudes and the kinetic energy of the conduction electrons increases (Figure 3-b). Increasing in lattice vibrations and kinetic energy of the conduction electrons will heat up the magnetic material. This phenomenon is known as direct magnetocaloric effect [38], which is analogous to the adiabatic compression of a gas in the vapor-compression cooling cycle (Figure 4). In adiabatic compression of a gas, the molecules come closer to each other and as a result they have less freedom to move. The decrease in the positional disorder results in a corresponding contribution to the entropy decrease. The decrease in the entropy associated with positional disorder is compensated by the entropy contribution of the kinetic energy of the gas (i.e. they start to move faster), by increasing the velocity of constituent Molecules [38].
Figure 3: Behavior of magnetic and crystalline lattice subsystems of a paramagnetic material under the influence of external magnetic field. (a) Before applying a magnetic field, spins are randomly oriented and lattice vibrations are at moderate level. (b) In the presence of an external field, magnetic spins are aligned parallel to the field and lattice vibrations goes up and consequently the material will heat up (adapted from [29]).

Figure 4: Analogy between the adiabatic magnetization (demagnetization) of a ferromagnetic material near its Curie temperature and adiabatic compression (expansion) of a gas (adapted from [39])
In an adiabatic decreasing of the external magnetic field applied to a magnetic substance (PM or FM), magnetic entropy increases while the total entropy is kept constant by decreasing the electronic and lattice contributions to the total entropy. This process is analogous to an adiabatic expansion of a gas, in which the positional disorder and hence corresponding contribution to the entropy increases, while the total entropy of the system is kept constant by decreasing the velocity of constituent molecules. The decreasing of lattice and electronic contribution of the entropy results in cooling of the magnetic substance. During both adiabatic magnetization and demagnetization, MCE can be expressed as the adiabatic change in the temperature. If the substance is magnetized isothermally (the temperature of the system is kept constant), the total entropy decreases because of the decrease in magnetic entropy contribution.

2.1.2 Indirect (inverse) MCE

In antiferromagnetic (AFM) states there are two magnetic sub-lattices. All the magnetic moments of each sub lattice are parallel to each other, but the two magnetic sub-lattices are anti-parallel to each other. The total entropy of an AFM material is the sum of the entropies of its crystalline lattice (i.e. contribution of lattice vibrations) and the magnetic entropy contribution from the two magnetic sub-lattice.

When a magnetic field is applied in the direction of the moments of one sub-lattice, the magnetic field will force the magnetic moments of the second magnetic sub-lattice to rotate into the direction of the first sub-lattice [14]. This results in the increasing of the disorder of the magnetic spin arrangement and will cause an increase in the corresponding magnetic entropy. Therefore, unlike in PM and FM materials, magnetization of AFM materials will increase their magnetic entropy. In adiabatic magnetization of an AFM, increasing of the magnetic entropy is compensated by decreasing of the rest of the contributions to the total entropy (i.e. lattice and
electronic contributions) and the total entropy is kept constant. Thus, amplitudes of the lattice vibrations as well as the kinetic energy of the conduction electrons decreases. The decreasing of lattice and electronic contributions of the entropy results in cooling of the magnetic material. This phenomenon is called the inverse magnetocaloric effect [14]. In the isothermal magnetization of an AFM material, the total entropy of the system increases because of the increasing of the magnetic contribution to the entropy. Figure 5 (b) illustrates the increasing of the magnetic entropy and decreasing of the temperature in an isothermal and an adiabatic process, respectively, upon increasing the magnetic field from zero to a higher value.

![Graph showing magnetic entropy vs. temperature in direct and inverse MCE](image)

Figure 5: Magnetic entropy vs. temperature (schematics) in direct and inverse MCE observed in (a) Ferromagnetic material in the vicinity of its Curie temperature (b) antiferromagnetic material near its metamagnetic transition temperature, in two different magnetic fields \( H = 0 \) and \( H > 0 \), respectively (adapted from [14]).

2.1.3 Giant Magnetocaloric Effect (GMCE)

Giant Magnetocaloric Effect is a phenomenon which, occurs in magnetic materials that have a strong coupling between their crystallographic structure and magnetic state. Therefore, conventional MCE and GMCE are considerably different phenomena [14, 40]. Unlike in conventional MCE, there is a structural phase transformations associated with GMCE [40]. In this
section, the GMCE observed in some of the Ni-Mn-X based Heusler alloys will be discussed first. Upon applying a strong magnetic field, near the Curie temperature of these FM materials, they undergo first-order structural and magnetic phase transitions simultaneously [30]. When the applied magnetic field is increased, these materials transform from low-symmetry martensitic phase to a highly symmetric FM, austenitic phase. Depending on the magnetic state of the martensitic phase, aniferromgnetic or spin-glass, the GMCE needs to be discussed seperately. First, consider a tranformation from spin-glass martensitic phase to FM austenite. During this process the magnetic entropy of such materials decreases due to the alignment of magnetic moments with applied magnetic field. This results in heating up of the material. Simultaneously, the structural change from low-symmetric twinned martensitic phase to a high-symmetry austenitic phase increases the associated entropy contribution of the crystalline phase transformation. Because the total entropy is constant due to the process being adiabatic, the lattice and electronic entropy contributions go down by decreasing both the amplitude of lattice vibrations and kinetic energy of the conduction electrons. The result is a large cooling effect (Figure 6) [30].

In this process, the absolute amount of heat absorption due to structural transition from martensite to austenite, exceeds the heat released from the transformation of the magnetic sub-lattice. Therefore, upon magnetization, a giant magnetocaloric material cools down. Conversely, upon demagnetization process, the magnetic entropy decreases when transforming from FM to spin-glass state and results in a cooling of the material. Concurrently, first-order phase transformation from a high symmetry austenite to a low-symmetry martensite decreases the lattice entropy. As the absolute amount of heat released due to structural transition exceeds the amount of heat absorption due to magnetic phase transformation, a net heating of the magnetic material results. In the martensitic transformation of spin-glass martensitic phase to FM austenitic phase,
the observed GMCE, $\Delta S_{\text{GMCE}}$ is the difference between the entropy contribution of the crystallographic phase transformation ($\Delta S_{\text{str}}$) and the magnetic entropy change ($\Delta S_M$) (i.e. the minus sign of the Equation 1 applies) [30].

$$\Delta S_{\text{GMCE}} = \Delta S_{\text{str}} \pm \Delta S_M$$  \hspace{1cm} (1)

Figure 6: The schematic diagram of two competing contributions, magnetic spin alignment and first-order structural transition, to the GMCE in Ni-Mn-based Heusler alloys. The sample heats up due to alignment of the magnetic moments by the adiabatic magnetization (top row). Simultaneously, there is a large change in lattice and electronic contribution to the entropy due to the first-order phase transformation from low-magnetization and low-symmetric twinned martensitic phase to high-magnetization and high symmetric austenitic phase. Because the total entropy is constant due to process being adiabatic, there is a large cooling effect (bottom row). These two competing contributions to GMCE resulting in net cooling (adapted from [30]).

Now consider a transformation of an AFM martensitic state to a FM austenitic phase [41]. In this case, increasing of the applied magnetic field will cause the magnetic entropy increase; that is because AFM state is more ordered compared to FM state. This results in the cooling down of the material. Simultaneously, the structural change from low-symmetry twinned martensitic phase
to high-symmetric austenitic phase increases the associated entropy contribution of the crystalline phase transformation. Because the total entropy is constant due to process being adiabatic, the lattice and electronic entropy contribution goes down by decreasing both the amplitude of the lattice vibrations and kinetic energy of the conduction electrons. The result is a large cooling effect. In this case the total entropy of the GMCE, $\Delta S_{GMCE}$ is the sum of the magnetic entropy change ($\Delta S_M$) and the difference in the entropies of the two crystallographic phases ($\Delta S_{str}$) (i.e. the plus sign of the Equation 1 applies) [30].

2.2 Thermodynamics of the Magnetocaloric Effect (MCE)

2.2.1 Isothermal entropy change at constant pressure [41, 42]

The classical MCE is explained in terms of the total entropy change caused by the interactions of the magnetic spins of the subjected material to an applied magnetic field. To obtain a mathematical expression for the magnetocaloric potentials, the magnetic variables (i.e. applied magnetic field and magnetization of a magnetic material) could be coupled with the thermodynamic variables of the magnetocaloric material (i.e. entropy and temperature). The total entropy ($S_T$) of a magnetic material consists of four different contributions: electronic ($S_E$), lattice ($S_L$), magnetic ($S_M$), and nuclear ($S_N$). However, the atomic nuclear contribution to the total entropy is only important at very low temperatures. While the present discussion is focused on room-temperature magnetocaloric effect; therefore, for the current discussion of the total entropy, its contribution is negligible. Under constant pressure, all these entropy contributions to the total entropy are functions of both the temperature and the applied magnetic field. However, for the sake of the simplicity of this discussion, it is assumed that of the three entropy contributions, only the magnetic entropy depends on the applied magnetic field and the remaining contributions could be considered as variables independent of the magnetic field. By considering all these
approximations, the total entropy of a magnetic material can be expressed as in the Equation 2 [42]:

\[
S_{\text{tot}}(T,H)_p = [S_E(T) + S_L(T) + S_M(T,H)]_p
\]

Upon increasing the applied magnetic field (from \(H_1\) to \(H_2\); \(\Delta H = H_2 - H_1\)) at constant temperature and pressure, a large number of magnetic moments will align with the applied field. This results in a more ordered arrangement of the magnetic moments and causes a significant decrease in the magnetic entropy of the material. Because we assume that the rest of the contributions to the total entropy are unaffected by the changing of the magnetic field, the difference between the magnetic entropies caused by changing the applied magnetic field could be expressed by Equation 3. This process is called the isothermal magnetic entropy change at constant pressure which is represented by the vertical arrows in Figure 7.

\[
-\Delta S_M(T,\Delta H)_p = [S_M(T,H)_{H_2} - S_M(T,H)_{H_1}]_p = [S_{\text{tot}}(T,H)_{H_2} - S_{\text{tot}}(T,H)_{H_1}]_p
\]

2.2.2 Adiabatic temperature change at constant pressure

Alternatively, the MCE can also be expressed as the adiabatic temperature change at constant pressure. In an adiabatic process, the applied magnetic field to a magnetic material is increased from \(H_1\) to \(H_2\) at constant pressure while the total entropy of the system is kept constant. Again, similarly to the isothermal process, the magnetic entropy of the material is decreased due to the alignment of the magnetic moments with the applied magnetic field. However, because the total entropy of the system is maintained constant, the decrease in magnetic entropy is compensated for by an increase in the lattice and electronic contributions to the entropy. This heats
up the material. The resulting adiabatic temperature change $\Delta T_{ad}$ (a function of both temperature, $T$ and magnetic field difference, $\Delta H$) of the magnetic material can be given by Equation 4 [43]:

$$\Delta T_{ad}(T, \Delta H)_p = [T(S, H)_{H_2} - T(S, H)_{H_1}]_p$$

Figure 7: Entropy vs. temperature schematic diagram of a magnetic material that exhibits MCE in pure magnetic phase transitions (i.e. a second order phase transformation without a structural change in the material). Solid lines represent the total entropy of the material at two different applied magnetic fields, $H_1$ and $H_2$ ($H_2 > H_1 = 0$). Dotted lines from top to bottom represent magnetic entropy at $H_1$, magnetic entropy at $H_2$ and combination of lattice and electronic entropies respectively. The horizontal arrows indicate the adiabatic temperature change at a constant pressure and the vertical line indicates an isothermal magnetic entropy change at constant pressure, when the magnetic field changes from $H_2$ to $H_1$ (or vice versa). (adapted from [44])

Equations 3 and 4, i.e. the isothermal magnetic entropy change and adiabatic temperature change at constant pressure (both are functions of temperature and applied magnetic fields), characterize the values of MCE. To calculate isothermal change in entropy, the heat transferred in the isothermal process is needed. The measurements of the heat transfer in an isothermal process in very difficult as it involves the heat transfer between the system and its surrounding at constant...
temperature. Therefore, Equation 3 is rarely used to describe the MCE. However, by measuring the temperature change of a sample under applied magnetic fields $H_1$ and $H_2$ ($H_2 > H_1$), Equation 4 can be used to determine the MCE.

So far, the total entropy diagram was used to determine the characteristic values of MCE ($\Delta S_{iso}$ and $T_{ada}$). There are additional methods to characterize the values of the MCE. One of them is the indirect determination of the magnetocaloric potentials ($\Delta S_{iso}$ and $T_{ada}$) by using magnetization data [42]. Moreover, magnetocaloric potentials can also be expressed by analytical expressions in terms of specific heat capacity and total entropy of magnetocaloric materials. A. S. Andreenko et al. [45], K. A. Gschneidner et al. [8] and V. K. Pecharsky et al. [44], have discussed magnetocaloric potentials in terms of specific heat capacity and total entropy at constant pressure. In all these works, they have arrived at the same expressions for characteristic values of MCE by following slightly different procedures. Here, in the following discussion, the procedure which has been developed by Pecharsky et al. [44] will be discussed.

The magnetic free energy of a magnetic material is a function of temperature $T$, volume $V$, pressure $P$, and magnetic field $H$. The total differential of the magnetic free energy at constant pressure is given by Equation 5 [46]:

$$dF = -S_M dT - M dH$$  \hspace{1cm} 5

In the above equation $S_M$ is the magnetic entropy and $M$ is the magnetization of the material. By considering the partial derivatives of Equation 5, with respect to the temperature and the magnetic field, the following relations for the entropy (Equation 6) and the magnetization (Equation 7) can be obtained. Then, by manipulation of those equations [46], a relationship between the magnetic variables (magnetization and magnetic field) and the thermodynamic
variables (temperature and entropy) (Equation 9) [8] can be obtained in terms of a Maxwell’s relationship:

\[
S = -\left(\frac{\partial F}{\partial T}\right)_H
\]

\[
M = -\left(\frac{\partial F}{\partial H}\right)_T
\]

\[
\left(\frac{\partial S}{\partial H}\right)_T = -\left[\frac{\partial}{\partial H}\left(\frac{\partial F}{\partial T}\right)_H\right] = -\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial H}\right)_T\right] = \left(\frac{\partial M}{\partial T}\right)_H
\]

By integrating the Equation 9 [47], the following expression (Equation 10) could be obtained.

\[
\Delta S_m(T, \Delta H)_{\Delta M,P} = \int_{H_1}^{H_2} \left[\frac{\partial M(T,H)}{\partial T}\right]_{H,P} dH
\]

The isothermal magnetic entropy change at constant pressure is proportional to the change in magnetization with respect to temperature at a constant magnetic field and the change in the applied field. The heat capacity at a constant magnetic field is given by Equation 11 [47]:

\[
\frac{C_H}{T} = \left(\frac{\partial S}{\partial T}\right)_H
\]

By considering entropy as a function of temperature \( T \), and magnetic field \( H \), an infinitesimally small change in entropy can be given by Equation 12 [47].
During an adiabatic process, the entropy of the system is kept constant, hence for such a system, Equation 12 can be rewritten as Equation 13.

\[ dS = \left( \frac{\partial S}{\partial H} \right)_T \, dH + \left( \frac{\partial S}{\partial T} \right)_H \, dT \]

Equation 12

\[ \left( \frac{\partial S}{\partial H} \right)_T \, dH = -\left( \frac{\partial S}{\partial T} \right)_H \, dT \]

Equation 13

By considering Equations 9, 11, and 13 the following relationship can be obtained [45]:

\[ dT = -\frac{T}{C_H} \left( \frac{\partial M}{\partial T} \right)_H \, dH \]

Equation 14

Then integrating the right-hand side of the resulting Equation (14) [48], (from lower magnetic field, \( H_1 \) to higher magnetic field, \( H_2 \)), another expression for MCE in terms of the adiabatic temperature change at a constant pressure (Equation 15) can be obtained [16]:

\[ \Delta T_{Ad}(T, \Delta H) = -\int_{H_1}^{H_2} \frac{T}{C_H(T, H)} \left( \frac{\partial M(T, H)}{\partial T} \right)_H \, dH \]

Equation 15

Equation 15 cannot be solved analytically because both magnetization and heat capacity are dependent on the material. They are also analytically unknown as functions of temperature and magnetic field. However, MCE can be determined by numerical integration of Equation 15 if the magnetization and heat capacity data are known (either by experimental measurements of magnetization and heat capacity both as functions of temperature and magnetic field or by values obtained in theoretical calculation). Equation 15 helps to understand the behavior of MCE in solids.
as well as it gives a basic searching pathways for a better magnetocaloric material. According to the Equation 15, for a given magnetic field change; MCE depends on the derivative of the magnetization with respect to temperature and the heat capacity of a material. MCE is larger when the derivative of magnetization, with respect to the temperature, is large. In paramagnetic materials, $[\partial M(T, H)/\partial T]_H$ has it maximal near the absolute zero where they magnetized spontaneously. On the other hand, in ferromagnetic materials, $[\partial M(T, H)/\partial T]_H$ becomes highest in the vicinity of the magnetic ordering temperature, thus the MCE will be maximized at or just below the Curie temperature. Therefore, in the search for a suitable refrigerant for room temperature magnetic cooling systems, the search should be focused on ferromagnetic materials. Additionally, Equation 15 demonstrates that the heat capacity of the material is inversely proportional to the MCE. The heat capacity of ferromagnetic materials is quite large at the magnetic ordering temperature. Therefore, to obtain a maximum MCE, a material in which there is no overlap of the peaks of the heat capacity curve and $[\partial M(T, H)/\partial T]_H$ curves need to be considered [48].

2.3 Thermodynamics of the Giant Magnetocaloric Effect (GMCE)

In this section, author will discuss an alternative approach, which is adopted from work of V. K. Pecharsky et at. [41], to obtain the isothermal magnetic entropy change exhibited by second order magnetic phase transformation (i.e. a magnetic order-disorder transformations). Then, this method will be developed to express the isothermal entropy change observed in a first-order magneto-structural phase transformation, observed in some Ni-Mn based Heusler alloys.

From the second low of the thermodynamics, the heat capacity of a magnetic material at constant pressure and magnetic field is given by $C(T)_{H,P} = (\partial S/\partial T)_{H,P} T$ [47]. Where, S is the
entropy and \( T \) is the absolute temperature of the material. This expression can be modified to obtain an expression to the change in entropy under constant pressure \( P \) and constant magnetic field \( H \) (equation 16) in terms of the heat capacity and the absolute temperature.

\[
dS(T)_{H,P} = \frac{C(T)_{H,P}}{T} dT
\]

The total entropy of a system at any ambient temperature \( T \) and under a constant magnetic field can then be obtained by integrating equation 16 from a lower temperature \( T_i \) (\( T_i \) is approaching to zero) to \( T \). The total entropies at \( T \) under constant magnetic fields \( H_1 \) and \( H_2 \) are given in Equations 17 and 18, respectively.

\[
S(T)_{H_1,P} = \int_{T_i}^{T} \frac{C(T)_{H_1,P}}{T} dT
\]
\[
S(T)_{H_2,P} = \int_{T_i}^{T} \frac{C(T)_{H_2,P}}{T} dT
\]

According to the third law of the thermodynamics, the total entropies of Equations 17 and 18 at \( T_i \) are going to be a constant and magnetic-field independent when \( T_i \) approaches 0 K. In Equation 3, MCE is defined in terms of isothermal magnetic entropy change as a function of temperature for a given magnetic field difference. Hence, an expression for MCE associated with second-order magnetic phase transformation, in terms of the magnetic entropy change, can be obtained by substituting equations 17 and 18 in equation 3, and then integrating from \( T_1 = 0 \) K to ambient temperature \( T \).

\[
\Delta S_M(T)_{H,P} \approx \Delta S(T)_{H,P} = \int_{0}^{T} \frac{C(T)_{H_2} - C(T)_{H_1}}{T} dT
\]
From Equation 19, it is clear that the MCE will be greater for a greater difference in heat capacities under magnetic fields $H_1$ and $H_2$ between absolute zero temperature and $T$. Also, if the difference between heat capacities remains constant for any given temperature, the MCE (i.e. entropy change in this case) decreases with increasing temperature.

2.3.1 Giant magnetocaloric effect associated with first-order phase transformation

In the previous derivation, it was assumed that the total entropy of a magnetic material is a continuous function of temperature. However, this is only valid for magnetic materials that undergo second-order phase transformation, such as magnetic order-disorder transformations: where the heat capacity and magnetizations are continuous functions of temperature. In the martensitic transformations associated with first-order phase transformations, the total entropy, heat capacity, and magnetization are discontinuous in the vicinity of the phase transformation temperature.

Consider the S-T diagram of a magnetic material in the vicinity of the first-order phase transformation (Figure 8). In this particular magnetic material, the phase transformation temperature decreases with increasing magnetic field, which is a similar behavior to studied Ni-Mn-In, and Ni-Mn-In-Co alloys in this thesis. It is well documented in literature that in some Ni-Mn-X based Heusler alloys, the phase transformation temperature decreases with increasing applied magnetic field. Here are two examples: R. Kainuma et al. reported decreasing martensitic transformation temperature with increasing magnetic field in $Ni_{46}Mn_{41}In_{13}$ and $Ni_{45}Co_{5}Mn_{36.7}In_{13.3}$ alloys [49]. A similar behavior of the martensite transformation temperature was also reported in $Ni_{45}Co_{5}Mn_{38}Sb_{12}$ alloy [50].

Figure 8 demonstrates two first-order phase transformations of Ni-Mn-X based Heusler alloy transform from highly ordered, low magnetic martensitic phase (paramagnetic or spin glass)
to highly symmetric ferromagnetic austenitic phase under two magnetic fields $H_1$ and $H_2$ ($H_1 < H_2$). First-order phase transformation temperature from martensite to austenite decreases with increasing magnetic field in this alloy. Therefore, the phase transformation temperature $T_{pt,H_1}$ under magnetic field $H_1$ is higher than the phase transformation temperature $T_{pt,H_2}$ under the higher magnetic field $H_2$. The enthalpy of the transformation at the lower magnetic field $H_1$ is $\Delta E_{H_1}$. This enthalpy change results in a discontinuity of the entropy change and the discontinuous equilibrium change of entropy at $T_{pt,H_1}$ is $\Delta S_{H_1} = \Delta E_{H_1}/T_{pt,H_1}$. Similarly, the enthalpy associated with the phase transition at the higher magnetic field, $H_2$ is $\Delta E_{H_2}$, which results in a total discontinuous equilibrium entropy change of $\Delta S_{H_2} = \Delta E_{H_2}/T_{pt,H_2}$. The effect of magnetic field on the heat capacities both above and below the first-order phase transition temperature is very small.

Figure 8: Schematic diagram of S-T behavior of a Ni-Mn-X based alloy near first-order phase transition temperature at two different magnetic fields, $H_1$ and $H_2$ ($H_2 > H_1$). The red line represents entropy at higher magnetic field $H_2$, whereas the black line represents entropy at lower magnetic field $H_1$. $T_{pt,H_1}$ and $T_{pt,H_2}$ are phase transformation temperatures, at magnetic fields $H_1$ and $H_2$ respectively. Note that phase transition temperature decreases with increasing magnetic field. Figure is adapted from [41] and [51].
For a first-order phase transformations take place at constant pressure and temperature, the heat capacity of the material is infinite at the phase transformation temperature. This causes a discontinuity of the entropy at phase transformation temperature. To express the total entropy of the material which undergoes a first-order phase transformation, Equations 17 and 18 can be rewritten by including this discontinuity of the heat capacity at the transformation temperature. The characteristic values of GMCE (in terms of total entropy change) exhibited in this first-order phase transformations, under magnetic fields $H_1$ and $H_2$ are given Equations 20 and 21, respectively.

$$S(T)_{H_1,p} = \int_{T_{p,H_1}}^{T_{H_1}} \frac{C_l(T)_{H_1,p}}{T} dT + \frac{\Delta E_{H_1}}{T_{p,H_1}} + \int_{T_{p,H_1}}^{T} \frac{C_h(T)_{H_1,p}}{T} dT$$  \hspace{1cm} (20)

$$S(T)_{H_2,p} = \int_{T_{p,H_1}}^{T_{H_2}} \frac{C_l(T)_{H_2,p}}{T} dT + \frac{\Delta E_{H_2}}{T_{p,H_2}} + \int_{T_{p,H_2}}^{T} \frac{C_h(T)_{H_2,p}}{T} dT$$  \hspace{1cm} (21)

Where, $C_l(T)_{H_1,p}$ and $C_l(T)_{H_1,p}$ are the heat capacities of the magnetic material below the transformation temperatures under magnetic fields $H_1$ and $H_2$, respectively. Similarly, $C_h(T)_{H_1,p}$ and $C_h(T)_{H_2,p}$ are the heat capacities above the transformation temperatures under magnetic fields $H_1$ and $H_2$, respectively.

Now, consider a temperature $T_1$, below the phase transition temperature $T_{p,H_2}$ ($T_1 < T_{p,H_2}$). The total entropy change experienced by the magnetic material for a change in the magnetic field $\Delta H = H_2 - H_1$ is given be the following Equation 22.

$$\Delta S_M(T)_{\Delta H,p} \simeq \Delta S(T)_{\Delta H,p} = \int_0^T \left[ \frac{C_l(T)_{H_2} - C_l(T)_{H_1}}{T} \right] dT$$  \hspace{1cm} (22)
This is nothing but the magnetic entropy changes for any magnetic material without first-order phase transformation (i.e. magnetic order-disorder transformation). The entropy change is dependent on the difference between the heat capacities under two magnetic fields. Therefore, the entropy change is very low as there is no significant difference between heat capacities.

Now, consider the entropy change experienced by the magnetic material at $T_2$, a temperature in between the phase transformation temperatures under two magnetic fields $H_1$ and $H_2$ (i.e. $T_{pt,H_2} < T_2 < T_{pt,H_1}$). At this temperature, under the lower magnetic field $H_1$, the Ni-Mn-X based alloy in the martensitic state and when magnetic field is changed to the higher value $H_2$, it transforms into austenic phase. Therefore, to find the total entropy change across the phase transformation, from martensitic state to austenitic state, we need to consider the heat capacities in the both phases as well as the enthalpy change associated with this transformation. The total entropy change will be given by Equation 23.

$$\Delta S_M(T)_{\Delta H,F} \approx \Delta S(T)_{\Delta H,F} = \int_{0}^{T_{pt,H_2}} \frac{[C^l(T)_{H_2} - C^l(T)_{H_1}]_p}{T} dT + \int_{T_{pt,H_2}}^{T} \frac{[C^h(T)_{H_2} - C^h(T)_{H_1}]_p}{T} dT + \frac{\Delta E_{H_2}}{T_{pt,H_2}}$$

And when $T > T_{pt,H_1}$ the MCE can be expressed in terms of change in magnetic entropy as (Equation 24):

$$\Delta S(T)_{\Delta H,F} = \int_{0}^{T_{pt,H_2}} \frac{[C^l(T)_{H_2} - C^l(T)_{H_1}]_p}{T} dT + \int_{T_{pt,H_2}}^{T_{pt,H_1}} \frac{[C^h(T)_{H_2} - C^h(T)_{H_1}]_p}{T} dT + \int_{T_{pt,H_1}}^{T} \frac{[C^h(T)_{H_2} - C^h(T)_{H_1}]_p}{T} dT - \left( \frac{\Delta E_{H_1}}{T_{pt,H_1}} - \frac{\Delta E_{H_2}}{T_{pt,H_2}} \right)$$
Generally, the heat capacities of two phases are slightly different. Under the assumption of that the heat capacities under a constant magnetic field are equal (i.e. $C_l(T) \approx C_h(T) = C(T)$) the above equations, 22, 23, and 24 can be simplified into the following formats:

$$\Delta S_M(T)_{\Delta H,p} \approx \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]}{T} dT$$  \hspace{1cm} (25)

$$\Delta S_M(T)_{\Delta H,p} \approx \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]}{T} dT + \frac{\Delta E_{H_2}}{T_{pt,H_2}}$$  \hspace{1cm} (26)

$$\Delta S_M(T)_{\Delta H,p} \approx \int_0^T \frac{[C(T)_{H_2} - C(T)_{H_1}]}{T} dT - \left( \frac{\Delta E_{H_1}}{T_{pt,H_1}} - \frac{\Delta E_{H_2}}{T_{pt,H_2}} \right)$$  \hspace{1cm} (27)

In some magnetocaloric materials, for example $Gd$ [48] and $Gd_5(Si_xGe_{1-x})_4$ [17] in a broad temperature range, except in the vicinity of the phase transition temperature, the heat capacity is independent of the applied magnetic field. For such materials, Equation 27 can be further simplified by assuming that the heat capacities below and above the phase transformation temperatures under different magnetic fields are the same at every temperature except the transition temperatures. When $C(T)_{H_1} = C(T)_{H_2}$ at everywhere except the transition temperature, the magnetic entropy is zero in the ideal case, or negligibly small in practice. The magnetic entropy of the GMCE associated with first-order phase transformations in the vicinity of the transformation temperature, $T_{pt,H_2} < T < T_{pt,H_1}$, becomes (Equation 28):

$$\Delta S_M(T)_{\Delta H,p} \approx \frac{\Delta E_{H_1}}{T_{pt,H_1}} \approx \frac{\Delta E_{H_2}}{T_{pt,H_2}}$$  \hspace{1cm} (28)

This discussion concludes that for a first-order phase transformation, the magnitude of GMCE is highly dependent on the entropy (or enthalpy) changes of the phase transformations
under both high and low magnetic fields. A large GMCE could be anticipated in Ni-Mn based alloys which exhibit a large discontinuity of the entropy (or enthalpy) in their magnetic field-induced martensitic phase transformations. The phase transformation temperatures of those alloys need to be strongly dependent on the magnetic field. However, the heat capacities, both above and below the phase transformation temperature, should be magnetic field independent [41].

To apply the result obtained for the GMCE associated with first-order phase transformation Equation 26 to studied magnetocaloric material, or any other similar material based on Heusler alloys, behavior of the heat capacity under external magnetic fields is needs to be studied. If the heat capacity of such a material is weakly dependent on the applied magnetic field, Equation 28 can be used to evaluate the MCE. Otherwise Equation 27, which is more accurately accounts for the dependence of the heat capacities on applied fields, could be used.
CHAPTER 3

MARTENSITIC PHASE TRANSFORMATIONS IN Ni-Mn BASED HEUSLER ALLOYS AND THEIR ROLE AS MAGNETOCALORIC MATERIALS

3.1 Introduction

In the previous chapter, the contributions of the magnetic and structural phase transformations to the GMCE were discussed. This chapter starts with an introduction of the martensitic phase transformations and follows the theory of the martensitic phase transformations. Then the possible crystalline structures and magnetic states of both austenitic and martensitic phases of the Ni-Mn-X based Heusler alloys are discussed. Also, the factors that effect on the crystalline structures and magnetism of these alloys such as composition, X-element, and number of electrons per atom (e/a) ratio are discussed.

3.1.1 Martensitic phase transformations

In iron-carbon alloys, the gamma phase above the critical eutectoid temperature is described as “austenite” which is named after Sir Robert-Austen [52]. Upon rapid cooling of this alloy, it transforms into a low-symmetric phase called martensite. The name “martensite” was used to designate the hard microstructures of quenched steel by Adolf Martens, who conducted the first studies on the martensitic phase transformations of steel in the 19th century [53]. Not only steel but also many other materials such as non-ferrous alloys, minerals, ceramics, some polymers, and some liquefied gasses demonstrate the martensitic transformations under favorable conditions [54].
Martensitic transformations are solid-state, first order, structural phase transformations, occur when the quenching rate of the molten alloy is rapid enough to prevent any diffusions of atoms into the solid [55]. Therefore, these transformations are diffusionless and atoms experience a cooperative moment when they transform to one phase to the other [55]. Because of this cooperative moment of atoms, martensitic transformations are also known as “military” transformations. They also are called “shear-like”, or “displacive” transformations. However, in these military transformations, atoms do not move more than their interatomic distances and hence they retain their relationship with neighboring atoms. Because of the diffusionless nature of the martensitic transformations, they are instantaneous and martensite grains nucleate and grow in the austenitic matrix at a large rate (~1000 m/s in steel). Consequently, for all the practical purposes, martensitic transformations are considered as time independent [55].

3.1.2 Theory of the martensitic transformation

The theory of the martensitic transformation provides explanations how does the martensitic formation progress in a material. The transformation rate depends on both the nucleation and growth processes of the product (martensitic in a forward transformation) phase. The slower process among these two determines the transformation rate. Martensitic nucleation occurs at structural imperfections in the parent austenitic phase such as insoluble impurities, grain boundaries, and dislocations. Usually, the nucleation process is slower than the growth process and hence nucleation governs the rate of a martensitic phase transformation [55].

3.1.2.1 Martensitic volume fraction by Koistien and Marburger relation

The volume fraction of martensitic phase, \( f_M \), is dependent on the degree of undercooling below the martensitic start temperature. The athermal character of these martensitic phase
transformations is given by the Koistien and Marburger relation [56]. The Equation 29 gives the volume fraction of the martensitic phase as a function of the temperature below the martensitic phase transformation,

\[ f_M = 1 - \exp \left( \beta (M_S - T) \right) \]

where, \( \beta \approx -0.011 \), \( M_S \) is the martensitic start temperature and \( T \) is the temperature (below martensitic start). It is clear that the fraction of martensite is not a function of time and also there is no thermal activation is needed to take place for the martensitic phase transformation. These type of transformations, in which the yield of the martensite is only dependent on the temperature rather the time spent at that temperature are described as athermal phase transformation [57, 58].

Equation 29 represents the variation of the volume fraction of the martensitic phase below the martensitic start temperature, which is in this case is 600 K. This equation does explain the behavior of the martensitic volume phase fraction above the martensitic start temperature, \( M_S \). However, it does not distinguish the difference between the variation of martensitic phase fraction in the austenitic (from martensitic to austenite) and martensitic (from austenite to martensite) phase transformations. That is, it does not differentiate the inherited hysteresis of the first-order phase transformations. The equation does not give any information about the nature of the phase transformation above the martensitic start temperature. Also, it is not possible to identify all the characteristic temperatures observed in a martensitic phase transformation, except \( M_S \), on the graph. Therefore, a better equation is needed to represent the true nature of the martensitic phase transformations, observed experimentally.
Figure 9: The volume fraction of the martensitic phase as a function of temperature given by the Koistinen and Marburger equation [56]. Note: the highest temperature is the martensitic start temperature which is chosen to be 600 K in this case.

3.1.3 Characteristic temperatures and kinetic equation of martensitic phase transformation in Heusler alloys

Mainly there are four characteristic temperatures (features) which could be identified in a martensitic phase transformation: martensitic start $M_S$ and martensitic finish $M_F$ in the martensitic phase transformation and austenitic start $A_S$ and austenitic finish $A_F$ temperatures in the austenitic phase transformations. The characteristic temperatures and their definitions are given in Table 1.

<table>
<thead>
<tr>
<th>Characteristic temperature Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martensite start</td>
<td>$M_S$</td>
<td>where the transformation from austenite to martensite begins on cooling.</td>
</tr>
<tr>
<td>Martensite finish</td>
<td>$M_F$</td>
<td>where the transformation from austenite to martensite finishes on cooling.</td>
</tr>
<tr>
<td>Austenite start</td>
<td>$A_S$</td>
<td>where the transformation from martensite to austenite begins on heating.</td>
</tr>
<tr>
<td>Austenite finish</td>
<td>$A_F$</td>
<td>where the transformation from martensite to austenite finishes on heating.</td>
</tr>
</tbody>
</table>

There are a number of different techniques to determine the characteristic temperatures of a martensitic phase transformation. Differential Scanning Calorimetry (DSC) is one such a technique where it measures the amount of energy (heat) absorbed/released by a sample, when it
is heated/cooled. DSC technique provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat release) processes. Those data are analyzed to identify the characteristic features of the martensitic phase transformations such as hysteresis and temperatures. Such a DSC curve of $Ni_{50}Mn_{37}Sb_{13}$ alloy which demonstrates all the characteristic temperatures of the martensitic and austenitic phase transformations is given in Figure 10 [59]. It clearly represents the hysteresis associated with this phase transformation.

![DSC curve of Ni$_{50}$Mn$_{37}$Sb$_{13}$ alloy](image)

Figure 10: DSC curve of $Ni_{50}Mn_{37}Sb_{13}$ alloy which demonstrates a martensitic and austenitic phase transformations with thermal hysteresis [59].

Magnetization measurements of a $Ni$-$Mn$-$X$ alloy, as a function of temperature under a constant magnetic field, can also be used to identify the features of the martensitic phase transformation. For alloys which demonstrate a merged magneto-structural phase transformation (i.e. there are two phase transformations, magnetic and structural, which take place simultaneously), the magnetization data (thermomagnetization curve) can be used to identify the characteristic temperatures of the martensitic phase transformation. Otherwise, the magnetization curve (i.e. magnetization vs. temperature under constant magnetic field) gives the characteristic features of the pure magnetic phase transformation.
Such a set of thermomagnetization curves of $Ni_{45}Co_{5}Mn_{36.6}In_{13.4}$ alloy under three magnetic fields 0.5, 2, and 7 T, is given in Figure 11 [32]. When temperature is increased, the alloy transforms from non-magnetic martensitic phase to ferromagnetic austenitic phase under all these magnetic fields. The characteristic temperatures of the magneto-structural phase transformation take place under 7 T field are marked Figure 11. Those temperatures are determined by extrapolating the linear parts of the thermomagnetic curve as shown here. By following the same procedure, the characteristic temperatures of the martensitic phase transformation under other magnetic fields (i.e. 0.5 and 2 T) could also be identified. As seen in many of those Ni-Mn based Heusler alloys, the martensitic phase transformation temperature of this alloy decreases with increasing magnetic field [30].

![Figure 11: Thermomagnetization curves of $Ni_{45}Co_{5}Mn_{36.6}In_{13.4}$ alloy under 3 magnetic field 0.5, 2, and 7 T magnetic fields. Characteristic temperatures of the martensitic and austenitic phase transformations under 7 T field are determined by extrapolating the linear parts of the thermomagnetic curve as shown here [32].](image)

These are the two methods which are widely used to determine the characteristic temperatures of the martensitic phase transformations. Additionally, phase fractions of each phase
in a martensitic phase transformation could be calculated by analyzing the diffraction data of the material which undergoes in the martensitic phase transformation. This data could be plotted as a function of the temperature and from this curve, the characteristic temperatures can be determined. This is the main technique used in this thesis work to identify the characteristic features of the martensitic phase transformations of the studied alloys.

3.1.4 Kinematic equation of the martensitic phase transformations

Many constitutive laws have been proposed to simulate the characteristic properties of the martensitic phase transformations. Among them, phenomenological models based on the internal variables, such as characteristic temperatures of the martensitic phase transformation, are widely used in practical engineering [60]. The first phenomenological model, based on the first and the second laws of thermodynamics, was introduced by Tanaka et al. in 1982 [61]. Following this work, successive models have been proposed by Brinson (1993) [62] and Zhu et al. (2002) [63]. Here, the most updated version of the phenomenological models, introduced by Li et al. (2013) [60] is discussed.

In the work of Li et al., the properties of the martensitic transformation (i.e. characteristic temperatures) of the Ti-49.5 wt % Ni were obtained through DSC measurements (similar to what is shown in Figure 12). Apart from the characteristic temperatures of a martensitic transformation (i.e. $M_S$, $M_F$, $A_S$, and $A_F$), a number of additional parameters were presented to describe the nature of the martensitic transformation more realistically. They are $T_A$, $T_M$, $A$, and $M$, where, $T_A$ and $T_M$ are the temperatures at which the martensitic phase fraction is 50% in the martensitic and austenitic transformations, respectively. $A \equiv (A_F - A_S)/2e$, $M \equiv (M_S - M_F)/2e$, and $e$ is the natural constant. These parameters are illustrated in Figure 12, a graph of variation of the austenitic phase fraction with the temperature in both martensitic (blue curve) and austenitic (red curve)
transformations. Martensitic phase fraction of a material at a certain temperature could be calculated by several different techniques such as X-ray or neutron powder diffraction, DSC curves, and thermomagnetization data. The procedure of the conversion of DSC data to martensitic phase fraction is given elsewhere [60].

Figure 12: Variation of austenitic phase fraction of a magnetic material, which undergoes a first-order phase transformation, while heating (red line) and then cooling (blue line) as a function of temperature. The characteristic temperature of the martensitic and austenitic transformations (i.e. $A_S$, $A_F$, $M_S$ and $M_F$) are obtained by extrapolating the linear parts of the thermogram. $T_A$ and $T_M$ are the temperatures at which the martensitic phase fraction is half in martensitic and austenitic transformations, respectively.

Li et al. (2013) [60] have established six different equations to simulate martensitic transformations stimulated under different driving forces such as temperature and stress and both temperature and stress, simultaneously. However, here only two equations will be given, which describe the variation of martensitic phase fraction in a martensitic and austenitic phase transformations take place upon changing the temperature of the material. The martensitic phase transformations under applied stress and both temperature and applied stress are out of the scope.
of this thesis work and hence the corresponding equations govern those martensitic phase transformations will not be discussed.

The kinematics equation of the phase transformation from austenitic phase to twinned martensitic phase (austenitic transformation) is given by Equation 30,

\[
f_M = \frac{1 - f_{M_0}}{1 + \exp\left(\frac{T - T_M}{M}\right)} + f_{M_0}
\]

where, \(f_{M_0}\) is the initial phase fraction of the twinned martensitic phase. The kinematics equation of the phase transformation from twinned martensitic to austenitic phase is given by Equation 31.

\[
f_M = \frac{f_{M_0}}{1 + \exp\left(\frac{T - T_A}{A}\right)}
\]

These equations accurately represent the variation of the martensitic phase fraction as a function of the temperature in both martensitic and austenitic phase transformations.

3.2 Ni-Mn based Heusler alloy

Heusler alloys are ternary inter-metallic compounds, first discovered by German chemist and metallurgist Friedrich Heusler in 1903. These alloys composed of \(Cu\) and \(Mn\) with other constituent elements such as \(Sn\), \(Al\), \(Sb\) and \(Bi\). Heusler reported that these alloys were ferromagnetic, even though the composing elements such as \(Cu\), \(Sn\), \(Al\), \(B\) and \(Bi\) are not ferromagnetic by themselves [64].

In \(Ni-Mn-X\) Heusler, the third element (\(X\)) such as \(Ga\), \(In\), \(Sn\), \(Sb\), and \(Al\) are coming from the groups IIIA-IVA of the periodic table. They undergo martensitic phase transformations upon changing the external parameters applied to the alloys such as temperature, pressure, and magnetic
field. These alloys exhibit unique properties in the vicinity of their structural transformation temperature because of these field-induced martensitic phase transformations. They undergo attractive phenomena such as super-elasticity [4], magnetic shape memory effect [3] and giant magnetocaloric effect [65]. The properties and effects exhibited by Heusler alloys around their transition temperature make them very suitable for numerous applications. One such application is the magnetic cooling based on the GMCE.

3.2.1 Crystal structure of Ni-Mn based Heusler alloys

3.2.1.1 Austenitic crystalline structures

Above phase transformation temperature, i.e. in the austenitic phase, despite their chemical composition and X atom, most of the Ni-Mn-X Heusler alloys have L2₁ crystalline structure. This structure belongs to Fm̅3m space group. As shown in Figure 13, L2₁ structure consists of four interpenetrating face centered cubic (fcc) sub-lattices [66]. The origins of those four sub-lattices are located at (0, 0, 0), (1/4, 1/4, 1/4), (1/2, 1/2, 1/2), and (3/4, 3/4, 3/4) positions of the L2₁ structure. In the stoichiometric compositions, i.e. NiₓMnᵧX₂₅ (for example Ni₂MnGa), Ni atoms occupy two sub-lattices, which have origins at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4). Generally, these positions are called regular Ni crystallographic sites. In Wyckoff notation, these crystallographic sites are identified as 8c positions. Mn atoms occupy the sub-lattice which has its origin located at (0, 0, 0). In Wyckoff notation the crystallographic sites belong to this sub-lattice are identified as 4b sites. In general, they are called regular Mn crystallographic sites. The X (= Ga, In, Sn, Sb) atom occupy the remaining fcc sub-lattice and the atomic positions belong to this sub-lattice are called 4b sites in the Wyckoff nation. The last fcc structure has it origin located at (1/2, 1/2, 1/2) [64]. Alternatively, L2₁ structure can be realized as a combination of two ordered binary compounds AB
$A = Ni$ and $B = Mn$) and $AC$ ($A = Ni$ and $C = X$) with Cubic $B2$ structure. This $B2$ structure itself is also recorded as the austenite crystalline structure of some of the off-stoichiometric $Ni-Mn-X$ Heusler alloys [40]. $B2$ structure belongs to $Pm\bar{3}m$ space group. Recorded crystalline structures of some of the $Ni-Mn-X$ based Heusler alloys with their chemical composition and other crystallographic information are summarized in Table 2.

Table 2: Reported crystallographic information of austenitic phase of the Ni-Mn-X Heusler alloys

<table>
<thead>
<tr>
<th>Reference number</th>
<th>Crystal structure</th>
<th>Composition</th>
<th>Lattice constants</th>
<th>Crystal system (space group)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[40]</td>
<td>$L2_1$</td>
<td>$Ni_{0.50}Mn_{0.24}In_{0.24}$</td>
<td>6.071 90</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td></td>
<td>$B2$</td>
<td>$Ni_{0.50}Mn_{0.37}In_{0.16}$</td>
<td>3.004 90</td>
<td>$Pm\bar{3}m$</td>
</tr>
<tr>
<td>[67]</td>
<td>$L2_1$</td>
<td>$Ni_{0.50}Mn_{0.30}Ga_{0.2}$</td>
<td>- 90</td>
<td>-</td>
</tr>
<tr>
<td>[68]</td>
<td>$L2_1$</td>
<td>Ni-Mn-Ga</td>
<td>5.780 90</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>[69]</td>
<td>$L2_1$</td>
<td>Ni-Mn-Ga</td>
<td>N/A N/A N/A</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>[70]</td>
<td>$L2_1$</td>
<td>$Ni_{0.45}Co_{0.05}Mn_{0.30}In_{0.133}$</td>
<td>N/A N/A</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>[71]*</td>
<td>$L2_1$</td>
<td>$Ni_{0.5}Mn_{0.25}Ga_{0.25}$</td>
<td>5.8127 90</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Ni_{0.5}Mn_{0.25}(Al_{0.025}Ga_{0.225})$</td>
<td>5.8111 90</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Ni_{0.5}Mn_{0.25}(Al_{0.025}Ga_{0.2})$</td>
<td>5.8094 90</td>
<td>$Fm\bar{3}m$</td>
</tr>
</tbody>
</table>

*Based on theoretical calculations

Figure 13: $L2_1$ crystalline structure of the stoichiometric $Ni-Mn-X$ Heusler alloy. This structure belongs to $Fm\bar{3}m$ space group.
3.2.1.2 Martensitic crystalline structures

\( \text{Ni}_2\text{MnGa} \) is the only \( \text{Ni}-\text{Mn} \) based Heusler alloy with stoichiometric composition 2:1:1, that undergoes in a martensitic phase transformation upon cooling [3]. In this case, essentially there is no volume change between the austenitic and martensitic structures, across this phase transformation [72]. Therefore, in this martensitic transformation, the simple relationship between austenitic crystalline structure \( L2_1 \) and martensitic crystalline structure \( L1_0 \) could be visualized easily (Figure 14-a). Also, off-stoichiometric \( \text{Ni}-\text{Mn}-X \) alloys (\( X: \text{Ga, In, Sn, Sb} \)) with low \( X \) concentration undergo in martensitic phase transformation and transform into tetragonal \( L1_0 \) structure (Figure 14-b). This \( L1_0 \) structure is the ground state structure of the \( \text{Ni}_{50}\text{Mn}_{50} \) compound and it belongs to \( I 4/mmm \) space group.

In all other \( \text{Ni}-\text{Mn} \) based alloy, martensitic phase transformations are demonstrated by off-stoichiometric alloys. The phase transformation temperature is dependent on the chemical composition and on the \( X \) element. In the martensitic transformations of off-stoichiometric \( \text{Ni}-\text{Mn}-X \) alloys, a volume change is observed across the phase transformations [73]. With this volume change across the martensitic phase transformations of off-stoichiometric alloys, the crystallographic relationship between the two phases, austenitic and martensitic, becomes complex [43].

Depending on the composition and \( X \) element of the \( \text{Ni}-\text{Mn}-X \) alloy, possible crystalline structures of the martensitic phases range from un-modulated structures to highly-modulated structures such as 5-, 6-, 7- and 10\( M \) modulated structures. Here, \( M \) stands for the monoclinicity resulting from the distortion associated with the modulation, whereas the integer value (for example 5 in the 5\( M \) modulated structure) gives the number of basic \( L1_0 \) units along the \( C \) axis (110 direction in the \( L2_1 \)) of the modulated structure [29]. A summary of the literature survey of
possible crystal structures of Heusler alloys in martensitic phase, depending on the composition and the X element, is given in Table 3.

Figure 14: Some of the reported crystalline structures of the \(\text{Ni-Mn-X} \ (X = \text{In, Ga, Sn, Sb})\) Heusler alloys in the austenitic and the martensitic phases. (a) The austenitic \(L2_1\) structure and the relationship between this structure and tetragonal \(L1_0\) structure. (b) Tetragonal \(L1_0\) structure. (c) and (d) are the top view of the (010) plane of the \(7M\) and \(5M\) modulated monoclinic structures obtained by shearing the tetragonal cell, respectively. Note: in these modulate structures \(\text{Mn}\) (green) and \(X\) (red) atoms are in the (010) plane, whereas the \(\text{Ni}\) atoms (blue) are in (0 2 0) plane, which is parallel to the (010) plane.
Table 3: Reported crystallographic information of the martensitic phase of the Ni-Mn-X Heusler alloys

<table>
<thead>
<tr>
<th>Ref. Num.</th>
<th>Crystal structure/Modulation</th>
<th>Composition</th>
<th>Crystal system (space group) and lattice parameters</th>
<th>Crystallographic system SPACE group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a(Å)</td>
<td>b(Å)</td>
</tr>
<tr>
<td>[40]</td>
<td>5M</td>
<td>Ni₀₅₁Mn₀₃₃In₀₁₅₅</td>
<td>4.385</td>
<td>5.592</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td>Ni₀₄₉₆Mn₀₃₅₄In₀₁₄₈</td>
<td>4.391</td>
<td>5.882</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>Ni₀₄₉₉₆Mn₀₄₀₂In₀₉₉</td>
<td>4.284</td>
<td>5.811</td>
</tr>
<tr>
<td></td>
<td>Un-modulated</td>
<td>Ni₀₄₉₆Mn₀₄₅In₀₈₉</td>
<td>7.593</td>
<td>7.593</td>
</tr>
<tr>
<td>[67]</td>
<td>10M</td>
<td>Ni₀₅₀₅₆Mn₀₂₆₄Ga₀₂₀</td>
<td>4.222</td>
<td>5.507</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni₀₅₇₅₆Mn₀₂₁₂₅Ga₀₂₅</td>
<td>4.220</td>
<td>5.539</td>
</tr>
<tr>
<td>[69]</td>
<td>5M</td>
<td>Ni₀₅₅₅₆Mn₀₂₅₅Ga₀₂₀</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>Ni₀₅₄₅₆Mn₀₂₆₄Ga₀₂₃₅</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>10M</td>
<td>Ni₀₄₅₅₆Mn₀₃₇₄Ga₀₁₇₁</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td>Ni₀₅₅₅₆Mn₀₲₇₅₆Ga₀₂₁₁</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Un-modulated</td>
<td>Ni₀₄₅₅₆Mn₀₳₇₅₆Ga₀₁₇₁</td>
<td>7.75</td>
<td>7.75</td>
</tr>
<tr>
<td>[74]</td>
<td>5M</td>
<td>Ni₀₅₅₅₆Mn₀₂₅₅Ga₀₂₀</td>
<td>N/A</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>Ni₀₅₃₅₆Mn₀₂₆₄Ga₀₂₀</td>
<td>4.26</td>
<td>5.43</td>
</tr>
<tr>
<td></td>
<td>5M &amp; 7M</td>
<td>Ni₀₅₀₅₆Mn₀₂₅₅Ga₀₂₃₅</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td>Ni₀₅₅₅₆Mn₀₁₅₅₆Ga₀₂₅₈</td>
<td>4.3</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>Ni₀₅₃₅₆Mn₀₂₆₄Ga₀₂₃₂</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>10M &amp; unmod.</td>
<td>Ni₀₄₇₅₆Mn₀₃₇₄Ga₀₁₇₁</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td>Ni₀₅₅₅₆Mn₀₂₅₅Ga₀₂₁₁</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>[35]</td>
<td>5M &amp; 7M</td>
<td>Ni₀₆₄₅₆Mn₀₄₁₃₆</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The magnetic and structural phase transformation temperatures as a function of the number of valance electrons per atom (e/a ratio) for Ni-Mn-X alloy are given in the sections (a) for X = Sn, (b) for X = In, and (c) for X = Ga of Figure 15. The e/a ratio is calculated by using Equation 32.

\[
\frac{e}{a} = \frac{(\text{Ni comp. in at. %} \times e_{\text{Ni}} + \text{Mn comp. in at. %} \times e_{\text{Mn}} + X \text{ comp. in at. %} \times e_{X})}{100}
\]

Where, \(e_{\text{Ni}}, e_{\text{Mn}}, \text{and } e_{X}\) are the number of valance electrons in Ni, Mn, and X element, respectively. The compositions of the constituent elements in at. % are labeled in upper axis of the graph. From this graph (Figure 15) it is evident that the crystalline structure of the martensitic phase evolves from \(L1_0\) structure for the alloys with high e/a ratio and shifts to \(14M\) and then \(10M\) with decreasing e/a ratio and increasing concentration of the X element. That is, the martensitic
structure is highly dependent on the chemical composition (i.e. e/a ratio) of the alloy and the X species.

Figure 15: The magnetic and structural phase diagrams of (a) Ni-Mn-Sn, (b) Ni-Mn-In, and (c) Ni-Mn-Ga Heusler alloys. The open circles (in all diagrams) and small black circles in Ni-Mn-Ga phase diagram represent martensitic and pre-martensitic transition temperatures, respectively. The triangles represent magnetic phase transformation temperatures. Martensitic phase transformation temperature decreases with increasing X species concentration. Crystalline structure of martensitic phase is dependent on the e/a ratio and the different regions corresponding to the different martensitic structures are separated by vertical dashed lines [43].

Figure 16 summarizes the variation of martensitic transformation temperatures and Curie temperatures of Ni-Mn-X alloys, where X is Ga, Ni, Sn and Sb, as a function of valance electron concentration per atom (e/a ratio). All curves start from Ni50Mn50 alloy (e/a ratio is 8.5), the base composition which is common to all these materials, which transforms to the L10 martensitic structure at about 975 K from austenitic B2 type structure [76]. The martensitic transformation temperature $M_S$ of the Ni-Mn-X alloys decrease with decreasing e/a ratio as a result of alloying with X element. Slope of the $M_S$ vs e/a ratio for different alloy series is different. However, it is significantly higher for all the alloys as the lowest is 80 K per 0.1 drop of e/a ratio. The dependence
of the $M_S$ temperature on the e/a ratio could be understand by considering the different binding forces arising in each alloy series as the $X$ species have different crystalline structures in their elemental forms.

As $Mn$ concentration increases (i.e. increasing of e/a), it could be expected more $Mn-Mn$ nearest neighbors and hence shorter $Mn-Mn$ interatomic distances. Therefore, the increasing of the AFM interactions with the increasing e/a ratio decreases the FM nature as well as the Curie temperature of the austenitic phase of these alloys.
3.2.2 Magnetic properties of Ni-Mn-X based Heusler alloys

3.2.2.1 Magnetization curves

In all Ni-Mn based Heusler alloys (which undergo martensitic transformations) there is a drop in the temperature dependence of the magnetization, M(T), at martensitic start temperature, even under a small magnetic field ~10 mT [40, 77]. This phenomenon is observed even under significantly higher magnetic field (~5 T) in all mentioned alloys above, except Ni-Mn-Ga. In Ni-Mn-Ga alloys, above certain field, magnetization drops when it is transforming from martensitic to austenitic phase [78].

The magnetization data under two extreme magnetic fields, 0.05 T and 5 T, of Ni-Mn-X (X = In, Ga, Sn, and Sb) alloys as a function of temperature in zero field cooling (ZFC), field cooling (FC), and field heating (FH) routines are given in Figure 17. Here $T_C^A$ and $T_C^M$ are the Curie temperatures of the austenitic and martensitic phases, respectively.

Under 0.05 T field, all Ni-Mn-X alloys ordered ferromagnetically just below the $T_C^A$. When temperature is decreased further down, magnetization decreases again and the temperature where the falling of the magnetization start is identified as martensitic start temperature $M_S$. Similarly, under the assumption of that the crystalline and magnetic phase transformations are merged, other characteristic temperatures (martensitic finish $M_F$, austenitic start $A_S$, and austenitic finish $A_F$) of the martensitic and austenitic transformations are identified from the features of the magnetization curves as shown in Figure 17-a.

Figure 17-(a) demonstrates the behavior of magnetization of $Ni_{50}Mn_{34}In_{16}$ alloy as a function of temperature under low magnetic field. This is a representative of the magnetization vs temperature curve for all Ni-Mn-X alloys. The local minima of the heating and the cooling curves are the austenitic start, $A_S$, and martensitic finish, $M_F$, temperatures, respectively. Below the $M_F$,
magnetization increases with decreasing temperature because of the ferromagnetic ordering of the martensitic phase. The Curie temperature of the martensitic phase, $T_{CM}^M$, could be identified only in FC and FH curves.

![Graph showing magnetization under different conditions](image)

Figure 17: Magnetization of Ni-Mn-X alloys as function of temperature in ZFC, FC and FH routines under two magnetic fields in the extreme ends. Magnetization of (a) Ni$_{50}$Mn$_{34}$In$_{16}$ and (b) Ni$_{50}$Mn$_{27}$Ga$_{23}$ alloys in very low magnetic field (0.05 T). (c) Magnetization of Ni-Mn-X alloys (X = Ga, In, Sn, and Sb) under high magnetic field of 5 T [40, 43].

There is no such feature in the ZFC magnetization curves and it deviate from other two curves just below the $T_{CM}^M$. ZFC magnetization decreases as temperature decreases because of two reasons. The major contribution is that the magnetization anisotropy of the martensitic phase below $T_{CM}^M$ and without a field the alloy does not order ferromagnetically. The other reason could be the pinning of the ferromagnetic matrix by antiferromagnetic components in different spin configuration to have lower magnetization in the absence of a magnetic field. The situation is entirely different in the case of Ni-Mn-Ga alloys (Figure 17-b). Magnetization of Ni-Mn-Ga seems to be temperature-independent below $T_{CM}^M$. Because of the higher twin-boundary mobility and
stronger anisotropy of the magnetization of Ni-Mn-Ga alloys compared to other Ni-Mn-X alloys, martensitic variants could be aligned along the easy axis by a such a small magnetic field.

Under a higher applied field (5 T), all the Heusler alloys except Ni-Mn-Ga have higher magnetization in the austenitic phase because they ordered ferromagnetically below their austenitic Curie temperature $T_C^A$ (Figure 17-c). When temperature is decreased from $T_C^A$, again there is an abrupt drop in magnetization at the $M_S$ temperature in the forward martensitic transformation. Similarly, there is an abrupt rise in the magnetization at $A_F$ in the austenitic phase transformation. The reason for the drop of the magnetization at the $M_S$ is the development of the local antiferromagnetic ordering associated with the changing of the $Mn-Mn$ bond length. Two phases, austenite and martensite, have different crystalline structures. Usually, in the austenitic phase, there are two types of $Mn-Mn$ exchange interactions: $Mn$ atoms reside in their regular sites (4a) interact ferromagnetically and antiferromagnetically with other $Mn$ atoms in the regular $Mn$-sites (4a) and X atomic sites (4b), respectively [79]. However, in the martensitic phase, these alloys assume distorted tetragonal, monoclinic, or orthorhombic structures. Upon phase change the atomic distance between neighboring $Mn$ atoms changes [80] hence the shorter $Mn-Mn$ interatomic distances would results in enhanced $AFM$ interactions compared to that of in the austenitic phase. Therefore, a large degree of magnetic frustrations could be observed in the low temperatures in the martensitic phase [81]. Additionally, giant magnetoresistance [82, 83] and exchange bias effects [84, 85] observed in these alloys further substantiate the existence of the antiferromagnetic interactions in these Heusler alloys.

In all Ni-Mn-X alloys, except Ni-Mn-Ga the magnetization of the martensitic phase is significantly lower than that of the austenitic phase. In the case of Ni-Mn-Ga alloys, magnetization
increases in the martensitic phase as temperature decreases because of the high twin-boundary mobility of the martensitic variants overcome the competition of the non-FM entities [86].

3.2.2.2 Magnetic moments and magnetic interactions between the constituent atoms

In Ni-Mn-X and Ni-Mn-Co-X alloys, all the constituent atoms except X species (In, Ga, Sn, and Sb) carry magnetic moments. Among them, Mn atoms carry the largest magnetic moments and the magnetic properties of these alloys are mainly determined by their magnetic moments. The contribution of Ni and Co atoms to the observed magnetization is relatively small [34].

In the austenitic phase, magnetic moments of Mn atoms in the regular Mn-sites couple ferromagnetically with the weak magnetic moments of Ni atoms [66]. Mn atoms in Ni-sites couple ferromagnetically with their nearest neighbor Mn atoms that are located at Ga sites [33]. Magnetic interactions of Ni and Mn with X atoms are very small compared to Mn-Mn and Mn-Ni interactions, and hence are negligible [87]. Almost all of these Ni-Mn based Heusler, austenitic phase exhibits a ferromagnetic ordering. This is because of the large number of Mn-Mn FM interactions between Mn atoms in the 4a sites and Mn-Ni FM interactions between Mn in 4a and Ni in 8c sites. They overcome the AFM interactions such as Mn-Mn atoms in regular Mn sites (4a) and X atoms sites (4b) [33, 87].

As discussed in the previous section, depending on the composition and X species, martensitic phase of these alloys assume number of complex modulated structures which belong to tetragonal, monoclinic, and orthorhombic crystalline systems. Upon martensitic phase change the interatomic distance between neighboring Mn atoms changes [80] hence the shorter Mn-Mn interatomic distances would results in enhanced AFM interactions compared to that of in the austenitic phase. Depending on the composition of the alloy, the competition between FM and AFM interactions in the martensitic phase could results in different magnetic states such as
ferrimagnetism [87], antiferromagnetism [88], and spin glass [89, 90] or may be highly complex magnetic states such as super spin glass and super-ferromagnetic state [91].

3.3 Technological important phenomena exhibited by Ni-Mn based Heusler alloys

Some Heusler alloys undergo recoverable martensitic phase transformation upon changing external parameters, including applied stress, temperature and magnetic field. Upon this phase transition, they recover from large deformation and return to their original shape. The shape recovery upon changing the temperature or applied stress is called conventional Shape Memory Effect (SME), while the shape recovery upon changing the applied magnetic field is called Magnetic Shape Memory effect (MSM) [92].

Discovery [3] and developments relating to the MSM effect [93] open new research areas focusing on the developments of more efficient devices based on Shape Memory Effect, such as actuators and sensors. This is because controlling the SME with a magnetic field is very convenient and effective when compared with controls based on temperature and applied stress. The phenomena responsible for MSM effect is the magneto-structural coupling between magnetic and martensitic variants (twin related structural domains) in the mesoscopic length scale. This phenomenon causes a change in the length of the material due to re-orientation of the martensitic variants upon applied magnetic field [43]. Figure 18 represents the mechanism of the MSM effect schematically. Below the martensitic transformation temperature, material is heterophase (a composition of several twin related martensitic variants). Magnetic domains present within each of these twinned martensitic variants and the directions of the magnetization vector in each magnetic domain are along the easy axis of the magnetization. The magnetic variants are organized in a way that minimizes the magnetostatic energy [94].
Figure 18: Schematic representation of the mechanism of Magnetic Shape Memory Effect observed in the magnetic material which has high-enough magneto-crystalline anisotropy in martensitic phase to cause a rotation of martensitic variants upon applying a magnetic field (adapted from [43]).

When magnetic field is applied to the material, magnetic domains within each martensitic variant align with the applied magnetic field if the magnetic anisotropy is weak. However, for a material with high degree of magnetic anisotropy, magnetic energy should increase by an amount great enough to rotate the magnetic domains towards the applied magnetic field. If the energy required to move the structural domain boundaries is considerably low, rotation of martensitic twinned variants along the field direction take place, rather than the rotation of magnetic domains. Rotation is facilitated by the difference in Zeeman effects between the variants. This results in a
martensitic structure where all variants are aligned in the same direction. Upon heating, this transforms to austenitic phase and recovers the original shape of the material [43].
CHAPTER 4

EXPERIMENTAL DESCRIPTION

4.1 Studied alloys

Six Ni-Mn-X based alloys; one Ni-Mn-In, three Ni-Mn-In-Co, and two Ni-Mn-Ga alloys, were studied by Rutherford backscattering spectrometry (RBS), neutron and synchrotron diffraction techniques, and magnetic measurements. In this chapter, the experimental techniques will be discussed considering their advantages and limitations particularly in regards the current study. Then the details of each experiment carried out at each facility will be given.

The composition of Ni-Mn-In and Ni-Mn-In-Co alloys were determined by RBS technique. Whereas the compositions of Ni-Mn-Ga alloys were determined by Energy Dispersive X-ray Spectroscopy (EDS) technique. Designations of these alloys with their constituent elements are given in Table 4.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition</th>
<th>Technique used to determine the composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-1</td>
<td>Ni\textsubscript{50}X\textsubscript{25+Y}Mn\textsubscript{25-X-Y}In\textsubscript{25-X-Y}</td>
<td>RBS</td>
</tr>
<tr>
<td>Co-73</td>
<td>Ni\textsubscript{50+X}Mn\textsubscript{25+X-Y}In\textsubscript{25+X-Y}Co\textsubscript{Z}</td>
<td>RBS</td>
</tr>
<tr>
<td>Co-74</td>
<td>Ni\textsubscript{50+X}Mn\textsubscript{25+X-Y}In\textsubscript{25+X-Y}Co\textsubscript{Z}</td>
<td>RBS</td>
</tr>
<tr>
<td>Co-76</td>
<td>Ni\textsubscript{50+X}Mn\textsubscript{25+X-Y}In\textsubscript{25+X-Y}Co\textsubscript{Z}</td>
<td>RBS</td>
</tr>
<tr>
<td>Ga-S1</td>
<td>Ni\textsubscript{50+X}Mn\textsubscript{25+X-Y}Ga\textsubscript{25+Y}</td>
<td>EDS</td>
</tr>
<tr>
<td>Ga-S2</td>
<td>Ni\textsubscript{50+X}Mn\textsubscript{25+X-Y}Ga\textsubscript{25+Y}</td>
<td>EDS</td>
</tr>
</tbody>
</table>
4.2 Casting, heat treatments and preparation of the alloys

The alloys were fabricated in our collaborators’ laboratory and the author will provide only a brief description. All alloy samples were cast by an arc-melting furnace under an argon atmosphere. Details of the heat treatment process is largely unknown to the author. However, all the alloys except Co-76 alloy, underwent heat treatments. The Co-76 alloy was used in all the experiments in as-cast state.

4.3 Rutherford backscattering spectrometry (RBS) [95]

Rutherford backscattering spectrometry (RBS) is a nuclear scattering technique that is widely used to analyze surface layers of solid materials. In RBS, the target material is bombarded with a high-energy ion beam (typically, the kinetic energy of the incident beam is in the range of a few MeV), and the energy of backscattered projectile ions is measured using an energy sensitive solid-state detector. A silicon surface barrier detector was used in the current series of experiments. From the measured energy spectrum of the backscattered ions, the composition of the target material and the depth profile (few micrometers) of constituent elements can be determined quantitatively. The main advantage of RBS analysis, when compared with other quantitative analytical techniques such as energy-dispersive X-ray spectrometry, is that this method does not require a standard or reference samples [95, 96]. Additionally, RBS technique gives a good depth resolution of up to several micrometers (typically, the depth is about 2 μm for $He^{2+}$ ions and about 20 μm for incident protons). Although RBS technique is considered a non-destructive analytical method, some properties of the samples such as surface roughness may be altered during the sample preparation process. RBS technique is sensitive to heavy elements, and therefore chemical composition could be determined accurately when the sample consists of heavy elements.
The scattering geometry used in the present study, IBM geometry, is shown in Figure 19.

In this geometry, the incident and scattered beams as well as the normal to the sample surface are all in the same plane. The relationship between the incident ($\alpha$), exit ($\beta$), and scattering angles ($\theta$) is given by Equation 33 and displayed in Figure 19 (b).

\[ \alpha + \beta + \theta = 180^\circ \]  

Equation 33

Figure 19: (a) The IBM geometry of the RBS experiment. (b) The relationship between the incident ($\alpha$), exit ($\beta$), and scattering ($\theta$) angles (adapted from [95]).

The relationship between the energy of incident ion, $E_0$, and scattered ion $E_1$, in the laboratory frame of reference is given by Equation 34. Where $K$ (Equation 35) is the kinematic factor, and $M_1$ and $M_2$ are the masses of the incident ions and the target atoms, respectively.

\[ E_1 = KE_0 \]  

Equation 34
\[ K = \frac{M_1^2}{(M_1 + M_2)^2} \left\{ \cos \theta \pm \sqrt{\left( \frac{M_2}{M_1} \right)^2 - \sin^2 \theta} \right\}^2 \] 35

In this experiment, the target nucleus is at rest. In almost all cases, the target atoms are heavier than the incident ion, and Equation 35 is then used with a “+” sign. When, the incident ion is heavier than the target atoms, Equation 35 is used with a “−” sign. For two different elements with mass difference \( \Delta M_2 \) present in the target, the energy difference \( \Delta E_i \) between backscattered ions is given by Equation 36.

\[ \Delta E_i = E_0 \left( \frac{dK}{dM_2} \right) \Delta M_2 \] 36

The larger the difference between the masses of the incident ion and target atoms, higher the energy resolution between the scattered ions from these target atoms. Also, if there is a significant difference between the atomic masses of the constituent atoms in the target sample, a clear separation between the edges, produced by these target atoms, could be seen in the RBS spectrum. As a result, the depth profile composition of such a material could be determined accurately.

4.3.1 RBS experimental description

The RBS data of these alloys were collected at Western Michigan University’s 6 MV Van de Graff accelerator laboratory. To get the maximum resolution between the back scattered ions from the target elements (i.e. Ni, Mn, In, Ga and Co), ion beam type, ion beam energy, angles of incidence and angles of scattering were pre-determined by calculations based on the above kinematic equations (Equations 33-36). Additionally, a simulation of the experiment and data
analysis was carried out using “SIMNRA”, an ion beam analyzing software [97]. Based on the pre-calculation, to get the maximum resolution in the RBS spectrum, 15 MeV \( O^{4+} \) ion beam was selected at a scattering angle of 150\(^0\). The data of the In-1 alloy were collected using both 2.5 MeV \( He^{2+} \) and 15 MeV \( O^{4+} \) ion beams at a scattering angle of 150\(^0\). A \( He^{2+} \) beam was used as a trial run, just to identify the constituent elements in the alloy sample. The chemical composition was calculated using the RBS data collected using 15 MeV \( O^{4+} \) ion beam. For the rest of the alloys, RBS data were collected using 15 MeV \( O^{4+} \) beam only at a scattering angle of 150\(^0\). Experimental setup of the RBS experiments performed in the linear accelerator laboratory at WMU, is shown in Figure 20.

![Figure 20: Rutherford backscattering spectrometry experimental set-up at WMU linear accelerator laboratory.](image)

The surface of the alloy, which was irradiated by ion beam, was prepared by polishing it to have a mirror like finish to the surface. 5.0-micron aluminum oxide powder was used as the abrasive. Also this sample preparation procedure removes any oxidation on the sample surface.
4.4 Synchrotron X-ray diffraction

Synchrotron radiation is extremely bright electromagnetic radiation that is produced in the booster ring (part 3 in Figure 21-a) of a synchrotron. Inside these booster rings, electrons are circulated and boosted by microwaves generated by radio frequency cavities. Electrons are produced by an electron gun (part 1 in Figure 21-a) and then accelerated to the booster ring by a linear accelerator (part 2 in Figure 21-a). Synchrotron radiation is produced by wiggling ultra-relativistic high-energy electrons (travelling with speeds close to the speed of light) with a device called undulator, which are in the straight parts of the storage ring of synchrotrons. Synchrotron radiation covers a broad band of electromagnetic radiation, wavelengths ranging from about 0.1 nm to 1000 nm, allowing the user to select the desired wavelength for their experiment [98]. High-energy, X-ray photons have great penetrating power into materials, that facilitates the structural studies of bulk materials. In addition, continuous spectrum, high flux and brightness, and coherence are some of the unique properties of synchrotron radiation, which make it an essential tool to explore various materials [99]. Moreover, synchrotron diffraction technique has the following advantages over conventional X-ray diffraction techniques: a single spectral line eliminates the problem associated with $K_\alpha$ doublets and spectral line shapes, an easy wavelength selection maximizes the peak-to-background ratio, simple Gaussian profiles for all the peaks in the diffraction pattern for refinement of the instrumental parameters and that makes the profile fitting relatively easier, and greater precision in lattice parameters [100]. Another advantage of synchrotron diffraction over the conventional X-ray diffractometer is that, in some synchrotron facilities, diffraction data can be collected under various experimental conditions. In some facilities, experimental conditions of the sample such as applied magnetic field could be controlled. Also, applied stress to the sample could be controlled by a suitable apparatus supplied by user.
Another important advantage of the synchrotron diffraction, especially in the current study, is that it allows the user to distinguish In atom from other atoms present in the studied alloys (i.e. Mn, Ni and Co). This is because the atomic number of In is relatively high, compared to that of Mn, Ni and Co. In the current study synchrotron diffraction is used to determine the crystallographic information, site occupancies, and chemical composition of the alloys as well as the influence of the applied magnetic field on crystal structures and phase transformation temperatures of these Heusler alloys.

![Synchrotron facility diagram](image)

Figure 21: (a) Structural features of a synchrotron facility: 1- electron gun, 2 - linear accelerator (LINAC), 3 - booster ring, 4 - storage ring, 5 - beamline, and 6 - end station. (b) Schematic diagram of the experimental set-up in the end station.

### 4.4.1 Synchrotron X-ray experimental description

In-situ synchrotron X-ray diffraction measurements of the polycrystalline Ni-Mn-X based alloys were carried out at beamline 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory (Figure 22). The details of the experiments performed in the 11-ID-C beamline are summarized in Table 5.
The wavelength of the X-ray at 11-ID-C beamline was 0.010798 nm in the experiment of the \textit{In}-1 alloy. For the rest of the alloys, the synchrotron data were collected at the same beam line using X-ray with the wavelength of 0.010804 nm. Diffraction data of the \textit{In}-1 sample were collected under 2 different applied magnetic fields (2 and 4 T) and without an applied field. Under each magnetic field, data were collected at temperature steps of 2 °C while heating up from 290 K to 314 K and then cooling back to 290 K. Synchrotron data of the \textit{Co}-73 alloy were collected under 3 magnetic fields (2, 4, and 6 T) and without an applied magnetic field.

Figure 22: Experimental setup to collect synchrotron diffraction data of the alloys (under no magnetic field) at the beamline 11-ID-C of the Advanced Photon Source.

Under each magnetic field, data were recorded while heating and then cooling the sample in steps of 5 K. Also, for the \textit{Co}-73 alloy, diffraction measurements were performed at 220 and 230 K while changing the applied magnetic field to the alloy from 0 to 6.5 T and back to 0 T. For
all other alloys (i.e. Co-74, Co-76, Ga-I and Ga-2), data were collected under no applied magnetic field while heating from 100 K up to 400 K and then cooling down back to 100 K.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Wavelength used (nm)</th>
<th>Temperature range while heating (K)</th>
<th>Temperature range while cooling (K)</th>
<th>Magnetic field (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-I</td>
<td>0.010798</td>
<td>290-314 (2 K steps)</td>
<td>314-290 (2 K steps)</td>
<td>0</td>
</tr>
<tr>
<td>Co-73</td>
<td>0.010804</td>
<td>205-300 (in steps of 5 K)</td>
<td>230-300 (in steps of 5 K)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220-300 (in steps of 5 K)</td>
<td>300-185 (in steps of 5 K)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210-240 (in steps of 5 K)</td>
<td>300-175 (in steps of 5 K)</td>
<td>6</td>
</tr>
<tr>
<td>Co-74</td>
<td>0.010804</td>
<td>100-400 K (in steps of 10 K)</td>
<td>400-100 (in steps of 10 K)</td>
<td>0</td>
</tr>
<tr>
<td>Co-76</td>
<td>0.010804</td>
<td>100-400 K (in steps of 10 K)</td>
<td>100-400 (in steps of 10 K)</td>
<td>0</td>
</tr>
<tr>
<td>Ga-S1</td>
<td>0.010804</td>
<td>100-400 K (in steps of 10 K)</td>
<td>100-400 (in steps of 10 K)</td>
<td>0</td>
</tr>
<tr>
<td>Ga-S2</td>
<td>0.010804</td>
<td>100-400 K (in steps of 10 K)</td>
<td>100-400 (in steps of 10 K)</td>
<td>0</td>
</tr>
</tbody>
</table>

4.5 Neutron diffraction

Neutrons are electrically neutral, spin half particle and carry magnetic moments of magnitude $-9.65 \times 10^{-27} JT^{-1}$ [101]. The electrical neutrality of neutrons allows them to penetrate electron clouds and interact with the nuclei via short-range strong nuclear forces. In comparison to other scattering techniques such as X-ray and electron scattering, neutrons penetrate deeper into the materials. Therefore, neutron diffraction technique provides the information on the bulk of a material. Additionally, in neutron diffraction, neutrons interact with magnetic moments of unpaired elections if present in the material via dipole-dipole interactions between magnetic moments of neutrons and atoms with unpaired electrons [102]. A schematic of different possible interactions of X-rays, electrons, and neutrons, with matter showing relative penetration depth are given in Figure 23.
Neutron diffraction technique offers several advantages over X-ray diffraction techniques in the study of the structural arrangement of Heusler alloys. First, the scattering amplitudes of the constituent atoms in the studied Heusler alloys \((\text{Ni, Mn, In, Co and Ga})\) for neutrons are significantly different (Table 6 [103]). Specifically, \(\text{Mn}\) has negative scattering length for neutrons, while \(\text{Ni and Co}\) have positive scattering lengths. However, the scattering lengths of \(\text{Co}\) and \(\text{Ni}\) are significantly different (see Table 6). They are closely positioned in the periodic table (atomic number of \(\text{Mn, Co, and Ni}\) are 25, 27, and 28 respectively), and therefore hardly distinguishable using X-ray diffraction technique. Because \(\text{Mn}\) site occupancy is highly correlated to the magnetic properties of the Heusler alloys, it is critical to know the site occupancies as precisely as possible. Neutron diffraction is the best available technique for the determination of site occupancies in the studied Heusler alloys because of the difference between the bound coherent neutron scattering lengths of their constituent atoms.

Additionally, magnetic moments of the neutrons interact with the magnetic moments of atoms with unpaired electrons in the magnetic materials. Most of the constituent elements in Heusler alloys \((\text{Ni, Mn, and Co})\) are transition metals and have unpaired electrons in their 3d electron shells. The interactions between the unpaired electrons of the constituent elements are the origin of the observed magnetic properties of the Heusler alloys. Therefore, a neutron diffraction technique could be used to investigate the magnetic structure of these Heusler alloys. If there is antiferromagnetic ordering present in the martensitic phase, there will be additional magnetic Bragg peaks, separated from crystalline peaks due to an enlargement of the magnetic unit cell compared to the crystalline unit cell [104].
Figure 23: Different interactions take place in a material when it is exposed to a beam of neutron, X-ray, and electron. Both X-ray and electron beams interact with the electrons in the material by electromagnetic interactions and electrostatic interactions, respectively. Due to the strong nature of these interactions, neither X-rays nor electrons penetrate deep into the material. On the other hand, neutron beam, which is electrically neutral, interacts with atomic nuclei via short-range strong nuclear forces and unpaired electrons in the material via dipole-dipole interaction between magnetic moments. Due to this short-range interaction, neutrons penetrate deep into the material (adapted from [102]).

Table 6: Bound coherent neutron scattering lengths of several elements present in Heusler alloys [103]

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Natural abundance (%)</th>
<th>Coherent scattering length (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (25)</td>
<td>Mn</td>
<td>100.0</td>
<td>-3.73</td>
</tr>
<tr>
<td>Co (27)</td>
<td>Co</td>
<td>100.0</td>
<td>2.49</td>
</tr>
<tr>
<td>Ni (28)</td>
<td>$^{58}\text{Ni}$</td>
<td>68.27</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>$^{60}\text{Ni}$</td>
<td>26.10</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>$^{61}\text{Ni}$</td>
<td>1.13</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>$^{62}\text{Ni}$</td>
<td>3.59</td>
<td>-8.7</td>
</tr>
<tr>
<td></td>
<td>$^{64}\text{Ni}$</td>
<td>0.91</td>
<td>-0.37</td>
</tr>
<tr>
<td>Ga (31)</td>
<td>$^{69}\text{Ga}$</td>
<td>60.10</td>
<td>7.88</td>
</tr>
<tr>
<td></td>
<td>$^{71}\text{Ga}$</td>
<td>39.90</td>
<td>6.40</td>
</tr>
<tr>
<td>In (49)</td>
<td>$^{113}\text{In}$</td>
<td>4.30</td>
<td>4.07</td>
</tr>
<tr>
<td></td>
<td>$^{115}\text{In}$</td>
<td>95.70</td>
<td>4.01</td>
</tr>
</tbody>
</table>
4.5.1 Constant wavelength (CW) neutron diffraction [105]

In the constant-wavelength powder diffraction technique, a monochromatic beam of neutrons produced in a nuclear reactor is used. The wavelength is selected using a monochromator. Most of the monochromators are single crystals made of silicon, copper, germanium, or pyrolytic graphite. The single crystal is correctly oriented to the incoming white neutron beam in order to diffract a mono-energetic beam of neutrons toward the sample. The elastically scattered neutrons from the sample are detected by suitable neutron detectors (Helium-3 gas), and recorded as a function of angle by rotating the detector, sample or both detector and sample at a constant speed.

4.5.1.2 Experimental description of (CW) neutron diffraction

In the current study, high-resolution CW neutron diffraction data of the Co-76 alloy were collected at the HB-2A diffractometer at Oak Ridge National Laboratory (https://neutrons.ornl.gov/powder). Data were collected at different temperatures in the range from 50 to 600 K while heating the alloy sample. The incident beam of neutron with the wavelength $\lambda = 0.1538$ nm was selected from the (115) plane of a Ge monochromator at a take-off angle of 90°. A photograph and a schematic diagram of the HB-2A instrument is shown in Figure 24. The detector bank of this instrument consists of 44 $^3$He tubes, each covers 3 cm (diameter) by 12 cm (effective length) area. The detector bank assembly can be rotated up to 35° to move it to a desired starting point and measurements can be made in the range $(2\theta)$ from 0° to 155° [106].
4.5.2 Time-of-Flight (TOF) neutron diffraction [107]

One of the advantages of the Time-of-Flight (TOF) neutron diffraction technique is that there are no low intensity issues like that associated with the constant-wavelength neutron diffraction technique. In the TOF neutron diffraction technique, the intensity of the incident beam is very high because, most the neutrons (a beam of white neutrons) produced in the spallation process are present in the incident neutron beam to the sample. A beam of white neutrons consists of a spectrum of neutrons with all the possible kinetic energies in a particular energy range.

In the first step of the spallation process, primary protons, which trigger the spallation process, are produced in a linear accelerator or LINAC. In the LINAC, negatively charged hydrogen ions are accelerated and their electrons are stripped off by allowing them to pass through a foil. Then pulses of neutrons are produced by striking these high-energy protons into a heavy metal target, a container of liquid mercury. These protons are then guided to a ring (i.e. a proton accumulation ring) where, protons are accumulated in bunches and accelerated to ultra-high velocities.
The pulses of neutrons, which are freed by the spallation process, are slowed down to desired velocities in a moderator and guided through a beamline to a specialized neutron diffraction instrument. These neutrons with different energies travel at different velocities, and therefore have different wavelengths. The relationship between the wavelength and velocity of neutrons is given by the de Broglie’s relationship \( \lambda = \frac{h}{mv} \). Here \( h \) and \( m \) are the Planck’s constant and mass of the neutron, respectively. In the spallation process, all the neutrons in a given pulse are generated at the same time, say \( t_0 \). If the length of the flying path \( L \) of the neutrons is known, a relationship between wavelength of the neutrons and time \( t \) taken for the neutrons to travel from the source to the detector via sample is given by Equation 37.

\[
\lambda = \frac{ht}{mL} \tag{37}
\]

A relationship between the d-spacing of the lattice planes and time of flight can then be obtained using Bragg law \( \lambda = 2d \sin \theta \). This relationship is given is Equation 38.

\[
\frac{ht}{mL} = 2d \sin \theta \Rightarrow d = \left( \frac{h}{2mL \sin \theta} \right) t \tag{38}
\]

It can be realized from the above relationship that the diffraction angle is constant; thus, the Bragg equation can be given in the following format (Equation 39):

\[
\lambda_{hkl} = 2d_{hkl} \sin \theta \tag{39}
\]

Therefore, the whole range of d spacing (Bragg reflections) of a sample can be measured at a fixed scattering angle \( 2\theta \) [107].
4.5.2.1 Experimental description

The schematic diagram of the TOF neutron diffraction experimental setup is shown in Figure 25. Time of flight (TOF) neutron diffraction data of the \textit{In-I} sample was collected at the Los Alamos’ Spectrometer for Materials Research at Temperature and Stress (SMARTS) instrument (http://lansce.lanl.gov/lujan/instruments/SMARTS.shtml). SMARTS facilitates collecting neutron diffraction data under the application of a variable magnetic field.

![Schematic diagram of the TOF neutron diffraction experimental setup.](image)

Figure 25: Schematic diagram of the TOF neutron diffraction experimental setup. A white beam of neutron incidents on the sample and scattered. Scattered neutron are detected by bank of detectors located at a fixed distance from the sample. The total length of the flight path is equal to the algebraic sum of the length from source to the sample $L_{CS}$, and length from the sample to the detector $L_{SD}$ (adapted from [107]).

As shown in Figure 26-b, the sample is placed in between thermally isolated compression platens that the temperature of the sample is changed conductively. These platens are placed inside of an aluminum vacuum chamber (Figure 26-b). The incident, diffracted, and transmitted neutron beams enter and exit from the vacuum chamber via four rectangular aluminum windows, which are at 90° to each other and positioned at 45° with respect to compression platens [108].
Figure 26: (a) Schematic diagram of the custom aluminum vacuum chamber with cryogenic loading capability. (b) Aluminum vacuum chamber with a copper cold mass. Samples are placed inside the vacuum chamber. Diffracted neutron beams exit from the vacuum chamber through the aluminum windows [108].

In the current experiment, neutron diffraction data of the In-I sample were collected at different temperature steps in the temperature range of 258 - 353 K under two applied magnetic fields (0 and 2 T) and no applied stress to the sample. Additionally, another set of data was collected within the same temperature window without the sample and under no applied magnetic field. There were two purposes of the second set of data. One was to determine the contribution of the sample environment to the diffraction patterns. The other was to determine the temperature of the sample more accurately in terms of the lattice constant of the copper. The calculated values of the lattice constant of Cu compared with the standard values and then the temperature of the sample was determined by thermal expansion coefficient of the Cu.

4.6 Superconducting Quantum Interference Device (SQUID) magnetometer

SQUID magnetometers are based on a super conduction quantum interface device in which one or two Josephson junctions are used as magnetic field sensors. The SQUIDs based on one and two Josephson junctions are called AC (rf) SQUIDs and DC SQUIDs, respectively. The physics
phenomenon that occurs in a Josephson junction is the quantum tunneling effect, which was proposed by B. D. Josephson in 1962 and experimentally observed in 1964 by Anderson and Rowell [109].

4.6.1 Operation of SQUID [69, 70]

Superconducting magnets immersed in a liquid helium bath create a uniform magnetic field over the whole area, which covers the sample-measuring region and superconducting pickup coils. The magnetic field of the superconducting magnet can be kept at a constant value (for DC magnetic measurements) or varied by superimposing a small AC driven magnetic field (for AC magnetic measurements), depending on the type of measurements to be performed. The sample is magnetized by the superconducting magnetic field, and there is no flux change in the DC magnetic field in the pickup coils when the sample is stationary. When the sample is moved between the two counter-wound pickup coils, the flux through the coils changes, inducing a current in the pickup coils. The change in flux (and in turns the induced current in pickup coil) is proportional to the magnetic moment of the sample. The pickup coil is inductively coupled to the superconducting quantum interference device, which is located away from the sample in the liquid helium bath. This results in the superconducting circuit transferring the magnetic flux from the sample to an AC SQUID device. This device acts as a magnetic flux-to-voltage converter and the collected voltage signal is then amplified and read out by the magnetometer's electronics.

4.6.2 DC magnetometry [69, 71]

As described above, the sample is magnetized by a constant magnetic field, and the magnetic moment of the sample is measured by an inductive technique. In this technique, measurements are performed by moving the sample relative to the pickup coil, either by one-time
extraction or by vibrating the sample. Superconductive pickup coils give highly sensitive measurements, which are independent of the sample extraction speed.

4.6.3 AC magnetometer [69, 71]

In AC magnetometer, a small AC drive magnetic field is superimposed upon the applied DC magnetic field. This AC drive magnetic field causes time a dependent magnetic moment in the sample. The AC magnetic moment induces a current in the pickup coil so that magnetic measurements of the sample can be made without any sample movement.

4.6.3.1 Low frequency measurements

At very low frequencies of an AC driven magnetic field, the magnetic measurements are very similar to DC magnetic measurements. For very small amplitudes of AC drive magnetic field compared to the DC magnetic field, the induced AC moment can be given by Equation 40 [110].

\[ M_{AC} = (dM/dH) \cdot H_{AC} \sin(\omega t) \]  

Where \( dM/dH \), \( H_{AC} \), and \( \omega \) are the slope of the \( M(H) \) curve (called the susceptibility), the amplitude of the AC driven magnetic field, and the frequency of the AC magnetic field, respectively. From Equation 40, it is evident that the AC magnetic measurements are very sensitive to the small variation in the magnetization. This is because the measurements are sensitive only to the variation of the magnetization with respect to the applied field \( (dM/dT) \) and not to the absolute value of the magnetization. Therefore, small magnetic variation in the sample can be identified even when the absolute magnetization of the sample is very large. Different parts of the magnetization curve are accessed by changing the DC applied magnetic field.
4.6.3.2 High frequency measurements [110]

Due to the dynamic effect of the magnetic moment of the sample, an AC magnetic moment does not follow the DC magnetization curve at higher frequencies. This effect can be detected by magnetometer electronics. Thus, AC magnetometry of a sample at higher AC drive frequencies gives two measurements of the magnetic susceptibility. One is the magnitude of the susceptibility ($\chi$) and the other is the phase difference between susceptibility and driven signal ($\phi$). Alternately, this can be understood as the real part (in phase) and the imaginary part (out of phase) of the susceptibility. The real part of the susceptibility, $\chi'$, is the slope of the $M(H)$ curve, while the imaginary part of the susceptibility, $\chi''$, represents the dissipative processes in the sample. The relationship between the real and the imaginary parts of the susceptibility and phase difference between them is given by the set of Equations 41 [110].

\[
\begin{align*}
\chi' &= \chi \cos \phi \\
\chi'' &= \chi \sin \phi \\
\chi &= \chi' + i\chi'' \\
|\chi| &= \sqrt{\chi'^2 + \chi''^2} \\
\phi &= \arctan\left(\frac{\chi''}{\chi'}\right)
\end{align*}
\]

In different magnetic materials, the imaginary part of the susceptibility corresponds to different processes. In conductive materials, the dissipation process responsible for the imaginary susceptibility is eddy currents. A spin-glass magnetic nature can be characterized by AC susceptibility measurements. Spin glass is irreversible and a highly metastable state due to the random interaction between disordered magnetic spins present in the material below a certain temperature called freezing temperature. Above the freezing temperature, the material is paramagnetic and the freezing temperature is identified by the presence of cusp (Figure 27) at
freezing temperature in the $\chi'$ vs. temperature curve [111]. Spin-glasses give rise to a nonzero imaginary susceptibility, due to relaxation and irreversibility of magnetic moments.

In ferromagnetic materials, irreversible domain walls movement or absorption due to permanent moments gives rise to non-zero imaginary susceptibility measurements. Additionally, susceptibility measurements can be used to determine the magnetic phase transition temperatures of magnetic materials because both $\chi'$ and $\chi''$ are very sensitive to magnetic phase changes. All these phenomena which occur in magnetic materials can be probed using AC magnetometer.

Figure 27: Zero field AC susceptibility vs. temperature measurements of CuMn (1 at% Mn) powder. The freezing temperature is identified by the presence of cusp at that temperature. The inset demonstrates the frequency dependence of cusp from 2.6 Hz (represent by triangles) to 1.33 kHz (represent by squares) [111].
Figure 28: (a) Schematic diagram of a variable temperature susceptometer (electronic circuit of the SQUID is not shown for clarity). (b) The SQUID response, when the sample is moved up and down through the superconducting detection coil, as a function of sample position height (adapted from [112]).

4.6.4 Magnetic Property Measurement System (MPMS)

Magnetic Property Measurement System (MPMS) Quantum Design used in this study consists of a superconducting solenoid magnet, which is immersed in liquid helium and produces a magnetic field up to 7 T (http://www.qdusa.com/products/mpms3.html). The sample is placed in the center of the superconducting magnet. The sample container is filled with helium at low pressure, and its temperature can be controlled. The maximum sample size that fits into this instrument is 9 mm. The sample temperature can be varied between 2 to 400 K and is thermally isolated from its surroundings. The sample can be moved up and down and can be rotated inside the superconducting pickup coils, which are inductively coupled to the SQUID. The whole measuring system is computer-controlled and can be operated 24 hours a day. Instrument execution is automatic according to pre-programmed measuring sequences without user intervention (except for refilling of liquid helium and changing of the samples) [113].
4.6.4.1 Thermomagnetic measurements of the studied alloys

Thermomagnetic measurements of Co-76 alloy were carried out in SQUID magnetometer at University of Michigan. Data were collected using MPMS in ZFC (cooling), FC (warming), and FC (cooling) paths under 2 different magnetic fields (0.05 and 0.1 T) in the temperatures range from ~1.9 K to 100 K. Thermomagnetic measurements of the Co-73, Co-74, and Co-76 alloys were carried out using a Variable sample magnetometer (VSM). Data were collected in ZFC (cooling), FC (warming), and FC (cooling) routines in a range of temperature under 4 different magnetic fields. Summary of the thermomagnetic measurements of these alloys are given in Table 7.

4.6.4.2 Susceptibility measurements of In-1 alloy

Real and imaginary parts of the susceptibility of the In-1 alloy were determined by AC-SQUID measurements conducted at the The Hebrew University, Israel. The amplitude of the measurements was $5.0 \times 10^{-6}$ T and data were collected under different frequencies in the range 73 to 1465 Hz.

Table 7: Summary of the thermomagnetic measurements

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Instrument</th>
<th>Temperature range (K)</th>
<th>Applied magnetic fields (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZFC (Cooling)</td>
<td>FC (Warming)</td>
</tr>
<tr>
<td><em>In-1</em></td>
<td>AC SQUID</td>
<td>100 - 1.8</td>
<td>1.8 - 100</td>
</tr>
<tr>
<td>Co-76</td>
<td>SQUID</td>
<td>100 - 1.8</td>
<td>1.8 - 75</td>
</tr>
<tr>
<td>Co-73</td>
<td>VSM</td>
<td>400 - 100</td>
<td>100 - 400</td>
</tr>
<tr>
<td>Co-74</td>
<td>VSM</td>
<td>400 - 100</td>
<td>100 - 400</td>
</tr>
<tr>
<td>Co-76</td>
<td>VSM</td>
<td>400 - 100</td>
<td>100 - 400</td>
</tr>
</tbody>
</table>
4.7 Data analyzing software

Neutron and synchrotron diffraction data analyses were performed using General Structure Analysis System (GSAS) [114] and POWDER CELL [115] software. Both GSAS and POWDER CELL are based on the Rietveld refinement method [116]. The Rietveld method is a crystallographic and magnetic structure refinement technique. The principle is to minimize a function $M$ (given by equation 42) which calculates the difference between the theoretically calculated profile $y^{calc}$, based on a model built on the previous knowledge of the material and instrument, and observed diffraction data, $y^{obs}$.

$$M = \sum_i w_i \left( y_{i}^{obs} - \frac{1}{c} y_{i}^{calc} \right)^2$$  \hspace{1cm} 42$$

where $w_i$ is the statistical weight and $c$ is the overall scale factor [116].

SARAh representational analysis and SARAh refine software were used to determine the magnetic structure from neutron diffraction data. The representational analysis is based on simple matrix calculations, that is used to find the model magnetic structures which can be possible from magnetic phase transformations (second-order phase transformations). SARAh representational analysis software performs these calculations automatically. The models based on these calculations are used as starting magnetic structures in the magnetic structure refinements. SARAh refine software can be used simultaneously with GSAS to perform the magnetic structure refinements [117].

4.8 Summary of the performed experiments

A summary of the experiments carried out on each alloy is given in the following Table 8. RBS and synchrotron diffraction measurements were performed on all six alloys. However, the
neutron diffraction data and magnetic measurements were carried out only in selected alloys because of the limitations of access to those experimental facilities.

Table 8: Summary of the studies performed on each alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Alloy Type</th>
<th>RBS</th>
<th>Neutron diffraction</th>
<th>Synchrotron diffraction</th>
<th>Magnetic measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-1</td>
<td>Ni-Mn-In</td>
<td>Yes</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>Co-73</td>
<td>Ni-Mn-In-Co</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Co-74</td>
<td>Ni-Mn-In-Co</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
</tr>
<tr>
<td>Co-76</td>
<td>Ni-Mn-In-Co</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Ga-1</td>
<td>Ni-Mn-Ga</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
</tr>
<tr>
<td>Ga-2</td>
<td>Ni-Mn-Ga</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 5

RESULTS

5.1 Chemical compositions of the studied alloys

Chemical composition of the studied Heusler alloys was determined independently by Rutherford Backscattering Spectrometry (RBS) analysis, Energy-Dispersive X-ray Spectroscopy (EDS) analysis, and by site occupancy refinements of the austenitic phase using either neutron or synchrotron diffraction data or both. In the case of the In-1 alloy, both neutron and synchrotron data were refined to get the site occupancies of the austenitic phase and the results were used in the calculations of the composition. For the Co-76 alloy, constant wavelength neutron diffraction data were used to refine the site occupancies to get the composition. For the rest of the alloys, i.e. Co-73, Co-74, Ga-S1, and Ga-S2, synchrotron diffraction data were refined in order to get the composition by site occupancies.

RBS experiments of the Ga-S1 and Ga-S2 alloys were not very successful and the energy resolution between the back scattered ions from constituent elements (Ni, Mn, and Ga) was not sufficient to get an accurate composition of the alloys. The main reason for this was the small sample size compared the diameter of the smallest possible ion beam. Therefore, in the case of the Ga-S1 and Ga-S2 alloys, EDS analysis was used to determine the chemical compositions.

In the RBS analysis, it was found that the Co-74 alloy is inhomogeneous. It was reported that the excess heat treatments to Ni-Mn-X alloys could cause segregation of the solid solution to stoichiometric and other phase with different compositions [118]. Even though there was no phase
with the stoichiometric composition in the analyzed region by the RBS, the observed inhomogeneity could be a result of excess heat treatments. Because of the inhomogeneity of the sample, it was not used in any further investigations. According to the EDS analysis, the Ga-S2 alloy has almost identical chemical composition to the Ga-S1 alloy, and as a result the crystalline structures of the austenitic phase as well as two martensitic phases (intermediate 7M monoclinic phase and low temperature tetragonal \( L1_{0} \)) are exactly the same as that of the Ga-S1 alloy. Also, they undergo similar martensitic phase transformations. Therefore, only the chemical composition and crystalline structures of the Ga-S2 alloy will be presented.

5.1.1 Depth profile composition by RBS technique

In order to get a maximum resolution between backscattered ions by constituent elements of the samples in the RBS spectrum (specially, to get as wide as possible separation between \( Mn \) and \( Ni \) edges, because they have similar atomic masses), a calculation was performed to determine the best ion beam. This calculation was based on Equations 34, 35, and 36, and the most appropriate ion type, its charge, and incident and scattering angles, out of the available resources, were determined. According to the calculations, 15 MeV O4+ ion beam was used at scattering angles of 140°, 150°, and 165° to collect the RBS spectra of these alloys. RBS data were analyzed using SIMNRA [97] to determine the composition of the alloys. The error analysis of the elemental composition calculations was also performed using the auto fit function available in the SIMNRA software.

5.1.1.1 Depth profile composition the \( In-1 \) alloy (\( Ni_{45}Mn_{43}In_{12} \))

Two RBS spectrums of the \( In-1 \) alloy, which resolved all elements in the sample, were obtained using a 15 MeV O4+ ion beam in different scattering angles, 150° (Figure 29-a) and 140°
Different scattering angles were used to examine any improvement of the resolution in the RBS spectrum, however, such an improvement was not observed.

Figure 29: Experimental and simulated (by SIMNRA [97]) RBS spectrum of the In-I alloy (a) with scattering angle of 150° and (b) scattering angle of 140°. Data were collected using 15 [MeV] O^{4+} ion beams.

Indium composition of the In-I alloy was determined more accurately compared to that of Mn and Ni. This is because, even with different scattering angles, the In edge in the RBS spectrum was identified clearly (Figure 29-a and -b) due to the relatively large mass difference between In and the other atoms (Ni and Mn) in this alloy. Summary of the calculations of the composition of the In-I alloy is tabulated in Table 9, including the uncertainties of the measurements. The uncertainties of the chemical composition results were obtained by the “Fit Spectrum” option available in the SIMNRA ion beam analyzing program [97].
5.1.1.2 Depth profile compositions of Ni-Mn-In-Co alloys

In order to calculate the compositions of these alloys more accurately as well as to investigate the homogeneity of the samples, RBS data of the Ni-Mn-In-Co alloys (Co-73, Co-74, and Co-76 alloys) were collected on two positions of each sample surface. In order to get the maximum resolution between the scattered ions from Ni, Mn, and Co atoms, RBS data were collected at scattering angle of 150° using a 15 MeV O\textsuperscript{4+} ion beam. The scattering angle and the energy of the ion beam were based on the pre-calculations which are governed by the experiment kinematics (Equation 35 and 36). The observed and simulated RBS spectrums of the Co-73 alloy are shown in Figure 30. There was a good agreement between the observed and simulated data. All the edges belong to the constituent elements, except that of the Co, were clearly identified in the RBS spectrum of the Co-73 alloy. This is the case for all the alloys with Co and the Co edge was identified with the aid of the simulated RBS spectrum. The chemical composition of the alloy was determined by RBS technique to be \(Ni_{52}Mn_{25}In_{16}Co_7\). Calculations of the composition and relative uncertainties of the measurements were given in Table 10.

<table>
<thead>
<tr>
<th>Scattering Angle (°)</th>
<th>Counts with the uncertainty</th>
<th>composition with percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ni)</td>
<td>(Mn)</td>
</tr>
<tr>
<td>140</td>
<td>48991±223</td>
<td>46943±2</td>
</tr>
<tr>
<td>150</td>
<td>44930±345</td>
<td>43140±2</td>
</tr>
</tbody>
</table>

Table 10: Summary of the RBS analysis of Co-73 alloy

<table>
<thead>
<tr>
<th>Position</th>
<th>Number of counts with uncertainties (x 10\textsuperscript{4})</th>
<th>Calculated Elemental Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ni)</td>
<td>(Mn)</td>
</tr>
<tr>
<td>1</td>
<td>649±2.59</td>
<td>309±1.90</td>
</tr>
<tr>
<td>2</td>
<td>631±2.31</td>
<td>304±1.96</td>
</tr>
</tbody>
</table>
Figure 30: Experimental and simulated (by SIMNRA [97]) RBS spectra of Co-73 alloy. Data were collected using a 15 [MeV] O\(^{4+}\) ion beam.

In the case of the Co-74 alloy, it was found that the sample is not homogeneous and its composition varies with the depth from the surface. Therefore, the RBS data were analyzed by dividing the sample into thin layers and the composition of each layer was obtained by refining the RBS data separately for each layer (Figure 31). The examined thickness of the sample by O\(^{4+}\) was divided into four layers and calculated compositions of each layer were summarized in Table 11.

### Table 11: Summary of the RBS analysis of the Co-74 alloy

<table>
<thead>
<tr>
<th>Layer</th>
<th>Layer thickness ((10^{15}) atoms/cm(^2))</th>
<th>Number of counts with uncertainties</th>
<th>Composition with percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Ni)</td>
<td>(Mn)</td>
</tr>
<tr>
<td>I</td>
<td>1018.2</td>
<td>456±2</td>
<td>380±3</td>
</tr>
<tr>
<td>II</td>
<td>1037.4</td>
<td>453±4</td>
<td>393±3</td>
</tr>
<tr>
<td>III</td>
<td>1036.5</td>
<td>408±3</td>
<td>413±3</td>
</tr>
<tr>
<td>IV</td>
<td>5487.4</td>
<td>2187±18</td>
<td>2087±17</td>
</tr>
</tbody>
</table>
Figure 31: Experimental and simulated (by SIMNRA [97]) RBS spectra of the Co-74 alloy. Data were collected using 15 [MeV] O⁴⁺ ion beams.

Even though the Co-76 alloy was used in the experiments in the as-cast state, there was no inhomogeneity of the sample along the depth from the surface which was examined in the RBS experiment. There is a good agreement between experimental and simulated RBS spectrums (see Figure 32).

Table 12: Summary of the RBS analysis of the Co-76 alloy

<table>
<thead>
<tr>
<th>Position</th>
<th>Number of counts with uncertainties</th>
<th>Calculated compositions with percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>1 (x 10⁷)</td>
<td>776±2.1</td>
<td>734±1.1</td>
</tr>
<tr>
<td>2 (x 10¹³)</td>
<td>679±2.7</td>
<td>641±2.1</td>
</tr>
</tbody>
</table>

The composition of the alloy was calculated to be \( Ni_{41}Mn_{30}In_{12}Co_8 \) and the results of the RBS calculations are tabulated in the Table 12.
Figure 32: Experimental and simulated (by SIMNRA [97]) RBS spectra of the position 1 of the Co-76 alloy. Data were collected using 15 [MeV] O\(^{4+}\) ion beams with incident and scattering angles 0° and 150°.

5.1.1.3 Depth profile compositions of Ni-Mn-Ga alloys

RBS data of the Ni-Mn-Ga alloys (Ga-S1 and Ga-S2) were collected only on one position of each sample surface because of the smaller sample dimensions compared to the smallest beam diameter available (which is 1 mm). For both alloys, RBS data were collected at a scattering angle of 150° using a 15 MeV O\(^{4+}\) ion beam.

In the case of the Ga-S1 alloy sample, there was a poor agreement between observed and simulated RBS spectrums (Figure 33) when compared to the RBS results of the Ni-Mn-In and Ni-Mn-In-Co alloys. Because of this poor agreement, the composition of the alloy was not calculated using the RBS spectrum of this alloy.

In the case of the Ga-S2 alloy, only the Ga edge was identified and it was almost impossible to identify the edges of Ni and Mn in the observed RBS spectrum. The reason for the poor RBS data could be the smaller sample size compared to the size of the ion beam. Therefore, this data was not used to calculate the composition by SIMNRA. In the case of Ni-Mn-Ga Heusler alloys,
the RBS is a not a reliable technique to calculate the chemical composition because all their elements are situated very close to each other in the periodic table (because of the similar atomic masses). Therefore, there was a poor resolution between the backscattered ions from those constituent elements $Ni$, $Mn$, and $Ga$.

![Experimental and simulated (by SIMNRA [97]) RBS spectra of the $Ga$-$S1$ alloy. Data were collected using 15 [MeV] $O^{4+}$ ion beams.](image)

5.1.1.4 EDS analysis of the $Ga$-$S1$ and $Ga$-$S2$ alloys

Because of the energy resolution issues in the RBS analysis of $Ni$-$Mn$-$Ga$ samples, their chemical composition was determined by the EDS technique and confirmed by the site occupancy refinements of the synchrotron diffraction data of these alloys. The EDS experiments were carried out at Aalto University, Finland by one of our collaborator, Dr. Yanling Ge. The quantitative EDS analysis was performed using standard of all the elements present on the alloy specimen (i.e. $Ni$, $Mn$, and $Ga$). The summary of the EDS analysis, with elemental composition with standard deviations, is given in Table 13.
5.2 Crystalline structure and site occupancies of the austenitic phase

To start Rietveld refinements, a preconceived model, which is based on previous crystallographic knowledge of similar materials, of the expected crystal structure was used in the GSAS EXPGUI program [114]. This is the initial or the starting structure of the first refinement cycle. In order to get a convergence in the successive refinement cycles, the starting structure should be reasonably close to the actual structure. The initial crystallographic information of the starting structure in the refinements such as crystalline system, space group, lattice parameters, and position of the atoms was taken from the literature by surveying the crystallographic information of alloys with similar compositions.

In these studied Heusler alloys, austenitic phase fraction increases with increasing temperature and the applied magnetic field. Therefore, in order to determine the crystalline structure and site occupancies of the austenitic phase, the diffraction pattern which was collected at the highest temperature and under the highest magnetic field was analyzed first.

The site occupancies of the magnetic atoms (mainly Mn) are critical as they determine the magnetic states. During the martensitic phase transformation, which is diffusionless, atoms keep their relative neighborhood unchanged. Consequently, once the site occupancies of the austenitic phase are known, those in the martensitic phase can be determined using the relationship between the crystalline structures. Therefore, for all these studied alloys, site occupancies of the austenitic phase were determined in the Rietveld refinement of diffraction data with the aid of the known compositions determined by the RBS analysis (for In-1, Co-73, Co-74, and Co-76) and EDS.
analysis (Ga-S1 and Ga-S2). Then, these site occupancy results were used in the refinements of the complicated martensitic crystalline structures by considering the relationship between the austenitic and martensitic crystalline structures.

5.2.1 Crystalline structures of the austenitic phase of the In-1 alloy (Ni_{45}Mn_{43}In_{12})

For the sake of simplicity of the refinements, it was assumed that at 314 K and under magnetic field of 4 T, the sample was single phase austenite. The refinements started by assuming the $L2_1$ crystal structure with lattice parameters were those found in literature [40]. However, the broad peak near the 2-theta = 2.5° (for the wavelength = 0.010798 nm) in the synchrotron diffraction pattern did not agree with this model (Figure 34).

![Synchrotron diffraction pattern](image)

Figure 34: Observed and calculated synchrotron diffraction patterns of the In-1 alloy at 314 K under 4 T applied magnetic field to the sample. Almost all the observed Bragg peaks belong to the cubic $L2_1$ structure. There is a small percentage (~6 %) of martensitic phase present under these conditions.
A subsequent set of refinement cycles, assuming a mixture of $L2_1$ and $B2$ also failed to resolve the problem in that 2-theta region. An agreement between observed and refined intensities was only obtained when introducing a mixture of $5M$ and $7M$ modulated martensitic structures. Observed and calculated diffraction data for a successful Rietveld refinement cycle (of the synchrotron data collected at 314 K under a 4 T field) is shown in Figure 34. The refined value of the austenitic phase fraction is about 94%, and the rest are the traces of the martensitic phase. According to the refinement results, the austenitic crystalline structure of the $In-I$ alloy is cubic $L2_1$ (Figure 35), which belongs to $Fm\bar{3}m$ space group. The lattice constant is 0.60176 nm at 314 K under a 4 T field.

![Image](image_url)

Figure 35: Austenitic, cubic $L2_1$ structure of the $In-I$ alloy at 314 K under 4 T applied field. Also, it represents the site occupancies the 3 atoms, $Ni$, $Mn$, and $In$ in the regular crystallographic sites.

5.2.1.1 Site occupancies of the $In-I$ alloy ($Ni_{45}Mn_{43}In_{12}$)

Site occupancies of the $In-I$ alloy were calculated by Rietveld refinements of both synchrotron and neutron diffraction data, collected at 314 K under a 4 T magnetic field and at 316 K under a 4 T magnetic field, respectively. At a given temperature, the austenitic phase fraction is higher under a higher applied magnetic field, and therefore, the diffraction data collected under a 4 T magnetic field (which is the highest magnetic field tested with for this alloy) was refined.
In the site occupancy refinements, it was assumed that all the crystallographic sites were fully occupied. The refinements based on this assumption were more stable compared to those carried out without constraining each site occupancy value to a unity. This sample has excess Mn when compared with the stoichiometric Ni$_2$MnIn alloy. Therefore, it was assumed that all regular Mn-sites were fully occupied with Mn atoms. The In composition of the alloy was found to be about 12%, which was approximately half of that of the stoichiometric alloy (25%). Because of the low In concentration, the regular In-sites which are not occupied by In could be filled by either Mn or Ni atoms. However, the Ni composition was only about 45%, which is less than that of stoichiometric Heusler alloys (Ni$_2$MnIn). Therefore, one possibility is that a portion of the excess Mn was occupying the regular In-sites, with the Ni-sites which were not occupied by Ni were filled by the remaining portion of excess Mn atoms. The other possibility considered was that a portion of the Ni atoms were occupying the regular In-sites, while all the Ni-sites which were not occupied by Ni atoms were filled by the excess Mn atoms. There were other possibilities of occupying a crystallographic site such as some portion of all three atoms occupying all available crystallographic sites. Site occupancy refinements of the austenitic phase of the In-1 alloy were carried out considering all these different possibilities. However, the site occupancy refinements were converged for only one way of occupying these crystallographic sites by the constituent atoms and that is presented in Table 14.

As mentioned in the experimental section, Mn has negative coherent scattering length for neutrons. Therefore, between synchrotron and neutron diffraction data, neutron data have the highest power of resolution to distinguish between Mn and Ni, which occupy the same crystallographic site. On the other hand, in the case of regular In-sites, both Mn and In occupy these sites. Atomic masses of Mn and In are significantly different and therefore, synchrotron
diffraction technique could be used to resolve In and Mn occupying the same crystallographic site. Because of this reason, in Rietveld site occupancy refinements, both synchrotron and neutron data were refined iteratively. The results of the site occupancy refinements of synchrotron diffraction data collected at 314 K under a 4 T magnetic field are summarized in Table 14.

According to these results, only about 90% of the regular Ni-sites were occupied by Ni atoms, while the rest of the Ni-sites were occupied by Mn atoms. Also, about 50% of the regular In-sites were occupied by Mn atoms and the rest, about 50% of regular In-sites were occupied by In atoms. All the regular Mn-sites were occupied by Mn atoms only. There were very little or no Ni atoms found in other crystallographic sites.

Table 14: Summary of the iterative site occupancy refinements of synchrotron (314 K, 4 T) and neutron (316 K, 4 T) data of the In-1 alloy

<table>
<thead>
<tr>
<th>Atom</th>
<th>Description</th>
<th>Wyckoff position</th>
<th>Coordinate</th>
<th>Multiplicity</th>
<th>Site occupancy</th>
<th>U&lt;sub&gt;iso&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Mn in Mn-site</td>
<td>4 a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0000</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni in Ni-sites</td>
<td>4 b</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>8</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn in Ni-site</td>
<td>4 b</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn in In-site</td>
<td>8 c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>In</td>
<td>In in In-site</td>
<td>8 c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>4</td>
</tr>
</tbody>
</table>

Site occupancy results were used to determine the composition of the alloy. At high temperatures (314 K and 316 K), the phase fraction of martensitic phases was small (less than 6%). Therefore, calculated composition of the martensitic phase at this temperature could be associated with some experimental errors. Overall composition was calculated by averaging the weighted composition of each element in each phase by that phase fraction of the particular phase. This method was followed to obtain the chemical composition of the In-1 alloy accurately, because at 314 K (from Synchrotron results) and 316 K (from neutron results) the phase fraction of the austenitic phase is about 94%. The phase fractions of martensitic phases are less than 5% at these temperatures and the way the calculations were done to get the final composition will minimize.
the errors associated with small phase fraction values in the martensitic phases. Compositions calculated by Rietveld refinements were in good agreement with the values calculated by RBS analysis.

Table 15: Composition of the In-1 alloy based on the Rietveld refinements of the synchrotron and neutron diffraction data with the agreement factors of the final refinement cycle

<table>
<thead>
<tr>
<th>Data type and experimental condition</th>
<th>Phase fractions</th>
<th>Composition of Austenitic phase</th>
<th>Agreement factors of the refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Austenite</td>
<td>7M</td>
<td>5M</td>
</tr>
<tr>
<td>Synchrotron at 314 K under 4 T field</td>
<td>94.07</td>
<td>1.69</td>
<td>4.24</td>
</tr>
<tr>
<td>Neutron at 316 K under 2 T field</td>
<td>95.06</td>
<td>2.01</td>
<td>2.95</td>
</tr>
</tbody>
</table>

The agreement factors of the Rietveld refinements are defined as in the following equations, 1, 2, and 3 [114]:

\[
R_P = \frac{\sum |I_0 - I_C|}{\sum I_0} \tag{43}
\]

\[
R_{WP} = 100 \sqrt{\left( \frac{\sum w_i(I_0 - I_C)^2}{\sum w_i I_0^2} \right)} \tag{44}
\]

\[
\chi^2 = \sum w_i (I_0 - I_C)^2 / (N_{obs} - N_{var}) \tag{45}
\]

Where, \( I_0 \) and \( I_C \) are observed and calculated intensities, respectively. \( w_i \) is the weight assigned to each intensity. \( N_{obs} \) and \( N_{var} \) are the total number of observations and the number of variables in the least square refinement, respectively. Finally, the \( \chi^2 \) is the goodness of the fit and when it is close to 1 (less than 5), the calculated diffraction pattern is considered to be in good agreement with the observed diffraction pattern. Agreement factors for each refinement cycle are automatically calculated by GSAS EXPGUI.
5.2.2 Crystalline structures and site occupancies of the austenitic phase of the Ni-Mn-In-Co alloys

In the austenitic phase of these alloys, for a wide range of compositions, the crystalline structure is cubic \(L2_1\) [30, 119, 120]. However, the cubic \(B2\) structure is also reported as the crystalline structure of the austenitic phase of the \(Ni_{50-x}Mn_{37}In_{13}Co_x\) ribbons when \(x\) is between 5.5 and 7 [120]. In the casting process, the cooling rate of the ribbons are much higher compared that to bulk alloys. Therefore, there is a lesser probability that the all the constituent atoms come to their equilibrium positions in the austenitic phase during this cooling process. The \(B2\) structure of the ribbons may arise because of the random distribution of constituent atoms (especially \(Mn\) and \(X\) atoms) in the ribbons.

5.2.2.1 Crystalline structures and site occupancies of the austenitic phase of the \(Co-73\) and \(Co-74\) alloys

The crystalline structure of the austenitic phase of the \(Co-73\) and \(Co-74\) alloys was determined by analyzing their synchrotron data collected at 300 K under a 6 T magnetic field and at 400 K under no applied magnetic field, respectively. Observed and calculated (by the Rietveld refinements) diffraction patterns of the \(Co-73\) and \(Co-74\) alloys are given in Figure 36-(b) and Figure 36-(c), respectively. Under these experimental conditions, both alloys are single phase austenite with a cubic \(L2_1\) crystalline structure which belongs to the \(Fm\bar{3}m\) space group.

In the case of the \(Co-73\) alloy, the diffraction patterns of the austenitic phase (at 300 K) under 2 magnetic fields, 4 (Figure 36-a) and 6 T (Figure 36-b), were examined in order to study the effect of the magnetic field on the crystalline structure. Under both magnetic fields, the crystalline structure of these alloys is the same. However, there is a noticeable difference in the intensities of the Bragg peaks belonging to (400) and (422) planes of the \(L2_1\) structure. This implies
that there are some influences from the applied magnetic field on the preferred orientation of this alloy sample.

Figure 36: Observed and calculated synchrotron diffraction patterns of the Co-73 alloy collected at 300 K under (a) 4 T and (b) 6 T magnetic fields. (c) Observed and calculated synchrotron diffraction patterns of the Co-74 alloy collected at 400 K under no applied field. Under these conditions, the austenitic crystalline structure of the two alloys is cubic $L2_1$ ($Fm\bar{3}m$ space group).

In the case of Ni-Mn-In-Co alloys, the synchrotron diffraction technique is not the best tool to determine the site occupancies of the austenitic phase. Synchrotron radiation is sensitive to the atomic mass of the material’s constituent elements. As a result, X-rays could not be used to differentiate Mn, Co, and Ni atoms, which occupy the same crystallographic site, because all these atoms have similar atomic masses. Therefore, in the case of the Co-73 and Co-74 alloys, additional constraints were used in the site occupancy refinements of the austenitic phase. The composition of the alloys was constrained to the value determined by the RBS technique. Additional constraints were used to avoid the complexity of the refinements; Co atoms were allowed to occupy only in regular Ni-sites [121] and indium atoms were limited to their regular sites.
In the refinements of the Co-73 alloy, it was found that the In-site is occupied by ~65% of In and ~35% of Mn. Over 65% of the Mn atoms were found in their regular sites, and the rest in In-sites. Ni atoms were found in both regular Ni- (~86%) and Mn-sites (~35%). The site occupancy results of the austenitic phase of the Co-73 alloys were summarized in Figure 37.

5.2.2.2 Crystalline structures and site occupancies of the austenitic phase of the Co-76 alloy (Ni₄₁Mn₃₉In₁₂Co₈)

The austenitic crystalline structure of the Co-76 alloy was determined by analyzing constant wavelength (λ = 0.15374 nm) neutron diffraction data. At all temperatures, well above the martensitic transformation temperature (300 K), i.e. 400 K, 450 K and 600 K, the crystalline structure was found to be cubic L2₁, which belongs to the Fm\overline{3}m space group (the unit cell is shown in Figure 38). At 300 K and 350 K the alloy is a mix of an L2₁ austenite and a 6M modulated monoclinic martensite. However, the phase fraction of the 6M modulated martensite phase was different, ~40% and 5% at 300 and 350 K, respectively.
Figure 38: A schematic representation of the average site occupancies of the cubic austenitic phase of the Co-76 alloy.

As a part of the refinement process, the lattice constant of the $L2_1$ structure was calculated at 5 steps in the range of temperatures from 300 to 600 K, and the lattice constant increases linearly with increasing temperature. The linear thermal expansion coefficient of the Co-76, in the above temperature range was calculated by the gradient of the graph of austenitic lattice constant vs. temperature (Figure 39). In this temperature range, the linear thermal expansion coefficient of the Co-76 alloy is $9.0 \times 10^{-6} \text{ K}^{-1}$, which is about 70% of that of pure Ni ($1.44 \times 10^{-5} \text{ K}^{-1}$) [23]. The agreement factor of this graph ($R^2$) is 1.

Rietveld refinements of the neutron diffraction data, collected at two different temperatures 600 K and 300 K, are shown in Figure 40-a and Figure 40-b, respectively. Calculated diffraction patterns at each temperature show a good agreement with the observed diffraction patterns. At 600 K, almost all the observed peaks belong to the austenitic phase with a cubic $L2_1$ crystalline structure. Two phases, austenite and $6M$ modulated martensite, coexist at 300 K. The phase fraction of the austenitic phase at 300 K is about 60%.
Figure 39: Variation of the lattice parameter of the austenitic structure of the Co-76 alloy with the temperature.

Figure 40: Refinements of neutron diffraction data at (a) 600 K and (b) 300 K (under no applied magnetic field). At 600 K the alloy is a single-phase austenite with a cubic $L2_1$ crystalline structure. Similar diffraction patterns were observed at 450 and 400 K. At 300 K, the alloy is a mixture of austenitic and martensitic phases. However, the martensitic contribution is small. The hkl values of the Bragg peaks of the austenitic, $6M$, and $8M$ martensitic phases are labeled in black, red, and blue, respectively.

One of the main aspects of the Rietveld refinements of the neutron diffraction data of the Co-76 alloy was to accurately investigate the site occupancies of substituted Co atoms. This is important as different possible magnetic interactions of the Co atoms with other atoms with
magnetic properties (Ni and Mn) are highly correlated to the magnetic properties of the both austenitic and martensitic phases. Three different crystallographic sites, 4a, 4b, and 8c which are regular crystallographic sites of Mn, In and Ni, respectively, are available to be occupied by the substituted Co atoms.

Neutron diffraction techniques are the best available tools for the determination of site occupancies, as the scattering amplitudes of the constituent atoms in the studied Heusler alloy (Ni, Mn, Co and In) for neutrons are significantly different. The bound scattering lengths of Ni, Mn, Co and In are 10.3, -3.73, 2.49 and 4.01 fm, respectively [103]. Therefore, in order to determine the occupation of substituted Co atoms as well as the other atoms, Ni, Mn, and In, in all three crystallographic sites, site occupancy refinements of the neutron diffraction data were carried out. In the Rietveld refinements, all the possible ways to occupy a crystallographic site by each atom were considered. The results of the site occupancy refinements of the austenitic phase and the composition of the alloy were tabulated in Table 16.

Table 16: Summary of the site occupancy refinement in the austenitic phase of the Co-76 alloy

<table>
<thead>
<tr>
<th>Occupation of Wyckoff positions (%)</th>
<th>Element</th>
<th>Ni</th>
<th>Mn</th>
<th>In</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a (4 atoms per unit cell)</td>
<td>4.23±0.07</td>
<td>95.77±0.07</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4b (4 atoms per unit cell)</td>
<td>0</td>
<td>53.37±0.48</td>
<td>46.67±0.06</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>8c (8 atoms per unit cell)</td>
<td>79.11±0.03</td>
<td>4.11±0.04</td>
<td>0</td>
<td>16.78±0.01</td>
<td></td>
</tr>
</tbody>
</table>

| Composition (%)                  | 40.59±0.05    | 39.29±0.06    | 11.75±0.02    | 8.37±0.01     |

From these results, it was found that almost all (~97%) of the substituted Co atoms occupy the Ni-sites (8c) and the rest appear in the Mn-sites (4a). This shows a good agreement with the formation energy calculations of the austenitic phase carried out by J. Bai et al. in order to study the site preference of the substituted Co in the Ni-Mn-Ga alloy [121]. The In-sites (4b) are occupied by both Mn and In atoms. About 47% of the 4b crystallographic sites are occupied by In atoms and the rest are filled with Mn atoms. Mn atoms occupy all three crystallographic sites. However,
most of the Mn atoms are concentrated in 4a-sites. These site occupancy results obtained at all three temperatures (600, 450 and 400 K), at which the alloy was fully austenite, were averaged to get the chemical composition of the sample and it was determined to be Ni$_{41}$Mn$_{39}$In$_{12}$Co$_8$. So, the composition of the alloy found by Rietveld refinements is in good agreement with the value obtained by RBS analysis.

5.2.3 Crystalline structures and site occupancies of the austenitic phase of the Ni-Mn-Ga alloys

A number of constrains were imposed on the site occupancy refinements of the synchrotron diffraction data of the Ni-Mn-Ga alloys. According to the EDS analysis, the Ga composition of the alloy is 25%. Consequently, all the regular Ga-sites (4b) were constrained to be occupied only by Ga atoms. Also, in both these alloys, there is an excess Ni concentration compared to that of the stoichiometric Ni$_2$MnGa alloy. Because of the excess Ni concentration, it was assumed that all the regular Ni-sites (8c) were occupied only by Ni atoms. Finally, the site occupancies of the regular Mn-sites were calculated according to the composition determined by the EDS technique (i.e. Ni$_{53.5}$Mn$_{21}$Ga$_{25.5}$ and Ni$_{54}$Mn$_{21}$Ga$_{25}$) Those models (with the constraints discussed above) were used as the staring models of the site occupancy refinements of the Ga-S1 and Ga-S2 alloys.

Observed and calculated synchrotron diffraction patterns of the Ga-S1 alloy collected at 390 K and the Ga-S2 alloy collected at 380 K under no applied magnetic field are shown in Figure 41-a and Figure 41-b, respectively. As expected the diffraction patterns are almost identical because of the very similar chemical composition. For both alloys under these conditions, the austenitic crystalline structure is cubic $L2_1$ and site occupancies were determined based on these diffraction patterns.
Figure 41: Observed and calculated synchrotron diffraction patterns of (a) \textit{Ga-S1} alloy collected at 390 K and (b) \textit{Ga-S2} alloy collected at 380 K under no applied magnetic field. For both alloys under these conditions, the austenitic crystalline structure is cubic \textit{L2$_1$}.

Table 17: Composition of the \textit{Ga-S1} and \textit{Ga-S2} alloys based on the Rietveld refinements of the synchrotron diffraction data with the agreement factors of the final refinement cycle.

<table>
<thead>
<tr>
<th>Alloy and experimental condition</th>
<th>Atom</th>
<th>Site occupancy at each Wyckoff position (and multiplicity)</th>
<th>Composition</th>
<th>Agreement factors of the final refinement cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Ga-S1} at 390 K, 0 T</td>
<td>\textit{Ni}</td>
<td>0.1481 0 0.998 0</td>
<td>\textit{Ni$<em>{53.6}$Mn$</em>{21.4}$Ga$_{25.0}$}</td>
<td>\textit{\chi}$^2$ $R_{WP}$ $R_P$</td>
</tr>
<tr>
<td></td>
<td>\textit{Mn}</td>
<td>0.8519 0 0</td>
<td>0.92 5.22 3.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>\textit{Ga}</td>
<td>0 1.00 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textit{Ga-S2} at 380 K, 0 T</td>
<td>\textit{Ni}</td>
<td>0.1581 0 1.00</td>
<td>\textit{Ni$<em>{53.6}$Mn$</em>{21.4}$Ga$_{25.0}$}</td>
<td>1.26 5.4 4</td>
</tr>
<tr>
<td></td>
<td>\textit{Mn}</td>
<td>0.8419 0 0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3 Martensitic crystalline structure of the studied $Ni-Mn-X$ based Heusler alloys

For all these studied alloys, in order to determine the crystalline structure of the martensitic phase, the approximate martensitic transformation temperature was determined. This was done by careful examination of all the diffraction patterns of each alloy, which were collected upon cooling the samples. After finding the approximate martensitic finish temperature of that particular alloy, martensitic structures of each alloy were found by analyzing a diffraction data pattern which was collected well below that temperature. In addition to the martensitic phase transformation temperature, there is other information which could be extracted by examining the raw diffraction patterns. One piece of vital information is the evidence of an inter-martensitic phase transformation exhibited by some of these alloys. The entropy change associated with the inter-martensitic phase transformations could be utilized to enhance the observed magnetocaloric effect in these alloys.
5.3.1 Martensitic crystalline structures of the *In-1* alloy (*Ni$_{45}$Mn$_{43}$In$_{12}$*)

Some of the selected diffraction patterns of the *In-1* alloy, which were collected while heating from 290 to 314 K under no applied magnetic field, are shown in Figure 43. This set of diffraction patterns demonstrates the evolution of the austenitic phase from modulated martensitic phases. It is evident from these diffraction patterns that at 290 K, the alloy is in the martensitic phase and upon heating, it starts an austenitic transformation around 305 K. At 314 K, the alloy completes its reverse martensitic transformation.

In order to determine the martensitic crystalline structure of the *In-1* alloy, its diffraction data collected at 290 K under no applied magnetic field were selected and analyzed by the Rietveld refinement method. As mentioned in the previous section, the martensitic phase transformation temperature decreases with an increasing magnetic field. Therefore, selecting a diffraction pattern which was collected under no magnetic field and in the lowest temperature where data were collected ensures that the diffraction pattern will have the highest contribution from the martensitic phase. Choosing a set of diffraction data which represents only the pure martensitic phase (or minimal contribution from the austenitic phase) makes the refinements much easier by avoiding the complications arising from the presence of mixed phases.

The Rietveld refinements of the diffraction data collected below the martensitic transformation temperature were done in a similar way to what was done in the austenitic phase. A starting structure was introduced to the GSAS EXPGUI software. To find a significantly close starting structure, all the possible structures of the martensitic phase of *Ni-Mn-X* based Heusler alloys found in the literature were considered. The summary of the literature survey was provided in Chapter 3 (Table 3). The theoretical constructed diffraction patterns of the surveyed martensitic structures were compared with the experimental diffraction data collected at 290 K (under 0 T).
All constructed diffraction patterns using the POWDER cell crystallographic analyzing software, the observed synchrotron diffraction pattern of In-1 at 290 K, and the lattice parameters and other crystallographic information of the surveyed martensitic structures are summarized in Table 18.

Figure 43: Raw diffraction patterns of the In-1 alloy collected while heating from 290 K to 314 K under no applied magnetic field. It is evident from these diffraction patterns that at 290 K, the alloy is in the martensitic phase (or phases) and upon heating, it starts its austenitic transformation around 305 K.
Table 18: POWDER CELL simulated diffraction data patterns (in the 2-theta range from 2° to 4° when the wavelength is 0.010798 nm) of different martensitic crystal structures of Heusler alloys reported in the literature and the synchrotron diffraction pattern of In-1 at 290 K

<table>
<thead>
<tr>
<th>Martensitic phase/phases</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>B</th>
<th>Diffraction pattern (2θ, 2° - 4° for λ = 0.010798 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental synchrotron diffraction pattern of In-1 alloy at 290 K (NOTE: good agreement for the mixture of 5M and 7M modulated martensite)</td>
<td>5M</td>
<td>4.41(6)</td>
<td>5.63(6)</td>
<td>21.72(6)</td>
<td>89.99°</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>4.31(6)</td>
<td>5.66(6)</td>
<td>28.89(6)</td>
<td>90.03°</td>
</tr>
<tr>
<td>POWDER CELL diffraction pattern of mixture of 5M and 7M modulated martensite space group - P 1 2/m 1 [41]</td>
<td>5M</td>
<td>4.4</td>
<td>5.6</td>
<td>21.2</td>
<td>88.5°</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td>4.3</td>
<td>5.8</td>
<td>30.0</td>
<td>93.5°</td>
</tr>
<tr>
<td>POWDER CELL diffraction pattern of 5M modulated martensite space group P 1 2/m 1 [40, 69, 71, 74]</td>
<td>4.4</td>
<td>5.6</td>
<td>21.2</td>
<td>88.5°</td>
<td></td>
</tr>
<tr>
<td>POWDER CELL diffraction pattern of 7M modulated martensite space group P 1 2/m 1 [40, 71, 74]</td>
<td>4.3</td>
<td>5.8</td>
<td>30.0</td>
<td>93.5°</td>
<td></td>
</tr>
<tr>
<td>POWDER CELL diffraction pattern of 10M modulated martensite space group P 1 2/m 1 [75]</td>
<td>4.222</td>
<td>5.507</td>
<td>42.22</td>
<td>93.3°</td>
<td></td>
</tr>
</tbody>
</table>
None of the patterns obtained for a single phase of martensite showed an agreement with the experimental data collected at 290 K. All theoretically constructed diffraction patterns by the POWDER CELL had only three large peaks in the 2-theta range from 2.7° to 3.1° (for wavelength $= 0.010798$ nm). However, the experimental data of the In-I alloy have six relatively large peaks around the 2-theta range. Thus, the refinement carried out using these single phase martensitic structures did not converge.

In the next step, a mixture of martensitic structures, 5M and 7M modulated martensite instead of a single phase of martensite, was used. This theoretical diffraction pattern of a mixture of 5M and 7M modulated monoclinic structures demonstrates six Bragg peaks similar to that in the experimental data. Therefore, this model, a mixture of 7M and 5M martensitic phases, was used as the starting structure in the Rietveld refinement of the synchrotron diffraction data collected at the martensitic phase (at 290 K). A convergence was obtained from this model after refining lattice parameters, atomic positions, background, and the texture of the sample.

In the Rietveld refinements of the modulated martensitic structures of the studied Heusler alloys a number of constraints were imposed on each starting structure. The main purpose of these constraints is the simplification of the refinement cycles and retention of the physical meaning of the refined crystallographic information (or to avoid unrealistic crystalline structures) of these alloys.

Similar to the constraints used by Righi [67, 69] in the refinement of the modulated structures of the martensitic phase of the Ni$_2$MnGa alloy, the following steps were taken to reduce the number of parameters in the refinements.

1. Lattice modulation occurs along the [001] crystallographic direction of the monoclinic unit cell (this corresponds to the [110] direction in the austenite structure).
2. Both x- and y-coordinates of all atoms in the martensitic phase were allowed to refine, while the z-coordinate was kept constant.

3. Because the modulation along [001] involves the periodic transversal displacements of (00l) atomic layers, the amplitude of modulation of every atom in that particular plane is the same.

Schematic diagrams of the starting crystalline structure of the $7M$ modulated martensite and refined crystalline structure of the synchrotron diffraction data at 290 K under 4 T magnetic field (alloy has the same crystal structure under no magnetic field and 2 T magnetic fields) are shown in Figure 44-a and Figure 44-b, respectively. These schematic diagrams were generated by DRAWxtl [122], software used in conjunction with GSAS to visualize the refined crystalline structures at any stage of the refinement process. Schematic diagrams of the starting crystalline structure of the $5M$ modulated martensite and the refined crystalline structure of the synchrotron diffraction data are given in Figure 45-a and Figure 45-b, respectively. Both structures, $7M$ and $5M$ modulated, belong to the monoclinic $P \bar{1} 2/m \bar{1}$ space group and the rest of the refined crystallographic information is given in Table 20.

Figure 44: $7M$ modulated martensitic unit cells. (a) A typical structure (based on the literature survey), used as the initial structure in GSAS refinements [69]. (b) Refined structure for the $7M$ modulated martensite, at 290 K and an applied magnetic field of 4 T based on synchrotron diffraction data of In-1 alloy. In Zhdanov notation, this has the stacking sequence (42626).
Figure 45: $5M$ modulated martensitic unit cells. (a) The typical model structure found in the literature survey used as the initial structure in GSAS refinements [69]. (b) Refined structure for the $5M$ modulated martensite of the $In-1$ alloy, which has the stacking sequence ($\overline{2}422$).

Figure 46 demonstrates the observed and calculated diffraction patterns of the $In-1$ alloy, which were collected at 302 K, however, under different magnetic fields. Figure 46-(a) represents the diffraction data collected under a 2 T magnetic field and Rietveld analysis revealed that under these conditions the alloy was a mixture of austenitic and martensitic phases. This figure clearly represents the Bragg peaks belonging to each phase. Figure 46-b represents the diffraction data collected under no applied magnetic field and under these conditions the alloy was entirely in the martensitic phase. Thus, these two diffraction patterns, which were collected under two magnetic fields, show clearly the influence of an applied magnetic field on crystalline structures as well as the martensitic phase transformation temperature of these alloys. Upon increasing the applied magnetic field to this alloy, more and more martensitic variants transform into the austenitic phase. The phase transformation temperature decreases with increased magnetic field.

5.3.2 Martensitic crystalline structures of the $Ni-Mn-In-Co$ alloys

By following a similar analytical procedure to that used for the $In-1$ alloy at the beginning of the Rietveld refinements, a starting model (based on the previous crystallographic knowledge of the similar Heusler alloys) of the expected crystal structure was used in the GSAS EXPGUI
program [123]. Crystallographic information such as crystal system, space group, lattice parameters, etc. of different possible starting structures of each phase was found in the literature and used as the starting model in the refinements.

Figure 46: Observed and calculated synchrotron diffraction patterns of the In-1 alloy at 302 K (a) under applied magnetic field of 2 T and (b) under no applied magnetic field. The insets show an enlarged portion of the diffraction patterns (from 2.6° to 3.2°), which include the characteristic bunch of Bragg peaks belonging to the modulated martensitic crystalline structure. Under a 2 T field, the majority of the alloy is in the austenitic phase. Whereas, under no applied field, three phases, austenite, 7M modulated martensite, and 5M modulated martensite coexist. Phase fractions of austenitic, 7M, and 5M phases are about 19%, 45%, and 36%, respectively.

Depending on the Co concentration as well as the composition of other elements, the martensitic crystalline structure could be a single phase or a mix of two phases of modulated or non-modulated structures. Non-modulated $LI_0$ [124], 5M modulated orthorhombic [50, 120], 5M
modulated monoclinic [30, 119, 120], 6M modulated martensite [124], 7M modulated monoclinic [30, 50, 120] and a mix of 5M and 7M modulated martensite are the possible crystalline structures of the martensitic phase of the Ni-Mn-X-Co (X = In, Sb) alloys, reported in the literature.

5.3.2.1 Martensitic crystalline structures of the Co-73 and Co-74 alloys

Observed diffraction patterns (with normalized intensities) of the Co-73 alloy, which were collected under no applied magnetic field while it was cooling from 300 K to 210 K, are displayed in Figure 47. At 300 K, the alloy was entirely in the austenitic phase. Upon cooling, this alloy started to transform into a martensite around 285 K and at 210 K it completed the transformation. A similar behavior was observed in the diffraction patterns of the Co-74 alloy which were also collected while cooling under no applied magnetic field.

Figure 47: Observed diffraction patterns of the Co-73 alloy collected while it was cooling under no applied magnetic field. Note the intensity of the diffraction patterns was normalized with respect to the highest peak in each diffraction pattern.
By examination of raw diffraction patterns of the Co-73 and Co-74 alloys, it was assumed that the alloys are in the pure martensitic phase below 220 K. Therefore, diffraction patterns collected at 220 K and 205 K were analyzed to determine the crystalline structures of the Co-73 and Co-74 alloys, respectively.

Figure 48: Rietveld refinements of synchrotron diffraction data of (a) Co-73 alloy collected at 220 K and (b) Co-74 alloy collected at 205 K. At these temperature (under a zero-applied magnetic field) the alloys were a mix of two martensitic phases: 5M and 7M modulated monoclinic. An enlarged portion of the diffraction patterns, (from 2.6 to 3.2) which are the characteristic set of peaks of the modulated martensite, are given in the inset of the graph.
Rietveld refinement results of the Co-73 and Co-74 alloys are shown in Figure 48. There is not a significant difference between the observed diffraction patterns of the Co-73 (Figure 48-a) and Co-74 (Figure 48-b) alloys and hence similar crystalline structures were anticipated. The refinements revealed that the crystalline structures of both alloys belong to the monoclinic \( P \bar{1} 2/m \) space group. The martensitic phase of these two alloys is a mixture of \( 7M \) and \( 5M \) modulated monoclinic structures. In the case of the In-1 alloy, the lattice parameter of the two alloys are slightly different. The crystallographic information and schematic diagrams of the crystalline structures of these two alloys are summarized in Table 20.

5.3.2.2 Martensitic crystalline structures of the Co-76 alloy (\( Ni_{41}Mn_{39}In_{12}Co_{8} \))

Constant wavelength neutron diffraction data, that were collected while heating the Co-76 alloy under no applied magnetic field in the range of temperatures from 50 to 450 K, are given in Figure 49. From this diffraction data patterns, it is evident that the alloy undergoes an austenitic phase transformation at around 315 K. At 250 K, the observed diffraction patterns indicate that the alloy is in the pure martensitic phase. Therefore, the diffraction pattern collected at 250 K was used to determine the martensitic crystalline structure. The crystalline structure of the Co-76 alloy at various temperatures in the range from 250 K to 450 K was found by Rietveld refinements of neutron diffraction data.

In the search for the crystalline structure of the martensitic phase of this alloy, all the possibilities reported in literature were tried out as the starting structures for the Rietveld refinement cycles. Convergence of the refinements was obtained only for a mix of \( 6M \) and \( 8M \) modulated monoclinic martensite structures. In the refinements of modulated martensite structures, all the constraints which were used in the refinements of the modulated martensitic
structures of Ni-Mn-In) were made in order to reduce the number of refinement parameters [67, 69].

The crystalline structure of the martensitic phase was a mix of modulated monoclinic structures belonging to the P 1 2/m 1 space group. The two structures have quite similar lattice parameters in the a and b crystallographic directions. However, the lattice parameter c and the modulations are very different from each other. Crystalline structures of the 8M and 6M modulation phases are given in Table 20. Lattice parameters of austenite L21, 6M, and 8M modulated monoclinic martensite and agreement factors of the Rietveld refinements are all summarized in Table 19.

Figure 49: Growing of the austenitic phase (at 450 K alloy is pure austenite) from pure martensitic phases (at 50 K).
Table 19: Agreement factors of the Rietveld refinements and lattice parameters

<table>
<thead>
<tr>
<th>Tem. (K)</th>
<th>Composition</th>
<th>Lattice parameters</th>
<th>Agreement factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>600</td>
<td>Austenite</td>
<td>6.007</td>
<td>6.007</td>
</tr>
<tr>
<td>300</td>
<td>Mix of austenite and 6M martensite</td>
<td>(L2_1) 5.980</td>
<td>5.980</td>
</tr>
<tr>
<td></td>
<td>6M</td>
<td>4.410</td>
<td>5.558</td>
</tr>
<tr>
<td>250</td>
<td>Mix of 6M and 8M martensite</td>
<td>6M 4.397</td>
<td>5.539</td>
</tr>
<tr>
<td></td>
<td>8M</td>
<td>4.426</td>
<td>5.579</td>
</tr>
</tbody>
</table>

Rietveld refinements of neutron diffraction data collected at 250 K are shown in Figure 50. At this temperature the alloy is a mix of two phases: 6M modulated and 8M modulated martensite, both belonging to the P 1 2/m 1 monoclinic space group.

Figure 50: Rietveld refinements of neutron diffraction data collected at 250 K. At this temperature the alloy is a mix of two martensitic phases: 6M and 8M martensite. The numbers marked in black and red are the (hkl) values of the peaks of 6M and 8M modulated phases, respectively. There is a good agreement between experimental and calculated diffraction patterns based on a mixture of modulated martensitic phases.
5.3.3 Martensitic crystalline structures of \(Ni-Mn-Ga\) alloys

A set of selected synchrotron diffraction patterns of the \(Ga-S1\) alloy, which were collected while cooling (from 395 to 100 K) the alloy under zero applied magnetic field, is shown in Figure 51. The \(Ga-S2\) alloy, which has a very similar chemical composition to the \(Ga-S1\) alloy, exhibits an almost identical set of diffraction patterns, which were collected while it was cooling from 400 to 100 K. Therefore, these two alloys were analyzed simultaneously in order to determine the crystallographic properties in the mentioned temperature range above.

Figure 51: Variation of the observed diffraction pattern of the \(Ga-S1\) alloy while the sample was cooling from 395 K to 100 K. At 395 K the alloy is in the austenitic phase (cubic \(L2_1\)) and upon cooling it transforms into an inter-martensitic \(7M\) modulated monoclinic phase. Further cooling down to 100 K, it completely transforms into a tetragonal \(L1_0\) structure.

In the examination of the observed diffraction patterns of this alloy in the temperature range 395 K to 100 K, despite the small variations in each diffraction pattern, they could be mainly categorized into three groups. Starting from 395 K and down to around 315 K the first category of diffraction patterns could be identified as the austenitic phase because of the simplicity of the
diffraction patterns in this region. The middle region was predicted as a modulated monoclinic or tetragonal phase by comparing it to the martensitic diffraction patterns of the Co-73 and Co-74 alloys. Around 200 K and below, the observed diffraction pattern is entirely different from that of the rest of the temperature region. This diffraction pattern has a smaller number of Bragg peaks compared to the intermediate martensitic diffraction pattern. However, when compared to the austenitic diffraction pattern, this low temperature martensitic pattern is more complicated. Therefore, a less complicated non-modulated crystalline structure such as tetragonal or orthorhombic structure was anticipated for this phase.

Figure 52: Observed and calculated synchrotron diffraction patterns of the Ga-S1 alloy (a) at 300 K and (b) at 100 K under no applied magnetic field to the sample. At 300 K, the alloy is in an inter-martensitic phase, which is a 7M modulated structure. When the temperature goes down, this transforms into the $L1_0$ tetragonal martensitic phase.

The Rietveld refinements revealed that the inter-martensitic phase of both Ga-S1 and Ga-S2 alloys is a 7M modulated monoclinic structure. This structure belongs to the $P 1 2/m$ space group. The crystalline structure of the lower temperature martensitic phase is tetragonal and belongs to $I 4/m m m$ space group.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>Structure and stacking sequence according to the Zhdanov notation</th>
<th>Lattice Parameters (α = γ = 90°)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-1</td>
<td>7M</td>
<td><img src="image" alt="7M structure" /> (25622)</td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td><img src="image" alt="5M structure" /> (2342)</td>
<td>4.312(6)</td>
<td>5.658</td>
</tr>
<tr>
<td>Co-73</td>
<td>7M</td>
<td><img src="image" alt="7M structure" /> (23432)</td>
<td>4.275(6)</td>
<td>5.492</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td><img src="image" alt="5M structure" /> (2343)</td>
<td>4.409(6)</td>
<td>5.634</td>
</tr>
<tr>
<td>Co-74</td>
<td>7M</td>
<td><img src="image" alt="7M structure" /> (22622)</td>
<td>4.272(6)</td>
<td>5.507</td>
</tr>
<tr>
<td></td>
<td>5M</td>
<td><img src="image" alt="5M structure" /> (12421)</td>
<td>4.505(6)</td>
<td>5.767</td>
</tr>
<tr>
<td>Co-76</td>
<td>8M</td>
<td><img src="image" alt="8M structure" /> (2224222)</td>
<td>4.426(6)</td>
<td>5.579</td>
</tr>
<tr>
<td></td>
<td>6M</td>
<td><img src="image" alt="6M structure" /> (214132)</td>
<td>4.397(6)</td>
<td>5.539</td>
</tr>
<tr>
<td>Ga-S1 &amp; Ga-S2</td>
<td>L10</td>
<td><img src="image" alt="L10 structure" /></td>
<td>3.882(6)</td>
<td>3.882</td>
</tr>
<tr>
<td></td>
<td>7M</td>
<td><img src="image" alt="7M structure" /> (2534)</td>
<td>4.249(6)</td>
<td>5.467</td>
</tr>
</tbody>
</table>
Figure 53: Observed and calculated synchrotron diffraction patterns of the Ga-S2 alloy (a) at 100 K and (b) at 280 K under no applied magnetic field to the sample. At 100 K, the alloy is in the low temperature martensitic phase, which is the $L1_0$ tetragonal martensitic phase. When the temperature goes up this transforms into a 7M modulated monoclinic structure.

5.4 Phase fraction analysis

Austenitic and martensitic phase fractions of four alloys (In-1, Co-73, Co-76, and Ga-S1) were calculated using the Rietveld refinements of their diffraction data. The purpose of this analysis was to study the martensitic phase transformations of the Ni-Mn-X Heusler alloys from many aspects; the influence of an applied magnetic field on the phase transformation temperature, behavior of the thermal hysteresis as a function of the applied magnetic field, and examination of a possible magneto-structural phase transformation. In the case of the In-1 and Co-73 alloys, synchrotron diffraction data, which were collected under different magnetic fields and in a wide range of temperatures (in the vicinity of the martensitic phase transformation), were analyzed to find out the influence of an applied magnetic field on the martensitic phase transformations. On the other hand, for the Co-76 and Ga-S1 alloys, diffraction data were collected only under no applied magnetic field. Therefore, data were analyzed to study the behavior of the austenitic and martensitic phase transformations while heating and cooling and under no applied magnetic field.
For all these alloys, thermograms of the martensitic phase transformations were constructed using phase fractions of each phase present at every temperature that diffraction was performed. Then, these thermograms were used to determine the four characteristic temperatures of the crystalline phase transformations: austenitic start ($A_S$), austenitic finish ($A_F$), martensitic start ($M_S$), and martensitic finish ($M_F$).

5.4.1 Phase fraction analysis of the In-1 alloy ($Ni_{45}Mn_{43}In_{12}$)

The synchrotron diffraction data of the In-1 alloy were analyzed to determine the phase fraction of each phase at selected temperatures in the range from 290 to 314 K (data were collected under no applied magnetic field and while heating the alloy). This procedure was repeated for the rest of the diffraction data collected under 2 and 4 T magnetic fields. At each temperature step and under all three magnetic fields, it was found that the alloy had a mix of three phases. Those phases are cubic austenite with $L2_1$ structure, $7M$ modulated martensite, and $5M$ modulated martensite. Both martensitic phases belong to the $P 1 2/m 1$ space group of the monoclinic crystalline system. However, under all three magnetic fields, the austenitic phase fraction was essentially zero below 294 K. Upon heating, the phase fraction of the cubic phase increases with increasing temperature starting from 294 K. Simultaneously, phase fractions of the martensitic phases decrease with increasing temperature. However, there is one exception: under all applied magnetic fields, the phase fraction of the $5M$ modulated martensitic phase decreases with the temperature from 294 K down to 290 K. Also, it was observed that at each temperature, but under different applied magnetic fields, the phase fraction in the alloy is different. At a given temperature, the phase fraction of the austenitic phase increases with an increasing magnetic field and as a result, the phase fraction of the martensitic phases decreases with the increasing magnetic field. These observations will be explained in the next chapter under section 6.2.1.
Variation of the austenitic and martensitic phase fractions while heating the \textit{In-1} alloy in the temperature range from 290 K to 314 K, under all three magnetic fields are shown in Figure 54. The characteristic temperatures of the martensitic to austenitic phase transformations, austenitic start ($A_S$) and austenitic finish ($A_F$), were determined using intersections of the lines obtained by extrapolating the linear parts of the thermograms. Determination of the characteristic temperatures, $A_S$ and $A_F$, under a 4 T magnetic field is demonstrated in Figure 54. The characteristic temperatures of the forward phase transformation (i.e. austenite to martensite while cooling the alloy), martensitic start ($M_S$) and martensitic finish ($M_F$), were not calculated because there were no diffraction data available while cooling the alloy.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure54.png}
\caption{Variation of the austenitic (white symbols) and martensitic (blue symbols) phase fractions under 0, 2, and 4 T magnetic fields in the vicinity of the first-order phase transformation of \textit{In-1} alloy. \textit{Note}: the dotted lines are just guide lines for the data points.}
\end{figure}

Austenitic phase transformation temperature (or equilibrium temperature of the two phases), $T_{Eq}$, was defined as the temperature at which the phase fraction of the austenitic phase is
50%. Additionally, the rate of the phase transformation as a function of the temperature was determined by calculating the gradient of the linear parts of the thermograms in each case (the line segment AB in the case of no applied magnetic field; see Figure 54). All the characteristic temperatures and the rates of the martensitic phase transformations, under all three magnetic fields are summarized in Table 21.

Table 21: Variation of austenitic transformation temperature of the In-1 alloy with applied magnetic field

<table>
<thead>
<tr>
<th>Magnetic field (T)</th>
<th>°Austenitic transformation temperature, T_{50%} (K)</th>
<th>A_S (K)</th>
<th>A_F (K)</th>
<th>Change of T_{Eq} (K)</th>
<th>^bAustenitic phase transformation rate (% per K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>304.0±0.25</td>
<td>301.25±0.25</td>
<td>305.75±0.25</td>
<td>reference</td>
<td>10.66±0.35</td>
</tr>
<tr>
<td>2</td>
<td>302.5±0.25</td>
<td>300.5±0.25</td>
<td>304.25±0.25</td>
<td>-1.5±0.35</td>
<td>11.42±0.35</td>
</tr>
<tr>
<td>4</td>
<td>299.25±0.25</td>
<td>298.0±0.25</td>
<td>300.25±0.25</td>
<td>-3.25±0.35</td>
<td>20.00±0.35</td>
</tr>
</tbody>
</table>

°Austenitic phase transformation temperature (or equilibrium temperature) is defined as the temperature at which the phase fraction of austenitic phase is 50%.

^bAustenitic phase transformation rate was calculated by taking the ratio of the difference in the austenitic phase fraction at A_S and A_F and the difference in A_S and A_F.

Under zero applied magnetic field, an abrupt change in phase fractions takes place in the temperature interval between 302 and 304 K. The austenitic phase transformation temperature, T_{Eq}, under these experimental conditions is 305.75±0.25 K. When the magnetic field is increased, the martensitic phase transformation temperature decreases (Table 21). Also, austenitic start (A_S) and finish (A_F) temperatures decrease with the increasing magnetic field. Although the martensitic transformation temperature decreases with the increasing magnetic field, the relationship between the transformation temperature and applied magnetic field is not linear. When the applied magnetic field is increased from 0 to 2 T, the martensitic transformation temperature reduces by ~1.5 K, whereas an increase of the magnetic field from 2 to 4 T results in a decrease of the martensitic transformation temperature ~ 3.25 K.
5.4.2 Phase fraction analysis of the Co-73 alloy ($Ni_{52}Mn_{25}In_{16}Co_7$)

Both synchrotron diffraction data and thermomagnetic measurements of the Co-73 alloy were analyzed in order to investigate any magneto-structural phase transformations. As discussed in the previous section, this alloy undergoes a crystalline phase transformation from the martensitic phase to the austenitic phase upon heating. Also, the thermomagnetic measurement, which will be discussed in section 5.5.1, shows a magnetic phase transformation. Both crystalline and magnetic phase transformations were studied as a function of the applied magnetic field. Then, these phase transformations were compared in order to get a better understanding of the coupled magneto-structural phase transformations.

5.4.2.1 Crystalline phase transformations of the Co-73 alloy ($Ni_{52}Mn_{25}In_{16}Co_7$)

In order to investigate the characteristics of the martensitic phase transformations (such as phase transformation temperatures, thermal hysteresis accompanied with these phase transformations, and the effects on the phase transformation temperature by applied magnetic field), phase fractions of the Co-73 alloy were calculated by the Rietveld refinements of the diffraction data collected under various experimental conditions. A summary of selected synchrotron diffraction data (magnetic field and the range of temperatures), which were selected for the above analysis, is given in Table 22.

The austenitic phase of the Co-73 alloy is cubic $L2_1$. Upon cooling, it transforms into a mixture of martensitic phases, $7M$ and $5M$ modulated monoclinic ($P 1 2/m$ 1). Phase fractions of all these phases, under different experimental conditions, were determined by analyzing the synchrotron diffraction data. The results of the phase fraction analysis of the Co-73 alloy are summarized in Figure 55. It demonstrates the variation of the austenitic phase fraction while
heating (from 200 to 300 K) the alloy under 4 magnetic fields (0, 2, 4, and 6 T) and then cooling (back to 200 K) under 3 magnetic fields (2, 4, and 6 T).

Figure 55: Variation of the austenitic phase fractions between 200 and 300 K, under various experimental conditions. In the case of zero applied field to the alloy, data were collected only while heating the material. In all other cases, data were available while heating from 200 K to 300 K and then cooling back to 200 K.

Table 22: Experimental conditions of analyzed synchrotron diffraction data of the Co-73 alloy

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Applied magnetic field to the alloy (T)</th>
<th>Temperature range</th>
<th>While heating (K)</th>
<th>While cooling (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>205-300</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.010804</td>
<td>2</td>
<td>230-300</td>
<td>300-200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>220-300</td>
<td>300-185</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>210-255</td>
<td>300-175</td>
<td></td>
</tr>
</tbody>
</table>

Upon heating the alloy under no applied magnetic field, the austenitic phase transformation starts around 255 K. The alloy completes its austenitic phase transformation around 290 K. Under a 2 T applied field, the austenitic phase transformation starts around 245 K and it finishes around
280 K. That implies a decreasing of the characteristic temperatures of the austenitic phase transformation when increasing the applied magnetic field. Similarly, there is a clear decrease of the $A_S$ and $A_F$ temperatures while increasing the magnetic field to 4 and 6 T.

Upon cooling under a 2 T applied magnetic field, a forward martensitic phase transformation started at around 275 K. Under higher magnetic fields of 4 and 6 T, the forward phase transformation temperatures, $M_S$ and $M_F$, decreased. That is, both forward and austenitic phase transformation temperatures shift towards lower temperatures as the applied magnetic field to the alloy is increased.

There is another important observation that can be made from the graphs of variation of the austenitic phase fraction versus temperature under different magnetic fields. As shown in Figure 55, the austenitic phase fraction above the austenitic finish temperature, $A_F$ (i.e. above 290 K in all the cases), is different under different magnetic fields. When there is no applied magnetic field, the highest value of the austenitic phase fraction is about 85% and that value increases to about 98% when the applied magnetic field is increased to 6 T. That shows an increasing of the austenitic phase fraction with the increasing magnetic field. With an increasing magnetic field, more and more martensitic variants transform into the austenitic phase. This trend is not limited to the austenitic phase. In the martensitic phase (that is below the $M_F$), the austenitic phase fraction is higher under a higher magnetic field. All these observations confirm the large impact of an applied magnetic field on the martensitic phase transformation of this alloy. These observations will be discussed under the discussion section of the dissertation.

5.4.3 Phase fraction analysis of the Co-76 alloy ($Ni_{41}Mn_{39}In_{12}Co_{8}$)

The evolving of the austenitic phase (at 450 K) from pure martensitic phases (at 250 K) is demonstrated in Figure 49 (section 5.3.2.2). The diminishing of the martensitic Bragg peaks and
the growing of the austenitic Bragg peaks can be observed as the temperature increases from 250 to 450 K. In order to determine the contribution of each phase to the observed diffraction pattern, the phase fractions at temperatures in the range from 50 to 600 K were calculated from the neutron diffraction refinements. The variation of the normalized phase fractions with temperature is given in Figure 56. The entire temperature range can be classified into three main regions. In the first region, between 600 K and 350 K, the alloy is a single-phase austenite. All the observed Bragg peaks belong to the cubic $L2_1$ structure and have no trace of the martensitic phase.

![Figure 56: Variation of the phase fractions of the austenite, total martensite, 6M, and 8M martensitic phases with temperature (50-600 K). The phase fraction of the 6M phase is higher than that of the 8M phase in all the studied temperatures except 50 K.](image)

In the second region (i.e. from 350 to 270 K), three phases, austenitic, 6M, and 8M martensitic phases, co-exist. The experimental and calculated diffraction patterns at 300 K (i.e. in the second region) is given in Figure 26-b (section 5.2.2.2). At this temperature, the austenitic
phase still dominates the diffraction pattern and the contribution from the $8M$ modulated phase is minimal. However, there is a significant contribution from the $6M$ modulated martensitic phase. At 270 K the weight fraction of the $8M$ phase is less than 15% and it increases with further temperature decrease. The martensitic transformation temperature ($T_M$), defined as the temperature at which the phase fraction of the martensitic phase is 50%, is approximately 295 K.

In the final region (i.e. from 270 down to 50 K), two martensitic phases with $6M$ and $8M$ modulations coexist. Here, the weight fraction of the $6M$ phase decreases with decreasing temperature ($6M$ is the dominant martensitic phase just below the transformation temperature). The decrease in the $6M$ phase is compensated by an increase in the fraction of the $8M$ martensite. At 50 K, the fractional ratio of the $8M$ to $6M$ phases is about 60% to 40%. It could be suggested that this behavior of the martensitic phase results from the entropy of the structures; the somewhat higher order of the $8M$ phase is energetically favorable at low temperatures because of its lower entropy compared to the $6M$ modulation.

5.4.4 Phase fraction analysis of the $Ga-S1$ alloy ($Ni_{53.6}Mn_{21.4}Ga_{25}$)

In section 5.3.3, the crystalline structures of the $Ga-S1$ and $Ga-S2$ alloys were discussed. From that discussion, it was concluded that in addition to the martensitic phase transformation from the cubic ($L2_1$) austenitic phase to the $7M$ modulated monoclinic martensite, there is another phase transformation (around 275 K) from the $7M$ modulated monoclinic phase to a non-modulated tetragonal phase. This transformation takes place between two martensitic phases and is thus called “inter martensitic phase transformation”.

Both alloys, the $Ga-S1$ and $Ga-S2$, exhibit the same kind of forward and reverse martensitic and inter-martensitic phase transformations upon cooling and heating the alloys, respectively. The similarities of the phase transformations of these two alloys could be anticipated as they have
similar chemical compositions. Additionally, both alloys have an excess Ni concentration and a deficiency of Mn when compared to the stoichiometric Ni$_2$MnGa alloy. Since they undergo the same type of phase transformations (i.e. from L2$_1$ to 7M modulated and then from 7M modulated to L1$_0$ upon cooling), one of them, the Ga-S1, was fully analyzed in order to study the intermartensitic phase transformations in detail.

5.4.4.1 Inter-martensitic phase transformations in the studied Ni-Mn-Ga alloys

Before starting the refinements, approximate phase transformation temperatures were determined by investigating the synchrotron diffraction patterns collected while heating the alloy from 100 to 400 K. In this investigation, despite the small variations in each diffraction pattern, they were categorized into five groups as shown in Figure 57. Those five temperature ranges and the phases present in each range are summarized in Table 23.

<table>
<thead>
<tr>
<th>Temperature range (K)</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-340</td>
<td>Cubic L2$_1$</td>
</tr>
<tr>
<td>340-325</td>
<td>Cubic L2$_1$ + 7M modulated monoclinic</td>
</tr>
<tr>
<td>325-315</td>
<td>7M modulated monoclinic</td>
</tr>
<tr>
<td>315-215</td>
<td>7M modulated monoclinic + Tetragonal L1$_0$</td>
</tr>
<tr>
<td>215-100</td>
<td>Tetragonal L1$_0$</td>
</tr>
</tbody>
</table>
Figure 57: Variation of the observed diffraction patterns of the \textit{Ga-Si} alloy while cooling from 395 to 100 K. At 395 K, the alloy is in the austenitic phase (cubic \textit{L2$_1$}) and upon cooling, the alloy transforms into the inter-martensitic \textit{7M} modulated monoclinic phase. Upon further cooling down to 100 K it transforms into a tetragonal \textit{L1$_0$} structure.

Phase fractions of each phase were determined by the Rietveld refinements. Then, using those results, thermograms of the martensitic and austenitic (of the 1$^{\text{st}}$ phase transformation) as well as inter-martensitic phase transformations were constructed. All six thermograms of \textit{L2$_1$} cubic, \textit{7M} modulated martensite, and tetragonal \textit{L1$_0$} phases are given in Figure 58. From Figure 58, two phase transformations could be identified while heating and then cooling of the \textit{Ga-Si} alloy. Upon cooling (from 400 K), around 310 K the alloy transforms from a cubic \textit{L2$_1$} austenitic phase to a \textit{7M} modulated martensitic phase. This is the forward martensitic phase transformation of this alloy. Upon further cooling, at around 260 K, the second phase transformation takes place from the \textit{7M} modulated monoclinic to a tetragonal \textit{L1$_0$} phase. The second phase transformation is the inter-martensitic phase transformation exhibited by some \textit{Ni-Mn-Ga} alloys [125, 126].
Upon heating, around 280 K, the alloy undergoes a phase transformation from the
tetragonal $L1_0$ to the $7M$ modulated monoclinic phase. Upon further heating, the alloy undergoes
an austenitic phase transformation from the $7M$ modulated martensitic phase to the cubic $L2_1$
phase.

The characteristic temperatures of the austenitic ($A_S$, $A_F$) and martensitic ($M_S$, $M_F$) phase
transformations were determined by the intersections of the lines obtained by extrapolating the
linear parts of the thermograms of the cubic $L2_1$ phase (Figure 59-a). In a similar fashion the phase
transformation temperatures of the inter-martensitic phase transformation ($IM_S$, $IM_F$) and
temperatures of the phase transformation from the tetragonal $L1_0$ to the monoclinic phase ($M_S$, $M_F$)
were determined (Figure 59-b). Four additional temperatures, two for the martensitic phase
transformation and two for the inter-martensitic phase transformation, were defined.

$T_{MH}$ and $T_{MC}$ are the temperatures at which the phase fraction of the martensitic phase is
half of the maximum value, upon heating and cooling of the alloy, respectively. These values are
taken as the martensitic phase transformation temperatures. $T_{IMH}$ and $T_{IMC}$ are the temperatures
at which the phase fraction of the tetragonal $L1_0$ martensitic phase is half of the maximum value, upon heating and cooling of the alloy, respectively. All these temperatures are given in Table 24.

Figure 59: Variation of the phase fractions of the (a) cubic, (b) $7M$ modulated monoclinic, and (c) tetragonal $L1_0$ phases with temperature upon heating (red) and cooling (blue) of the $Ga-Si$ alloy. Characteristic temperatures of the martensitic and inter-martensitic phase transformations were determined by the intersections as shown here.

<table>
<thead>
<tr>
<th>Phase transformation</th>
<th>Characteristic temperatures of the phase transformations (K)</th>
<th>Hysteresis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marten.</td>
<td>$A_S$ or $M_S^{<em>}$ $A_F$ or $M_F^{</em>}$ $M_S$ or $IM_S$ $M_F$ or $IM_F$</td>
<td>$T_{MC}$ or $T_{IMC}$ $T_MH$ or $T_MH$</td>
</tr>
<tr>
<td></td>
<td>$330.0\pm0.5$ $346.0\pm0.5$ $322.0\pm0.5$ $301.0\pm0.5$ $307.5\pm0.5$ $332.0\pm0.5$</td>
<td>$24.5\pm0.7$</td>
</tr>
<tr>
<td>Inter-marten.</td>
<td>$265.0\pm0.5$ $295.0\pm0.5$ $264.0\pm0.5$ $241.0\pm0.5$ $257.0\pm0.5$ $282.0\pm0.5$</td>
<td>$25.0\pm0.5$</td>
</tr>
</tbody>
</table>

Thermal hysteresis of the both phase transformations, martensitic and inter-martensitic, were calculated by taking the differences between $T_{MH}$ and $T_{MC}$ and between $T_{IMH}$ and $T_{IMC}$, respectively. The thermal hystereses of the two transformations are very close, $\sim 25$ K. Because of the similar hysteresis, the separation between the martensitic and inter-martensitic transformation temperatures while heating and then cooling, are the same. In each case, heating and cooling, the separation between the two phase transformations is $\sim 50$ K.
5.5 Magnetism of the austenitic and martensitic phases of the In-1, Co-73, and Co-76 alloys

The magnetic natures of these alloys were determined by different techniques. In the case of the Co-73 and Co-76 alloys, the thermomagnetic measurements were analyzed to study the magnetic nature of their austenitic and martensitic phases. AC-susceptibility measurements of the In-1 alloy were used to determine its magnetic nature in both austenitic and martensitic phases. Additionally, neutron diffraction data of the In-1 and Co-76 alloys were analyzed in order to confirm the observed magnetic nature in their martensitic phases.

5.5.1 Thermomagnetic measurements of the Co-73 alloy (Ni_{52}Mn_{25}In_{16}Co_{7})

Figure 60 displays the behavior of the mass magnetization as a function of the temperature (in the range from 125 to 325 K) in FC (cooling), and FC (heating) routines under four applied magnetic fields (0.005, 1, 2, and 3 T). All these thermomagnetic curves demonstrate a sharp increase of the magnetization around a certain temperature upon heating and sharp decrease of the magnetization upon cooling of the alloy. This indicates a magnetic phase transformation from a phase with a lower magnetization to a ferromagnetic phase upon heating and a ferromagnetic to a low magnetic phase upon cooling. From Figure 60, it can be seen that the magnetic phase transformation temperatures decrease with an increasing magnetic field. The weak magnetization in the martensitic phase is almost constant below some temperature in the martensitic phase. The behavior of the magnetization curve in the martensitic phase could be due to a low magnetization state such as antiferromagnetic or spin-glass.

Under the 0.005 T magnetic field, the magnetization of the ferromagnetic austenitic phase increases at a very slow rate. This is because the 0.005 T magnetic field is not sufficient to saturate the ferromagnetic austenitic phase. However, in the case of higher magnetic fields (1 to 3 T), magnetization comes to a maximum value upon heating. This is where the alloy completes the
magnetic phase transformation from a low magnetization state to a ferromagnetic state. Above this temperature, the magnetization of the alloy gradually decreases with increasing temperature. This is because heating the alloy in the austenitic phase will cause a decrease in the ferromagnetism due to thermal agitation.

Figure 60: Thermo-magnetization curves under four magnetic fields (.005, 1, 2, and 3 T).

5.5.2 The magnetic nature of the Co-76 alloy (Ni$_{41}$Mn$_{39}$In$_{12}$Co$_8$)

5.5.2.1 Thermomagnetic measurements of the Co-76 alloy (Ni$_{41}$Mn$_{39}$In$_{12}$Co$_8$)

Figure 60 demonstrates the behavior of the mass magnetization of the Co-76 alloy as a function of the temperature in the range from 100 to 400 K while undergoing ZFC (heating) and FC (cooling) routines under four applied magnetic fields (0.005, 1, 2, and 3 T). All these thermomagnetic curves demonstrate a sharp change in the magnetization in both ZFC (heating) and FC (cooling) paths. The temperature around which the sharp change in the magnetization takes place decreased with an increasing magnetic field in both ZFC (heating) and FC (cooling) paths. A higher magnetization in the higher temperatures (e.g. approximately above 270 K upon heating
under 1 T field) confirms a ferromagnetic ordering in the austenitic phase. A weak magnetization in lower temperatures is almost constant below a certain temperature in the martensitic phase. The observed lower magnetization in the martensitic phase compared to that of the austenitic phase could be due to a magnetic state such as an antiferromagnetic or a spin-glass.

5.5.2.2 Magnetic phase transformation of the Co-76 alloy (Ni_{41}Mn_{39}In_{12}Co_{8})

Thermomagnetic measurements indicate a magnetic phase transformation of the Co-76 alloy from a ferromagnetic phase to a phase with a low magnetization. The characteristic temperatures of the magnetic phase transformation were defined by the intersections of the lines obtained by extrapolating the linear parts of the thermomagnetic curves (Figure 61). The characteristic temperatures of the pure magnetic phase transformation are ferromagnetic start ($F_{MS}$), ferromagnetic finish ($F_{MF}$), lower magnetization state start ($L_{MS}$), and lower magnetization state finish ($L_{MF}$). These characteristic temperatures of the thermo-magnetic curve obtained under the 3 T field are shown in Figure 61. Additionally, two characteristic temperatures, $T_{h(50)}$ and $T_{c(50)}$, were defined. Here, $T_{h(50)}$ is the temperature at which the magnetization of the alloy is equal to the average value in the FC heating path, while $T_{c(50)}$ is the temperature at which the magnetization of the alloy is equal to the average value in the FC cooling path. All the characteristic temperatures of the magnetic phase transformations are listed in Table 25.
Figure 61: Thermo-magnetization curves under different magnetic fields (.005, 1, 2, and 3 T). The characteristic temperatures of the magnetic phase transformation (associated with a crystallographic phase transformation) were determined by extrapolating the linear parts of the thermomagnetic curves. The characteristic temperatures of the magnetic phase transformation under a 3 T field are given in the diagram. Magnetic phase transformation temperatures decrease with an increasing field.

<table>
<thead>
<tr>
<th>Magnetic Field (T)</th>
<th>$F_M$</th>
<th>$F_M'$</th>
<th>$^{a}L_M$</th>
<th>$^{a}L_M'$</th>
<th>$T_c(50)$</th>
<th>$T_h(50)$</th>
<th>Thermal Hysteresis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>293 ± 0.5</td>
<td>319 ± 0.5</td>
<td>286 ± 0.5</td>
<td>249 ± 0.5</td>
<td>267 ± 0.05</td>
<td>306 ± 0.05</td>
<td>39.0 ± 0.05</td>
</tr>
<tr>
<td>1</td>
<td>308 ± 0.5</td>
<td>320 ± 0.5</td>
<td>287 ± 0.5</td>
<td>267 ± 0.5</td>
<td>278 ± 0.05</td>
<td>314 ± 0.05</td>
<td>36.0 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>300 ± 0.5</td>
<td>313 ± 0.5</td>
<td>279 ± 0.5</td>
<td>259 ± 0.5</td>
<td>270 ± 0.05</td>
<td>308 ± 0.05</td>
<td>38.0 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>295 ± 0.5</td>
<td>308 ± 0.5</td>
<td>271 ± 0.5</td>
<td>250 ± 0.5</td>
<td>260 ± 0.05</td>
<td>302 ± 0.05</td>
<td>42.0 ± 0.5</td>
</tr>
</tbody>
</table>

$^{a}LM$ – Low magnetization state

The hystereses associated with the magnetic phase transformations were calculated by taking the difference between $T_h(50)$ and $T_c(50)$. The magnetic phase transformation temperature decreases with the increasing magnetic field. However, the associated thermal hysteresis of the magnetic phase transformation increases with the increasing field in the range 1 to 3 T. Also in this range, the thermal hysteresis is linearly proportional to the applied magnetic field and there is
an increment in the thermal hysteresis of ~2 K/T. The characteristic temperatures of the magnetic phase transformation under the 0.005 T field deviate from the rest. Also, the thermal hysteresis under these conditions is close to that of under 2 T.

5.5.2.3 Neutron diffraction analysis of martensitic phases of the Co-76 alloy ($Ni_{41}Mn_{39}In_{12}Co_8$)

To further investigate the magnetic state of the martensitic phase, neutron diffraction data of this alloy collected at temperatures below 250 K were analyzed in detail. Three of the constituent atoms of this alloy ($Mn$, $Co$, and $Ni$) have magnetic moments due to their unpaired electrons, and those magnetic moments interact with the neutrons’ spin. If there is an antiferromagnetic ordering present in the martensitic phase, there will be additional magnetic Bragg peaks, separated from crystalline peaks due to an enlargement of the magnetic unit cell compared to the crystalline unit cell [104].

Figure 62 demonstrates a chemical unit cell and an enlarged magnetic unit cell seen by the neutron below the Neel temperature of this material. There is one type of atom and the unit cell is simple tetragonal. However, below the Neel temperature, these magnetic atoms in the 100 plane align parallel to each other and they align antiparallel to the magnetic moments in the adjacent planes. Consequently, the dimensions on the magnetic unit cell are different from the chemical unit cell. In this case the lattice parameter in the $x$ direction of the magnetic unit cell is twice the chemical unit cell (changes from $a$ to $2a$).

As described in section 5.3.2.2, the refinement of the neutron diffraction data, which were collected below the martensitic phase transformation temperature, was carried out with a mixture of two martensitic phases ($8M$ and $6M$ modulated monoclinic belonging to the $P 1 2/m$ 1 space group). The observed diffraction patterns are in good agreement with the calculated diffraction patterns by Rietveld refinements using these model structures (Figure 63). All peaks in the
observed diffraction pattern were identified as the Bragg peaks belonging to either $8M$ or $6M$ modulated monoclinic phases. There were no extra peaks which could belong to an antiferromagnetic ordering. As previously discussed, an antiferromagnetic unit cell, if present, would not be the same size as the crystallographic unit cell (e.g. Figure 62). Therefore, the possibility of an antiferromagnetic ordering in the martensitic phase can be ruled out.

Figure 62: The chemical and magnetic unit cells of a hypothetical antiferromagnetic material $M$, below its Neel temperature. Above the Neel temperature, the structure of $M$ is the same by either X-ray or neutrons scattering. Below Neel temperature additional reflections appears in the neutron diffraction pattern from antiferromagnetic ordering and these magnetic reflections double the unit cell in the $a$ direction.

5.5.2.4 DC SQUID measurements of the Co-76 alloy ($Ni_{41}Mn_{39}In_{12}Co_{8}$)

Thermomagnetic measurements demonstrate a very low magnetization in the martensitic phase under all measured magnetic fields. The possibility of antiferromagnetic ordering in the martensitic phase was excluded by the neutron diffraction results of the martensitic phase; however, there is no sufficient evidence to confirm the magnetic nature of the martensitic phase just below the martensitic transformation. In order to investigate the magnetic nature at very low temperatures (below 100 K), another set of DC SQUID magnetization measurements were carried out in the temperature range from ~1.9 to 100 K. The experimental procedure of the DC SQUID
measurements of the Co-76 alloy is summarized in Table 26. This experimental procedure was adapted from Chamberlin et. al. [127].

Figure 63: Rietveld refinements of the neutron diffraction data collected at 250 K. At this temperature, the alloy is a mix of two martensitic phases: 6M and 8M modulated monoclinic. The numbers marked in black and red are the (hkl) values of the peaks belong to the 6M and 8M modulated phases, respectively.

Table 26: Summary of the DC SQUID measurements of the Co-76 alloy

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Preparation</th>
<th>ZFC heating</th>
<th>FC cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cooled from 100 to ~ 2 K under 0.001 T field</td>
<td>Change MF to 0.01 T at ~ 2 K and heated to 100 K</td>
<td>Cooled to 2 K from 100 K under 0.01 T</td>
</tr>
<tr>
<td>2</td>
<td>Cooled from 100 to ~ 2 K under 0.001 T field</td>
<td>Change MF to 0.05 T at ~ 2 K and heated to 100 K</td>
<td>Cooled to 2 K from 100 K under 0.05 T</td>
</tr>
</tbody>
</table>

Consider the ZFC and FC heating routines of the thermomagnetic curves of the Co-76 alloy under 0.005 T field shown in Figure 64-a. These curves separate (starting around ~ 285 K, just below the transformation temperature from the ferromagnetic state to a phase with lower magnetization) indicating an irreversible behavior of the magnetization. Separation between the
curves gets wider as temperature decreases. Such a splitting of the ZFC and FC curves could be attributed to the coexisting of the ferromagnetic and antiferromagnetic interactions in the martensitic phase of this alloy [40, 77].

![Thermomagnetic measurements](image)

**Figure 64:** Thermomagnetic measurements of the Co-76 alloy in ZFC (heating), FC (heating), and FC (cooling) paths. (a) Splitting between ZFC and FC curves (starting around 285 K and getting wider as temperature decreases) indicates a coexisting of the antiferromagnetic and ferromagnetic interaction in the martensitic phase. (b) Cusp like features in both ZFC curves under 0.01 and 0.05 T fields indicate a spin-glass-like magnetic nature below ~ 19 K.

Under both magnetic fields, 0.01 and 0.05 T, cusp-like maxima were observed in the mass magnetization in the ZFC heating path at around 19 K. In addition, there is a splitting between ZFC heating and FC cooling thermomagnetic curves. These features indicate a spin-glass-like magnetic nature of this alloy at very low temperatures [89, 90, 127]. From these thermomagnetization curves, the glass transition temperature was identified to be ~19 K (Figure 64-b). Therefore, one of the potential magnetic nature of the martensitic phase of this alloy (from transformation temperature (~300 K) down to ~20 K) is an exchange bias interaction as suggested in [91]. The observed magnetic nature of the Co-76 alloy, in both austenitic and martensitic phases, will be discussed and explained in the next chapter using the site occupancies, interatomic
distances, and exchange interactions of the atoms with a magnetic moment (\(Mn\), \(Ni\), and \(Co\)) in different crystallographic sites.

5.5.3 Magnetic nature of the \(In\)-\(I\) alloy (\(Ni_{45}Mn_{43}In_{12}\))

The crystalline structures of the \(In\)-\(I\) alloy were determined by analyzing its synchrotron diffraction data, which were collected under various experimental conditions. Therefore, one of the main goals of the TOF neutron diffraction experiment was to determine the magnetic nature of the martensitic phase of the \(In\)-\(I\) alloy. Crystallographic information of the austenitic and martensitic phases of the \(In\)-\(I\) alloy such as space groups, crystalline systems, unit cells, lattice parameters, and thermal parameters were obtained from the Rietveld refinements of the synchrotron diffraction data. Therefore, the crystallographic information determined from the synchrotron diffraction data analysis was used as the starting parameters in the Rietveld refinements of the neutron diffraction data of the \(In\)-\(I\) alloy.

5.5.3.1 Determination of the actual temperature of the \(In\)-\(I\) alloy sample in the neutron diffraction experiment

In the TOF neutron diffraction experiment, the \(In\)-\(I\) alloy sample was placed inside the custom aluminum vacuum chamber (Figure 26-b, section 4.5.2.1). In order to determine the exact contribution of the alloy sample to the observed diffraction pattern, another set of diffraction data, under the identical experimental conditions except the sample, was collected. First, the neutron diffraction data of the sample environment (without the sample), were analyzed. The main contribution to the diffraction pattern of the sample environment (without the alloy) came from copper. These observed \(Cu\) peaks were due to the neutrons which were diffracted by the \(Cu\) thermal contacts and copper cold mass (Figure 26-b in chapter 4). Also, there was a significant contribution
from the aluminum chamber. Aluminum peaks could be coming from the aluminum windows of the vacuum chamber which are also shown in Figure 26-b. However, this is unexpected because the bound scattering cross section of the aluminum is only 1.495 barn [103], which is a small value to acquire noticeable diffraction peaks.

To determine the temperature of the sample accurately, the lattice constant of the Cu was refined at each temperature step from the Bragg peaks of Cu in the diffraction data of the sample environment. The calculated lattice parameters at different temperatures were compared with the reported values in the literature [128]. Then the temperature of the copper thermal contacts was calculated using the lattice parameters at each temperature and the thermal expansion coefficient of copper, \( \alpha = 14.87 \times 10^{-6} \, ^\circ\text{C}^{-1} \) [128].

The actual temperature of the sample should be the same as that of copper thermal contacts. Consequently, the actual temperature of the sample at each temperature step were determined by following the above procedure. There was a significant difference between the calculated and nominal temperatures of the sample. Actual temperature (based on the lattice parameter and thermal expansion coefficient) was always \( \sim 10 \, ^\circ\text{C} \) higher than the nominal value. The results obtained from the above calculations of sample temperature are summarized in Table 27.

5.5.3.2 Rietveld refinements of the neutron diffraction data of the martensitic phase of the In-1 alloy (\( \text{Ni}_{45}\text{Mn}_{43}\text{In}_{12} \))

The crystallographic information of the 7M and 5M modulated martensitic phases of the In-1 alloy (which were obtained from the analysis of synchrotron diffraction data) was used as the starting structures in the neutron data refinements. The Bragg peaks, which were coming from the sample background (i.e. from aluminum vacuum chamber and copper thermal contacts), were analyzed using the known lattice parameters of these phases by examining the neutron diffraction
data of the sample environment (at the same temperature). In the refinements of the neutron diffraction data of the sample at a particular temperature, lattice parameters of all above phases (i.e. aluminum, copper, 7M, and 5M modulated martensitic phases) were kept constant. These constants (lattice parameters) at a particular temperature were determined by the synchrotron diffraction analysis of the In-1 alloy and neutron diffraction analysis of the sample background at the same temperature. Additionally, thermal parameters of all phases and fractional coordinates of all atoms in every phase were kept constant. Site occupancies of the martensitic phase were constrained to the values found in the austenitic phase (by iterative site occupancy analysis of synchrotron and neutron diffraction data in the austenitic phase) by considering the relationship between the crystalline structure of two phases, austenitic and martensitic.

Table 27: The actual temperature of the sample calculated by lattice parameter of copper

<table>
<thead>
<tr>
<th>Data file ID</th>
<th>Nominal temp. (K)</th>
<th>Actual temp. (K)</th>
<th>Lattice parameter (nm)</th>
<th>Uiso (nm)</th>
<th>Temp. Difference (°C)</th>
<th>Percent change of temp. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58555</td>
<td>251</td>
<td>258</td>
<td>0.361275</td>
<td>0.000726</td>
<td>7</td>
<td>2.79</td>
</tr>
<tr>
<td>58558</td>
<td>271</td>
<td>281</td>
<td>0.361394</td>
<td>0.000753</td>
<td>10</td>
<td>3.69</td>
</tr>
<tr>
<td>58568</td>
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<td>58564</td>
<td>331</td>
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<td>4.23</td>
</tr>
<tr>
<td>58566</td>
<td>353</td>
<td>372</td>
<td>0.361888</td>
<td>0.000921</td>
<td>19</td>
<td>5.38</td>
</tr>
</tbody>
</table>

As shown in Figure 65 and Figure 66 there was a good agreement between observed neutron diffraction intensities collected at 309 K under 0 and 2 T magnetic fields, respectively. Those calculated intensities were based on the known crystallographic information of the 7M, 5M martensite, copper and aluminum phases in each temperature step.
Figure 65: Observed and calculated neutron diffraction patterns of the In-1 alloy. Data were collected at 309 K under no applied magnetic field to the alloy. Under these conditions, the alloy is just below the martensitic phase transformation temperature.

Under 2 T magnetic field, at 309 K the In-1 alloy was in the austenitic phase. All the observed Bragg peaks were identified in the diffraction pattern collected under a 2 T magnetic field. However, in the case of no applied magnetic field, at 309 K, the In-1 alloy was in the martensitic phase (mix of 5M and 7M). Under these conditions, there is one Bragg peak at d-spacing = 0.3178 nm, which could not be identified as belonging to any of the above crystallographic phases (austenitic, 7M, 5M, copper, and aluminum phases). The crystalline structures of the martensitic phases, 7M & 5M, and the austenitic phase were determined by analyzing the synchrotron diffraction data of the In-1 alloy sample. The contributions of the sample environment (from Cu and Al) to the diffraction pattern are also well known from the refinements of the neutron diffraction data of the sample environment (without the alloy). Therefore, this extra peak which appears in the neutron diffraction pattern, was collected below the martensitic
transformation temperature, should be due to an antiferromagnetic ordering of the martensitic phase.

Figure 66: Observed and calculated (by Rietveld refinements) neutron diffraction data of the In-1 alloy. Data were collected at 309 K under 2 T applied magnetic field. Under these conditions, alloy is in the austenitic phase. However, there are some traces of the martensitic phase/phases.

At the final stages of the refinements, two new magnetic-only phases were introduced to GSAS with the aid of a complementary program to GSAS, called SARAh refine [117]. These were magnetic only phases of the 5M and 7M modulated martensitic phases. After a number of different propagation vector (trial and error), \( K = 1/2, 0, 0 \) was used as the propagation vector in both phases. The lattice parameters and atomic positions of the new magnetic phases were calculated by SARAh representational analysis software [117]. The lattice parameters of the new magnetic phases were the same except the lattice parameter “\( a \)” which was twice as that of the martensitic phases. That is, the magnetic unit cell is twice the size of the crystalline unit cell.
From the magnetic refinements, it was found that the peak positions of the unidentified peaks coincide with the antiferromagnetic Bragg peaks of the $5M$ modulated antiferromagnetic phase. Those antiferromagnetic Bragg peaks were a family of planes $(115)$ & $(115)$. However, there was no good agreement between the observed and calculated peak intensities of the magnetic peaks. After the magnetic refinements, the preferred orientations and peak profile parameters of all the phases were allowed to refine to get a better match between the observed and calculated diffraction patterns.

From this neutron diffraction data analysis of the $In-1$ alloy, it was found that there is an antiferromagnetic ordering in the martensitic phase of this alloy. By the investigation of other diffraction patterns (which were collected below the martensitic phase transformation temperature), this antiferromagnetic ordering was found in all the temperatures below the martensitic phase transformation.

5.5.3.3 AC-Susceptibility measurements vs. magnetic ordering

In the AC-susceptibility measurements of the $In-1$ alloy, which is shown in Figure 67, an abrupt drop of the magnetization was observed around 305 K. Above this temperature the magnetization is significantly higher. This indicates a magnetic phase transformation around 305 K. Because of the high magnetization, it can be concluded that the higher temperature phase (above 305 K) is ferromagnetic. From phase fraction analysis of this alloy, it was concluded that the austenitic finish temperature under no applied magnetic field is ~305 K. Therefore, it can be concluded that the austenitic phase of this alloy is ferromagnetically ordered.
Figure 67: Imaginary susceptibility ($\chi''$) measurements of the In-I alloy as a function of temperature under different frequencies. Data were collected under a magnetic field of 0.05 Oe.

The abrupt drop of magnetization around the martensitic phase transformation indicates the change in the magnetic ordering through the phase transformation. The austenitic phase is ferromagnetic and it transforms into a phase with a much lower magnetization, compared to the austenitic phase. The possible magnetic states in the martensitic phase could either be antiferromagnetic or spin-glass. However, it was also observed that the cusp (onset) of the susceptibility vs. temperature curves (Figure 67) was frequency independent. This is solid evidence to rule out the possibility of a spin-glass nature in the martensitic phase, because the onsets of the imaginary susceptibility curves are independent of the frequency of the applied AC field [111]. This leaves only one possibility: the antiferromagnetic ordering in the martensitic phase.

As discussed, the results of the Rietveld refinements of the neutron diffraction data demonstrate some magnetic Bragg peaks belonging to the 5$M$ modulated antiferromagnetic phase.
Thus, AC-susceptibility and neutron diffraction results agree and it can be concluded that the magnetic ordering of the martensitic phase of the In-1 alloy is antiferromagnetic.

5.5.3.4 Martensitic phase transformation temperature

As shown in Figure 68, at 309 K, when the applied magnetic field was zero, all the major peaks observed in the diffraction patterns were martensite (i.e. (020), (021), (0 3 15) of the 7M modulated martensite and (212), (2 2 10) of the 5M martensite). A family of antiferromagnetic peaks of the martensitic phase, (115) & (115), and antiferromagnetic peak (612) of the martensitic phase, were also observed very clearly in this diffraction pattern. The contribution of the austenitic phase to the diffraction pattern was minimal. On the other hand, in the presence of a magnetic field of 2 T, there were no traces of magnetic peaks in the diffraction pattern (Figure 65). Also, all major martensitic peaks observed in the diffraction pattern under no magnetic field were diminished. At 309 K and under an applied field, the majority of the larger peaks in the diffraction pattern (Figure 66) were austenite (e.g. (220), (422), (600), (640) and (660) of the austenitic phase).

The refinement of the diffraction data collected at the same temperature (309 K) but under different magnetic fields (0 T and 2 T) clearly indicates the large effect of the applied magnetic field on the martensitic transformation. Variations of the normalized intensity (with respect to the maximum peak in each diffraction pattern) of several diffraction peaks with temperature under no applied magnetic fields and 2 T are shown in Figure 68. These graphs demonstrate the shift of transformation temperature to a lower temperature with an increased magnetic field. Similar behavior of the sample was observed from the phase fraction analysis of the synchrotron diffraction data. Therefore, two results confirm the shift in transformation temperature to a lower value with an increasing magnetic field.
5.6 Effect of the applied magnetic field on the martensitic phase transformation

In order to investigate the effect of an applied magnetic field on the martensitic phase transformation of the Co-73 alloy, diffraction data were collected under constant pressure (atmospheric pressure) and at a constant temperature (at 220 K) while increasing the applied magnetic field gradually from 0 to 6.5 T and then decreasing back to 0 T. The observed diffraction patterns under each magnetic field (in steps of 0.5 T) while increasing the field from 0 to 6.5 T, are shown in Figure 69.
Figure 69: The observed diffraction patterns of the Co-73 alloy under different magnetic fields (in steps of 0.5 T) while increasing from 0 to 6 T. The experiment was carried out at constant temperature (220 K) and under atmospheric pressure. These diffraction patterns demonstrate the growth of the austenitic phase from the martensitic phase upon increasing the magnetic phase.

From the observed diffraction patterns (Figure 69), it was concluded that the Co-73 alloy was in the martensitic phase at 220 K and under no applied magnetic field. Upon increasing the magnetic field, the alloy gradually transformed into the austenitic phase, and around 6 T, the alloy completed its austenitic phase transformation.

In order to study these magnetic field-induced martensitic phase transformations quantitatively, the diffraction data were analyzed by Rietveld refinements to determine the phases and their fractions under each magnetic field. Refinements of the diffraction data, collected at 220
K under a zero field, is shown in Figure 48-a (in section 5.4.2). A convergence for the refinements was obtained for a mixture of 7M and 5M modulated monoclinic structures. Under 6.5 T, the alloy was in the austenitic phase with a cubic $L2_1$ structure. The alloy has the same structure when it was at 300 K under a zero applied magnetic field. Rietveld refinements of the data collected under these extreme experimental conditions, at 220 K under 6.5 T and at 300 K under 0 T, are identical. The phase fractions of the austenitic and martensitic phases under different fields between 0 and 6.5 T (in steps of 0.5 T) were calculated. Variations of the austenitic and martensitic phase fractions upon increasing and then decreasing the applied magnetic field are shown in Figure 70.

Figure 70 demonstrates a complete austenitic phase transformation upon increasing the field from zero to 6.5 T, and a complete martensitic phase transformation upon decreasing the field from 6.5 T to zero. Four characteristic magnetic fields were defined by following a procedure similar to that of defining the characteristic temperatures in a temperature-induced martensitic phase transformation. Four characteristic magnetic fields - austenitic start ($A^M_{s}$), austenitic finish ($A^M_{F}$), martensitic start ($M^M_{s}$), and martensitic finish ($M^M_{F}$) - were determined by the intersections of the lines obtained by extrapolations of the linear parts of the austenitic phase fraction verses magnetic field curves (Figure 70). The magnetic hysteresis associated with the magnetic field-induced martensitic phase transformation was determined by taking the average of ($A^M_{s} - M^M_{F}$) and ($A^M_{F} - M^M_{s}$). The characteristic magnetic fields and the magnetic hysteresis associated with this phase transformation is given in Table 28.
Figure 70: Variation of the austenitic (red) and total martensitic (blue) phase fractions with the applied magnetic field at 220 K while increasing the field from 0 to 6.5 T and then decreasing back to 0 T. Around the phase transformation, the magnetic hysteresis is ~0.1 T.

Table 28: Characteristic magnetic fields

<table>
<thead>
<tr>
<th>Characteristic magnetic fields (T)</th>
<th>Magnetic Hysteresis (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s^M$</td>
<td>$A_F^M$</td>
</tr>
<tr>
<td>4.80±0.05</td>
<td>5.80±0.05</td>
</tr>
</tbody>
</table>

Complete martensitic and austenitic phase transformations of this alloy were observed upon changing the temperature from 300 K to 200 K and then 200 K to 300 K, respectively. Therefore, temperature and magnetic field could be drive the martensitic phase transformations in this alloy [129].
CHAPTER 6

DISCUSSION

6.1 Chemical composition and site occupancies

It is very important to determine the chemical composition of the studied alloys accurately because their crystallographic, magnetic, and magnetocaloric properties are highly dependent on the composition and constituent atoms [43, 130]. Therefore, the best technique in each case, depending on the constituent elements and sample size, was used to determine the composition of the studied alloys.

Three characterization techniques, Rutherford Backscattering Spectrometry (RBS), Energy Dispersive X-ray Spectroscopy (EDS), and Rietveld refinements, were used to determine the chemical composition of the studied alloys. When comparing RBS and EDS techniques, they both have advantages and disadvantages, depending on the nature of the needed analysis. RBS can be used to calculate the depth profile (typically, the depth is about 2000 nm for $He^{2+}$ ions [95]) and elemental concentration of almost all the elements [131].

The RBS technique needs no standards to calculate the elemental composition [96, 131]. On the other hand, to conduct a quantitative analysis by EDS, calibrations standards (i.e. standards with known similar chemical compositions for each element in the sample to be analyzed) are needed [131, 132]. The Ga-S1 and Ga-S2 alloys were analyzed by EDS because the smart magnetic alloy research group at Aalto University in Finland, where the EDS experiment carried out, has the appropriate standards and calibrated EDS.
The preparation procedure of a sample for the RBS experiment constitutes mainly of polishing the surface so that is smooth enough (roughness of the surface should be less than 100 nm) for good resolution in the RBS spectrum [132]. In the current study, the inadequate sample preparation (roughness) could have affected the accuracy of the RBS data analysis.

*Ni* and *Mn* are present in all studied alloys. In the RBS spectra, the corresponding edges were identified clearly in each sample. Because of the significant difference between the atomic mass of *In* and other constituent elements of studied alloys, the *In* concentration was determined more accurately compared to other elements. In the case of the *Ni-Mn-Ga* alloys, the atomic mass difference between *Ga* and the other elements is small (atomic mass in a.m.u.: Mn = 54.93, *Ni* = 58.69, Ga = 69.72, and In =114.41). Therefore, RBS works better for *Ni-Mn-In* alloy compared to *Ni-Mn-Ga* alloys.

6.1.1 Site occupancies in the austenitic phase of the studied alloys

Despite the difference in the chemical composition of the studied alloys, their austenitic crystalline structure is cubic *L2*$_1$. This is the most common structure reported in the literature (See the references in Table 2, section 3.2.1.1). There are three crystallographic sites which could be occupied by the constituent atoms of the studied Heusler alloys. Site occupancies of the constituent atoms were determined by Rietveld analysis of the diffraction data (neutron or synchrotron or both). The synchrotron diffraction technique is a good tool to distinguish the *In* atom from the rest of the constituent atoms (i.e. *Mn*, *Ni* and *Co*) of the *In-1*, *Co-73*, *Co-74*, and *Co-76* alloys, because of the significant mass difference between *In* and other elements. On the other hand, *Mn*, *Co*, and *Ni* are closely positioned in the periodic table (the atomic numbers of *Mn*, *Co*, and *Ni* are 25, 27, and 28, respectively), and therefore not effectively distinguishable using an X-ray diffraction technique. Because X-rays are sensitive to the electron cloud of the atoms, it cannot distinguish
between atoms with similar atomic numbers effectively. On the other hand, in the neutron diffraction technique, the scattering amplitudes of the constituent atoms in the studied Heusler alloys \((\text{Ni, Mn, In, Co and Ga})\) for neutrons are significantly different (Table 6 [103]). Specifically, \(\text{Mn}\) has a negative scattering length for neutrons, while \(\text{Ni and Co}\) have positive scattering lengths. A negative scattering length indicates that the scattered neutron wave function is out of phase with respect to the incident neutron wave function. This shows a good contrast between \(\text{Mn and Ni}\) and hence they could be distinguished effectively. Also, the scattering lengths of \(\text{Co and Ni}\) are significantly different (bound scattering lengths of \(\text{Ni}\) and \(\text{Co}\) are 14.4 and 2.39 fm, respectively [103]).

Considering the capabilities of neutron and synchrotron diffraction techniques, both neutron and synchrotron diffraction data were used to determine site occupancies of the \(\text{In-1}\) alloy. From iterative site occupancy refinements of the neutron (to distinguish \(\text{Ni and Mn}\) in the same crystallographic sites) and synchrotron diffraction data (to distinguish \(\text{In and Mn}\) in the same crystallographic sites), site occupancies of the \(\text{In-1}\) alloy were determined. Also, site occupancy refinements of the \(\text{Co-76}\) alloy is considered reliable because results were based on its neutron diffraction data. The chemical composition of these two alloys, determined by the site occupancy refinements are in good agreement, with the chemical composition calculated by the RBS technique.

For the rest of the studied alloys (i.e. \(\text{Co-73, Ga-S1, and Ga-S2}\)), site occupancies were determined by Rietveld analysis of their synchrotron diffraction data. As previously discussed, synchrotron radiation does not distinguish between elements with similar atomic numbers. Therefore, synchrotron diffraction has limitations with regards to the determination of the site occupancies of \(\text{Ni, Co, and Mn}\) atoms in the \(\text{Ni-Mn}\) based Heusler alloys. In the site occupancy
refinements of these alloys, several constraints had to imposed to avoid unrealistic results for the chemical composition. All the constraints were based on the pre-determined chemical composition of these alloys (composition determined by RBS in the case of the Co-73 alloy and compositions determined by EDS in the case of the Ni-Mn-Ga alloys).

In the case of the Ni-Mn-Ga alloys, both have excess Ni and deficiency of Mn. The excess Ni atoms were found to occupy the regular Mn-sites. The Ga atoms occupy only their regular sites. The majority of the Mn atoms stay in their regular sites and only very few were found to occupy Ga-sites (Table 17). The results are based on the synchrotron diffraction data of the Ga-S1 and Ga-S2 alloys and their compositions. These site occupancy results are in a good agreement with the site occupancies of some Ni-Mn-Ga alloys with similar compositions [33, 133]. Both site occupancy refinement results were based on neutron diffraction data studies of two series of Ni-Mn-Ga alloys conducted independently by P. J. Lázpita et. al. [33] and M. Barandiarán et. al. [133], respectively.

The site occupancies of the studied alloys with their chemical composition are summarized in Table 29. Also, the agreement factors of the final Rietveld refinement cycle of the site occupancy refinements are given in Table 29. In all these alloys, Mn atoms occupy both regular Mn sites (4a) and regular In sites (4b). In the case of the In-1 alloy, Mn atoms occupy all three crystallographic sites. In contrast, this is not the case with the Ga-S1 and Ga-S2 alloys. There is a deficiency of the Mn atoms in those alloys, and, therefore, they occupy only their regular sites (4a). In the cobalt substituted alloys, Co-73 and Co-76, cobalt atoms tend to occupy the regular Ni-sites (they have similar atomic radii). This trend of Co atoms, (i. e. the preference of occupying the regular Ni-sites) has been predicated by J. Bai et al. [121] by the formation energy calculations of the austenitic structure of Ni-Mn-Ga alloys.
Table 29: Composition of the studied Heusler alloys based on the site occupancy refinements of their austenitic phase (cubic $L2_1$)

<table>
<thead>
<tr>
<th>Alloy and experimental condition</th>
<th>Atom</th>
<th>Percentage site occupancy (%)</th>
<th>Chemical composition</th>
<th>Agreement factors of the final refinement cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$4a$ (4) $4b$ (4) $8c$ (8)</td>
<td></td>
<td>$\chi^2$ RP WP</td>
</tr>
<tr>
<td><strong>In-1 at 316 K, 2 T</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>-  -  89.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>100.0 50.6 10.4</td>
<td>Ni$<em>{44.9}$Mn$</em>{42.8}$In$_{12.3}$</td>
<td>2.7 3.3 2.8</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>0  49.4  -</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Co-73 at 300 K, 6 T</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>36.5 - 86.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>63.5 36.4 -</td>
<td>Ni$<em>{52.1}$Mn$</em>{25.1}$In$<em>{15.9}$Co$</em>{6.9}$</td>
<td>4.6 6.9 4.4</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>- 63.6 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>- - 14.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Co-76 at 600 K, 0 T</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>95.8 53.4 4.1</td>
<td>Ni$<em>{48.6}$Mn$</em>{39.3}$In$<em>{11.7}$Co$</em>{8.4}$</td>
<td>3.0 4.8 3.5</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>- 46.7 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>- - 16.8</td>
<td></td>
<td></td>
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<tr>
<td><strong>Ga-S1 at 390 K, 0 T</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>14.8 - 99.8</td>
<td>Ni$<em>{33.6}$Mn$</em>{21.4}$Ga$_{25.0}$</td>
<td>0.9 5.2 3.6</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>85.2 - 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>- 100.0 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ga-S2 at 380 K, 0 T</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>15.8 - 100.0</td>
<td>Ni$<em>{33.4}$Mn$</em>{21.1}$Ga$_{25.0}$</td>
<td>1.3 5.4 4.0</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>84.2 - -</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>- 100.0 -</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Site occupancies of the constituent atoms with a magnetic moment are important because they may provide a semi-quantitative explanation of the observed magnetic properties of the studied alloys. The magnetocaloric performance of these alloys strongly depends on the magnetic nature of their austenitic and martensitic phases. The origin of the magnetism in the austenitic and martensitic phases could be understood semi-quantitatively by analyzing the exchange bias interactions between the constituent atoms with magnetic properties. The magnetic nature of the austenitic and martensitic phases could be explained semi-quantitatively when the site occupancies and crystalline structures are known. The procedure will be discussed, and the observed magnetic nature of the In-1 and Co-76 alloys will be explained in section 6.8.
6.1.2 Neutron diffraction experiments and magnetic structure

Based on the thermomagnetic measurements of the Co-76 alloy and AC-susceptibility measurements of the In-1 alloy, it was concluded that both are ordered ferromagnetically in their austenitic phase (below their Curie temperature). As discussed in the experimental description section, neutron diffraction can provide information about the magnetic structure of the studied alloys. However, in the case of the In-1 and Co-76 alloys, ferromagnetic ordering of the austenitic phase could not be confirmed by the neutron diffraction analysis. This is because ferromagnetic ordering does not give any additional magnetic Bragg peaks, separated from the crystalline Bragg peaks in the observed diffraction patterns of the austenitic phase of these alloys. Instead, the ferromagnetic Bragg peaks coincide with the crystalline Bragg peaks and contribute to the peak intensities of the observed peaks. In the neutron diffraction data refinements of the austenitic phase, a magnetic only phase was introduced to the GSAS EXPGUI [123] by the SARAh representation analysis program. No additional improvement to the calculated diffraction pattern was obtained by magnetic refinements in the case of either alloy.

The neutron diffraction data of the Co-76 alloy were collected under no applied magnetic field. Under these experimental conditions, the spontaneous magnetization below the Curie temperature is very low (the mass magnetization of the austenitic phase of the Co-76 alloy is very low, about 1 emu/g, even under 50 Oe applied magnetic field). This could be the reason for the very low or no ferromagnetic ordering contribution in the neutron diffraction pattern of the Co-76 alloy in the austenitic phase. The neutron diffraction data of the austenitic phase of the In-1 alloy were collected under a 2 T magnetic field, and even then, there was no noticeable change in the observed diffraction pattern by adding a magnetic phase. It was reported that the magnetic intensity negligible when compared with the nuclear intensity in the neutron diffraction measurements of
off-stoichiometric Ni-Mn-Ga alloys, which are ferromagnetic in the austenitic phase [33]. Consequently, it was not possible to fit the magnetic contribution of the neutron scattering even in a single-crystalline sample [33].

An antiferromagnetic ordering of the martensitic phase of the In-1 alloy was confirmed by the neutron diffraction analysis (with the aid of the synchrotron diffraction results under the same experimental conditions) by the identification of extra magnetic Bragg peaks (coming from the antiferromagnetic ordering) in the observed diffraction pattern. On the other hand, for the Co-76 alloy, neutron diffraction data analysis of the martensitic phase could not be confirmed any antiferromagnetic ordering.

6.1.3 Martensitic phase transformations and crystalline structures of the studied alloy

All studied alloys undergo martensitic phase transformations upon cooling. Only Ni-Mn-Ga alloys undergo intermartensitic phase transformation upon further cooling to very lower temperatures. Except for the Ni-Mn-Ga alloy (which will be discussed in the following section), the martensitic phase of these alloys is a mixture of two modulated phases. The martensitic phase of the Co-76 alloys is a mixture of 6M and 8M modulated monoclinic structures, while that of In-1, Co-73, and Co-74 alloys is a mixture of 5M and 7M modulated monoclinic structures (P 1 2/m 1). A summary of the martensitic phase transformation of all studied alloys is given schematically in Figure 71.
Figure 71: Summary of the martensitic phase transformations of the studied Ni-Mn based Heusler alloys. (Intermartensitic phase transformations of the Ni-Mn-Ga alloys will be discussed in the section 6.1.3.1).

The contribution to the GMCE from the lattice entropy change in the first-order structural phase transformations of some Ni-Mn based alloys is more than 50% [30]. All the studied alloys undergo first-order structural phase transformations, and the associated lattice entropy changes with each transformation could be qualitatively compared. The lattice entropy difference between the cubic and modulated phases increases with increasing modulations (e.g. the lattice entropy difference between the cubic austenitic structure and 8M modulated martensitic structure is higher than that between the cubic austenitic structure and 7M modulated monoclinic structure). This is because the higher modulated phases are more ordered and hence less symmetric than a phase with lower modulations. When considering the martensitic phase transformations of the Co-76 (e.g. from cubic to 8M) and Co-73 (e.g. from cubic to 7M) alloys, the lattice entropy change of the Co-76 alloy is higher than that of the Co-73 alloy. However, in each of these alloys, due to co-existence of two modulated phases, the behavior of the lattice entropy is unclear.
In a similar fashion, the lattice entropy change of the first-order martensitic phase transformations of the In-1 and Co-76 alloys could be compared. Even though the lattice entropy change of the first-order phase transformation of the Co-76 alloy is greater than that of the In-1 alloy, the magnetic entropy change of the Co-76 alloy works against the lattice entropy change, similar to the reported results (of series of Ni-Mn-In-Co alloys, with similar composition to the Co-76) [30]. This is because the alloy transforms from a lower magnetization phase (presumably spin-glass-like) to a ferromagnetic phase, upon applying a magnetic field with sufficient strength, resulting in a decrease of the magnetic entropy.

On the other hand, the In-1 and Ga-S1 alloys transform from a highly ordered magnetic state to a less ordered magnetic state in the magnetostructural phase transformations, upon heating. The In-1 alloy transforms from an antiferromagnetic state to a ferromagnetic state while the Ga-S1 alloy transform from a ferromagnetic state to a paramagnetic state, respectively. In both cases, magnetic entropy and lattice entropy change upon transformation work together to enhance the observed magnetocaloric effect. Therefore, conceptually they are expected to better perform as magnetocaloric materials. However, to rank them according to their magnetocaloric potentials, their magnetocaloric effects need to be measured systematically, under the same experimental conditions.

6.1.3.1 Inter-martensitic phase transformations in the studied Ni-Mn-Ga alloys

Upon cooling, some Ni-Mn-Ga alloys undergo both martensitic (from a parent austenitic phase to an intermediate martensitic phase) and at a lower temperature an inter-martensitic phase transformations (from a modulated martensitic structure to a more stable non-modulated martensitic phase) [125, 134]. The studied Ni-Mn-Ga alloys in this work, the Ga-S1 and Ga-S2, exhibit both martensitic and inter-martensitic phase transformations.
Compared to the martensitic phase transformation temperature, inter-martensitic phase transformations of Ni-Mn-Ga alloys take place at much lower temperatures, resulting in a large temperature gap between two phase transformations [125]. For example, V. A. Chernenko et al. [125] have reported inter-martensitic phase transformations in Ni-Mn-Ga alloys, with a separation between the two transformations of more than 100 K, with a large hysteresis. The large separation between the two phase transformations eliminates the possibility of enhancing the magnetocaloric effect by utilizing the entropy associated with multi-structural transformations. On the other hand, the separation between the equilibrium temperatures of the two successive phase transformations in the Ga-S1 alloy is only ~50 K, and the hystereses in both phase transformations are less than 25 K. Therefore, these two-successive phase transformations could be considered for use to enhance the magnetocaloric effect by utilizing the entropy associated with multi-structural phase transformations in this alloy. This will be discussed in detail in the future studies section.

6.2 Magnetic field-induced martensitic phase transformations

Complete austenitic and complete martensitic phase transformations of the Co-73 alloy were observed at 230 K upon changing the magnetic field from 0 to 6.5 T and then back to 0 from 6.5 T, respectively. Similar austenitic and martensitic phase transformations of the same alloy were observed upon changing the temperature from 230 K to 300 K and then back to 230 K, respectively. Figure 72 compares the two austenitic phase transformations that started at the same initial conditions: 0 T at 230 K. The temperature-induced phase transformation is represented by closed circles, while the magnetic field-induced phase transformation is represented by open circles. Similar to what was reported by Shamberger et al. in Ni-Mn-Sn alloys, it could be concluded that the temperature and the applied magnetic field are both driving forces for the austenitic and martensitic phase transformations of this alloy [129].
In the temperature-induced austenitic transformation, at ~271.5 K (i.e. 41.5 K above the starting temperature), the austenitic phase fraction reaches 50%. The same austenitic phase fraction 50%, in the magnetic field-induced phase transformation, is achieved by increasing the magnetic field from 0 to 5.15 T. In the temperature-induced austenitic phase transformation, there is no significant change in the austenitic phase fraction up to 250 K, then within the next 40 K, the alloy completes its austenitic transformation. Similarly, there is almost negligible increase of the austenitic phase fraction in the magnetic field-induced phase transformation until the magnetic field reaches ~ 2.5 T, then increasing the magnetic field to 6.5 T result in complete austenitic transformation.
In the magnetic refrigeration process, these alloys undergo magnetic field-induced phase transformations, and a complete phase transformation delivers the maximum work available to the refrigeration process [129]. By choosing the correct starting temperature of the austenitic phase transformation ($A_S$), the magnetic field-induced phase transformation could be made more effective. In this alloy, 250 K can be taken as the starting point of the austenitic phase transformation. This temperature is very close to the austenite start temperature of this alloy under a 2 T magnetic field, and under this magnetic field the alloy finishes its austenitic phase transformation around 275 K. Therefore, a complete phase transformation could be obtained under a lower magnetic field (~2 T).

6.2.1 Dependence of the martensitic transformation temperature on the applied magnetic field

The forward martensitic phase transformation temperatures (i.e. austenite to martensite upon cooling) of the In-1 alloy decrease with an increasing magnetic field. Also, both austenitic and martensitic phase transformation temperatures of the Co-73 alloy decrease with an increasing magnetic field. Conversely, as our group reported, the martensitic phase transformation temperature of the Ga-SI alloy increases with an increasing magnetic field [2]. All these observations confirm the strong dependence of the martensitic phase transformation temperature on the applied magnetic field to these alloys, under which the phase transformation takes place. The dependence of the martensitic transformation temperature on the applied magnetic field can be described qualitatively using the Clausius-Clapeyron equation [135]:

$$\frac{dT_0}{dH} = -\frac{\Delta M}{\Delta S}$$
Where, $\Delta M = M^A - M^M$ is the difference between the magnetization of the two phases, austenite and martensite, respectively. Similarly, $\Delta S = S^A - S^M$ is the difference between the entropies of the austenitic ($S^A$) and martensitic ($S^M$) phases. The $dT_0/dH$ gives the rate of change of the transformations temperature with the applied magnetic field.

Both In-1 and Co-73 alloys are ferromagnetic in their austenitic phase at temperatures below the Curie temperature. In the reverse phase transformation, both alloys transform into austenitic phases with very higher magnetization compared to that of their martensitic phases (the In-1 alloy is confirmed as antiferromagnetic in the martensitic phase). Therefore, in both cases, the magnetization of the martensitic phase is negligible compared to the austenitic phase (i.e. $M^M \ll M^A$) and results in a positive $\Delta M$.

Next, the difference between the entropies of the martensitic ($S^M$) and the austenitic ($S^A$) phases needs to be considered. In both alloys, the crystalline structure of the austenitic phase is cubic $L2_1$, which is more symmetric than the modulated monoclinic martensitic crystalline structures. Therefore, a positive entropy change results from a phase transformation from the low symmetry of the modulated martensitic phase(s) to a highly symmetric austenitic phase. W. Ito et al. [119] have investigated the entropy change ($\Delta S = S^A - S^M$) of a series of Ni-Mn-In alloys and a series of Ni-Mn-In-Co alloys. The calculated entropy change of all these austenitic phase transformations of Ni-Mn-In and Ni-Mn-In-Co alloys (i.e. from martensite to austenite phase transformation upon heating) are positive [119]. Upon applying a magnetic field, Ni-Mn-In alloys transform from a martensitic to austenitic phase causing a positive entropy change [28].

In the case of the In-1 and Co-73 alloys, with a positive $\Delta M$ and $\Delta S$, the rate $dT_0/dH$ is going to be negative. This indicates a negative temperature change upon a positive magnetic field.
change to them. Therefore, as the applied magnetic field increases, the phase transformation temperature further decreases.

Upon heating the Ga-1 alloy, it transforms from a ferromagnetic martensitic phase to a paramagnetic austenitic phase [2]. This results in a negative $\Delta M$. On the other hand, the entropy change is positive in the austenitic phase transformation because it transforms from a modulated monoclinic martensitic phase to a higher symmetry cubic phase. This negative change in the magnetization and positive change in the entropy indicate an increasing of the phase transformation temperature upon increasing the applied magnetic field to the Ga-SI alloy.

6.3 Simulation of the austenitic and martensitic transformations of the Ni-Mn based Heusler alloys

As presented in chapter 5, variations of the phase fractions of the austenitic and martensitic phases with temperature during phase transformations of the In-1, Co-73, Co-76, and Ga-SI alloys were studied. In the cases of the In-1 and Co-73 alloys, the study was extended to investigate the behavior of the austenitic and martensitic phase fractions under different applied magnetic fields. In this section, the behavior of the phase fraction of the austenitic phase of the Co-73 with temperature will be simulated using kinematic equations, representing the austenitic and martensitic phase transformations.

Starting with the kinematic equations introduced by Li et al. (2013) [60], which were discussed in section 3.1.4, two new empirical equations will be developed to simulate the thermograms of the crystallographic phase transformations of the Co-73 alloy. Then, the way to use these equations to construct the martensitic thermograms for austenitic and martensitic phase transformations under certain experimental conditions will be discussed.
6.3.1 Kinematic equations representing the martensitic phase transformations of the Co-73 alloy (Ni_{52}Mn_{25}In_{16}Co_{7})

In order to investigate the martensitic phase transformations of the Co-73 alloy in detail and quantitatively under all 4 applied magnetic fields, the normalized austenitic phase fraction (with respect to the highest phase fraction value in each phase transformation) was plotted against the temperature. Then, the following kinematic equations (47 and 48) were used to fit the observed data points of the normalized austenitic phase fractions. The normalized austenitic phase fraction during the phase transformation to austenite is given by Equation 47. This equation was used to fit the data points in the austenitic phase transformations under 0, 2, 4, and 6 T magnetic fields. The fitting parameters, $T_0$ and $A_0$, were refined using Origin (a data analysis and graphics software) until there was a good agreement between experimental data points and the fit curve (R-squared values are between 0.98 and 1). The function $M^A f_A$ in Equation 47 explains the behavior of the austenitic phase fraction during a phase transformation from a twinned martensite to an austenite (adapted from [60]).

$$\frac{f_{M_0}}{1 + \exp \left\{ \frac{(T_0 - T)}{A_0} \right\}}$$

Where $f_{M_0}$ is the initial martensitic phase fraction in the lowest temperature measured in the twinned martensitic phase, and which is taken as unity in all these cases because the phase fractions were normalized with respect to the highest phase fraction value. $T$ is the absolute temperature and $T_0$ is the phase transformation temperature, and is defined as the temperature at which the austenitic phase fraction is 50%. For the austenitic phase transformations, $A_0 = (A_F - A_S)/C_0$, where $A_S$ and $A_F$ are austenite start and finish temperatures, respectively. The normalized austenitic phase fraction during the phase transformation to martensite is given by
Equation 48. This equation was used to fit the data points in the martensitic phase transformations under 2, 4, and 6 T magnetic fields. The fitting parameters, $T_0$ and $M_0$, were determined by following the same procedure as in the austenitic phase transformations. Where $M_0 = (M_S - M_F)/C_m e$ where $M_S$ and $M_F$ are martensite start and finish temperatures, respectively. In both Equations 47 and 48, $e$ is the natural constant (2.71828) and $Ca$ (or $Cm$) is an empirical constant to be determined.

$$f_A^{\alpha-M} = \frac{1}{1 + \exp\left(\frac{T_0 - T}{M_0}\right)}$$

Figure 73 shows the variation of the normalized austenitic phase fraction with temperature while heating (from martensitic to the austenitic) and cooling (from austenitic to martensitic) under those 4 magnetic fields (0, 2, 4, and 6 T). The curve-fitting based on Equations 47 and 48 is in good agreement with the experimental data (R-squared values are between 0.98 and 1). The refined values of the fitting parameters, $A_0$, $M_0$, and $T_0$, are summarized in Table 30. The characteristic temperatures of the martensitic ($M_S$ and $M_F$) and austenitic ($A_S$ and $A_F$) phase transformations were determined by the intersections, which were obtained by extrapolating the linear parts of the thermograms. The determination of the four characteristic temperatures in the case of a 2 T magnetic field is demonstrated in Figure 73. All the characteristic temperatures of both austenitic and martensitic phase transformations under all four magnetic fields are given in Error! Not a valid bookmark self-reference.

The refined parameters, $A_0$ and $M_0$, gradually decrease with an increased magnetic field (column 2 of The characteristic temperatures of the martensitic ($M_S$ and $M_F$) and austenitic ($A_S$...
and $A_F$) phase transformations were determined by the intersections, which were obtained by extrapolating the linear parts of the thermograms. The determination of the four characteristic temperatures in the case of a 2 T magnetic field is demonstrated in Figure 73. All the characteristic temperatures of both austenitic and martensitic phase transformations under all four magnetic fields are given in Error! Not a valid bookmark self-reference.

Table 30). These parameters depend on the difference between the two characteristic temperatures of each martensitic phase transformation. In the austenitic phase transformation, $A_0$ is proportional to the difference between the $A_F$ and $A_S$ temperatures; in the martensitic phase transformation, $M_0$ is proportional to the difference between the $M_S$ and $M_F$ temperatures.

The gradual decrease of these parameters with the increasing magnetic field indicates a decrease in the difference between the characteristic transformation temperatures of the respective phase transformations. The decrease of the difference between the phase transformation temperatures means the completion of the phase transformation occurred over a shorter temperature interval. That is, the rate of the phase transformation increases with an increased magnetic field. The parameters, $A_0$ and $M_0$, give a measure of the phase transformation rates. The rates of the austenitic and martensitic phase transformations are inversely proportional to $A_0$ and $M_0$, respectively.

The characteristic temperatures of the martensitic ($M_S$ and $M_F$) and austenitic ($A_S$ and $A_F$) phase transformations were determined by the intersections, which were obtained by extrapolating the linear parts of the thermograms. The determination of the four characteristic temperatures in the case of a 2 T magnetic field is demonstrated in Figure 73. All the characteristic temperatures of both austenitic and martensitic phase transformations under all four magnetic fields are given in Error! Not a valid bookmark self-reference.
Table 30: Least squares curve fitting parameters and characteristic temperatures of martensitic phase transformations of the Co-73 alloy

<table>
<thead>
<tr>
<th>Type of the transformation</th>
<th>( A_0 ) or ( M_0 ) (K)</th>
<th>Characteristic temperatures of the phase transformation (K)</th>
<th>( C_a ) or ( C_m ) Hysteresis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_0 ) A( _S ) A( _F ) M( _S ) M( _F )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 T (h)</td>
<td>6.80±0.33 268.26±0.39 254.5±0.5 281.0±0.5 - -</td>
<td>1.43±0.05</td>
<td>-</td>
</tr>
<tr>
<td>2 T (h)</td>
<td>7.16±0.17 261.32±0.20 248.5±0.5 276.5±0.5 - -</td>
<td>1.41±0.03</td>
<td>-</td>
</tr>
<tr>
<td>2 T (c)</td>
<td>6.96±0.21 254.28±0.23 - - 268.5±0.5 240.5±0.5</td>
<td>1.47±0.04</td>
<td>7.04</td>
</tr>
<tr>
<td>4 T (h)</td>
<td>3.93±0.18 247.02±0.20 239.0±0.5 255.0±0.5 - -</td>
<td>1.49±0.06</td>
<td>7.91</td>
</tr>
<tr>
<td>4 T (c)</td>
<td>4.14±0.26 239.11±0.26 - - 247.5±0.5 231.0±0.5</td>
<td>1.46±0.08</td>
<td></td>
</tr>
<tr>
<td>6 T (h)</td>
<td>3.16±0.37 224.40±0.42 218.0±0.5 231.0±0.5 - -</td>
<td>1.51±0.13</td>
<td>19.04</td>
</tr>
<tr>
<td>6 T (c)</td>
<td>3.45±0.30 205.36±0.22 - - 212.0±0.5 198.5±0.5</td>
<td>1.43±0.10</td>
<td></td>
</tr>
</tbody>
</table>

Figure 73: Variation of the normalized austenitic phase fraction of the Co-73 alloy as a function of temperature while heating (open symbols) and cooling (solid symbols) under 4 different magnetic fields (0, 2, 4, and 6 T). Solid (heating) and dash (cooling) lines are the fit lines for the martensitic thermograms. Fit lines are based on Equations 47 and 48.
The empirical constants $C_a$ and $C_m$ in the martensitic phase transformations were calculated using Equations 49 and 50, respectively.

$$C_m = (M_S - M_F)/(eM_0)$$  \hspace{1cm} 49
$$C_a = (A_S - A_F)/(eA_0)$$  \hspace{1cm} 50

The empirical constant $C$ (i.e. $C_a$ or $C_m$) for each case was determined by substituting the appropriate characteristic phase transformation temperatures and the appropriate fitting parameter ($A_0$ or $M_0$). The value of $C$, determined for each phase transformation, is also summarized in The characteristic temperatures of the martensitic ($M_S$ and $M_F$) and austenitic ($A_S$ and $A_F$) phase transformations were determined by the intersections, which were obtained by extrapolating the linear parts of the thermograms. The determination of the four characteristic temperatures in the case of a 2 T magnetic field is demonstrated in Figure 73. All the characteristic temperatures of both austenitic and martensitic phase transformations under all four magnetic fields are given in Error! Not a valid bookmark self-reference.

Table 30. The mean value of the empirical constant $C$ is 1.48±0.03. Therefore, the kinematic equations that represent the normalized austenitic phase fraction for the martensitic and austenitic phase transformations are given by Equations 51 and 52, respectively.

$$^{A\rightarrow M}f_A = \frac{1}{1 + \exp\left\{ \frac{1.48(T_0 - T)e}{M_S - M_F} \right\}}$$  \hspace{1cm} 51

$$^{M\rightarrow A}f_A = \frac{1}{1 + \exp\left\{ \frac{1.48(T_0 - T)e}{A_S - A_F} \right\}}$$  \hspace{1cm} 52
The above expressions can be used to predict the behavior of both martensitic and austenitic phase transformations of the Co-73 alloy. If the characteristic temperatures of the martensitic phase transformation are known (they can be determined by differential scanning calorimeter measurements [60]), the variation of the austenitic phase fraction with temperature could be fully described using those equations even under different magnetic fields.

6.3.2 Magnetic phase transformations of Co-73 alloy ($\text{Ni}_{52}\text{Mn}_{25}\text{In}_{16}\text{Co}_{7}$)

In the previous section, the crystalline phase transformation of the Co-73 alloy was discussed in detail. In this section, the magnetic phase transformation of this alloy will be discussed with the aid of the thermomagnetic measurements. From thermomagnetic measurements, it was concluded that, upon cooling, the alloy transforms from ferromagnetic phase to a phase with much lower magnetization.

Magnetization versus temperature data can be transformed to ferromagnetic phase fraction versus temperature data by considering that the magnetization is directly proportional to the ferromagnetic phase fraction. The conversion procedure of the magnetization data to ferromagnetic phase fraction is given in P. J. Shamberger’s work [129]. Variation of the ferromagnetic phase fraction of the Co-73 alloy with temperature, under 4 magnetic fields (0.005, 1, 2, and 3 T), is given in Figure 74.
Figure 74: Variation of the normalized ferromagnetic phase fraction with temperature of the Co-73 alloy. The characteristic temperatures of the magnetic phase transformations were determined by extrapolating the linear parts of the normalized thermomagnetic curves. Magnetic phase transformation temperatures decrease with an increasing field.

For the study of the characteristic of the magnetic phase transformations of the Co-73 alloy, magnetic phase transformation temperatures were defined as the intersections of the lines obtained by extrapolations of the linear parts of the magnetic phase fraction versus temperature graph. The characteristic temperatures of the magnetic phase transformation - ferromagnetic start, $FM_s$, ferromagnetic finish, $FM_F$, lower magnetic state start, $LM_s$, and lower magnetic state finish, $LM_F$, under all three magnetic fields (1, 2, and 3 T) - are shown in Figure 74. Additionally, two characteristic temperatures, $T_{1/2C}$ and $T_{1/2H}$, were defined. Similar to the characteristic temperature $T_0$ in the crystalline phase transformation, $T_{1/2C}$ and $T_{1/2H}$ are the temperatures at
which the ferromagnetic phase fraction is 50%, while cooling and heating the alloy, respectively. All the characteristic transformation temperatures are listed in Table 31.

From the magnetic phase fraction analysis of the Co-73 alloy, it was concluded that the magnetic phase transformation temperatures are highly dependent on the applied magnetic field. All four characteristic temperatures of the magnetic phase transformation, \( FM_s, FM_F, LM_s, \) and \( LM_F, \) decrease with an increasing magnetic field, except for the case of 0.005 T. As shown in Figure 75, the four characteristic temperatures under 0.005 T field deviate from the rest. A similar phenomenon was observed in the case of the Co-76 alloy.

<table>
<thead>
<tr>
<th>Magnetic field (T)</th>
<th>Characteristic temperatures of the phase transformation (K)</th>
<th>Hysteresis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>( T_{1/2}^C ) 236.0±0.5, ( T_{1/2}^H ) 275.0±0.5, ( FM_s ) 265.0±0.5, ( FM_F ) 287.0±0.5, ( LM_s ) 248.5±0.5, ( LM_F ) 224.0±0.5</td>
<td>39.0±0.7</td>
</tr>
<tr>
<td>1</td>
<td>( T_{1/2}^C ) 239.5±0.5, ( T_{1/2}^H ) 280.0±0.5, ( FM_s ) 275.0±0.5, ( FM_F ) 285.5±0.5, ( LM_s ) 246.5±0.5, ( LM_F ) 232.5±0.5</td>
<td>40.5±0.7</td>
</tr>
<tr>
<td>2</td>
<td>( T_{1/2}^C ) 225.0±0.5, ( T_{1/2}^H ) 271.0±0.5, ( FM_s ) 265.5±0.5, ( FM_F ) 276.5±0.5, ( LM_s ) 233.5±0.5, ( LM_F ) 217.0±0.5</td>
<td>46.0±0.7</td>
</tr>
<tr>
<td>3</td>
<td>( T_{1/2}^C ) 206.5±0.5, ( T_{1/2}^H ) 261.0±0.5, ( FM_s ) 255.5±0.5, ( FM_F ) 267.0±0.5, ( LM_s ) 217.5±0.5, ( LM_F ) 197.0±0.5</td>
<td>54.5±0.7</td>
</tr>
</tbody>
</table>

6.3.3 Magnetic phase transformation temperatures of the Co-73 alloy (\( Ni_{52}Mn_{25}In_{16}Co_7 \))

A very small magnetic field (0.005 T in this study) is not sufficient to saturate the alloy magnetically. Therefore, the alloy does not undergo a complete magnetic phase transformation [129]. On the other hand, under 1, 2, and 3 T magnetic fields the alloy undergoes a complete phase transformation. Therefore, the trend of the characteristic phase transformation temperatures is consistent for all magnetic fields including 1 T and above. The smallest magnetic field, which is sufficient to obtain a complete magnetic phase transformation in this alloy could be determined by investigating the magnetic phase transformations under small fields.

Similar to the thermal hysteresis in the crystalline phase transformation, there is a thermal hysteresis associated with the magnetic phase transformation, and it is strongly dependent on the
applied magnetic field. As the magnetic field increases the thermal hysteresis associated with the magnetic phase transformation increases. As shown in the inset of Figure 75 the relationship between the hysteresis and applied magnetic field is not linear. The relationship between the thermal hysteresis associated with the magnetic phase transformation and applied magnetic field was obtained by non-linear curve fitting of the calculated hysteresis data points. Equation 53 gives the relationship between the hysteresis and applied magnetic field and it could be approximated that the thermal hysteresis is proportional to the square of the applied magnetic field.

\[
\text{Thermal hysteresis} = 1.499 \left( \frac{K}{T^2} \right) \times B^2(T^2) - 0.503 \left( \frac{K}{T} \right) \times B(T) + 38.99\ (K)
\]

Figure 75: Behavior of the four characteristic phase transformation temperatures under 4 magnetic fields. The trend of the characteristic temperatures under 0.005 T field deviate from the rest (data points inside the oval). The inset represents the variation of the thermal hysteresis with an increased magnetic field.
6.4 Magnetostructural phase transformation of the Co-73 alloy (Ni_{52}Mn_{25}In_{16}Co_{7})

In the previous sections of this chapter, crystalline and magnetic phase transformations of the Co-73 alloy were discussed. In this section, the characteristic temperatures and hystereses of both phase transformations will be compared to investigate the possibility of any coupled magnetostructural phase transformations. For this purpose, variation of the austenitic phase fraction with temperature (in crystalline phase transformations) was compared with the variation of the ferromagnetic phase fraction with temperature (in magnetic phase transformations) under the same magnetic fields.

Magnetic phase transformation data were collected under 0.005, 1, 2, and 3 T magnetic fields. The crystalline phase transformation data were collected under 0, 2, 4, and 6 T magnetic fields. Therefore, the crystalline phase transformation data under 0 and 2 T magnetic fields were compared with the magnetic phase transformation data under 0.005 and 2 T magnetic fields, respectively. However, to compare the crystalline and magnetic phase transformations under higher magnetic fields, crystalline phase transformation information under 1 and 3 T magnetic fields were generated using the kinematic equations constructed in section 6.3.1 (Equations 51 and 52).

Equation 51 was used to simulate the variation of the austenitic phase fraction during the martensitic phase transformations under 1 and 3 T magnetic fields. The variation of the austenitic phase fraction in the austenitic transformation under 1 and 3 T magnetic fields were simulated using Equation 52. To use these equations, the parameters $M_0$ and $T_0^M$ for martensitic phase transformations and the parameters $A_0$ and $T_0^A$ for austenitic phase transformations had to be defined. Values of these parameters under 0, 2, 4, and 6 T magnetic fields were found by the analysis of the experimental data. The trend lines and their equations of these parameters under 0,
2, 4, and 6 T magnetic fields are given in Figure 76. Then the respective parameters, $M_0$, $A_0$, $T_0^M$, and $T_0^A$ for martensitic and austenitic phase transformations under 1 and 3 T magnetic fields were calculated by interpolation. Experimental (closed circles) and calculated (open circles) parameters $M_0$, $A_0$, $T_0^M$, and $T_0^A$, are shown in Figure 76.

![Figure 76](image.png)

Figure 76: Experimental (closed symbols) and calculated (open symbols) parameters, (a) $M_0$ and $A_0$, (b) $T_0^M$ and $T_0^A$ of the martensitic and austenitic crystalline phase transformations of the Co-73 alloy.

With these parameters, two sets of data of the variations of the austenitic phase fraction with temperature for 1 and 3 T magnetic fields were constructed. Then, the variation of the austenitic phase fraction and the variation of the ferromagnetic phase fractions with temperature under the same magnetic fields were compared as shown in Figure 77. This figure shows the variation of austenitic and ferromagnetic phase fractions with temperature under 4 magnetic fields. In Figure 77-a and -c (i.e. under ~0 and 2 T magnetic fields, respectively), both austenitic and ferromagnetic phase fraction data were determined experimentally. The phase fractions of the
austenitic phase under 1 and 3 T were determined by kinematic equations, 51 and 52 (Figure 77-b and -d).

![Graphs showing thermal hysteresis and phase transformations](image)

**Figure 77:** Comparison of the thermal hystereses and characteristic phase transformation temperatures of the crystalline and magnetic phase transformations of the Co-73 alloy. Variation of austenitic phase fraction and ferromagnetic phase fraction with temperature under (a) no applied magnetic field, (b) 1 T field, (c) 2 T, and (d) 3 T applied magnetic fields. In (b) and (c), normalized austenitic phase fraction data were constructed using kinematic Equations.

The thermograms of the crystalline phase transformations and magnetic phase transformations have different characteristic temperatures. Under all four magnetic fields, the thermal hysteresis loops of the crystalline phase transformations are smaller and are contained within the thermal hysteresis loops of the magnetic phase transformations. Also, the thermograms of the reverse phase transformations (crystalline and magnetic) upon heating are close to each
other when compared with those of the forward phase transformations which take place upon cooling. Furthermore, the crystalline and magnetic phase transformation temperatures were compared by calculating the differences $T_0^M - T_{1/2}C$ (for transformations while cooling) and $T_0^A - T_{1/2}H$ (for transformations while heating). The calculated values (Table 32) confirm that the characteristic temperature of austenitic phase transformations are closer to the characteristic temperatures of the $LM$ to $FM$ transformation than the characteristic temperatures of the martensitic phase transformation to the $FM$ to $LM$ transformations.

Table 32: Phase transformation temperatures and hysteresis associate with crystalline and magnetic phase transformations

<table>
<thead>
<tr>
<th>Field (T)</th>
<th>Reverse phase transformation (Heating)</th>
<th>Forward phase transformation (Cooling)</th>
<th>Thermal hysteresis (K)</th>
<th>Temperature difference between phase transformations (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_0^A$ (K)</td>
<td>$T_{1/2}H$</td>
<td>$T_0^M$ (K)</td>
<td>$T_{1/2}C$ (K)</td>
</tr>
<tr>
<td>0</td>
<td>268.5±0.5</td>
<td>275.0±0.5</td>
<td>-</td>
<td>234.5±0.5</td>
</tr>
<tr>
<td>1</td>
<td>266.5±0.5</td>
<td>280.0±0.5</td>
<td>255.5±0.5</td>
<td>239.0±0.5</td>
</tr>
<tr>
<td>2</td>
<td>262.0±0.5</td>
<td>271.0±0.5</td>
<td>255.0±0.5</td>
<td>225.0±0.5</td>
</tr>
<tr>
<td>3</td>
<td>256.5±0.5</td>
<td>260.5±0.5</td>
<td>249.0±0.5</td>
<td>206.0±0.5</td>
</tr>
<tr>
<td>4</td>
<td>247.0±0.5</td>
<td>-</td>
<td>239.0±0.5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>224.5±0.5</td>
<td>-</td>
<td>205.0±0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Under the studied magnetic fields (0.005, 1, 2, and 3 T), the difference between $T_0^A$ and $T_{1/2}H$ is at its maximum under a 1 T field, and then gradually decreases with an increased magnetic field. Under 3 T, the difference between $T_0^A$ and $T_{1/2}H$ is only 4.0 K, which is significantly smaller compared to the difference under no applied field (~6.5 K). Therefore, a merged magneto-structural transformation can be anticipated (upon heating) under a magnetic field greater than 3 T. To determine the magnetic field under which a merged magneto-structural reverse phase transformation is possible, equilibrium phase transformation temperatures, $T_0^A$ and $T_{1/2}H$, were plotted against the applied magnetic field.
Figure 78 represents the variation of the equilibrium phase transformation temperatures while heating, in magnetic (open circles) and crystalline (open squares), under an applied magnetic field to the alloy. Magnetic phase transformation temperatures under higher magnetic fields (4, 5, and 6 T) were determined by an extrapolation. Both magnetic and crystalline reverse phase transformation temperatures decrease with the applied magnetic field. However, the rates of decrease of the phase transformation temperature with the increasing magnetic field is not the same. Therefore, two curves intersect at ~3.9 T, where a merged magneto-structural phase transformation may be anticipated.

For magnetic field is greater than 1 T, the difference between $T_0^M$ and $T_{1/2}^C$ (i.e. the difference between the forward transformation temperatures) monotonically increases with the applied magnetic field. Therefore, the martensitic and the $FM$ to $LM$ magnetic phase transformations do not merge under any magnetic field because of the large difference between their thermal hystereses.
Figure 78: Variation of the phase transformation temperature upon heating, in both crystalline (squares) and magnetic (circles) phase transformations, with the applied magnetic field.

6.5 Thermal hystereses associated with magnetic and crystalline phase transformation of the Co-73 alloy (Ni$_{52}$Mn$_{25}$In$_{16}$Co$_{7}$)

The thermal hystereses associated with crystallographic and magnetic phase transformations under each magnetic field were calculated by taking the difference between $T_{0M}$ and $T_{0A}$ and between $T_{1/2H}$ and $T_{1/2C}$, respectively. A summary of these calculations is given in Table 32. Then, the thermal hystereses versus applied magnetic field were plotted and the trend line of the data points was determined by non-linear curve fitting (Figure 79).

Figure 79: Behavior of the thermal hysteresis associated with first-order crystalline phase transformation (open squares) and a second-order magnetic phase transformation (close circles) with applied magnetic field to the Co-73 alloy.

Thermal hystereses of the magnetic phase transformations are available only in the range of applied fields from 0.005 to 3 T. To compare the thermal hysteresis of a magnetic phase transformation, with first-order crystalline phase transformations, the thermal hysteresis under 4, 5, and 6 T magnetic fields were estimated by extrapolation of the trend line of thermal hysteresis
versus applied magnetic field. The thermal hysteresis of a magnetic phase transformation is increase monotonically with an increasing magnetic field. On the other hand, the thermal hysteresis of the first-order transformation reaches a minimum at 2.8±0.05 T fields.

6.5.1 Thermal hystereses and magnetocaloric effect of the Ni-Mn based Heusler alloys

Some Ni-Mn based Heusler alloys, which exhibit giant inverse magnetocaloric effects are promising as refrigerants for future magnetic cooling machines. The structural phase transformations proceed by nucleation and growth which lead to a hysteresis [136]. The hysteresis losses associated with a first-order phase transformation of these alloys reduce the useful magnetocaloric work by allowing only a limited fraction of the alloy to transform cyclically between the two phases; austenitic and martensitic, [30, 137, 138]. Therefore, it is important to analyze the hysteresis losses accurately when considering these materials as magnetic refrigerant [129, 139].

The Co-73 alloy exhibits a thermal hysteresis associated with both first-order and magnetic phase transformations. Compared to the thermal hysteresis associated with the first-order transformations, that of the magnetic phase transformations is significantly higher (about four times higher, under all studied magnetic fields). The thermal hysteresis of the magnetic phase transformations increases with an increasing magnetic field, whereas, that of a first-order transformation has a minimum around a 2.8 T field. An achievable magnetocaloric effect in these alloys increases when increasing the working magnetic field (i.e. the difference between the high and low magnetic fields). On the other hand, the hysteresis losses associated with the two transformations increase with an increasing magnetic field. In the case of the Co-73 alloy, to minimize the hysteresis losses, the magnetic field under which the thermal hysteresis becomes a minimum could be considered as the upper limit of the working magnetic field. However, more
systematic magnetocaloric measurements (as a function of the applied magnetic field) are needed to fully understand the true contribution of each component (entropy change and hysteresis losses) to the magnetocaloric effect.

The coupling temperature of the crystalline and magnetic phase transformations of the Co-73 alloy depends on the applied magnetic field under which the phase transformation takes place. A merged crystalline and magnetic phase transformation of this alloy could be anticipated upon heating the alloy under a ~3.9 T field. The entropy change associated with a first-order martensitic transformation reaches a maximum when the crystalline and magnetic phase transformations are coupled, if the magnetic disorder increases upon increasing the magnetic field. Nevertheless, the Co-73 alloy transforms from a lower magnetization (presumably a spin-glass-like) martensitic phase to a ferromagnetic austenitic phase. Therefore, the magnetic and structural entropy changes work against each other and hence the coupling of the two transformations reduces the magnitude of the magnetocaloric effect for this alloy.

6.6 Influence of the interatomic distances, site occupancies, and modulation of the martensitic phase on the observed magnetism of the studied alloys

The observed magnetic nature of the studied alloys (In-1 and Co-76) in both austenitic and martensitic phases will be examined and discussed in terms of the site occupancies and interatomic distances of the atoms carrying magnetic moments (i.e. Mn and Ni in the case of the In-1 alloy and Mn, Ni, and Co in the case of the Co-76 alloy). This is a semi-quantitative analysis and only the nature of the direct exchange interactions between the same type of atoms will be considered (i.e. Mn-Mn, Ni-Ni, and Co-Co). Also, the strength of interactions is compared qualitatively to understand the observed magnetism.
Both In-I and Co-76 alloys have excess Mn compared to a stoichiometric Ni₂MnX Heusler alloy and hence their magnetic properties are highly dependent on the Mn content due to the occupation of Mn atoms in different crystallographic sites [32, 77]. The relative neighborhood of all these atoms is conserved in the martensitic phase transformations upon cooling because martensitic phase transformations are diffusionless. Therefore, the site occupancy of a crystallographic site in the martensitic phase could be determined by considering the site occupancies of the austenitic phase and the relationship between the austenitic and martensitic crystalline structures. Over the martensitic transformations, the interatomic distance between the constituent atoms changes significantly due to the modulations of the martensitic phase [77, 85]. The change of the interatomic distance caused by the modulation of the martensitic phase transformation could significantly alter the magnetic nature entirely.

6.6.1 Observed magnetism of the In-I and Co-76 alloys (Ni₄₁Mn₃₉In₁₂Co₈)

It is well reported that below Tc the austenitic phase of Ni-Mn-In, Ni-Mn-Sn [28, 140], and in some Ni-Mn-Ga (the martensitic phase transformation temperature is lower than their Curie temperature) [141, 142] alloys is ferromagnetic. On the other hand, depending on the composition, in some Ni-Mn-Ga alloys the martensitic phase transformation temperature is above their Curie temperature and they are paramagnetic in their austenitic phase [78, 134]. Most of these alloys have a cubic L2₁ structure in the austenitic phase which belongs to the Fm̅3m space group. The lattice parameter of the cubic L2₁ structure is ~0.6 nm [80]. Comparing the In-I alloy with the Co-76 alloy under the same experimental conditions, the lattice parameter of the Co-76 alloy is slightly lower than that of the In-I alloy. The smaller lattice parameter of the Co-76 alloy could be explained by Co having a smaller atomic radius compared to In atoms. Therefore, substitution of Co in Ni-Mn-In alloys reduces their lattice constants in both austenitic and martensitic phases.
From thermomagnetic measurements of the Co-76 alloy and AC susceptibility measurements of the In-1 alloy, it was found that below the Curie temperature they order ferromagnetically in their austenitic phase. As presented in the results section, the In-1 alloy exhibits an antiferromagnetic ordering in its martensitic phase. The Co-76 alloy exhibits a very low magnetization in its martensitic phase and transforms to a spin-glass-like magnetic phase around ~ 19 K. Site occupancies of these two alloys, In-1 and Co-76, in the austenitic phase were determined by Rietveld refinements of diffraction data and presented in the results section. In the following sections, the observed magnetism in each alloy will be explained qualitatively in terms of the different possible exchange interactions between the same type of magnetic atoms (i.e. Mn-Mn, Ni-Ni, and Co-Co) by considering their site occupancies and interatomic distances.

6.6.2 Exchange interactions of magnetic materials [143, 144]

In this section, the basic theory of the exchange couple interactions of transition metals is discussed. Consider a pair of electrons 1 and 2, which are shared between two adjacent atoms \(a\) and \(b\) as shown in Figure 80. The space between the atoms which is shared by those electrons (\(a\) and \(b\)) could be considered an electron cloud. The wave function which describes the cloud of electrons is \(\psi\), and \(|\psi|^2 = \psi^*\psi\) gives its probability density. This cloud of elections is immersed in a potential \(V\) generated by the net charge of the two atoms \(a\) and \(b\) (each having a charge of \(+e\) by contributing an electron to the cloud). The coupling between two atoms by exchanging those two electrons is stable in time. Therefore, the wave function which describes the electrons 1 and 2, \(\psi\), must satisfy the time-independent Schrödinger equation in the presence of potential \(V\). The time-independent Schrödinger equation of the wave function which describes those two electrons is given by Equation 54.
\[ E\psi = \left[ -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) \right] \psi \]

In this equation, \( E \) is the total energy of the system and \( \nabla_1 \) and \( \nabla_2 \) are the Nabla operators of electrons 1 and 2, respectively. \( V(r_1) \) and \( V(r_2) \) are the Coulomb potentials of electrons 1 and 2, respectively. The potential \( V \) depends on the electron orbital configuration as well as \( r_1 \) (the distance to electron 1 from the centers of the two atoms) and \( r_2 \) (the distance to electron 2 from the centers of the two atoms). The center of the two atoms is the center of the line joining the nuclei of the atoms. The solution to the time-independent Schrödinger equation (54) depends on the nature of the potential, \( V \).

Figure 80: Schematic diagram of the exchange interaction (spin parallel) between two atoms \( a \) and \( b \) by sharing their electrons 1 and 2 in the 3d orbitals. Arrows indicate the spin of the electrons and in this case, they are aligned parallel to each other (adapted from [145]).

The total energy of the system \( E \) is the sum of three integrals, which are the Coulomb, overlap, and exchange integrals. For the present discussion (i.e. the exchange interactions of magnetic materials), only the exchange integral will be considered. The exchange integral depends on the spin state of the system (two electrons) and is given by Equation 55.
\[ J_e = \int \phi_a^*(1)\phi_b^*(2)V_{12}\phi_a(2)\phi_b(1)dr_1dr_2 \]

Where \( \phi \) represents the wave function of one atom without consideration of the spin contribution to the wave function and \( V_{12} \) is the Coulomb potential. For simplicity of discussion and for understanding of the Coulomb potential energy, a simplest case is considered here, which represents the Coulomb potential of the hydrogen molecule, \( H_2 \) (Equation 56).

\[ V_{12}(r_1, r_2) = \frac{e^2}{4\pi\varepsilon_0} \left[ \frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{2b}} \right] \]

In this equation, \( 1/r_{ab} \) and \( 1/r_{12} \) are proportional to the electrostatic repulsion between two positively charged atoms and between the two exchanged electrons, respectively. \( 1/r_{1a} \) and \( 1/r_{2b} \) represent the electrostatic attraction between electrons and the positively charged atoms. \( V_{12}(r_1, r_2) \) is a function of \( r_1 \) and \( r_2 \), and therefore, the exchange integral depends on the separation between atoms \( a \) and \( b \). The exchange integral has units of energy and could be positive or negative depending on the exchange energy contribution to the total energy of the system which will tend to assume a minimum value. If the energy contribution of the exchange integral to the total energy of the system favors the parallel alignment of the two spins, then \( J_e > 0 \) and results in a ferromagnetic coupling. On the other hand, if the exchange integral contribution to the total energy favors the antiparallel alignment of the two spins, then \( J_e < 0 \) and it causes an antiferromagnetic coupling. There are three types of exchange interactions which determine the nature of the magnetic interactions of a magnetic material. Direct exchange occurs when there is a magnetic interaction between the nearest neighbor atoms (e.g. antiferromagnetism in \( MnCl_2 \) via direct exchange interactions between \( Mn \) ions [146]). When the magnetic coupling occurs via intermediate atoms, it is named a super exchange interaction. The exchange interaction between


$Mn^{2+}$ ions via $O^{2-}$ ions is a well-known example of super exchange interactions [147]). The third kind of exchange interaction occurs in delocalized electrons in ferromagnetic metals.

The $Mn-O$ bond is largely ionic (~ 73%) and is ~27% covalent. In the ionic bond, oxygen accepts two electrons from $Mn$ and the resulting $Mn^{2+}$ and $O^{2-}$ create linear ion chains as shown in Figure 81-a. A fully occupied $p$-orbit of $O^{2-}$ is aligned in the direction of the $Mn-O-Mn$ axis. $Mn^{2+}$ contains five $3d$ electrons (one electron per orbit), which align parallel to each other. If a covalent bond between $Mn^{2+}$ and $O^{2-}$ is assumed to be energetically favorable, the only possible way of having one is by donating one electron from a fully occupied $p$-orbit of oxygen to a $d$-orbit of $Mn^{2+}$. As shown in Figure 81-b, if the spin-up electron in the $p$-orbit of $O^{2-}$ is donated to a $Mn^{2+}$ with all down spin $d$ electrons in the first covalent bond, a second covalent bond between the down spin electron of the $O^{2-}$ is possible only with a $Mn^{2+}$ with all spin-up $d$ electrons. In this way, $O^{2-}$ mediated antiferromagnetic super exchange interactions between $Mn^{2+}$ in MnO crystals.

![Figure 81](image)

Figure 81: (a) Schematic of a $Mn-O-Mn$ chain in the partial ionic bond direction. Fully occupied $p$-orbits of the $O^{2-}$ orient along this direction. (b) Schematic of the super exchange mechanism of $Mn-O-Mn$ mediated by $O^{2-}$ (adapted from [148]).

The dependence of the exchange integral $J_e$ on the ratio $R/r$ (the ratio of the atomic separation, 2 $R$, to the diameter of the incomplete d-electron shell, 2 $r$) is demonstrated in Figure 82 for some of the transition metals in their elemental form [143, 144]. This is called the “Bethe-Slater curve” (after Hans Albrecht Bethe and John Clarke Slater). The exchange integral $J_e$ depends strongly on the ratio $R/r$ and becomes positive for $R/r > 1.5$. The maximum of the curve
(i.e. the maximum of $J_e$) is at $R/r \approx 1.76$, where the ferromagnetic coupling is strongest. The coupling strength decreases with a further increase of $R/r$ ratio and at larger $R/r$ ratios it decreases to zero such as rare earth elements.

The exchange integral gives the coupling strength of two shared electrons with spin $\pm 1/2$ that belongs to their corresponding atoms. In most cases, there is more than one pair of shared electrons and in such situations, the total spin vectors of the corresponding atoms are considered to determine the so-called exchange energy (given by Equation 57).

$$E_{ex} = -2J_e S_1 \cdot S_2$$

Here $J_e$ is the exchange integral and $S_1, S_2$ are the spin vectors of the two atoms. Exchange energy always tends to get the minimum value possible by either parallel or antiparallel alignment of $S_1$ and $S_2$, depending on the sign of $J_e$. When $J_e$ is positive, $S_1$ and $S_2$ are parallel and the result is ferromagnetic coupling. On the other hand, when $J_e$ is negative, $S_1$ and $S_2$ are antiparallel and this results in an antiferromagnetic coupling. In situations where the exchange integral is very small, thermal fluctuations overcome the magnetic ordering even at lower temperatures and results in paramagnetism [143]. The Bethe-Slater curve explains the magnetic nature of transition metals in their elemental form. Table 33 summarizes the magnetic ordering of three transition metals (which are the constituent elements with magnetic properties of the studied alloys) in their elemental form by considering the nearest neighbor magnetic interactions with the aid of the Bethe-Slater curve.
Table 33: Data related to the Bethe-Slater curve for the elements with a magnetic moment in the study [144]

<table>
<thead>
<tr>
<th>Element</th>
<th>Incomplete inner shell/ electron configuration</th>
<th>Interatomic distance, $2R$ (nm)</th>
<th>d-shell diameter $2r$ (nm)</th>
<th>$R/r$</th>
<th>Magnetic ordering</th>
<th>$T_C$ or $T_N$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{25}$Mn</td>
<td>$3d^5 [Ar], 3d^5, 4s^2$</td>
<td>0.251</td>
<td>0.171</td>
<td>1.47</td>
<td>AFM (below 100 K)</td>
<td>100</td>
</tr>
<tr>
<td>$^{27}$Co</td>
<td>$3d^7 [Ar], 3d^7, 4s^2$</td>
<td>0.251</td>
<td>0.138</td>
<td>1.82</td>
<td>FM</td>
<td>1403</td>
</tr>
<tr>
<td>$^{28}$Ni</td>
<td>$3d^8 [Ar], 3d^8, 4s^2$</td>
<td>0.250</td>
<td>0.127</td>
<td>1.97</td>
<td>FM</td>
<td>631</td>
</tr>
</tbody>
</table>

Figure 82: The Bethe-Slater curve demonstrates the variation of the exchange integral $J_e$ with the ratio $R/r$ for elements with incomplete inner electron shells. Ferromagnetic interaction for $J_e > 0$ and antiferromagnetic interactions for $J_e < 0$ (based on the $R/r$ value in [144] and adapted from Ref. [143]).

6.6.3 Exchange interactions of the studied Heusler alloys

In this section the observed magnetism of the studied alloys will be examined and discussed qualitatively by considering the interatomic distances of atoms carrying a magnetic moment and exchange interactions between them. In this discussion, the following approximations were taken.
1. Only the interactions between the same type of atoms which occupy different crystallographic sites were considered. For example, in the case of Mn, the interactions between Mn atoms in regular sites with themselves and other Mn atoms in different crystallographic sites were considered. Also, the interactions between Mn atoms in other crystallographic sites (e.g. Mn in 4b and 8c-sites in the austenitic phase) with themselves were considered. Similarly, interactions between Co and Ni atoms in the same crystallographic sites and different crystallographic sites were considered.

2. The interactions between the different types of nearest neighbors were not considered. This is because of the lack of the exchange interaction data.

3. Only the nearest neighbor interactions were considered. Because of the larger distance to the next nearest neighbor, those interactions are weak to be considered in this examination.

The crystalline structures obtained from the Rietveld refinements of the In-1 and Co-76 alloys demonstrate significant differences in the interatomic distances between the atoms with a magnetic moment (i.e. Mn, Ni, and Co) in both austenitic and martensitic phases [77, 85]. This is true for all the alloys but only the In-1 and the Co-76 alloys will be discussed here in order to qualitatively shed light on the observed magnetic nature of these alloys. The difference in the interatomic distances between the austenitic and martensitic phases is a result of both differences in the crystalline structures of the two phases as well as modulations that is present in the martensitic crystalline structures during the phase transformation [89].

6.6.3.1 Ferromagnetic austenitic phase of the In-1 alloy (Ni_{45}Mn_{43}In_{12})

From the site occupancy refinements of the austenitic phase of the In-1 alloy, it was found that the Mn atoms occupy all three crystallographic sites with different proportions; 100% of the regular Mn-sites (4a), ~50% of the regular In-sites (4b), and ~10% of the regular Ni-sites (as shown in Figure 83). Also, Mn atoms carry the largest magnetic moments among the constituent atoms and the magnetic properties of these alloys are mainly determined by magnetic moments of Mn.
atoms [32, 34, 77]. Therefore, the possible interactions between Mn atoms with the nearest Mn atoms (in both similar and different crystallographic sites) in all crystallographic directions were considered and respective $R/r$ ratios were calculated to determine the possible magnetic couplings between those Mn atoms.

Figure 83: Austenitic $L2_1$ crystalline structure of the In-1 alloy at 314 K under 4 T field. The lattice parameter is 0.6018 nm. Site occupancies of the regular Mn (green), regular In (black), and regular Ni (silver) sites, and interatomic distances between different crystallographic sites are also shown.

Even though the magnetic moment of Ni is less than that of Mn (magnetic moment of Mn and Ni atoms in $Ni_2MnGa$ are ~3.85 and ~0.3 $\mu_B$, respectively [66]), interactions between Ni atoms (Ni atoms occupy only their regular sites) were also considered. However, the Ni-Mn interaction was not considered because the behavior of the exchange integral of Ni-Mn interactions is out of the scope of this work. Observed interatomic distance $2R$ (by Rietveld refinements) for both phases, austenitic (at 314 K, under 4 T) and martensitic (at 294 K, under no applied field), $R/r$ ratios, and the predicted magnetic interactions between the atoms in different crystallographic sites are summarized in Table 34.
Here, in the first column, the atoms in parentheses represent the crystallographic site of the atom outside the parentheses. For example, \( \text{Mn(Mn)}-\text{Mn(Ni)} \) represents the direct exchange interaction between \( \text{Mn} \) atoms in their regular sites with \( \text{Mn} \) atoms in the regular \( \text{Ni} \)-sites. The calculated values of \( \frac{R}{r} \) for the possible interactions between the same type of atoms, in the austenitic phase of the \( \text{In-1} \) alloy (at 314 K under 4 T), are marked on the Bethe-Slater curve in Figure 84.

![Figure 84: Comparison of the \( \frac{R}{r} \) ratios corresponding to the different interatomic distances in the austenitic phase of the \( \text{In-1} \) alloy (at 314 K and under 4 T field) with Bethe-Slater curve. \( \text{Mn(Mn)} \) strongly couples ferromagnetically with \( \text{Mn(In)} \). With other ferromagnetic coupling interactions, the austenitic phase should be ferromagnetic under these conditions.](image-url)
Table 34: Predicted magnetic interactions between the magnetic atoms in the *austenitic (Aust.)* and *martensitic (Mart.)* phases of the In-1 alloy based on the Bethe-Slater curve

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Interaction</th>
<th>Interatomic distance (2R \text{ (nm)})</th>
<th>Shell diameter (2r \text{ (nm)}) [144]</th>
<th>(R/r)</th>
<th>Predicted magnetic interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Mn)-Mn(Ni) (min)</td>
<td></td>
<td>0.2606</td>
<td>0.2432</td>
<td>0.171</td>
<td>1.52</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(Ni) (max)</td>
<td></td>
<td>-</td>
<td>0.2520</td>
<td>-</td>
<td>1.47</td>
</tr>
<tr>
<td>Mn(In)-Mn(Ni) (min)</td>
<td></td>
<td>0.2606</td>
<td>0.2432</td>
<td>0.171</td>
<td>1.52</td>
</tr>
<tr>
<td>Mn(In)-Mn(Ni) (max)</td>
<td></td>
<td>-</td>
<td>0.2520</td>
<td>-</td>
<td>1.47</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(In) (min)</td>
<td></td>
<td>0.3009</td>
<td>0.2650</td>
<td>0.171</td>
<td>1.76</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(In) (max)</td>
<td></td>
<td>-</td>
<td>0.2850</td>
<td>-</td>
<td>1.66</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(Mn) (min)</td>
<td></td>
<td>0.4255</td>
<td>0.4110</td>
<td>0.171</td>
<td>2.49</td>
</tr>
<tr>
<td>Ni(Ni)-Ni(Ni) (min)</td>
<td></td>
<td>0.3009</td>
<td>0.2829</td>
<td>0.127</td>
<td>2.37</td>
</tr>
<tr>
<td>Ni(Ni)-Ni(Ni) (max)</td>
<td></td>
<td>-</td>
<td>0.3370</td>
<td>-</td>
<td>2.65</td>
</tr>
</tbody>
</table>

According to Figure 84, interactions between the same types of atoms in the austenitic phase of the *In-1* alloy are coupled ferromagnetically. Among these exchange interactions, the strongest ferromagnetic ordering is between the \(Mn(Mn)\) and \(Mn(In)\). About 50% of regular \(In\)-sites are occupied by the \(Mn\) atoms. The ferromagnetic couplings between \(Ni(Ni)\) and \(Ni(Ni)\) are also contributing to the observed ferromagnetism of the austenitic phase. However, the ferromagnetic interactions between \(Mn\) atoms in their regular sites with themselves are very weak due to the significantly large separations between the regular \(Mn\)-sites. The possible exchange coupling interactions between the nearest neighbor \(Mn\) in all three crystallographic sites and \(Ni\) in their regular sites (at 314 K, under 4 T field) are shown in Figure 85, and all of these interactions are ferromagnetic. Therefore, it could be assumed that the observed ferromagnetism of the austenitic phase of the *In-1* alloy is primarily due to the ferromagnetic coupling between the \(Mn(Mn)\) and \(Mn(In)\).
Figure 85: The possible nearest neighbor exchange coupling interactions between Mn atoms in the regular Mn-, Ni-, and In-sites and between Ni atoms in their regular sites, in the austenitic phase. The relative strength of the ferromagnetic couplings is also given.

In addition, there is a significant contribution to ferromagnetism from the exchange interactions between Ni(Ni) and Ni(Ni). These interactions are shown in Figure 85 schematically, indicating the relative strength of the exchange interactions. This may explain the observed ferromagnetism of the austenitic phase of the In-1 alloy in the susceptibility measurements (Figure 67, section 5.5.2.3).

6.6.3.2 Antiferromagnetic martensitic phase of the In-1 alloy (Ni<sub>45</sub>Mn<sub>43</sub>In<sub>12</sub>)

In a modulated martensitic phase, the separation between two magnetic atoms is not a unique value such as in the austenitic phase. Separation between two atoms varies in a range of values depending on the occupied crystallographic site by that atom. For example, the distance between the Mn in regular Mn-sites, Mn(Mn), and Mn in regular Ni sites, Mn(Ni), varies in the range from 0.2432 to 0.2520 nm (Table 34). Therefore, the calculated $R/r$ value for an interaction
varies in a range of values, as shown in Figure 86. This figure displays the possible magnetic coupling between the same type of atoms in the martensitic phase of the *In-I* alloy at 294 K under no applied magnetic field.

Interatomic distances between the atoms carrying magnetic moments in the martensitic phase of the *In-I* alloy were calculated by martensitic crystalline structures obtained by Rietveld refinements. When compared to the austenitic phase of the *In-I* alloy, the distance between *Mn(In)* and *Mn(Ni)* and the distance between *Mn(Mn)* and *Mn(Ni)* atoms is shorter in the modulated martensitic phase [77, 85]. The magnetic couplings between those *Mn* atoms in the austenitic phase were weak ferromagnetic (Figure 84). Because of a shorter distance between those *Mn* atoms in the martensitic phase, the nature of the exchange couplings is antiferromagnetic ranging from weak (at *R/r* = 1.47) to strong antiferromagnetism (at *R/r* = 1.42). Compared to the austenitic phase, the exchange coupling between *Mn(Mn)* and *Mn(In)* in the martensitic phase is weak (Figure 86). This interaction in the martensite is weak due to the shorter distance between *Mn(Mn)* and *Mn(In)* atoms compared to that of the austenitic phase. The *R/r* value ranges from 1.54 to 1.66 resulting in weak to moderate ferromagnetic exchange interactions. The strongest ferromagnetic interaction (among the considered interactions) in the martensitic phase is significantly smaller compared to that of the austenitic phase. Additionally, there are two weak ferromagnetic interactions between *Mn(Mn)* and *Ni(Ni)* (Figure 86), which are the same magnitude as in the austenitic phase. By considering all these exchange interactions in the martensitic phase of the *In-I* alloy, it could be concluded that the strength of the ferromagnetic exchange interactions is weaker than that in the austenitic phase. Additionally, there is a strong antiferromagnetic interaction between *Mn(Mn)* and *Mn(Ni)* atoms, but only 10 % of *Mn* atoms are in the regular *Ni-sites*. Therefore, the overall magnetic nature of
the martensitic phase could be a weak antiferromagnetism as concluded by the neutron diffraction analysis [88].

Figure 86: Comparison of the $R/r$ ratios corresponding to the different interatomic distances in the martensitic phase of the In-I alloy (at 294 K and under no field) with Bethe-Slater curve. $Mn(Ni)$ strongly couples antiferromagnetically with $Mn(In)$. On the other hand, $Ni(Ni)$ coupled ferromagnetically.

6.6.3.3 Magnetic behavior of the Co-76 alloy ($Ni_{41}Mn_{39}In_{12}Co_8$)

The austenitic phase of the Co-76 alloy (at 350 K and under no applied field) has a cubic $L2_1$ structure with a lattice constant $a = 0.5984$ nm, which is smaller by 0.56% than that of the In-I alloy. Therefore, the interatomic distances between crystallographic sites are slightly shorter in the case of the Co-76 alloy compared to the In-I alloy. When compared with the In-I alloy, the Co-76 has Co atoms that carry a strong magnetic moment compared to Ni atoms. Still, the magnetic
moment of Mn atoms is stronger than that of Co in Heusler alloys [149]. All the substituted Co atoms occupy the regular Ni-sites (a similar trend is reported in [121]). Therefore, an extra exchange interaction between Co(Ni) and Co(Ni) exists in this alloy. Mn atoms occupy both regular Mn- and regular In-sites (but not the Ni-sites as in the case of the In-1 alloy). Also, almost all the Ni atoms occupy their regular sites. Exchange interactions between the same type of magnetic atoms in the austenitic phase of the Co-76 alloy were calculated in a similar fashion to the case of the In-1 alloy, considering site occupancies and the interatomic distances between them. The possible exchange interactions between the same type of atoms are shown in Figure 87 and listed in Table 35.

All the considered exchange interactions between the same type of atoms in the austenitic phase of the Co-76 alloy are ferromagnetic including very strong ferromagnetic exchange interactions of Co(Ni) with themselves and between Mn(Mn) and Mn(In). The site occupation of the Co atoms in the regular Ni-sites is only ~ 16 % and therefore its contribution to the overall ferromagnetism is not very large. However, the interaction between Co(Ni) is stronger than that of Ni(Ni) and Ni(Ni) because of the higher magnetic moment of Co compared to Ni [149]. This explains the observed ferromagnetism of the austenitic phase of the Co-76 alloy in the thermomagnetic measurements. Similarly, as in the case of the In-1 alloy, the interatomic distances between the magnetic atoms in the martensitic phase of the Co-76 alloy were calculated. The martensitic phase of the Co-76 alloy is a mixture of 6M and 8M modulated monoclinic structures. Because of the modulations of the martensitic phase, the interatomic distance between two atoms varies in a range of values. For example, the interatomic distances between Mn atoms in their regular site and Mn atoms in regular In sites were calculated using GSAS and DRAWxtl and the results are summarized in Table 35 and
Table 37, for the $8M$ modulated and $6M$ modulated martensitic phases, respectively. These interatomic distances vary in a range of values (from 2.722 to 3.322 nm in the $8M$ phase and from 2.522 to 3.322 nm in $6M$ phase). Thus, the $R/r$ ratios of all possible exchange interactions vary in a range of values. In the case of $Co(Ni)$-$Co(Ni)$ exchange interactions, the values of $R/r$ range from 1.42 to 1.90, resulting in an antiferromagnetic coupling for the smallest $R/r$ and a very strong ferromagnetic coupling for the largest $R/r$. The rest of the considered interactions are all ferromagnetic which are summarized in Table 35. This implies the coexisting of both ferromagnetic and antiferromagnetic exchange interactions in the martensitic phase of the $Co$-76 alloy. However, this qualitative analysis of the possible magnetic interactions between the same type of atoms (with magnetic properties) is not sufficient to determine the overall magnetic nature (i.e. ferromagnetic, antiferromagnetic, or spin-glass) of the martensitic phase of the alloy.

Table 35: Predicted exchange interactions between the magnetic atoms in the *austenitic* (*Aust.*)) and *martensitic* (*Mart.*)) phases of the $Co$-76 alloy based on the Bethe-Slater curve

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Aust. $2R$ (nm)</th>
<th>Mart. $2R$ (nm)</th>
<th>Aust. $2r$ (nm)</th>
<th>Mart. $2r$ (nm)</th>
<th>$R/r$ Aust.</th>
<th>$R/r$ Mart.</th>
<th>Predicted magnetic interaction Aust.</th>
<th>Predicted magnetic interaction Mart.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Mn)-Mn(In) (min)</td>
<td>0.2992</td>
<td>0.2730</td>
<td>0.171</td>
<td>1.74</td>
<td>1.60</td>
<td>FM</td>
<td>FM</td>
<td>FM</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(In) (max)</td>
<td>-</td>
<td>0.3290</td>
<td>0.171</td>
<td>-</td>
<td>1.92</td>
<td>-</td>
<td>FM</td>
<td>FM</td>
</tr>
<tr>
<td>Mn(Mn)-Mn(Mn) (min)</td>
<td>0.4231</td>
<td>0.4255</td>
<td>0.171</td>
<td>2.47</td>
<td>2.49</td>
<td>FM</td>
<td>FM</td>
<td>FM</td>
</tr>
<tr>
<td>Ni(Ni)-Ni(Ni) (min)</td>
<td>-</td>
<td>0.2590</td>
<td>0.127</td>
<td>-</td>
<td>2.04</td>
<td>-</td>
<td>FM</td>
<td>FM</td>
</tr>
<tr>
<td>Ni(Ni)-Ni(Ni) (max)</td>
<td>0.2992</td>
<td>0.3470</td>
<td>0.127</td>
<td>2.36</td>
<td>2.73</td>
<td>FM</td>
<td>FM</td>
<td>FM</td>
</tr>
<tr>
<td>Co(Ni)-Co(Ni) (min)</td>
<td>-</td>
<td>0.2590</td>
<td>0.182</td>
<td>-</td>
<td>1.42</td>
<td>-</td>
<td>AFM</td>
<td>AFM</td>
</tr>
<tr>
<td>Co(Ni)-Co(Ni) (max)</td>
<td>0.2992</td>
<td>0.3470</td>
<td>0.182</td>
<td>1.64</td>
<td>1.90</td>
<td>FM</td>
<td>FM</td>
<td>FM</td>
</tr>
</tbody>
</table>
Table 36: Number of nearest neighbor *Mn* atoms in the regular *In* sites for the *Mn* atoms in their regular sites in a given interatomic distance range of the *8M* modulated monoclinic martensitic structure of the Co-76 alloy (at 250 K under no applied magnetic field)

<table>
<thead>
<tr>
<th>Interatomic distance range (nm)</th>
<th>Number of nearest neighbors in the range</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.722 – 2.822</td>
<td>58</td>
</tr>
<tr>
<td>2.822 – 2.922</td>
<td>24</td>
</tr>
<tr>
<td>2.922 – 3.022</td>
<td>12</td>
</tr>
<tr>
<td>3.022 – 3.122</td>
<td>30</td>
</tr>
<tr>
<td>3.122 – 3.222</td>
<td>18</td>
</tr>
<tr>
<td>3.222 – 3.322</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 37: Number of nearest neighbor Mn atoms in the regular In sites for the Mn atoms in their regular sites in a given interatomic distance range of the 6M modulated monoclinic martensitic structure of the Co-76 alloy (at 250 K under no applied magnetic field)

<table>
<thead>
<tr>
<th>Interatomic distance range (nm)</th>
<th>Number of nearest neighbors in the range</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.522 – 2.622</td>
<td>6</td>
</tr>
<tr>
<td>2.622 – 2.722</td>
<td>0</td>
</tr>
<tr>
<td>2.722 – 2.822</td>
<td>6</td>
</tr>
<tr>
<td>2.822 – 2.922</td>
<td>6</td>
</tr>
<tr>
<td>2.922 – 3.022</td>
<td>12</td>
</tr>
<tr>
<td>3.022 – 3.122</td>
<td>6</td>
</tr>
<tr>
<td>3.122 – 3.222</td>
<td>6</td>
</tr>
<tr>
<td>3.222 – 3.322</td>
<td>24</td>
</tr>
</tbody>
</table>
Figure 87: Comparison of the $R/r$ ratios corresponding to the different interatomic distances in the austenite phase of the Co-76 alloy (at 350 K and under no field) with the Bethe-Slater curve. Mn(Mn) strongly couples ferromagnetically with Mn(In) and Co(Ni) couples together ferromagnetically. With other ferromagnetic coupling interactions, the austenitic phase should be ferromagnetic under these conditions.

In a summary, this simple approximated approach of explaining the magnetic nature of the In-1 and Co-76 alloys successfully predicted the observed ferromagnetism of the austenitic phase of these alloys. In the austenitic phase of both alloys, the main contribution to the observed ferromagnetism is coming from the exchange interactions between Mn(Mn) and Mn(In) atoms. There is a small contribution from the interactions between Ni atoms in their regular sites with themselves. In the case of the In-1 alloy, this approach is successful. This is because the magnetic moment of Mn atoms (~3.85 $\mu_B$) is approximately one order of magnitude higher than that of Ni (~0.3 $\mu_B$) [66]. Therefore, interactions between the same type of atoms is sufficient to explain the magnetism as there are only two types of atoms contributing.

In the case of the Co-76 alloy, there are three types of atoms, Mn, Ni, and Co, carrying a magnetic moment. Co atoms carry a strong magnetic moment compared to Ni atoms (e.g. magnetic moments of Co and Ni atoms in the Ni$_2$CoGa alloy are 1.55 and 0.16 $\mu_B$, respectively). However,
the magnetic moment of Mn atoms is stronger than Co in Heusler alloys (e.g. magnetic moments of Mn and Co atoms in the Co$_2$MnGa alloy are 2.72 and 0.76 $\mu_B$, respectively) [149]. Therefore, exchange interactions between Co(Ni) atoms with themselves give a significant contribution to the observed ferromagnetism. Consequently, the exchange interactions between different types of atoms (e.g. Mn and Co) may need to considered in the case of the Co-76 alloy.

Exchange interactions in the martensitic phase of these alloys are very complex due to the variation of the interatomic distances associated with modulation. Nevertheless, the shorter interatomic distances in the martensitic phase compared to that in the austenitic phase reduce the strength of the ferromagnetic interactions significantly. They even change into antiferromagnetic interactions in much shorter interatomic distances. The qualitative model is quite successful in explaining the antiferromagnetic ordering of the martensitic phase of the In-1 alloy. However, this model cannot explain the magnetic nature of the martensitic phase of the Co-76 alloy.

6.6.3.4 Magnetism of the martensitic phase of the Co-76 alloy (Ni$_{41}$Mn$_{39}$In$_{12}$Co$_8$)

According to the neutron diffraction analysis of this alloy, no antiferromagnetic ordering is expected in either martensitic phases in the temperature range from 300 down to 50 K. On the other hand, low magnetization observed in the thermomagnetic measurements of the martensitic phase confirms that no ferromagnetic ordering exists in the range of temperatures from 100 to ~ 300 K. Therefore, neither ferromagnetic nor antiferromagnetic ordering is present in the martensitic phase of the Co-76 alloy.

The ZFC and FC heating thermomagnetic curves of the Co-76 alloy under a 0.005 T field (shown in Figure 64-a) separate (starting around ~ 285 K just below the ferromagnetic to low magnetic phase transformation temperature), indicating an irreversible behavior of the magnetization in this region [28]. Separation between the curves gets wider as temperature
decreases. Such splitting is due to the coexisting of the ferromagnetic and antiferromagnetic interactions in the martensitic phase of this alloy [40, 77]. As shown in Figure 64-b, there are cusp like maxima in both ZFC curves (under 0.01 and 0.05 T). The susceptibility cusps are the key features of both spin-glass and antiferromagnetic transitions from a higher temperature paramagnetic phase [150]. This is probably due to a spin-glass-like magnetic nature in the martensitic phase of the Co-76 alloy below ~19 K [89, 90, 150]. The magnetic nature of the martensitic phase may be confirmed by AC-susceptibility measurements. Spin-glass and antiferromagnetic magnetic natures can be distinguished by AC-susceptibility measurements because the position of the cusps in a spin-glass state depends on the AC-driven frequency of the applied field in the measurements. Even though a paramagnetic nature could be a possibility between 285 K down to 20 K [151], it is highly unlikely to exist as a magnetic phase with higher entropy such as paramagnetic disorder below the ferromagnetic austenitic phase.
CHAPTER 7

CONCLUSIONS AND SUGGESTED FUTURE STUDIES

7.1 Conclusions

First, the main conclusions of this study will be presented. In the second half of this chapter, potential future studies of these alloys and their importance will be discussed.

7.1.1 Austenitic crystalline structures and site occupancies

1. All studied alloys have a $L2_1$ cubic structure in their austenitic phase. This structure belongs to the $Fm\bar{3}m$ space group.
2. Probably due to the lower concentrations of $In$ (in $In-1$ and $Ni-In-Mn-Co$ alloys) and stoichiometric concentration of $Ga$ (in $Ga-S1$ and $Ga-S2$ alloys), both atoms occupy only the $4b$ crystallographic sites in the austenitic phase.
3. When there is an excess $Mn$ (e.g. $In-1$ and $Co-76$ alloys), $Mn$ atoms occupy all three crystallographic sites with the highest preference given to their regular sites ($4a$). The majority of the rest occupy the $4b$-sites.
4. When there is an excess $Ni$ (e.g. $Co-73$, $Ga-S1$, and $Ga-S2$), the majority of $Ni$ occupy their regular sites ($8c$). The rest occupy the regular $Mn$-sites. In any of these alloys, $Ni$ atoms do not occupy the $4b$-sites.
5. In the $Co$ substituted alloys (i.e. $Co-73$ and $Co-76$), the $Co$ atoms prefer to occupy $Ni$-sites.

7.1.2 Martensitic phase transformations and martensitic crystalline structures

1. All studied alloys undergo martensitic and austenitic phase transformations upon cooling and upon heating, respectively.
2. The martensitic phase of the Ni-Mn-In and Ni-Mn-In-Co alloys is a mixture of modulated monoclinic structures: 5M and 7M modulated in the case of the In-1, Co-73, and Co-74; 6M and 8M modulated monoclinic in the case of the Co-76 alloy.

3. In addition to the martensitic phase transformation, the studied Ni-Mn-Ga alloys undergo a temperature-induced inter-martensitic phase transformation from 7M modulated monoclinic to a non-modulated tetragonal $L1_0$ phase ($I4/mnm$ space group) upon cooling. Crystalline structures of the austenitic and martensitic phases and their space groups, site occupancies of the austenitic phase, and chemical compositions of the studied alloys are summarized in Table 38.

Table 38: Summary of the crystalline structures of the austenitic and martensitic phases, site occupancies of the austenitic phase, and chemical compositions of the studied alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Atom</th>
<th>Percentage site occupancy (%)</th>
<th>Chemical composition</th>
<th>Crystalline structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-1</td>
<td>Ni</td>
<td>100.0</td>
<td>Ni$<em>{44.9}$Mn$</em>{22.8}$In$_{12.3}$</td>
<td>Cubic $L2_1$Fm$\bar{3}m$ By RBS</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.0</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>0.0</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td>Co-73</td>
<td>Ni</td>
<td>36.5</td>
<td>Ni$<em>{52.1}$Mn$</em>{25.1}$In$<em>{13.5}$Co$</em>{6.9}$</td>
<td>Cubic $L2_1$Fm$\bar{3}m$ By RBS</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>63.5</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>63.6</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>14.0</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td>*Co-74</td>
<td>Inhomogeneous</td>
<td>-</td>
<td></td>
<td>Mix of 5M &amp; 7M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td>Co-76</td>
<td>Ni</td>
<td>4.2</td>
<td>Ni$<em>{40.8}$Mn$</em>{39.3}$In$<em>{11.7}$Co$</em>{8.4}$</td>
<td>Cubic $L2_1$Fm$\bar{3}m$ By RBS</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>95.8</td>
<td></td>
<td>Mix of 6M &amp; 8M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>-</td>
<td></td>
<td>Mix of 6M &amp; 8M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>-</td>
<td></td>
<td>Mix of 6M &amp; 8M Monoclinic $P\bar{1}2/m\bar{1}$</td>
</tr>
<tr>
<td>Ga-S1</td>
<td>Ni</td>
<td>14.8</td>
<td>Ni$<em>{53.6}$Mn$</em>{21.4}$Ga$_{25.0}$</td>
<td>Cubic $L2_1$Fm$\bar{3}m$ By EDS</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>85.2</td>
<td></td>
<td>Non-modulated tetragonal $14/mnm$</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>-</td>
<td></td>
<td>Non-modulated tetragonal $14/mnm$</td>
</tr>
<tr>
<td>Ga-S2</td>
<td>Ni</td>
<td>15.8</td>
<td>Ni$<em>{53.9}$Mn$</em>{21.3}$Ga$_{25.0}$</td>
<td>Cubic $L2_1$Fm$\bar{3}m$ By EDS</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>84.2</td>
<td></td>
<td>Non-modulated tetragonal $14/mnm$</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>-</td>
<td></td>
<td>Non-modulated tetragonal $14/mnm$</td>
</tr>
</tbody>
</table>
7.1.3 Magnetic field-induced phase transformations

1. Both temperature and magnetic field drive the martensitic phase transformations of these alloys.
2. The Co-73 alloy undergoes magnetic field-induced complete austenitic and martensitic phase transformations at 230 K, upon changing the magnetic field from 0 to 6.5 T. The magnetic hysteresis of the magnetic field-induced phase transformations is very small (~0.1 T).
3. By choosing the correct starting temperature of the austenitic phase transformation ($A_s$), magnetic field-induced phase transformations could be made more practical.

7.1.4 Effects of the applied magnetic field on martensitic transformation temperature

Both martensitic and austenitic phase transformation temperatures strongly depend on the applied magnetic field. In the case of the In-1 and Co-73 alloys, the martensitic phase transformation temperature decreases with an increasing magnetic field. On the other hand, the martensitic transformation temperature of the Ga-SI alloy increases with an increased magnetic field. This phenomenon can be explained qualitatively using the Clausius-Clapeyron equation, $dT_0/dH = -\Delta M/\Delta S$. Table 39 summarizes the effect of an applied magnetic field on the martensitic phase transformation temperature of four of the studied alloys.
Table 39: Summary of the behavior of martensitic phase transformation temperature with applied magnetic field change according to Clausius-Clapeyron equation

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase</th>
<th>Crystalline structure</th>
<th>Magnetic nature</th>
<th>( \Delta S ) ( (S^A - S^M) )</th>
<th>( \Delta M ) ( (M^A - M^M) )</th>
<th>( \frac{dT_0}{dH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{In}-1</td>
<td>Mar. 5M &amp; 7M monoclinic</td>
<td>AFM</td>
<td>positive</td>
<td>positive</td>
<td>Negative: decrease with increasing field</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aus.</td>
<td>Cubic ( L_2 )</td>
<td>FM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textit{Co}-73</td>
<td>Mar. 5M &amp; 7M monoclinic</td>
<td>Low magnetization</td>
<td>positive</td>
<td>positive</td>
<td>Negative: decrease with increasing field</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aus.</td>
<td>Cubic ( L_2 )</td>
<td>FM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textit{*Co}-76</td>
<td>Mar. 6M &amp; 8M monoclinic</td>
<td>Paramagnetic</td>
<td>positive</td>
<td>positive</td>
<td>Negative: decrease with increasing field</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aus.</td>
<td>Cubic ( L_2 )</td>
<td>FM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textit{Ga}-\textit{Si}</td>
<td>Mar. 7M monoclinic</td>
<td>FM</td>
<td>positive</td>
<td>negative</td>
<td>Positive: increase with increasing field</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aus.</td>
<td>Cubic ( L_2 )</td>
<td>Paramagnetic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In the case of \textit{Co}-76, the \( dT_0/dH \) trend is predicted by known crystalline and magnetic data.

7.1.5 Magnetic behavior of the austenitic and martensitic phases

1. The \textit{In}-1, \textit{Co}-73 and \textit{Co}-76 alloys are ferromagnetic in their austenitic phase below the Curie temperature. On the other hand, the austenitic phase of the \textit{Ga}-\textit{Si} alloy is paramagnetic above the martensitic phase transformation temperature.

2. The magnetic nature of these alloys is very complex in the martensitic phase because of the highly ordered interatomic distances between the magnetic atoms due to the modulations of the martensitic phase.

Ferromagnetic, antiferromagnetic, and spin-glass-like magnetic natures are present in the martensitic phase of these alloys. The summary of the observed magnetism in both phases are given in...
3. Table 40.
### Table 40: Summary of the detected magnetic nature of four of the studied alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Chemical composition</th>
<th>Magnetism (Austenitic phase (below $T_C$))</th>
<th>Magnetism (Martensitic phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-1</td>
<td>Ni$<em>{44.9}$Mn$</em>{42.8}$In$_{12.3}$</td>
<td>ferromagnetic</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>Co-73</td>
<td>Ni$<em>{52.1}$Mn$</em>{25.3}$In$<em>{15.5}$Co$</em>{6.9}$</td>
<td>ferromagnetic</td>
<td>low magnetization (not identified)</td>
</tr>
</tbody>
</table>
| Co-76 | Ni$_{40.6}$Mn$_{39.3}$In$_{11.7}$Co$_{8.4}$ | ferromagnetic | paramagnetic below $M_f$ and above 19 K  
spin-glass-like below $\sim 19$ K |
| Ga-S1 | Ni$_{53.2}$Mn$_{22.1}$Ga$_{25.0}$ | paramagnetic | ferromagnetic |

#### 7.1.6 Relation between the magnetic nature and site occupancies of the studied alloys

The following conclusions were made by examination of the exchange interactions of the austenitic phases of the In-1 and Co-76 alloys, by considering the interatomic distances between constituent magnetic atoms.

1. $Mn(Mn)$-$Mn(In)$ interaction is stronger compared to others and hence provides the main contribution to the ferromagnetism in the austenitic phase.

2. The contribution of the $Ni(Ni)$-$Ni(Ni)$ interaction to the ferromagnetic ordering is small. On the other hand, in the case of the Co-76 alloy, the ferromagnetic contribution by the interactions between $Co(Ni)$-$Co(Ni)$ is significantly higher than that of $Ni(Ni)$-$Ni(Ni)$. The substitution of Co atoms in Ni-Mn-In alloys enhances the ferromagnetic nature of the austenitic phase by strong ferromagnetic interactions between $Co(Ni)$-$Co(Ni)$.

Also, the following conclusions were made in the examination of the exchange interactions in the martensitic phase of the In-1 and Co-76 alloys.

3. The interatomic distance between any two atoms varies significantly in the martensitic phase due to the modulations in the martensitic structures. As a result, the strength and even the sign of the exchange interactions change with the variation of the interatomic distance between the same types of atoms.

4. In the case of the In-1 alloy, the strength of the exchange interactions between $Mn(Mn)$-$Mn(In)$ varies in a range of values. All these values result in ferromagnetic coupling between Mn atoms. However, the strongest interaction in the martensitic phase is less than the $Mn(Mn)$-$Mn(In)$ interaction in the austenitic phase.
5. The exchange interactions between $\text{Mn(In)}$-$\text{Mn(Ni)}$ and $\text{Mn(Mn)}$-$\text{Mn(Ni)}$ are antiferromagnetic because of the reduced distance between the $\text{Mn}$ atoms in these sites. These interactions overcome the weak ferromagnetic interactions between the $\text{Mn(Mn)}$-$\text{Mn(In)}$ and the overall magnetism of the martensitic phase is antiferromagnetic.

6. In the case of the $\text{Co-76}$ alloy, the interaction between $\text{Co(Ni)}$-$\text{Co(Ni)}$ is antiferromagnetic. Also, all the ferromagnetic exchange interactions become weaker in the martensitic phase. This may suggest the coexisting of both ferromagnetic and antiferromagnetic exchange interactions in the martensitic phase.

7.1.7 Kinematic equations representing the martensitic phase transformations

Two kinematic equations (Equations 58 and 59) were constructed to represent the normalized austenitic phase fraction for the martensitic and austenitic phase transformations.

$$
\begin{align*}
\text{A-M} f_A &= \frac{1}{1 + \exp \left\{ \frac{1.48e (T_0 - T)}{M_S - M_F} \right\}} \\
\text{M-A} f_A &= \frac{1}{1 + \exp \left\{ \frac{1.48e (T_0 - T)}{A_S - A_F} \right\}}
\end{align*}
$$

1. These expressions can be used to predict the behavior of both martensitic and austenitic phase transformations of the $\text{Co-76}$ alloy under different magnetic fields.
2. In the case of the $\text{Co-73}$ alloy, the empirical constant $C$ is $1.48 \pm 0.03$ for both austenitic and martensitic phase transformations.
3. To use them in general, the behavior of this empirical constant in the martensitic and austenitic phase transformations in other $\text{Ni-Mn-X}$ Heusler alloys needs to be studied.
7.1.8 Thermal hystereses associated with crystalline and magnetic phase transformations of Ni-Mn-X based alloy and the coupled magneto-structural phase transformations

Thermal hysteresis associated with crystalline (for Co-73 alloy) and magnetic (for both Co-73 and Co-76 alloys) phase transformation was studied as a function of an applied magnetic field. The following conclusions were made from that study.

1. In both alloys, the thermal hysteresis associated with a magnetic phase transformation increases (with growing rate) with an increased magnetic field. The thermal hysteresis is approximately proportional to the square of the applied magnetic field.
2. The thermal hysteresis associated with the first-order phase transformation has a minimum under a ~2.8 T magnetic field.
3. In the studied range, the hysteresis associated with the magnetic phase transformation is about 4 times higher than that of the crystalline phase transformation.
4. Characteristic temperatures of both crystalline and magnetic phase transformations decrease with an increasing magnetic field, but in different rates. Thus, the difference between the equilibrium temperatures of the crystalline and magnetic phase transformation (upon heating) decreases with an increased magnetic field, and a merged magneto-structural phase transformation is anticipated around 3.9 T.
5. Because of the large difference in the hystereses, the crystalline and magnetic phase transformations upon cooling do not merge under any magnetic field.

7.1.9 Evaluation of the studied alloy according to their anticipated magnetocaloric performances

All the studied alloys undergo first-order structural and magnetic phase transformations. By considering the lattice entropy and magnetic entropy changes, the total entropy (i.e. GMCE) associated with these transformations were qualitatively compared and the following conclusions may be made.

1. The lattice entropy difference between austenitic (cubic) and modulated martensitic phases increases with increasing modulations.
2. In magnetic phase transformations, entropy increases when the transformation is from a highly ordered magnetic state to a less ordered magnetic phase (e.g. antiferromagnetic to ferromagnetic).

3. In the case of Co substituted Ni-Mn-In alloys, magnetic entropy change works against the lattice entropy change because, they transform from a lower magnetization (presumably spin-glass-like) modulated martensitic phase to a ferromagnetic austenitic phase.

4. In the case of the In-1 and Ga-S1 alloys, both magnetic and lattice entropy changes increase when they transform from their martensitic to austenitic phases (e.g. In-1 transforms from an antiferromagnetic modulated martensite to a ferromagnetic austenite).

5. Conceptually the In-1 and Ga-S1 alloys are more suitable as magnetocaloric materials considering the total energy output in their phase transformations.

6. To rank them according to their magnetocaloric potentials, their magnetocaloric effects need to be measured systematically. Also, thermal hysteresis losses associated with both phase transformations need to be considered.

7.2 Future studies of the Ga-S1 alloy (Ni_{53.6}Mn_{21.4}Ga_{25})

A number of techniques have been introduced to enhance the magnetocaloric effect associated with the first-order martensitic phase transformations in Ni-Mn-X alloys. One issue to overcome is the hysteresis associated with the first-order transformations causes an irreversible energy loss, and this lowers the magnetocaloric efficiency of the studied Ni-Mn-X Heusler alloys [30]. There is a new trend of enhancing the magnetocaloric effect by utilizing the entropy associated with multi-structural transformations in Ni-Mn-Ga alloys [24, 126]. A maximum magnetic entropy change of -30.0 J Kg^{-1} K^{-1} (under $\mu_0\Delta H = 5$ T) by magneto-multistructural transitions in melt-spun ribbons of the Ni_{52}Mn_{28}Ga_{22} alloy was reported [24]. In this form, this
alloy undergoes martensitic and inter-martensitic phase transformations from an austenite to a 7M modulated martensitic to a non-modulated tetragonal phase, respectively.

The studied Ni-Mn-Ga alloys undergo magneto-multistructural transitions with the separation between the equilibrium temperatures of the two successive phase transformations in only ~50 K, and the hystereses in both phase transformations are less than 25 K. All these conditions suggest that utilizing two successive phase transformations may result in higher GMCE. To optimize the GMCE of these alloys, extensive knowledge of two transformations is required, and in order to broaden this knowledge more studies could be performed by following the directions of this study.

The martensitic phase transformation of the Ga-S1 alloy is a coupled magneto-structural transformation, and upon cooling the alloy transforms from a paramagnetic austenitic phase to a ferromagnetic martensitic phase with a 7M modulated structure. The magnetic phase transformation temperature increases with increasing magnetic field [2]. However, the behavior of the crystalline (martensitic) phase transformation temperature under different magnetic fields is unknown. According to the thermomagnetic measurement, below the martensitic transformation, and down to 200 K there is no significant difference in the magnetization [125]. However, the 7M martensitic phase is only stable in a narrow temperature range (~ 50 K) and undergoes an inter-martensitic phase transformation to a non-modulated tetragonal phase upon cooling. The behavior of the inter-martensitic phase transformation under different magnetic fields is also unknown. Therefore, examination of the martensitic and inter-martensitic phase transformations under different magnetic fields is important. A neutron diffraction analysis of the Ga-S1 alloy under different magnetic fields could be suggested to investigate the behavior of the successive crystalline phase transformations. Additionally, isothermal magnetization measurements at
different temperatures in the range from 200 to 400 K (which covers the two transformations) could be suggested to investigate the possible magnetic phase transformations.
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APPENDICES

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A. Figure 2: A characteristic value of MCE (adiabatic temperature change) for the applied field difference of 2 T, for several of the most studied magnetocaloric materials at either their pure magnetic transition (second-order) temperature, represented by hatched pattern, or merged magneto-structural transition (first-order) temperature, represented by solid colors.

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transition, solid fill-pattern). Except for the Ni–Mn–In–(Co) alloy (solid pink), the given 1Tad data are taken from refs 1,18 and related references therein.

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B. **Figure 10:** DSC curve of the Ni\textsubscript{50}Mn\textsubscript{37}Sb\textsubscript{13} alloy which demonstrates a martensitic and austenitic phase transformations with thermal hysteresis
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C. **Figure 11**: Thermomagnetization curves of the Ni\textsubscript{45}Co\textsubscript{5}Mn\textsubscript{36.6}In\textsubscript{13.4} alloy under 3 magnetic field 0.5, 2, and 7 T magnetic fields.

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D. **Figure 15**: The magnetic and structural phase diagrams of (a) Ni-Mn-Sn, (b) Ni-Mn-In, and (c) Ni-Mn-Ga Heusler alloys.

E. **Figure 16**: Variation of the martensitic transformation temperature MS and Curie temperatures in the martensitic TCM and austenitic phases TCA of Ni-Mn-X alloys (X = Ga, In, Sn, and Sb) as a function of valance electron concentration per atom (e/a ratio).

F. **Figure 17**: Magnetization of Ni-Mn-X alloys as function of temperature in ZFC, FC and FH routines under two magnetic fields in the extreme ends. Magnetization of (a) Ni50Mn34In16 and (b) Ni50Mn27Ga23 alloys in very low magnetic field (0.05 T). (c) Magnetization of Ni-Mn-X alloys (X = Ga, In, Sn, and Sb) under high magnetic field of 5 T

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Figure 5. M (T) for Ni–Mn–Z Heusler alloys. (a) A typical low-field measurement (H = 50 Oe) represented by the data for Z as In. (b) A typical low-field measurement (H = 50 Oe) for Ni–Mn–Ga. (c) High-field H = 50 kOe M(T ) measurements for Z as Ga, In, Sn and Sb.

Figure 6. The e/a dependence of the martensitic transition temperature (Ms) and the Curie temperature in austenitic (T^A_C) and martensitic (T^M_C) states for Ni–Mn–Z Heusler alloys with Z as Ga, In, Sn and Sb.

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G. **Figure 24:** (a) A picture (https://neutrons.ornl.gov/powder) and (b) schematic diagram of the constant wavelength neutron diffractometer, HB-2A instrument, at Oak Ridge National Laboratory.

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H. **Figure 26**: (a) Schematic diagram of the custom aluminum vacuum chamber with cryogenic loading capability. (b) Aluminum vacuum chamber with a copper cold mass.
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I. **Figure 27**: (Zero field AC susceptibility vs. temperature measurements of CuMn (1 at% Mn) powder.)

**Susceptibility of the $\text{CuMn}$ spin-glass: Frequency and field dependences**

C. A. M. Mulder, A. J. van Duyneveldt, and J. A. Mydosh

Feb 1, 1981

FIG. 5 Zero-field susceptibility $X'$ as a function of temperature for sample IIc (Cu-0.94 at % Mn, powder). Measuring frequencies: Square - 1.13 kHz, Circle - 234 Hz, x - 10.4 Hz, and Triangle - 2.6 Hz
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