

Understanding the role of Z atom in influencing martensitic transformation in Ni-Mn-Z (Z = Ga, In, Sn, Sb) Heusler alloys

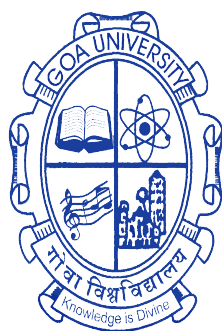
A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in Physics

IN THE SCHOOL OF PHYSICAL AND APPLIED SCIENCES

GOA UNIVERSITY



By

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OCTOBER 2025

DECLARATION

I, Nafea Manea Bhlos hereby declare that this thesis represents work which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

Place: Taleigao Plateau.

Date : 31-10-2025



Nafea Manea Bhlos

CERTIFICATE

I hereby certify that the above Declaration of the candidate, Nafea Manea Bhlos is true and the work was carried out under my supervision.



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Acknowledgment

The journey of completing this doctoral thesis has been one of the most challenging and rewarding endeavors of my life. It would not have been possible without the unwavering support, guidance, and encouragement of numerous individuals to whom I owe my deepest gratitude.

foremostly, I wish to express my profound appreciation to my supervisor (Prof. K. R. Priolkar). Thank you for your invaluable guidance, immense patience, and unwavering belief in me throughout this process. Your insightful feedback, constant encouragement, and intellectual generosity have been the cornerstone of this work. You have not only been a mentor, but also a great source of inspiration. For experimental assistance at XAFS beamlines, I sincerely thank Dr. Edmund Welter and Dr. Anuradha Bhogra at P65, PETRA III Synchrotron source, DESY - Hamburg.

My sincere thanks go to the members of my thesis committee, Dr. RajeshKumar Shankar Hyam and Dr. Ramesh V. Pai , for their time, thoughtful critiques and constructive suggestions, which have significantly strengthened this dissertation.

I extend my gratitude to the Goa University community for their financial support, which made this research possible.

This work would not have been the same without my colleagues and friends at the School of Physical and Applied Sciences. Thank you for creating a stimulating and collaborative environment. A special thanks to Dr. Elaine T. Dias and Dr. Bholanath Pahari for helping in the magnetization measurements.

I am indebted to all faculty of Goa University, and the staff of School of Physical and Applied Sciences, for their indispensable assistance and for always being ready to help. To my dearest friends, I thank you for your emotional support, for providing much-needed distractions, and for reminding me that there is a world outside of Heusler alloys and electron concentrations.

Finally, and most importantly, I reserve my deepest gratitude for my family. To my

parents, thank you for your unconditional love, endless sacrifices, and for instilling in me the values of perseverance and education.

To my wife Noha Inam , thank you for your endless patience, understanding and for being my pillars of strength. This achievement is as much yours as mine.

Dedicated to
My Parents

Contents

1	Introduction	1
1.1	Shape memory alloys:	1
1.1.1	Types of Shape Memory Effects:	2
1.2	Austenite and Martensite:	6
1.3	Heusler alloys:	8
1.3.1	Crystal Structure:	10
1.3.2	Electronic properties:	12
1.3.3	Magnetic properties:	14
1.4	Relation between e/a and Martensitic Transformation Temperature T_M : . .	15
1.5	Objectives:	20
	References:	24
2	Experimental Techniques	36
2.1	Introduction:	36
2.2	Sample Preparation:	36
2.3	Structural studies	37
2.3.1	Energy-Dispersive Analysis of X-ray (EDAX) spectroscopy:	37
2.3.2	X-ray diffraction (XRD):	39
2.3.3	Extended x-ray absorption Fine Structure (EXAFS):	42
2.3.4	Theoretical Foundations of EXAFS:	42
2.3.5	EXAFS Data Reduction:	45

2.4	Transport properties	46
2.4.1	Electrical Resistivity:	46
2.5	Differential Scanning Calorimetry (DSC):	47
2.6	Magnetization $M(T)$:	48
	References:	51
3	Control Parameters of Martensitic Phase Transition in Ni-Mn-Z Heusler	
	Alloys ($Z = \text{Ga, Sn}$)	55
3.1	Introduction:	55
3.2	Results:	59
3.3	Discussion:	70
3.4	Conclusion:	71
	References:	72
4	Effect of Rapid Quenching and Temper Annealing on Phase Stability	
	and Physical Properties of Ni-Mn-Z ($Z = \text{Ga, In}$)	77
4.1	Introduction:	77
4.2	Results:	79
4.3	Discussion:	85
4.4	Conclusion:	86
	References:	87
5	Role of local structural distortions in the variation of martensitic trans-	
	formation temperature with e/a ratio in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($Z = \text{In, Sn or}$	
	Sb) alloys	90
5.1	Introduction:	90
5.2	Results:	93
5.3	Discussion:	104
5.4	Conclusion:	107

References:	109
6 Effects of In doping in the martensitic alloy $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5}$	113
6.1 Introduction:	113
6.2 Results:	114
6.3 Discussion:	125
6.4 Conclusion:	127
References:	128
7 Summary and Future Work	131
7.1 Summary:	131
7.2 Future work:	134

List of Tables

3.1	EDAX composition, e/a ratio, martensitic transformation temperature (T_M) and magnetic ordering temperature (T_C) for the Ni-Mn-Ga and Ni-Mn-Sn alloys.	59
3.2	Structural phases and the respective lattice parameters for alloys.	61
3.3	Expected near neighbour environment, as per their austenitic crystal structure, around Mn and Ni atoms in the Mn-rich and Ni-rich Ni-Mn-Z alloys.	64
3.4	Local structural parameters like the type of bond, coordination number (C.N.), bond length (R), mean square disorder in bond distance (σ^2) obtained from Mn and Ni K EXAFS analysis in Ni-Mn-Ga and Ni-Mn-Sn alloys. C.N. was kept fixed at the crystal structure allowed value throughout the analysis. Bond distances belonging to the two phases in Ni-Mn-Sn alloys are separated by a horizontal line.	69
4.1	Nominal and EDAX-measured compositions of Ni-Mn-Ga and Ni-Mn-In alloys along with their e/a ratios and martensitic transformation temperatures.	79
4.2	Phase structures and corresponding lattice parameters of Ni-Mn-Ga and Ni-Mn-In alloys obtained by X-ray diffraction after rapid quenching and temper annealing, (NM) refers to non modulated tetragonal and (Hex) refers to hexagonal phase.	82

5.1	EDAX composition, e/a ratio, and the martensitic transformation temperature for $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn and Sb}$) alloys.	94
5.2	Lattice parameters obtained from Rietveld fitting for the X-ray diffraction patterns of all the alloys.	98
5.3	Bond length (R) and mean square radial disorder (σ^2) of the near neighbor correlations around Mn and Ni in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn, Sb}$) alloys. .	103
6.1	EDAX composition, e/a ratio, and the martensitic transformation temperature for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.	114
6.2	Lattice parameters obtained from Rietveld fitting for the X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.	119
6.3	Expansion of the unit cell volume with respect to x content.	120
6.4	Bond length (R) and mean square radial disorder ($\sigma^2(\text{\AA}^2)$) of the near neighbor correlations around Mn and Ni in $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.	122

List of Figures

1.1	Shape memory transformation between the austenite and martensitic phases.	2
1.2	A schematic of the shape memory effect cycle.	3
1.3	A schematic of the shape memory effect on (a) one-way, (b) two-way. . . .	5
1.4	A schematic of (a) shape memory effect, (b) Superelasticity (SE) effect. . .	6
1.5	Transformation from cubic austenite to tetragonal martensite, showing 110 plane distortion and formation of twinned plates.	8
1.6	Transformation pathways from the cubic $L2_1$ austenite phase to low-symmetry martensitic structures in Heusler Ni_2MnGa alloys. The schematic illus- trates how the parent cubic lattice distorts into modulated martensitic variants (10M, 14M) or the non-modulated tetragonal martensite, reflect- ing the reduction in crystallographic symmetry and stabilization of the martensitic phases. Adapted from [54].	12
1.7	phase diagram of Ni-rich in the Ni-Mn-Ga alloys.	17
1.8	Martensitic transformation temperature (T_M) versus e/a for Mn-rich Ni- Mn-Z alloys ($Z = Ga, In, Sn, Sb$). The four lines are for the four different Z elements. The slope increases from Ga to Sb, indicating that T_M becomes more sensitive to e/a for larger Z atoms, a trend attributed to increasing atomic size mismatch.	19

1.9	The magnetic and structural phase diagram of Ni–Mn–Z Heusler alloys with Z as (a) Ga, (b) In, (c) Sn and (d) Sb. The triangles and the circles correspond to the magnetic and martensitic transformation temperatures respectively. The regions corresponding to the different structures are separated by discontinuous lines. Small solid circles in (c) correspond to the premartensitic transition temperature. This graph has been reproduced from [69]	20
2.1	Pictures taken during the preparation of the alloy. (I) High-purity elements (Ni, Mn, Ga) are carefully weighed and placed on a copper hearth, preparing them for alloy formation. (II) The elements are melted together using an arc-melting furnace. (III) The resulting alloy button is removed from the furnace and allowed to cool. It is then cut into smaller pieces and (IV) about half of the sample is ground into a powder preparing it for further analysis or experiments. (V) Both the alloy pieces and the powder encapsulated quartz tube sealed under vacuum. (VI) The sealed quartz tubes were arranged inside the furnace for annealing.	38
2.2	Principle of Energy Dispersive X-ray Spectroscopy (SEM/EDAX)	39
2.3	The fundamental principle of Bragg diffraction	40
2.4	Schematic representation of an XAS spectrum, exhibiting absorption of the x-rays both within the 50 eV of the edge energy (XANES) and from some hundred to greater than 1000 eV energy beyond the absorption edge (EXAFS)	43
2.5	Schematic diagram of the EXAFS experimental setup	44
2.6	Diagram of four-probe resistivity	46
2.7	Differential Scanning Calorimetry (DSC) Diagram	47
2.8	DSC thermogram recorded at a heating rate of 10°C/min under nitrogen flow	48

2.9	Diagram of Magnetization $M(T)$ with $T(K)$ and $H(Oe)$	49
2.10	Schematics of (a) a DC SQUID sensor (two Josephson junctions in a superconducting loop) and (b) its integration into a SQUID magnetometer for magnetic moment measurements	50
3.1	Le-Bail refined x-ray diffraction patterns for Ni-Mn-Ga alloys recorded at room temperature.	60
3.2	Le-Bail refined x-ray diffraction patterns for Ni-Mn-Sn alloys recorded at room temperature.	60
3.3	DSC measurement of Ni-Mn-Ga and Ni-Mn-Sn alloys showing the thermal transition behavior.	62
3.4	Magnetization as a function of temperature under an applied field of 100 Oe during ZFC, FCC and FCW cycles for Ni-Mn-Ga and Ni-Mn-Sn alloys.	63
3.5	Magnitude of Fourier transforms of EXAFS (filled circles) along with the best fits (line) at the Mn and Ni K edges for Ni-Mn-Ga alloys.	67
3.6	Magnitude of Fourier transforms of EXAFS (filled circles) along with the best fits (line) at the Mn and Ni K edges for Ni-Mn-Sn alloys.	68
4.1	X-ray diffraction data for the alloys $Ni_2Mn_{1.8}Ga_{0.2}$ and $Ni_2Mn_{1.8}In_{0.2}$ in rapid quenched (RQ) and Temper annealing (TA).	80
4.2	X-ray diffraction data for the alloys $Ni_{2.46}MnGa_{0.54}$, $Ni_{2.46}MnIn_{0.54}$ and $Ni_{2.9}Mn_{0.1}Ga$, in rapid quenched (RQ) and Temper annealing (TA).	81
4.3	DSC thermogram showing the martensitic transformation behavior of alloys during heating and cooling cycles in both RQ and TA	83
4.4	ZFC, FCC and FCW curves for $Ni_2Mn_{1.8}Ga_{0.2}$, $Ni_2Mn_{1.8}In_{0.2}$ in (RQ) and (TA).	83
4.5	ZFC, FCC and FCW curves for $Ni_{2.46}MnGa_{0.54}$, $Ni_{2.9}Mn_{0.1}Ga$ in (RQ) and (TA).	84

4.6	ZFC, FCC and FCW and Resistivity curves in both sequence warming and cooling in (RQ) and (TA).	84
5.1	DSC thermograms of $\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$ $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ $\text{Ni}_2\text{Mn}_{1.34}\text{Sn}_{0.66}$ Ni_2MnSb $\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$ $\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$	94
5.2	Rietveld-refined XRD patterns of $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ ($x = 0.3\text{--}0.5$) recorded at room temperature.	95
5.3	Rietveld-refined XRD patterns of the alloys with same $e/a \approx 8.0$ recorded at room temperature.	96
5.4	Room-temperature X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($Z = \text{In}$, Sn , and Sb) alloys are presented, arranged according to their respective e/a ratios for comparative analysis.	97
5.5	Temperature-dependent magnetization (M-T) curves measured under 100 Oe applied field, showing zero-field-cooled (ZFC), field-cooled cooling (FCC), and field-cooled warming (FCW) protocols across 5 - 400 K.	100
5.6	Fourier transform magnitudes of EXAFS spectra (open circles) with theoretical fits (solid lines) for Ni and Mn K edges in Ni-Mn-In alloys.	101
5.7	Fourier transform magnitudes of EXAFS spectra (open circles) with theoretical fits (solid lines) for Ni and Mn K edges in Ni-Mn-Sn and Ni-Mn-Sb alloys.	102
5.8	Difference in the second nearest neighbor Mn-Z and Mn-MnZ as a function of e/a ratio in the Ni-Mn-Z alloys.	105
5.9	Variation of the nearest neighbor Ni-Mn and Ni-Z bond distances in the Ni-Mn-Z alloys as a function of e/a ratio.	106
6.1	Differential Scanning Calorimetry (DSC) curves for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), showing the martensitic and reverse transformations during heating and cooling.	115

6.2	the relation between x contents and martensitic transformation temperature T_M	116
6.3	XRD pattern of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2$) with Rietveld refinement. The observed data are shown as black points, the calculated profile as a red line, and the difference between them as a blue line. Bragg reflection positions are marked below the pattern.	117
6.4	XRD pattern of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.3, 0.4, 0.5$) with Rietveld refinement. The observed data are shown as black points, the calculated profile as a red line, and the difference between them as a blue line. Bragg reflection positions are marked below the pattern.	118
6.5	The relationship between unit cell volume and the martensitic transformation, showing that an increase in unit cell volume is associated with changes in the crystal structure.	120
6.6	the ZFC and FC $M(T)$ curves for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys in a magnetic field of 100 Oe.	121
6.7	The magnitude of Fourier transform of the EXAFS spectra recorded at 300 K at the Ni K and Mn K edges for the alloys $x = 0.0$, $x = 0.1$ and $x = 0.2$ in the series $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$	123
6.8	The magnitude of Fourier transform of the EXAFS spectra recorded at 300 K at the Ni K and Mn K edges for the alloys $x = 0.3$, $x = 0.4$ and $x = 0.5$ in the series $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$	124
6.9	The variation of Ni-In and Mn-In bond distances with x contents.	126

Chapter 1

Introduction

1.1 Shape memory alloys:

Shape-memory alloys (SMAs), a class of smart materials, can undergo significant deformation before returning to their original state (size or shape) when subjected to pressure, or magnetic field (if the alloys are magnetic) when thermally cycled across their critical temperature. A reversible, diffusion-free solid-state phase transition between two distinct crystalline phases is the basic mechanism underlying this extraordinary behavior, called as the shape memory effect. Firstly, in 1932, Arne Olander made observations of this phenomenon in (Au-Cd) alloys [1], and in 1941, Vernon officially came up with the term "shape memory" [2]. The history of shape memory alloys begins with this. Modern shape memory alloy technology was made possible by William Buehler and Frederick Wang's seminal discovery of the pronounced effect in a nickel-titanium alloy in 1962 [3,4]. As a result, the technological applications of these materials have proliferated, driving demand across various engineering domains. Its special qualities are now utilized by a wide range of sophisticated and commercial industries, including the automotive, and aerospace [5–8], and the micromotor and microelectromechanical systems (MEMS) sector. The shape memory effect is experimentally observed through a crystal transition between a low-temperature, low-symmetry martensite phase and a high-temperature, high-symmetry

austenite phase [9,10] which is represented by the martensitic start temperature M_s and the martensitic finish temperature M_f , and the austenitic start temperature A_s and the austenitic finish temperature A_f , during the warming cycle [11] as shown in Figure 1.1.

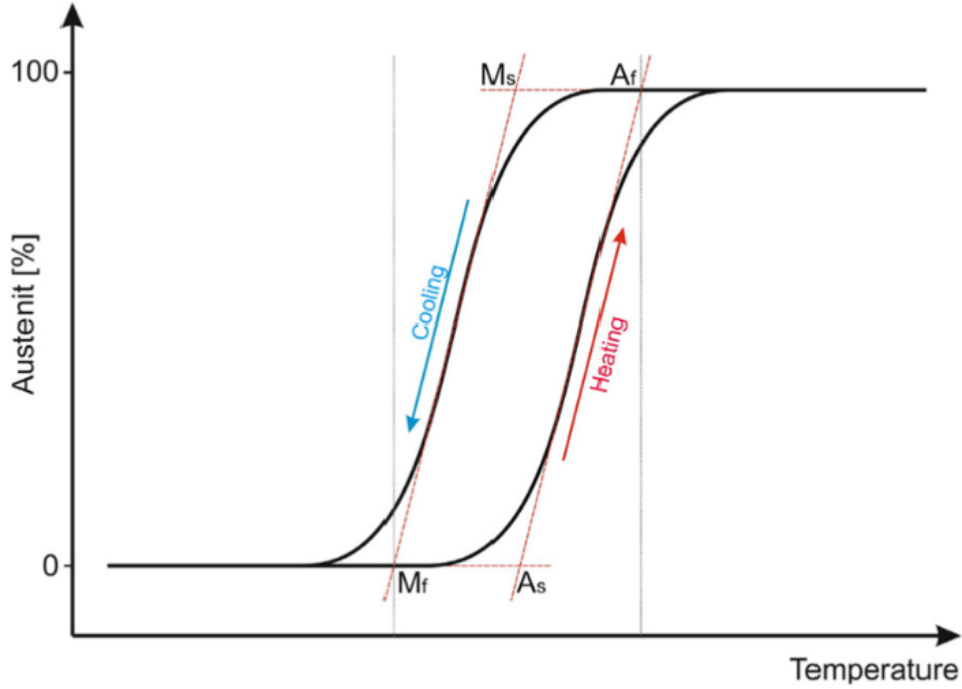


Figure 1.1: Shape memory transformation between the austenite and martensitic phases.

Two other martensite phase states are a self-adapting dual structure and an untwisted, distorted, and reoriented structure. The transition from the austenite phase to the martensite phase occurs when the material cools, and it reverses when the material heats up. This is because the austenite phase is thermodynamically stable at higher temperatures, while the martensite phase is stable at lower temperatures. Figure 1.2 shows the effect of shape memory [12].

1.1.1 Types of Shape Memory Effects:

Essentially, the shape memory effect occurs in two distinct phases of the crystal structure, including twinned, detwinned martensite, and austenite. is plastically deformed in its martensitic state, its original shape can be regained by simply heating it across its phase

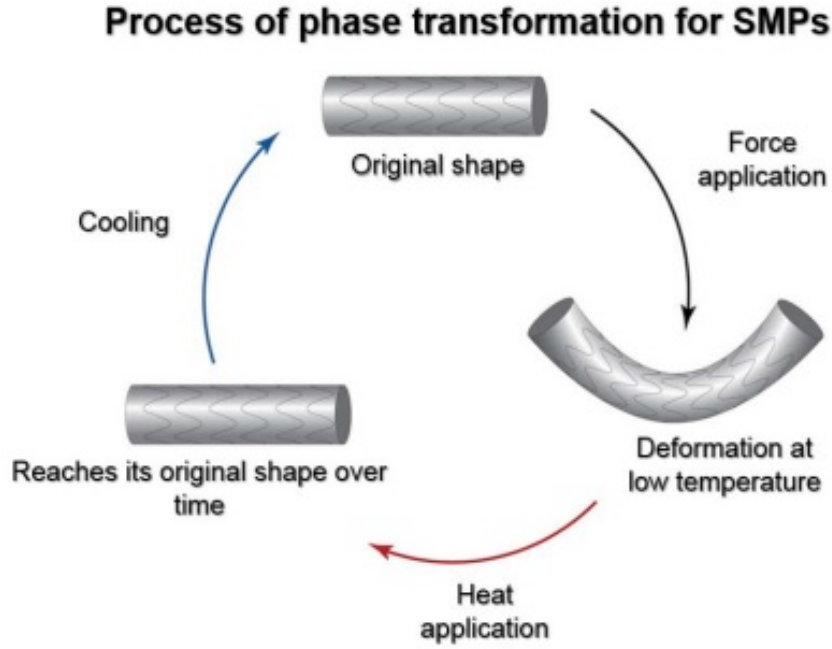


Figure 1.2: A schematic of the shape memory effect cycle.

transition temperature to austenitic state. It retains this shape even after cooling back to martensitic state. This transformation is possible even under high applied loads, resulting in high energy densities of the actuator [13]. The shape memory effect (SME) and pseudoelasticity (or superelasticity) are characterized by three fundamental behaviors.

1. One-Way Shape Memory Effect:

The effect of one-way shape memory can be defined as the ability of the material to recover its original shape when heated above a critical temperature, which is a fundamental thermodynamic behavior. A reversible, diffusionless solid-state phase transition between a low-symmetry martensite phase, and a high-symmetry austenite phase, which is stable at higher temperatures, controls this phenomenon. Twinned martensite, which is formed when the material is cooled below M_f , initiates the process. To accommodate significant strain, martensite variants undergo detwinning and reorientation due to mechanical deformation at temperatures lower than the A_s . Because the martensitic transformation is crystallographically reversible, while

heating above the A_f results in a reverse transformation that restores the parent austenite phase and the original shape [14, 15]. At higher temperatures, the intrinsic thermodynamic instability of deformed martensite drives the restoration process, leading to the spontaneous recovery of the original crystallographic structure [16].

2. Two-Way Shape Memory Effect:

The second type of shape memory effect is the two-way shape memory effect. The memory effect refers to a sophisticated thermomechanical behavior in which a material exhibits reversible shape changes between two distinct configurations during thermal cycling, independent of mechanical intervention. This transformation behavior is defined by the instantaneous transition to one-way shape memory when cooling below the M_f with a different alloy shape when heating above the A_f . The two-way effect, intrinsic and self-actuating, contrasts with the one-way effect, which necessitates external deformation to achieve a temporary shape. This feature gives the advantageous two-way effect for actuator applications [15]. The technique involves establishing a preferential internal stress field, typically achieved through thermomechanical training processes, including repeated deformation cycles or constrained aging [17]. This training presents stabilized lattice defects, dislocations, or precipitates that influence the formation of specific martensite variants during cooling, resulting in a macroscopic shape change [18]. Upon heating, recovery of the austenite phase predominates, restoring the material to its high-temperature state. The effect of Two-way shape memory is not an essential characteristic of original shape memory alloys [19]; rather, it is induced by particular processing techniques that deactivate the symmetry of the phase transformation, facilitating controlled and reversible motion. This effect is primarily for applications that necessitate repeated actuation solely driven by thermal cycles, including micro-positioning systems and adaptive structures [20]. Figure 1.3 shows the effect of shape memory on one-way and two-way transformations [21].

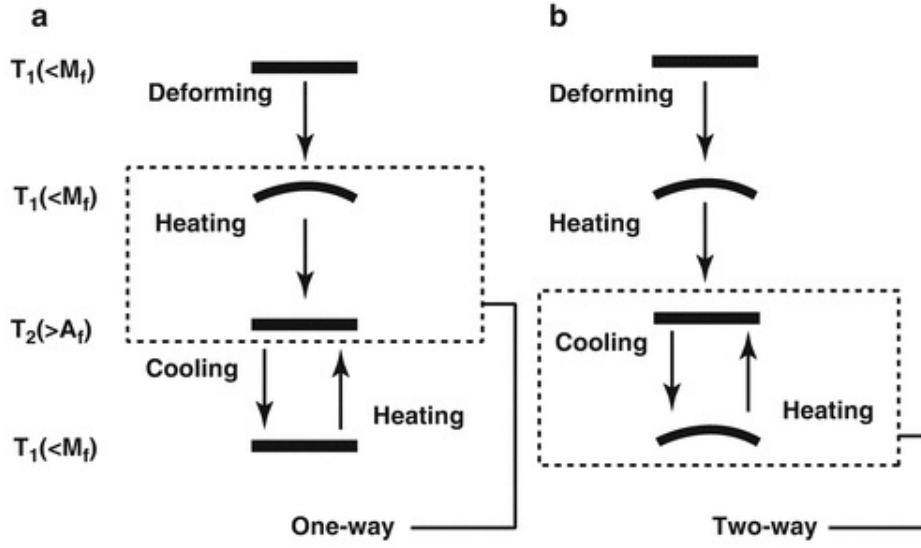


Figure 1.3: A schematic of the shape memory effect on (a) one-way, (b) two-way.

3. Pseudoelasticity (PE) or Superelasticity (SE):

One of the features of the shape memory features occurs when it is in the Austenite phase at high temperatures above the A_f [17]. This phenomenon is fundamentally distinct from the one-way shape memory effect, as it involves a fully mechanical, isothermal cycle where applied stress alone induces a reversible phase transformation without requiring a change in temperature. Here, the applied stress transforms the high-temperature austenite phase into stress-induced martensite (SIM) [18], accommodating significant strain—often up to (8-10%) in alloys like NiTi. This deformation is not plastic in the conventional sense, but rather results from a crystallographic reorganisation into a detwinned martensitic structure. While unloading the mechanical stress, the martensite phase becomes an unstable phase, which leads to the alloy returning to its original shape in the austenite state [15]. This difference in the curve transformation, observable as hysteresis in the stress-strain region, is repeatable over thousands of cycles, making pseudoelastic SMAs exceptionally valuable in applications that demand large elastic deformation ranges, such as biomedical implants, including self-expanding stents and archwires and seismic

dampers in civil engineering [22]. Figure 1.4, displays the shape memory effect and the Superelasticity (SE) effect of Ni-Ti alloy [23].

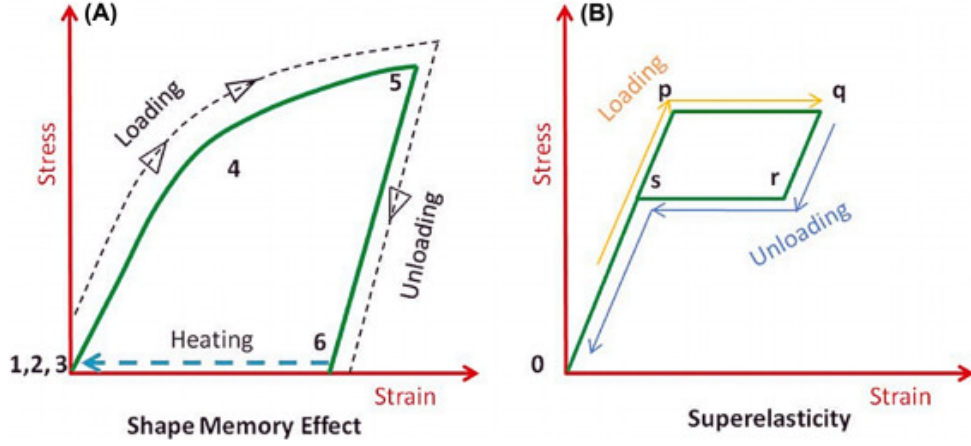


Figure 1.4: A schematic of (a) shape memory effect, (b) Superelasticity (SE) effect.

1.2 Austenite and Martensite:

The unique functional behavior of shape memory alloys stems from the way they transition between the austenite and martensitic phases. The high-temperature phase is austenite, which means that it remains stable at high temperatures and usually has a cubic structure with high symmetry ($B2$ or $L2_1$). But when the temperature drops, the parent lattice structure becomes less stable and quickly changes to a martensite phase at the martensitic start temperature M_s . The crystal structure of the lower symmetry phase is usually a tetragonal ($L1_0$), orthorhombic, or monoclinic and changes through a diffusionless, displacive mechanism [24]. Atomic changes occur in a coordinated manner without long-range diffusion, leading to a rapid and thermally driven change. The Bain strain model, which shows how the cubic lattice changes in a uniform way by compressing one axis and expanding the other two [25, 26] as shown in Figure 1.5. This change in crystal keeps some of the orientation relationships, which keeps a huge amount of stress on the material. The martensite phase makes several variations related to symmetry and is grouped as finely spaced twinned structures to handle this strain [26]. This creates

a microstructure that can change and keeps the shape of the original grain. The delicate energy balance between the twins changes when the alloy is mechanically loaded. This causes detwinning, which is when variations that are more favorable go up and those that are less favorable go down because the twin boundary moves. This change in orientation creates macroscopic strain without any dislocation motion, which leads to a reversible deformation. When the load is removed or the temperature starts to increase above the austenite finish temperature A_f , the detwinned martensite returns to its original structure as austenite. This reversible change is what makes the shape memory effect and superelasticity possible [27–29]. The habit plane, which is a mostly undistorted and unrotated intermolecular contact between austenite and martensite, is very important for transformation reversibility. The compatibility of the Bain strain with lattice-invariant shears (e.g., twinning or slide), as delineated by the Phenomenological Theory of Martensite (PTMT), gives rise to this phenomenon. The reversibility of the martensitic transformation, which is fundamental to the shape memory effect [30], is governed by the crystallographic compatibility between the austenite and martensite phases. The precise lattice correspondence ensures a low-energy transformation pathway characterized by minimal irreversible slip, thereby guaranteeing complete reversibility upon heating.

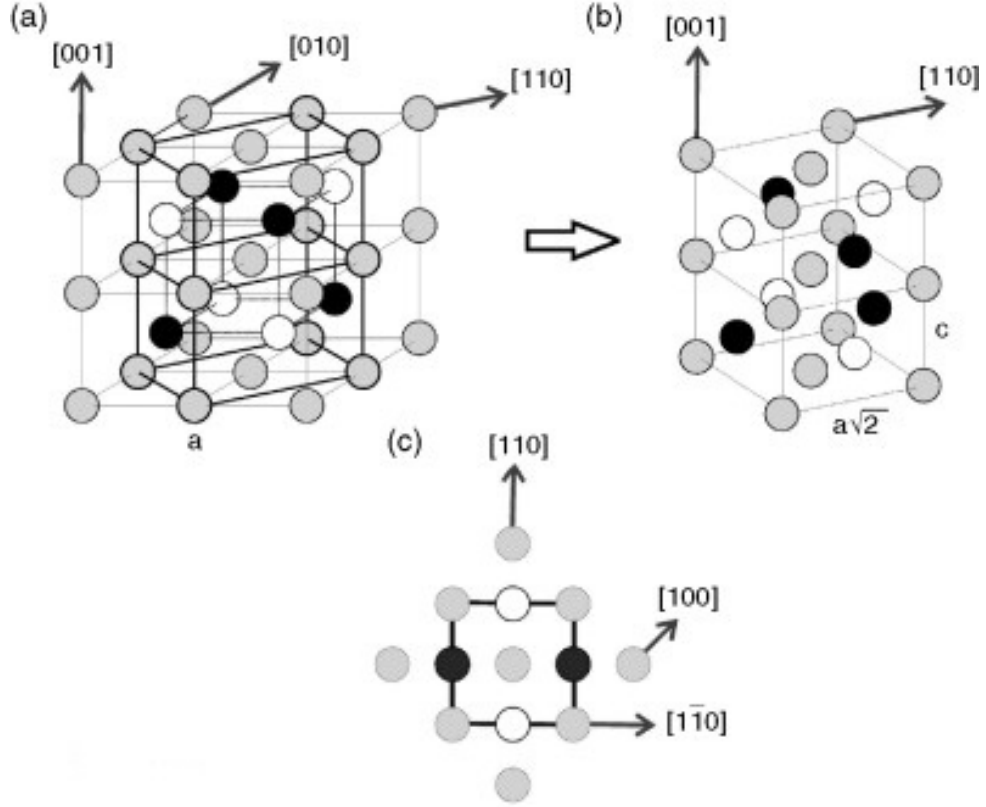


Figure 1.5: Transformation from cubic austenite to tetragonal martensite, showing 110 plane distortion and formation of twinned plates.

1.3 Heusler alloys:

Heusler alloys are ternary magnetic intermetallic compounds that crystallize in structure $L2_1$ and are generally expressed by the formula X_2YZ . The designation comes from the German mining engineer and chemist Friedrich Heusler, who investigated the alloy Cu_2MnSn in 1903 [31].

In Mn-based alloys, the Y element is often manganese, the X element is a transition metal such as cobalt, nickel, copper, or palladium, and the Z element is from Group III-V, including aluminum, gallium, silicon, tin, indium, or antimony. Magnetism in intermetallic alloys has been a prominent focus of substantial first-principle calculations, garnering increasing interest over time [32–34].

In the Heusler composition X_2YZ , where the X and Z elements are non-magnetic,

magnetization is predominantly restricted to the Mn sublattice. When the element X is cobalt or nickel, an extra magnetism manifests itself at the cobalt or nickel sites [35]. These alloys provide a distinctive opportunity to investigate manganese compounds in which the Mn atom is exclusively surrounded by other transition metals (X) as nearest neighbors and non-transition elements (Z) in the second coordination sphere. They are conventionally regarded as local moment systems, with the arrangement of the moments facilitated by the indirect exchange interaction of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type, mediated by the system's free electrons [36, 37]. First-principle band-structure computations for these alloys indicate that the 3d majority-spin levels of Mn are occupied and hybridize with the 3d states of the X atom, whereas the minority-spin 3d states of Mn reside above the Fermi level. The calculations indicated that, along with the long-range Mn-Mn interactions, the short-range magnetic X-Mn interaction is crucial for systems with significant magnetic moments on the X atoms, such as Co and Ni [32, 38]. These interactions not only facilitate the Mn-Mn interactions but also contribute to the establishment of the magnetic state. Recent comprehensive studies on Mn-based Heusler alloys, particularly those with $X = \text{Ni}$, have attracted considerable global attention [39]. The observation of a martensitic structural phase transformation within the ferromagnetic state of Ni_2MnGa has opened the field of magnetic shape memory technology. Since the discovery of ferromagnetic shape memory alloys (FSMA), several commendable evaluations have already emerged [40, 41]. For instance, the magnetically generated stresses in Ni-Mn-Al samples reached only 0.1% at a field strength of up to 7 T [42, 43]. The magnetic ordering of Ni-Mn-Al alloys is significantly influenced by the chemical ordering of the high-temperature phase, which varies with thermal treatment. Quenched samples possess a B2 structure of the austenite phase and display either antiferromagnetism or a spin glass state. The aging of samples post-quenching results in the development of the $L2_1$ structure of the austenite phase, characterized by ferromagnetic ordering with a Curie temperature T_c of around 330 K [44]. Ni_2MnAl possesses superior ductility and a greater structural transition temperature compared to Ni_2MnGa . The Ni-Mn-Ga alloys are ex-

tensively researched among other FSMA and serves as a prototype for the development of new FSMA. Consequently, the ensuing discussion of Ni-Mn based FSMA will primarily concentrate on the features demonstrated by the Ni-Mn-Ga system. Prior to further discussion on the physical features of these alloys, it is pertinent to note the importance of chemical composition of Ni-Mn-Ga Heusler alloys. Nearly all characteristics of these alloys demonstrated significant sensitivity to the chemical composition of the samples. The composition of the sample significantly influences the temperatures of phase transitions and the development of superstructures in both the austenite and martensite states. In general, magnetic shape memory alloys show a large change in magnetization when they change from the high-temperature austenite phase to the low-temperature martensite phase. For example, the magnetic transformation from ferromagnetic austenite to paramagnetic or antiferromagnetic martensite [45]. There is always a strong connection between the structural and magnetic configurations of the austenite and martensite phases. Magnetic transformation may occur in either the austenite or martensite phase, depending upon the alloy and its chemical composition. It is important to note that the martensitic transformation temperature and magnetostructural properties are affected by variations of the chemical composition alloys, such as doping of extra elements in the Heusler alloys [46–48].

1.3.1 Crystal Structure:

Fritz Heusler demonstrated that a material mixture with the chemical formula Cu_2MnAl exhibited ferromagnetic properties, despite being composed of non-magnetic elements. Ferromagnetic behavior is achieved via RKKY interaction between the third nearest neighbour Mn atoms mediated through the conduction electrons. The L2_1 structure is the most ordered structure of the X_2YZ Heusler alloys and is susceptible to site occupancy disorder. In a typical Heusler alloy, the X atoms occupy the $(0.25, 0.25, 0.25)$ and $(0.75, 0.75, 0.75)$ sites while the Y and Z atoms form a rock salt arrangement by occupying the $(0, 0, 0)$ and

(0.5,0,0) positions respectively. This subsequently results in the development of disordered phases. Based on the site occupation of X, Y and Z atoms, it is possible for other crystalline phases to emerge, including the fully disordered A2 phase and the partially disordered B2 and D03 phases. A random occupation disorder between the Y and Z atoms generates the B2 structure. While, the D03 structure is formed when the X and Y atoms are exchanged places in the unit cell. When every atom occupies a position in the unit cell at random, the completely disordered A2 phase takes place. Further, a 100% spin polarization is predicted from the band structure calculations performed on these Heusler alloys. The high degree of band polarization results in half metallic characteristics and potential applications in spintronics. [49].

Some of the Heusler alloys, especially those containing Mn are prone to a martensitic transformation. During cooling below the martensitic start temperature the structure begins to transform from high temperature structure high-symmetry structure to the low-symmetry structure due to the electronic, vibration and the elastic instabilities, resulting in a non modulated diffusionless shear distortion of the lattice structure, this process reduces the crystallographic symmetry and transform to the tetragonal (NM), Orthorhombic, or a modulated structure with a periodicity of modulation extending over 5 unit cells (5M) or 7 unit cells (7M), depending on the alloy chemical composition and the heat treatment conditions [50, 51]. These modulations can even be incommensurate with the lattice periodicity. This transformation entails coordinated shifts of atomic planes, lattice shear, and local distortions of the tetrahedral environments, which relieve elastic instabilities while preserving overall chemical order. Despite its small macroscopic volume change, the transformation induces a pronounced anisotropic distortion, generating substantial internal strain that is accommodated by forming multiple martensite variants or twins [52]. These changes in the crystal structure will decrease the elastic energy of the distorted lattice, resulting in a stable martensitic phase. The initiation of the transformation is often linked to the band Jahn–Teller mechanism, which is splitting the electronic states around the Fermi level energy is energetically favorable the lower-symmetry distorted

structures over the parent austenite phase [53]. Consequently, the transformation from cubic $L2_1$ to the martensitic state emerges from the delicate interplay of electronic structure, tetrahedral distortion, and crystallographic symmetry reduction. Figure 1.6 shows the martensitic transformation in Ni_2MnGa Heusler alloys, adopted from [54].

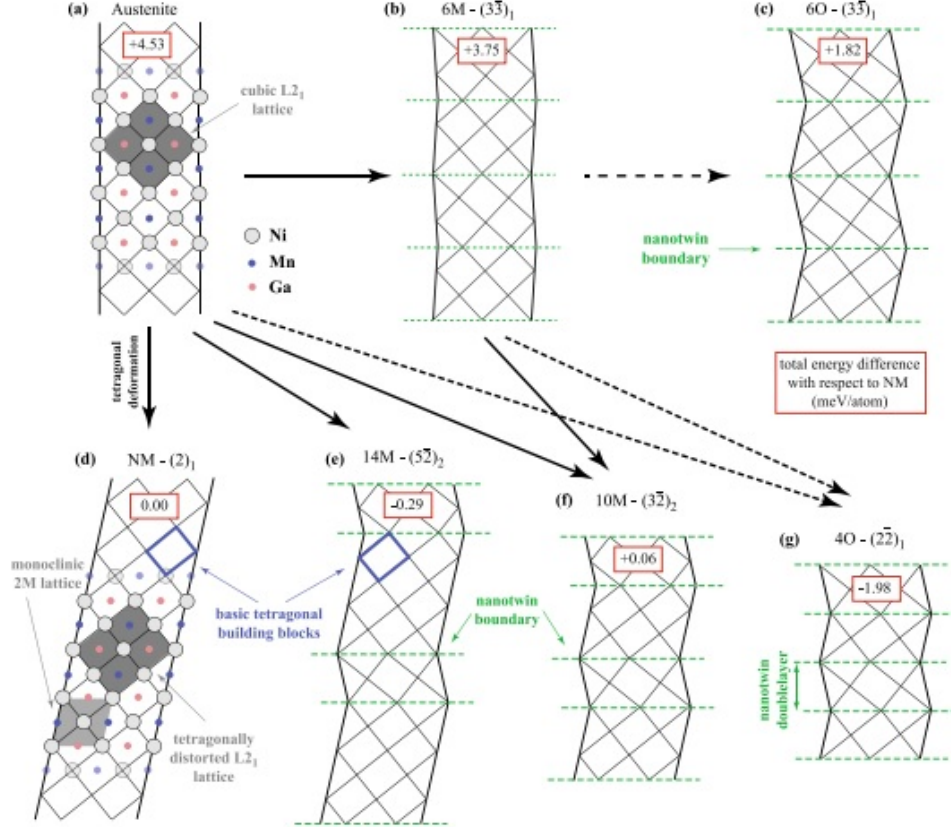


Figure 1.6: Transformation pathways from the cubic $L2_1$ austenite phase to low-symmetry martensitic structures in Heusler Ni_2MnGa alloys. The schematic illustrates how the parent cubic lattice distorts into modulated martensitic variants (10M, 14M) or the non-modulated tetragonal martensite, reflecting the reduction in crystallographic symmetry and stabilization of the martensitic phases. Adapted from [54].

1.3.2 Electronic properties:

Heusler alloys are distinct metallic systems, and the band structure calculations accurately represent their uniqueness, extensively addressed the hybridization characteristics and corresponding binding mechanisms of several Heusler alloys [55]. The calculations indicate

that the 3d majority-spin states of Mn are occupied and hybridized. The 3d state of X atom exist within the minority spin 3d states of Mn atom, which are located above the Fermi level energy. In addition, the p electrons of the Z atom are combined with the d electrons of the transition metals, exhibiting a filled band at the Fermi level [38]. The electronic structure of Ni_2MnGa reveals the peak in the density of states at the Fermi level, it was proposed that the redistribution of electrons around the Fermi level is the catalyst for the phase transition [56, 57]. The decrease in free energy from the re-population of these bands may surpass that necessary to induce the lattice distortion, making such a change energetically advantageous. Nonetheless, the bands operating at the Fermi surface are not discernible in the density of states DOS curves provided in this simulation. The Fermi level E_F is positioned slightly above a peak in the local DOS of the minority-spin Ni e_g band, while for the Mn band, E_F is located where the local DOS of majority and minority t_{2g} states is about equal. Upon structural deformation, the peak in the minority Ni conduction band is bifurcated, but minimal alteration is observed in the Mn bands around the Fermi surface. The closeness of Ni and Ga atoms results in the hybridization of Ni d states with Ga p states. The peak at E_F consists of the partially filled bands resulting from $p - d$ hybridization. The Ga atoms, which provide p electrons, create energetically favorable hybrid states with the d electrons of Ni. These states produce a maximum in the spin-down electronic density of states precisely at the Fermi level. The $p - d$ connection is thought to be covalent in nature. The alteration of the crystal structure induces the polarizability of the electron cloud between Ga 4p and Ni 3d states, leading to covalent connections between them. The phenomenon of electronic hybridization in Ni_2MnGa is examined through a basic model. The L_{21} state of Ni_2MnGa is characterized by four interpenetrating face-centered cubic lattices, with Ni atoms positioned in a body-centred (CsCl-type) configuration. This results in the alignment of the Ni-3d states with the associated crystal field. The Fermi level of Ni_2MnGa is situated within the trough of antibonding minority spin 3d states of Ni, indicating a precarious condition. The system circumvents this by undergoing a martensitic metamorphosis, including modulated

structures [41, 58]. Ni shows a larger change in magnetic moments compared to Mn, accompanied by a minor redistribution of moments [59]. The symmetry modification in alloys is accompanied by a magnetization distribution in the alloy that follows a band Jahn–Teller process, wherein unpaired electrons are redistributed among the 3d sub-bands with different symmetries due to lattice distortion. In the cubic phase, these unpaired electrons predominantly occupy states with overall e_g symmetry. During the tetragonal phase transition, the degeneracy of the e_g and t_{2g} bands is lifted, causing a redistribution of unpaired electrons that allows them to cross the Fermi level, thereby lowering the band energy. This structural transformation is driven by the Jahn–Teller band mechanism [60].

1.3.3 Magnetic properties:

The Heusler alloys Ni_2MnZ ($Z = \text{Al, Ga, In, Sn, Sb}$) display a ferromagnetic ground state with a Curie temperature, T_C , just above room temperature. Among these alloys with $Z = \text{In, Sn and Sb}$ do not undergo a martensitic transformation. Magnetization as a function of temperature and magnetic field are typical of a soft ferromagnet with magnetic moment saturating to a constant value at 1T field [61–63]. Ni_2MnGa orders ferromagnetically at $T_C = 373 \text{ K}$ [64,65]. In its ferromagnetic state, the alloy undergoes a martensitic transformation from L2_1 cubic phase to 5M modulated monoclinic phase [66]. At the martensitic transformation, the ferromagnetic order is retained making it one of the few ferromagnetic shape memory alloys. The shape memory effect arises due to increase in magnetic anisotropy in the martensitic phase. The tetragonal distortion induced due to martensitic transformation supports the reorientation of martensitic twins under the magnetic field [67,68]. The martensitic transformation temperature and the crystal structure of the martensitic phase are critically dependent on the stoichiometry of the alloy. The transformation temperature scales with average valence electron per atom (e/a) ratio. A small change in stoichiometry leading to higher e/a ratio leads to convergence of T_M and T_C giving rise to a large magnetocaloric effect at temperatures

just above room temperature (~ 330 K) making it versatile for applications in magnetic refrigeration [69, 70].

Martensitic transformation can also be induced in other Ni-Mn-Z ($Z = \text{In, Sn, Sb}$) alloys by realizing alloys of the type $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$. Presence of Mn in the Z sub-lattice gives rise to antiferromagnetic interactions between the second nearest neighbour Mn atoms. Unlike Ni-Mn-Ga, these Mn-rich Ni-Mn-Z alloys display inverse magnetocaloric effect [62, 71]. Initial theoretical calculations indicated RKKY interactions to be the cause of these AFM interactions [72, 73]. However, XMCD and EXAFS studies highlighted the role of Ni in AFM interactions in these Mn-rich intermetallics [74, 75]. EXAFS studies in particular showed the presence of local structural distortions [76–78]. Recently, temper annealing treatment brought out the metastability of these alloys and showed that these alloys disintegrate into L2_1 Ni_2MnZ Heusler and L1_0 NiMn phases [79]. Presence of such ferromagnetic and antiferromagnetic structural units in these Mn-rich Ni-Mn-Z alloys results in a complex magnetic ground states like super spin glass, cluster glass, etc. [80]. The magnetism of these alloys is distinctly different from Ni-Mn-Ga alloys.

1.4 Relation between e/a and Martensitic Transformation Temperature T_M :

The martensitic transformation temperature in Heusler alloys is influenced by the integration of electronic, magnetic, structural, and external forces. Generally, parameters such as the number of valence electrons per atom (e/a), atomic ordering, lattice instabilities, chemical composition, magnetic interactions, applied stress, cooling rate, presence of impurities, thermomechanical treatments, and external fields determine the stability of the austenite phase and the onset of martensite transformation [81–83]. Ni-Mn-Ga is widely regarded as a model system for elucidating the fundamental principles governing martensite transformations in Heusler alloys. In particular, the clear and predictable effect of

the e/a ratio on T_M observed in this system provides a crucial framework for analyzing and predicting phase stability in more complex quaternary alloys. Mathematically, the number of valence electrons per atom can be calculated by the following equation:

$$\frac{e}{a} = \frac{(10 \times \text{Ni}_{\text{at}\%} + 7 \times \text{Mn}_{\text{at}\%} + 3 \times \text{Ga}_{\text{at}\%})}{(\text{Ni}_{\text{at}\%} + \text{Mn}_{\text{at}\%} + \text{Ga}_{\text{at}\%})} \quad (1.1)$$

In general, the e/a ratio can be modified by increasing the number of each atom in the chemical composition of the alloys; for Ni-Mn-Ga alloys, it can be divided into two types, Ni-rich and Mn-rich, which can be defined as the substitution of Ni on both Mn and Ga sides, and for the case of Mn-rich, only Mn adds by the Ga side. Figure 1.7 shows the relationship between the ratio e/a with the martensitic transformation temperature and the magnetic transition in Ni-rich Ni-Mn-Ga alloys. The graph has been adopted from [41]

In Ni-rich Ni-Mn-Ga systems, the e/a ratio plays a role in controlling the martensitic transformation temperature, the first-order transformation temperature, which is denoted as T_M , and the magnetic transformation, which is denoted as T_C , both have been plotted as functions of the e/a ratio. When the Fermi surface of the alloys approaches the Brillouin zones, the martensitic transformation occurs [64]. The substitution of Ni as given in the above diagram leading to linear increasing the T_M from 200 K when $x = 0$ to 550 K at $x = 0.42$ with e/a ratio ≈ 8.2 . This linearity is a hallmark of a rigid-band-like filling mechanism, where the added electrons populate the existing band structure, shifting the Fermi energy to a region where the martensite's electronic energy is lowered more productively than that of the austenite [84]. The behavior of Ni-rich Ni-Mn-Ga alloys can be divided into three regions. When the nickel content is between 0.0 and 0.16, the transformation will occur in the ferromagnetic region, since the Curie temperature (T_C) is higher than the martensitic transformation temperature (T_M). However, when the nickel content is equal to 0.27, the martensitic transformation temperature will be $T_M = T_C$, which exhibits strong hysteresis due to coupled magnetostructural transformation [85,86].

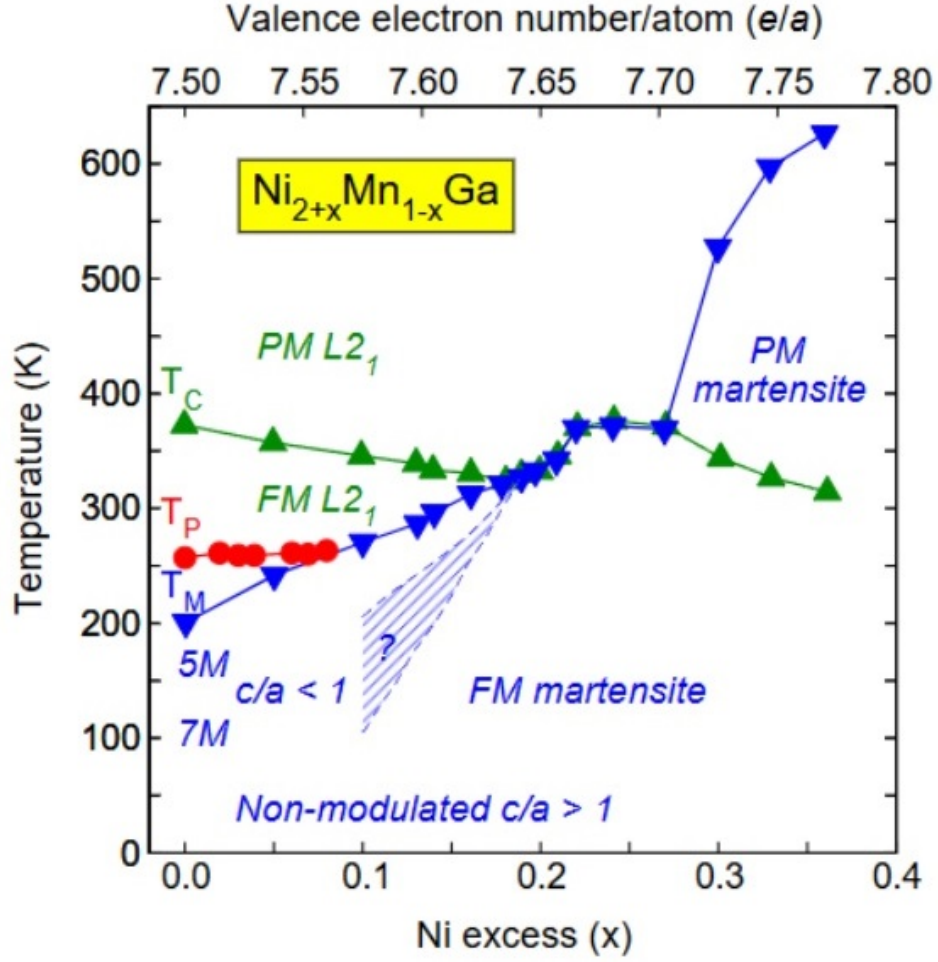


Figure 1.7: phase diagram of Ni-rich in the Ni-Mn-Ga alloys.

As can be seen in Figure 1.7, in the case of nickel-rich Ni-Mn-Ga alloys, when the nickel content increases, T_M increases sharply with the x content. When the Ni concentration is equal to or greater than 0.3, the transformation will shift to the paramagnetic state. As reported in previous neutron diffraction studies, the magnetic moment of Ni_2MnGa is mainly controlled by the Mn ions, which have a magnetic moment of $4\mu_B$ and are oriented along the $[111]$ plane. This value is greater than the magnetic moment of Ni ions in the compound, which is about $3\mu_B$ [87]. This is why $T_C = 376$ K in stoichiometric Ni_2MnGa . When increasing the content of Ni, the location of Mn will be replaced by the extra Ni, resulting in an increase in the distance between Mn and Mn, which will then lead to a decrease in the interaction between Mn and Mn, which will then result in a decrease in

T_C to 376K, and will merge with T_M [88–90]. Because of the increase in the concentration of manganese (Mn) in the stoichiometric structure, the interaction between manganese atoms (Mn-Mn) will be high in nickel-manganese-gallium alloys (Ni-Mn-Ga) that are rich in manganese. This will cause the magnetic transition temperature to shift to more than 376 K. The structure of Ni_2MnGa alloy is known to be composed of Ni atoms that occupy the corners of the unit cell, while Mn and Ga atoms are located in the center of the unit cell [91]. while, the excess amount of Ni atoms will be placed at the location of the Mn position in the center of the unit cell during the transformation to the tetragonal structure, which will be accompanied by a rise in T_M [92].

In case of Mn-rich Ni-Mn-Z (Z=In, Sn, Sb), the martensite transition temperature, known as T_M , and the magnetic transformation temperature, known as T_C , exhibit a similar behavior in relation to the e/a ratio, which starts at $e/a \approx 7.9 - 8.0$ [61,62]. The relationship between e/a and the transition temperatures is illustrated in Figure 1.8. The variability of the e/a ratio in Ni-Mn-Ga begins around 80 K for every 0.1 units, while for other elements of Z, such as Sb, this occurs at 270 K for every 0.1 units. This could be attributed to the fluctuation in composition of approximately 2 to 5%. Every Z atom possesses a unique crystallographic structure, as demonstrated by various research using X-ray diffraction (XRD). However, when Ni and Mn are alloyed with these atoms, the binding force will vary depending on the kind of Z atom used [69]. When the valence of electrons per atom (e/a) changes, the value of M_S also changes. These changes in M_S will have an impact on the value of T_C , which will subsequently cause a decrease in T_C in the austenite state. This decrease in T_C is a result of weakening of the ferromagnetic coupling as the manganese content in the composition of the alloy increases. The increase in manganese content will also result in a reduction in the distance between manganese atoms, leading to the appearance of antiferromagnetism and a further decrease in T_C . Ni-Mn-Z structural transformation occurs when the unit cell lattice is approximately 6 Å or less in size. However, the crystal structure of the alloy changes as a result of the addition of additional elements to the alloys, which may also have an impact on the martensitic

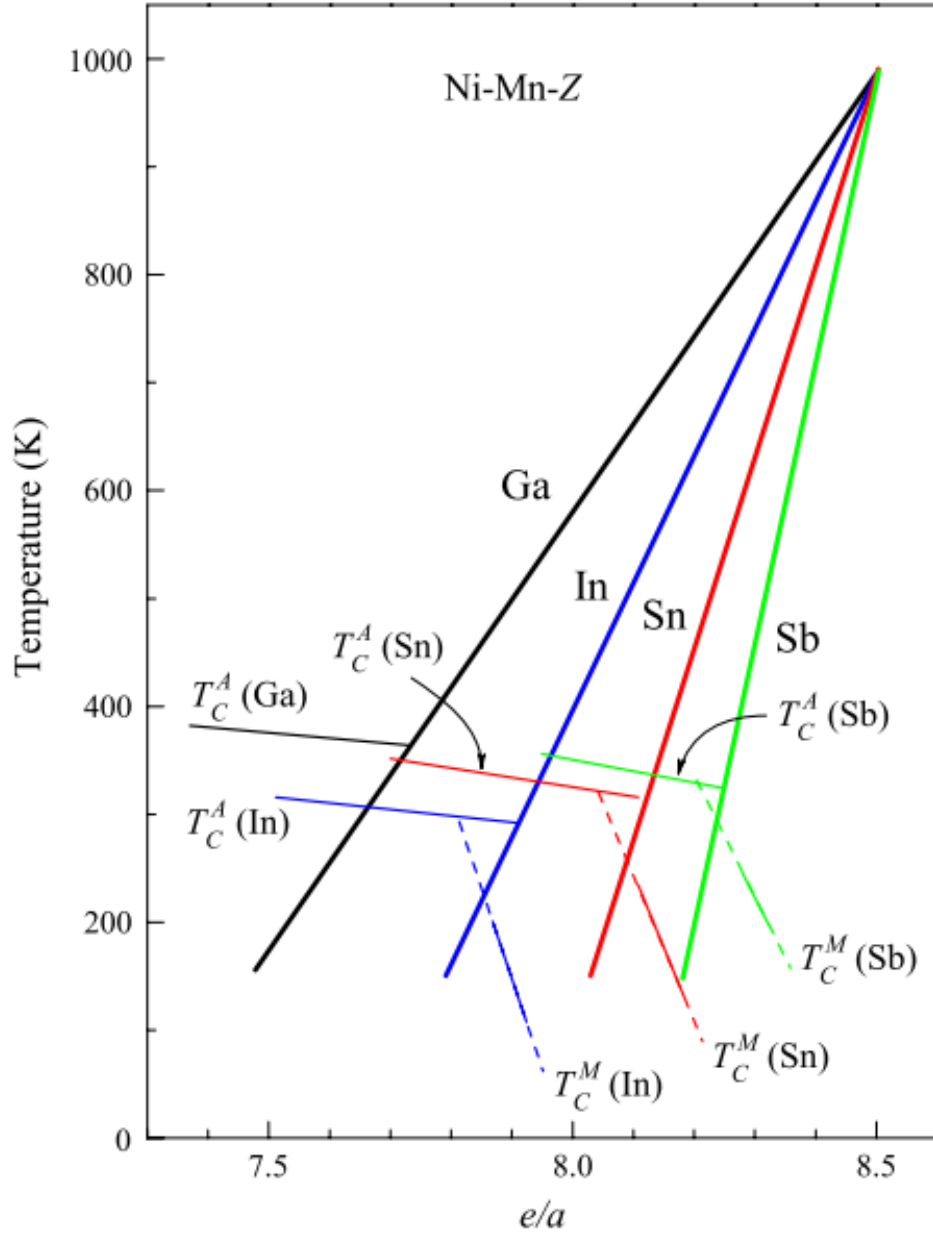


Figure 1.8: Martensitic transformation temperature (T_M) versus e/a for Mn-rich Ni-Mn-Z alloys ($Z = \text{Ga, In, Sn, Sb}$). The four lines are for the four different Z elements. The slope increases from Ga to Sb, indicating that T_M becomes more sensitive to e/a for larger Z atoms, a trend attributed to increasing atomic size mismatch.

transformation because the atoms of the various elements are of different sizes [93].

1.5 Objectives:

The main motivation of the present work is to identify the factors that infer the martensitic transformation temperature T_M in Ni-Mn based Heusler alloys and understand the behavior of these factors such as the number of valence electrons per atom e/a ratio, phase separation in the alloys and the effect of doping additional elements in the crystal structure of these alloys. Figure 1.8 shows the magnetic and martensitic transition temperatures of the Ni-Mn-Z Heusler alloys ($Z = \text{Ga, In, Sn, Sb}$) plotted as a function of the average valence electron concentration per atom (e/a).

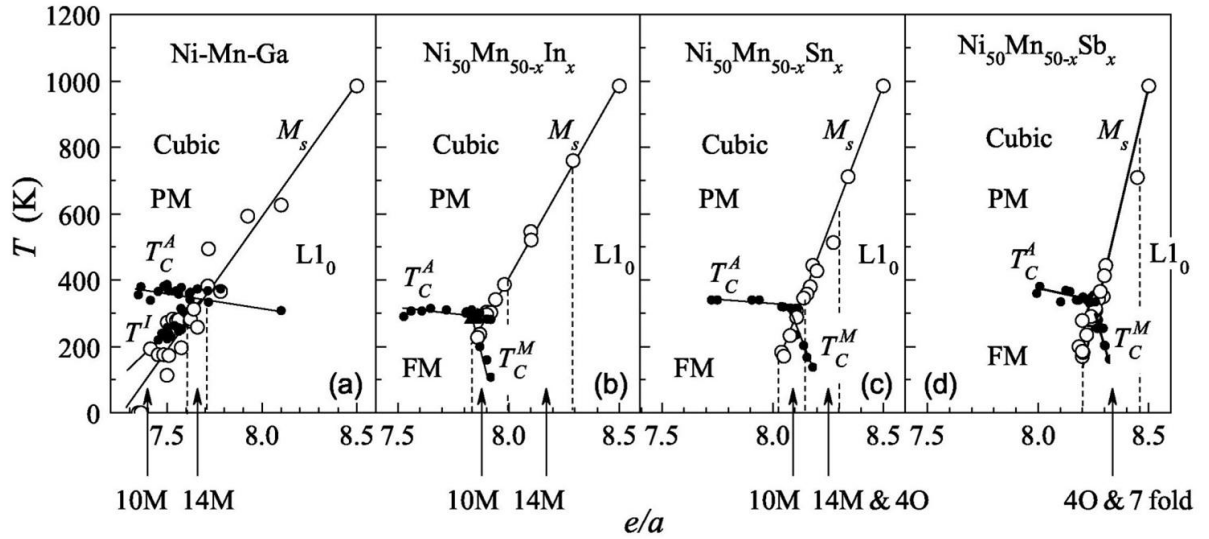


Figure 1.9: The magnetic and structural phase diagram of Ni-Mn-Z Heusler alloys with Z as (a) Ga, (b) In, (c) Sn and (d) Sb. The triangles and the circles correspond to the magnetic and martensitic transition temperatures respectively. The regions corresponding to the different structures are separated by discontinuous lines. Small solid circles in (c) correspond to the premartensitic transition temperature. This graph has been reproduced from [69]

As shown above, Figure 1.9 the magnetic and martensitic transition temperatures of the Ni-Mn-Z Heusler alloys ($Z = \text{Sn, In, Ga}$) plotted as a function of the average valence electron concentration per atom (e/a) ratio, T_C^A and T_C^M represent the ferromagnetic transition temperatures of the austenitic and martensitic phases, respectively, while M_s represents the martensitic start temperature. Except for Ni-Mn-Ga, all other Ni-Mn-Z

alloys the martensitic transformation occurs in off-stoichiometric compositions. Although there is no constraint on the elemental composition of Ni-Mn-Ga (Ni non-stoichiometry or Mn non-stoichiometry or both), the figure depicts only $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ alloy compositions (Mn non-stoichiometry) for Ni-Mn-In, Ni-Mn-Sn and Ni-Mn-Sb [69]. Therefore, one of the objectives of the present study would be to explore the presence / absence of the martensitic transition temperature in non-stoichiometric alloys (Ni_{2+x}) and update the above phase diagram. Although compositional off-stoichiometry introduces newer magnetic and structural interactions, observation of structural similarities in the austenitic and martensitic phases of these $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ alloys with Ni_2MnGa helps in describing martensitic transformation with similar structural relationships. In addition, detailed studies of the fine structure of x-ray absorption and circular magnetic x-ray dichroism have identified that a local structural distortion leading to hybridization between Ni3d and Mn3d states is responsible for martensitic transformation in such Mn non-stoichiometric alloys (Mn rich) [41, 94, 95]. Local structural distortion was also identified as the main factor responsible for martensitic transformation in Ni_2MnGa [76]. The present study focused on alloys and will thus enable verification of the importance of Mn nonstoichiometry in driving the system toward martensitic transformation. Secondly, Figure 1.9 also shows that the slope of the M_s versus e/a ratio is dependent on the type of Z atom. The role of Z atoms in mediating structural or magnetic interactions has been hitherto not understood. The proposed study would attempt to understand the same. Hence, the present work is undertaken with the following objectives:

1. Explore the possibility of martensitic transformation in Ni-Mn-Z alloys ($Z = \text{In, Sn, or Sb}$) as a function of the e/a ratio by introducing Ni non-stoichiometry.
2. Understand the role of Z atom in structural and magnetic interactions that affect the martensitic transformation in Ni-Mn-Z alloys.

The thesis consists of seven chapters and a brief overview of each chapter is as follows:

Chapter 1 describes an introduction to Shape memory, austenite and martensite phase,

Heusler alloys along with their structural and physical properties and the relation between martensitic transformation temperature with e/a ratio.

Chapter 2 provides a comprehensive explanation of the sample preparation process and the experimental techniques used to investigate the properties of the alloys.

Chapter 3 explaining the reasons for the absence of martensitic transition in Ni-rich Ni-Mn-Sn alloys. Here, a comparison of structural phase transitions in Ni-Mn-Ga and Ni-Mn-Sn alloys is made. In particular, we have studied, Ni-rich, $\text{Ni}_{2.1}\text{MnGa}_{0.9}$, $\text{Ni}_{2.2}\text{MnSn}_{0.8}$, $\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$ and $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$ alloy compositions and Mn-rich, $\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$ and $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$ alloys. In doing so, care is taken to ensure that all three Ni-Mn-Ga alloys and the three Ni-Mn-Sn alloys have the same e/a ratio.

Chapter 4 focuses on the effect of temper annealing treatment on phase stability for Ni-rich and Mn-rich, Ni-Mn-Ga, and Ni-Mn-In alloys and these results are described in Chapter 4. The samples employed in this study are $\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.46}\text{MnIn}_{0.54}$, $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$, $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$, $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ as compositions for this study, with respect of e/a ratio is same for alloys.

Chapter 5 discusses the behavior of M_s with respect to e/a ratio. The samples in this study were chosen to comply with three conditions:

1. Varying e/a ratio but with the same Z ($Z = \text{In}$) atom $\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$, $\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$, $\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$, $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$.
2. Varying the Z atom but the same e/a ratio (8.0) $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ $\text{Ni}_2\text{Mn}_{1.33}\text{Sn}_{0.67}$, Ni_2MnSb .
3. Varying Z atom with variation of the e/a ratio but with the same $M_s \approx 400$ K $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$, $\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$, $\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$.

Here we compared the difference between the second nearest neighbors Mn-Z and Mn-Mn_z and the distances of the nearest neighbor Ni-Mn and Ni-Z bonds in the transforming and non-transforming alloys.

Chapter 6 This chapter focuses on the effect of doping extra elements on martensitic transformation temperature T_M and the behavior of the unit cell expansion due to the size different of Z (Z = Ga, In), they alloys which have been chosen for this study are $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) with respect of e/a ratio (e/a =8) throughout the series.

Chapter 7 presents the summary of the accomplished work and the future plan.

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Chapter 2

Experimental Techniques

2.1 Introduction:

This chapter includes a complete review of alloy preparation procedures, including a brief description of the experimental approaches used to characterize the alloys and the data processing tools used. The chemical compositions of alloys were investigated using energy-dispersive analysis of X-ray spectroscopy (SEM-EDAX), while the crystal structure of the alloys was determined using X-ray diffraction (XRD). Magnetic and transport parameters were studied using the Magnetization Cryogenic S-700 SQUID magnetometer from 5 to 400 K, and four-probe resistivity was recorded in the range of 30 to 400 K. The first-order transformation temperature was calculated using differential scanning calorimetry (DSC). Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to investigate the local atomic structure and deformation of alloys.

2.2 Sample Preparation:

Polycrystalline alloys were synthesized at the School of Physical and Applied Sciences of Goa University using the arc-melting technique in a high-purity argon atmosphere devoid of oxygen. The stoichiometric amounts of raw elements, such as nickel (Ni) and

manganese (Mn), along with gallium (Ga), indium (In), tin (Sn), and antimony (Sb), were weighed, compressed, and then melted together on a water-cooled copper hearth. The ingots were subjected to four remelting processes, with each process including a flip, to achieve compositional uniformity. Thereafter, the alloys were sealed in evacuated quartz tubes under a vacuum of $\approx 10^{-6}$ mbar and subjected to a post-annealing heat treatment procedure, which involved keeping the alloys in a furnace for 48 hours at (750 °C). They were then rapidly quenched in ice water to preserve the desired microstructure. After the samples were removed from the furnace, they were cut in half using a low-speed diamond cutter. The first half was ground into powder for XRD and EXAFS measurements, while the remaining half was sectioned into small pieces for other purposes, such as SEM-EDAX, DSC, Resistivity, and Magnetization (SQUID). The alloys in the sixth chapter were prepared following the same thermal treatment protocol as previously described. However, a part of the alloys was quenched in ice water and again kept in the furnace at a temperature of (400 °C) for 96 hours, followed by cooling of the furnace to room temperature, known as temper annealing. A schematic of the sample preparation workflow is presented in Figure 2.1

2.3 Structural studies

2.3.1 Energy-Dispersive Analysis of X-ray (EDAX) spectroscopy:

After preparation and annealing of the alloys, the chemical compositions of the synthesized Heusler alloys were determined using energy-dispersive X-ray spectroscopy (EDAX). This technique provided localized elemental analysis to verify stoichiometric consistency between samples and detect potential segregation during high temperature processing [1,2]. The principle of energy dispersion is schematically illustrated in Figure 2.2 [3].

When a high-energy electron beam interacts with the sample, it ejects the inner-shell electrons (K or L shell) from constituent atoms, creating excited ionic states [4]. When

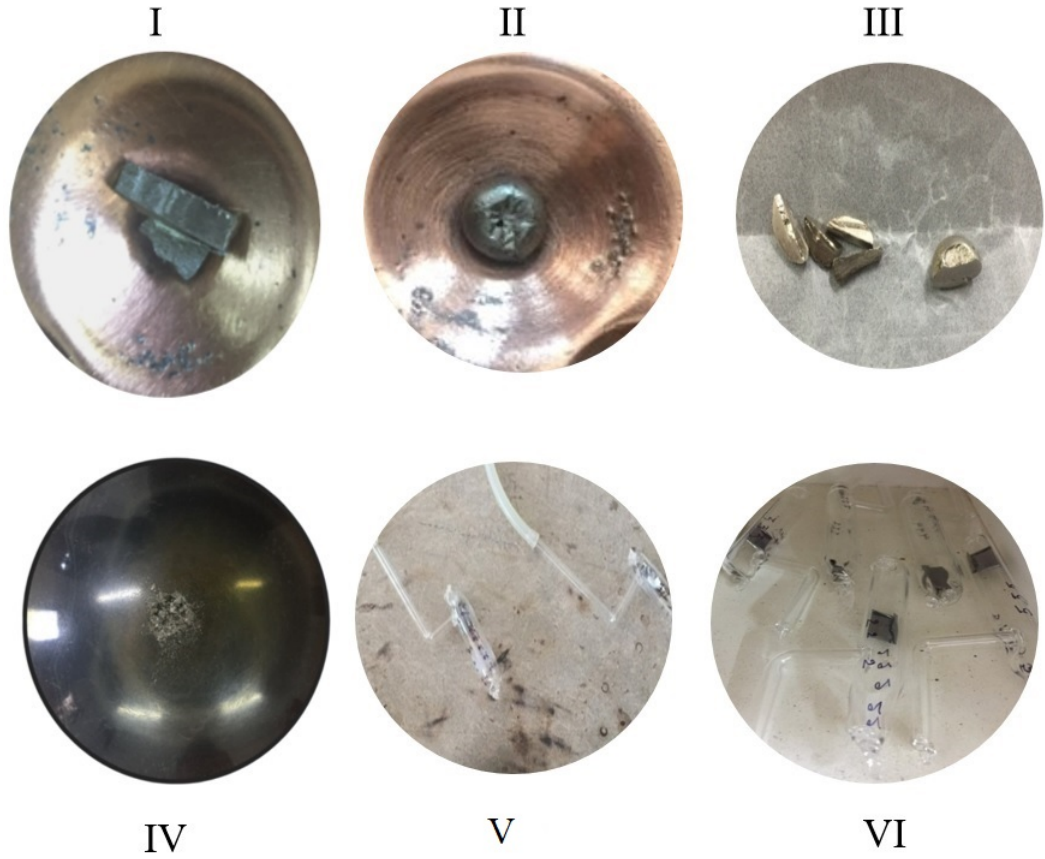


Figure 2.1: Pictures taken during the preparation of the alloy. (I) High-purity elements (Ni, Mn, Ga) are carefully weighed and placed on a copper hearth, preparing them for alloy formation. (II) The elements are melted together using an arc-melting furnace. (III) The resulting alloy button is removed from the furnace and allowed to cool. It is then cut into smaller pieces and (IV) about half of the sample is ground into a powder preparing it for further analysis or experiments. (V) Both the alloy pieces and the powder encapsulated quartz tube sealed under vacuum. (VI) The sealed quartz tubes were arranged inside the furnace for annealing.

these ions relax, outer-shell electrons transition to fill the vacancies, emitting characteristic X-ray photons with energies specific to each element's atomic structure [5]. The semiconductor detector, usually Si (Li) or SDD, collects these X-rays, and their energy spectra are resolved by pulse height analysis [6]. Elemental identification is achieved by matching peak positions to known emission lines, while quantification in weight or atomic percentage is derived from peak intensities.

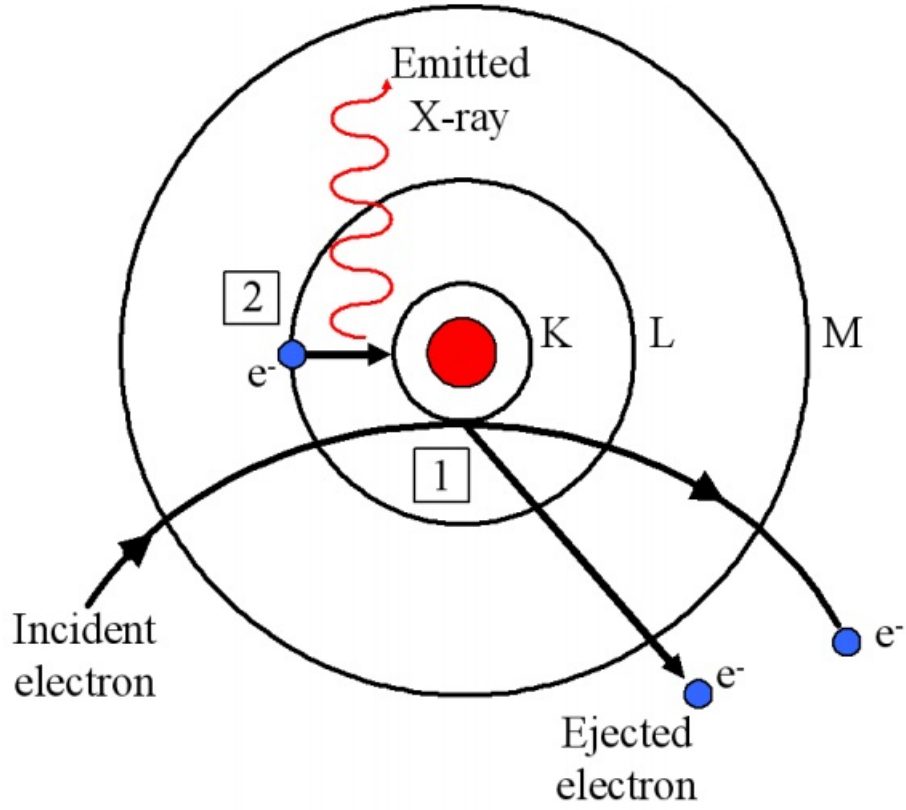


Figure 2.2: Principle of Energy Dispersive X-ray Spectroscopy (SEM/EDAX)

2.3.2 X-ray diffraction (XRD):

The structure of the alloys was studied using X-ray diffraction to determine the phase structure and check for impurities, with measurements taken at the School of Physical and Applied Sciences at Goa University, Goa. The annealed powder was measured by X-ray diffraction at room temperature within the $2\theta^\circ$ range from 20° to 100° with a speed of $2^\circ/\text{min}$ and a step size of 0.02° , using radiation ($\text{Cu K}\alpha$) on a Rigaku Smart Lab X-ray diffractometer.

XRD analysis of the synthesized Heusler alloys was conducted to identify their crystal structure and phase impurities. The core concept behind this method is the Bragg equation [7].

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

Where:

- n is the order of reflection
- λ is the wavelength of the incident wave
- d is the interplanar spacing
- θ is the angle of incidence

when ' d ' denotes the interplanar spacing in crystallography, θ represents the angle of incidence, and n being an integer multiple of the wavelength.

Figure 2.3 illustrates the fundamental principle of Bragg diffraction.

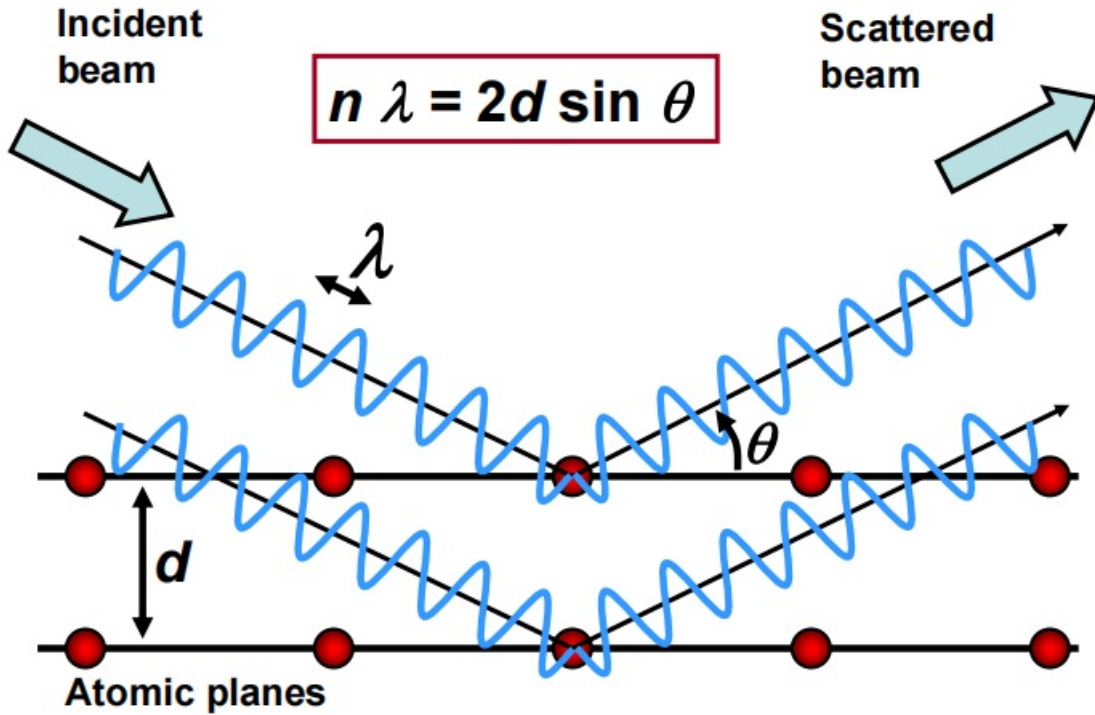


Figure 2.3: The fundamental principle of Bragg diffraction

Constructive interference occurs, producing distinct diffraction peaks. By analyzing the angular positions $2\theta^\circ$ and intensities of these peaks, we identify the dominant phases present in the alloys, calculate precise lattice parameters, and evaluate the degree of Heusler alloys. The presence of superlattice reflections at distinct $2\theta^\circ$ angles along with

their associated intensities is crucial in confirming the formation of the desired L2₁ ordered structure [8], whereas deviations from ideal peak positions suggest the possibility of secondary phases or compositional disorder arising from the synthesis process. The crystal structure of Heusler alloys was elucidated through high-precision XRD analysis conducted with the aid of JANA2020 [9, 10]. The process commenced with the Le Bail fitting, with diffraction peaks being modeled using the pseudo-Voigt profile equation [11].

$$P(2\theta) = \eta L(2\theta) + (1 - \eta)G(2\theta) \quad (2.2)$$

Here, η controls the Lorentzian-Gaussian contribution. This can be defined with critical reflections ($hkl = 1$) with fundamental (220) and symmetry sensitive peak key signatures (111) of the L2₁ Heusler alloys. The Rietveld refinement process was used to optimize the structure model, with the goal of minimizing the weighted profile factor R $R_{wp} \approx 2\%$, by iteratively adjusting the atomic coordinates, the thermal parameters and the occupancy of the site while maintaining the necessary relationship between intensity, which is crucial to detect atomic ordering. The convergence was confirmed through statistical metrics, including Bragg R χ^2 , and this ultimately led to the determination of the geometrically ordered atomic arrangement that characterizes these functional materials [12]. At room temperature, Stoichiometric Heusler alloys exhibit a cubic L2₁ crystal structure, as determined by JANA 2020. However, the analysis of modulated (martensitic) structures in the non-stoichiometric compositions poses a significant challenge because of their inherent complexity. Specifically, the main peaks of the modulated structure within the $2\theta^\circ$ range of 40° to 50° originate from a monoclinic structure, which complicates the analysis. The complexity in this system originates from replacing the typical periodic pattern with structures that exhibit satellite reflections caused by either displacive changes or variations in composition. The key issue involves accurately identifying the modulation wave vector $\vec{q}$, necessitating high-resolution diffraction data and meticulous parameter optimization to prevent misindexing. The strong relationship between

atomic displacement parameters and modulation functions often leads to difficulties with parameter correlations during refinement, thereby increasing the risk of overfitting [13]. JANA2020 resolves these issues by using a specialized superspace formalism, which allows the improvement of (3+d)-dimensional structural models, with d signifying the modulation dimensionality [14]. Refinement of successful outcomes requires strict enforcement of superspace symmetry constraints, precise determination of modulation amplitude parameters, and comprehensive testing via difference Fourier analysis. The computationally intensive process is greatly affected by the initial conditions, underscoring the importance of high-quality data and systematic refinement techniques.

2.3.3 Extended x-ray absorption Fine Structure (EXAFS):

Extended X-ray absorption fine structure (EXAFS) spectroscopy is an important technique for understanding the effect of local structural distortion of the neighbor-absorbed atom [15]. The alloy measurements were performed at room temperature on the edge of the Ni *K* edge (8333 eV) and Mn *K* edge (6539 eV), the P65 beamline at the Petra III synchrotron source, DESY, Hamburg, Germany, using a Si(111) double crystal monochromator. With the use of an ionization gas, the incident I_0 and the transmitted I_t energy photon were performed while two crystals were tuned up to 90% of maximum to control the higher-order harmonics. The absorbers have been prepared by coating a Scotch tape with an extremely fine alloy powder, and the thickness of the tape was adjusted by changing the number of layers to extract the absorption edge jump $\Delta\mu t \leq 1$.

2.3.4 Theoretical Foundations of EXAFS:

The spectrum of X-ray absorption is typically divided into two regions. The first is XANES near-edge x-ray spectroscopy and the second is EXAFS [16]. XANES has high sensitivity to formal oxidation states and coordination chemistry in the case of EXAFS used to determine the distortion of the local atomic structure, the distances between

neighboring atoms, and the number of coordination atoms [17]. As shown in Figure 2.4

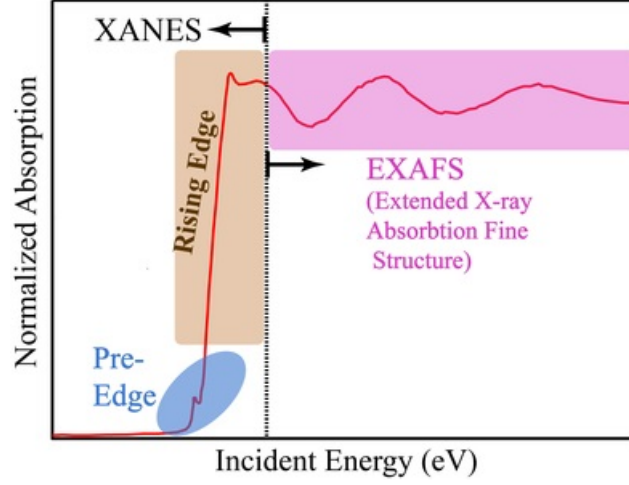


Figure 2.4: Schematic representation of an XAS spectrum, exhibiting absorption of the x-rays both within the 50 eV of the edge energy (XANES) and from some hundred to greater than 1000 eV energy beyond the absorption edge (EXAFS)

The absorption coefficient μ can be determined by Beer's law.

$$I = I_0 e^{-\mu t} \quad (2.3)$$

The core instrumentation for EXAFS measurements comprises a monochromator, slits, and ionization chambers. The energy selection of the incident X-rays is achieved via a double-crystal monochromator utilizing parallel silicon crystals operating on Bragg's law 2.1. Photons satisfying this condition at an angle θ are reflected by the first crystal, with the second crystal redirecting the beam. A potential drawback is the transmission of higher-order harmonics. Harmonic rejection is accomplished by either detuning the relative alignment of the monochromator crystals or by employing X-ray mirrors fabricated from high-atomic-number metals (e.g., Rh or Pt). Measurement of incident I_0 and transmitted I_t x-ray intensities is performed using gas-filled ionization chambers. Structurally, these are parallel plate capacitors maintained at high voltage and filled with a suitable gas. The X-ray beam ionizes this gas, and the liberated electrons are collected by the electric field, generating a current signal whose magnitude corresponds to the X-ray flux. The

composition of the gas fill is determined by the energy of the relevant absorption edge [18]. The main setup of EXAFS consists of a monochromator, slits, and ion chambers with an ionization gas. The purpose of the monochromator is to choose the x-ray energy that will be used in the alloy measurement [19]. The monochromator is made of one pair of crystals that are parallel to each other. In particular, only those wavelengths of X-ray photons that satisfy Bragg's condition at a specific angle get reflected from the surface of the first crystal. The second of the crystal acts as a mirror, which is used to keep the beam back to the original path. As mentioned above, the crystals have been tuned 99% to control the harmonics of higher order to pass through the experiment. Higher-order harmonics can be achieved by using x-ray mirrors made of metals such as Pt and Rh. The EXAFS measurement setup is illustrated schematically in Figure 2.5 [20].

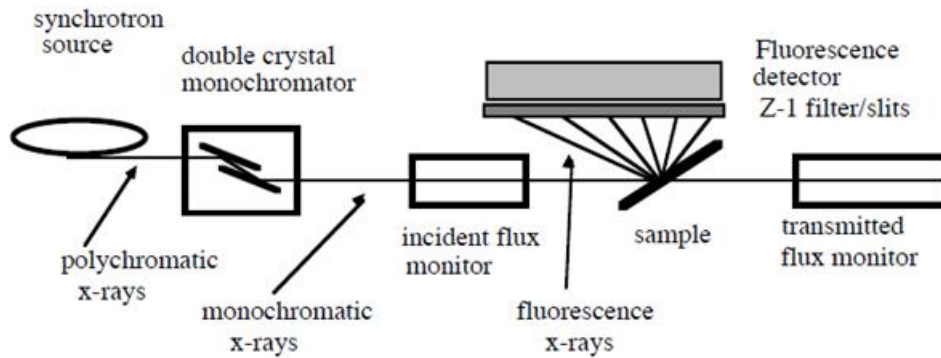


Figure 2.5: Schematic diagram of the EXAFS experimental setup

The ionization gas in the chamber is used to record the intensities of the transmitted and incident X-rays. Gas occupies the space between parallel plates in the ion chambers, which are kept at high voltage. When the beam of x-rays moves through the chamber, the gas will be ionized and will produce the electrons, which will be swept by the applied potential, producing a current that is proportional to the intensity of the x-rays. The gases that filled the chamber can be chosen depending on the energy at the edge.

2.3.5 EXAFS Data Reduction:

EXAFS data for alloys were obtained in transmission mode at the Ni-K and Mn-K edges. The full analysis has been performed by using the DEMETER suite, which consists of ATHENA and ARTEMIS software. Using the EXAFS equation [21], the parameters were selected to vary and should be less than the number of degrees of freedom. Firstly, convert the measured intensity to the x-ray absorber coefficient μ , then subtract the pre-edge background to get the true absorption signal, which is emitted by the absorber atom, by removing the extra signals that are not related to the target edge. The absorption edge energy E_0 is subsequently recognized as the maxima of the derivative of $\mu(E)$. Additionally, the post-edge background function is subtracted and $\mu_0(E)$ is estimated. $\chi(k)$ is then extracted using the formula:

$$\chi_i(k) = \frac{(N_i S_0^2) F_{\text{eff}_i}(k)}{k R_i^2} \sin [2k R_i + \varphi_i(k)] e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)} \quad (2.4)$$

Secondly, before modeling the EXAFS analysis, the structure of the alloys was discussed based on the main structure of the Heusler alloys $L2_1$, the R space and the K space were chosen during the fit to be in the range of (1.0-3.0) Å and (3.0-14.0) Å⁻¹ respectively. The chosen ranges are $R = (1.0, 3.0)$ Å and $k = [3.0, 12.0]$ Å⁻¹. For the given range of ‘ R ’ and ‘ k ’, there can be about 11 parameters that can be determined from the EXAFS data fitting. Generally, each coordination corresponds to three fitting parameters, ie, N , R , and σ^2 . The total number of fit parameters can be controlled by constraining parameters such as N , R , and σ^2 for different paths while fitting a single edge or even while fitting multiple edges recorded at different temperatures or for elements. In addition, fitting together more than one EXAFS edge to a common structural model can be advantageous in determining the local structural disorder around the absorber atom in a system. The EXAFS data modeling was performed using the ARTEMIS and ATHENA software package [22], the theoretical standards for each scattering path were calculated using calculations of the FEFF program [23].

2.4 Transport properties

2.4.1 Electrical Resistivity:

Resistivity measurements of Heusler alloys were performed to determine the first-order transformation temperature using a four-probe resistivity set-up [24]. This experiment was carried out over a temperature range of 20 K to 450 K at the School of Physical and Applied Sciences of Goa University. The setup consisted of a closed-cycle refrigerator connected to a Keithley 6221 DC current source, a Keithley 2182A nanovoltmeter, and a Lakeshore 325 temperature controller. The four-probe arrangement used included two probes for current and two for voltage [25], as depicted in Figure 2.6

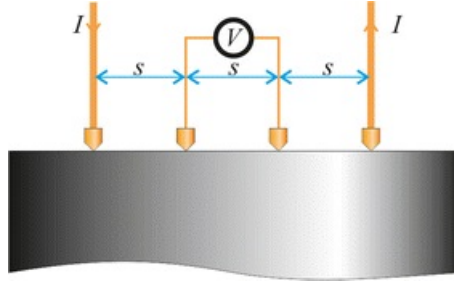


Figure 2.6: Diagram of four-probe resistivity

The sample was shaped into a rectangular shape and securely anchored on a high-purity copper measurement stage using a thermally conductive silver paint to ensure optimal electrical contacts. The surface of the sample was polished to a mirror finish (with a roughness of $\leq 1 \mu\text{m}$) prior to attachment. Following the mounting of the sample, electrical characterization was performed under a constant current of 100 mA, which was applied through the outer probe using A 6221 current source, while the voltage drop across the inner probes was measured. The temperature-dependent resistivity profiles were obtained by sweeping the sample temperature in 3 K–5 K increments, with a stabilization time of 6 to 90 seconds at each temperature to ensure thermal equilibrium. The Si diode sensor used in this application maintained temperature stability within ± 0.1 degrees during measurements [26], using the resistivity equation [27] and the raw of I – V

data being converted to resistivity values utilizing the geometric correction factor relevant to the sample dimensions while accounting for both instrumental resolution and thermal fluctuations via error propagation.

2.5 Differential Scanning Calorimetry (DSC):

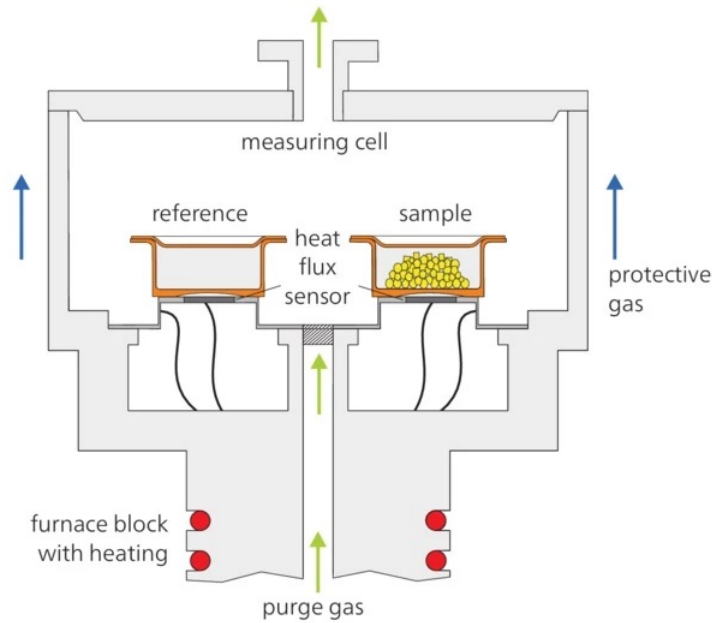


Figure 2.7: Differential Scanning Calorimetry (DSC) Diagram

DSC measures the difference in heat flow between the sample and the reference material as they undergo identical temperatures [28]. The main principle relies on the detection of energy changes during physical transformations or chemical reactions in samples [29].

DSC Principle:

The differential scanning calorimetry technique employs a reference, usually an empty aluminum pan, and a sample, which is sealed within another aluminum pan [30]. The experiment is conducted under conditions where the reference and sample experience nearly identical temperatures throughout the procedure. This technique evaluates the variable

amount of heat needed to raise or lower the temperature as a function of the current temperature [31]. During a phase transition in the sample, the amount of heat transferred to the sample varies compared to that of the reference, with the flow either increasing or decreasing depending on whether the process is endothermic or exothermic. It is essential to keep both the sample and the reference at the same temperature to maintain them. Differential scanning calorimeters can measure the amount of heat absorbed or released during transitions by comparing the heat flow between the sample and reference, defined by $\Delta\left(\frac{\partial H}{\partial t}\right)$, with H representing the enthalpy. A thermogram is obtained by graphically representing the rate of change in heat over time or at temperature. The DSC curve in Figure 2.8 shows exothermic and endothermic reactions as peaks and dips, respectively, the area under each peak indicating the heat given off or taken in during the transition [32].

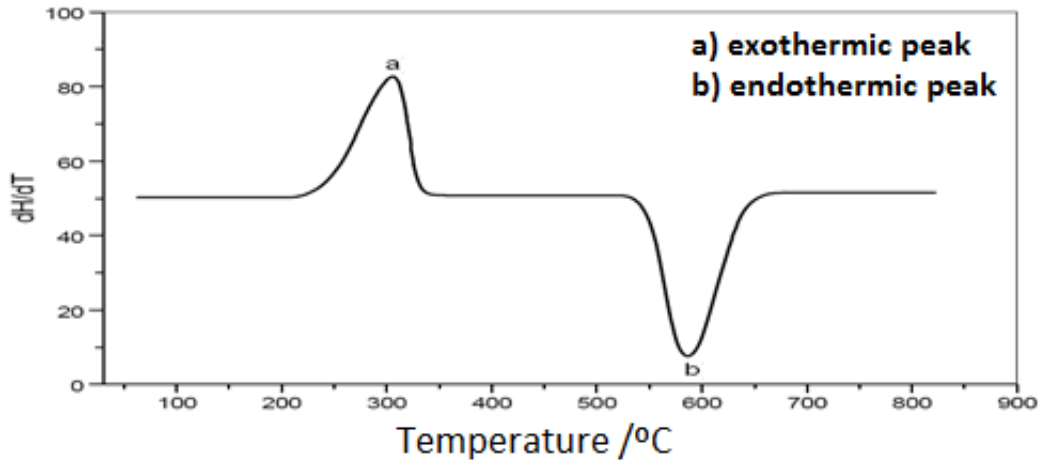


Figure 2.8: DSC thermogram recorded at a heating rate of 10°C/min under nitrogen flow

2.6 Magnetization $M(T)$:

Magnetization measurements $M(T)$ were performed in the temperature range of 5 K to 400 K using a SQUID magnetometer. The samples were first cooled in zero applied magnetic field, and then the ZFC (zero field cooled) data were recorded while warming in the

magnetic field of 10 mT, followed by subsequent cooling and warming cycles termed FCC (field cooled cooling) and FCW (field cooled warming), respectively. The magnetization as a function of temperature and magnetic field is shown in Figure 2.9, where (a) MT as a function of temperature for the Ni_2MnSb alloy exhibiting a paramagnetic to ferromagnetic transition, (b) AC susceptibility as a function of temperature [33].

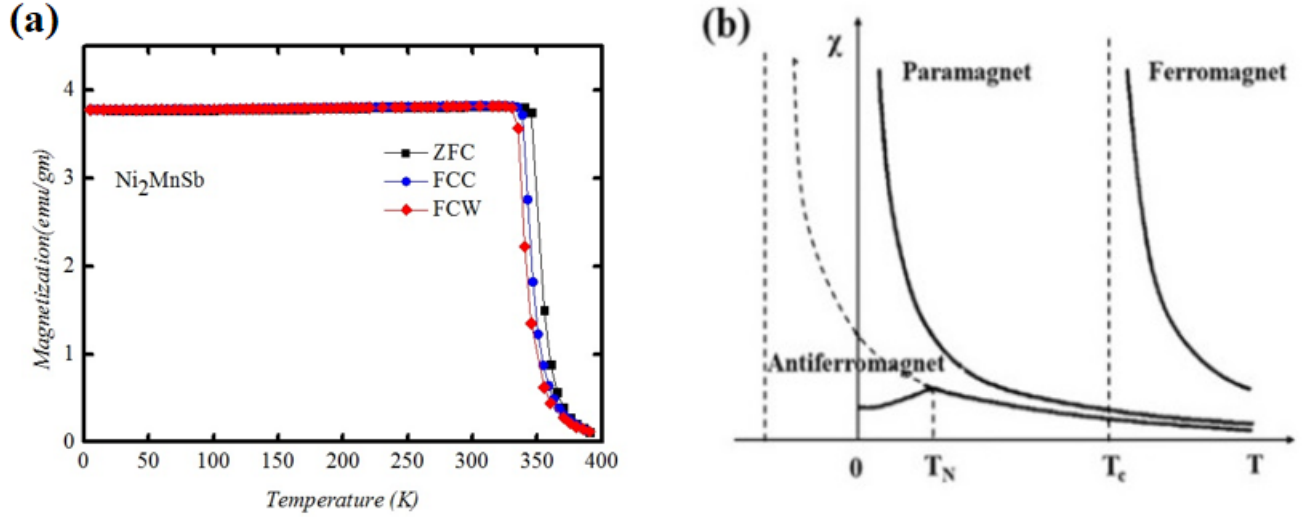


Figure 2.9: Diagram of Magnetization $M(T)$ with $T(K)$ and $H(\text{Oe})$

The SQUID sensor functions as a flux-to-voltage converter [34]. This device has a broad operational frequency range that extends almost from direct current (DC) to several gigahertz (GHz) [35]. The DC SQUID sensor comprises two half rings of superconducting material joined by a very thin nonconductive layer, resulting in two Josephson junctions in parallel configuration [36], as illustrated in Figure 2.10

The operation of a DC SQUID sensor is based on the principles of the Josephson effect, as described in Figure 2.10 and flux quantization. The Josephson effect is a phenomenon characterized by the flow of a current through a Josephson junction in the absence of an applied external voltage and forms the basis for the operation of SQUID sensors [37]. The flux quantization is also crucial because it allows the SQUID sensor to detect and measure magnetic flux with high sensitivity.

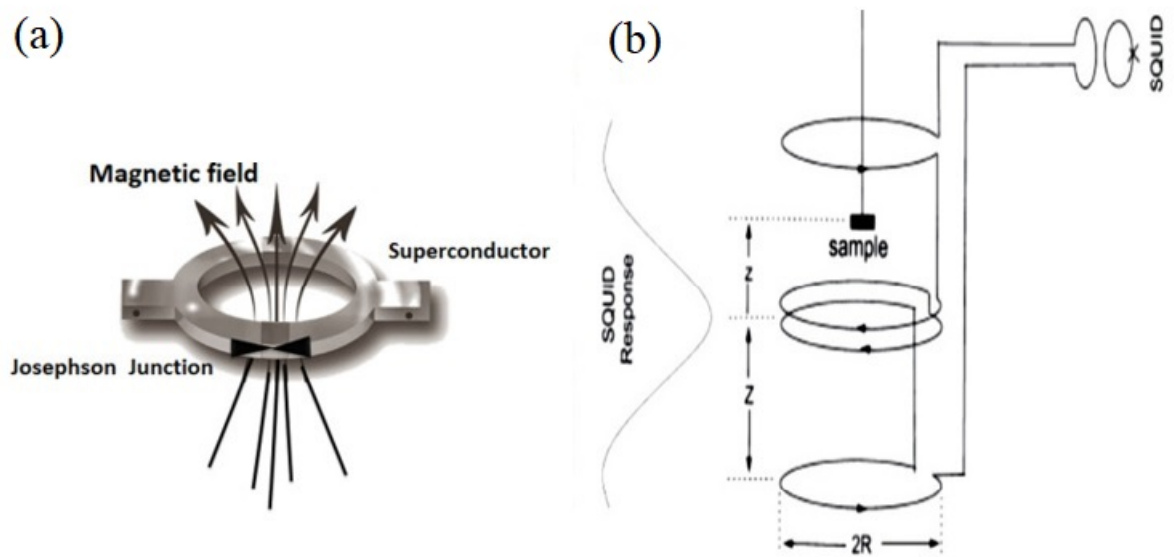


Figure 2.10: Schematics of (a) a DC SQUID sensor (two Josephson junctions in a superconducting loop) and (b) its integration into a SQUID magnetometer for magnetic moment measurements

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Chapter 3

Control Parameters of Martensitic Phase Transition in Ni-Mn-Z Heusler Alloys ($Z = \text{Ga, Sn}$)

3.1 Introduction:

The interesting functional properties exhibited by Ni-Mn-Z ($Z = \text{Ga, Sn, In, Sb}$) Heusler alloys with martensitic transformations have motivated fundamental investigations into their phase transition dynamics and structure-property relationships. One of these alloys, which exhibits fantastic magnetic application during the transformation process is Ni_2MnGa [1,2]. It undergoes a martensitic transformation below room temperature (T_M 202 K) in a ferromagnetically ordered state ($T_C = 370$ K) limiting its application as a ferromagnetic shape memory alloy at room temperature. Therefore, to improve the functional performance of these alloys, it is essential to identify key crucial parameters and systematically investigate their influence on the temperature of the martensitic transformation T_M and other related physical properties for a target application. This has motivated several researchers to identify factors that affect the martensitic transition temperature T_M in these alloys Ni-Mn-Z ($Z = \text{Ga, Sn, In, Sb}$). One of the factors that

leads to the variation of the transformation temperature T_M in Ni-Mn-Ga Heusler alloys is the chemical composition of the alloys [3–9]. The martensite transition temperature T_M can be scaled with the e/a ratio (which represents the number of valence electrons per atom in a material) and is given by the equation:

$$\frac{e}{a} = \frac{(10 \times \text{Ni}_{\text{at}\%} + 7 \times \text{Mn}_{\text{at}\%} + 3 \times \text{Ga}_{\text{at}\%})}{(\text{Ni}_{\text{at}\%} + \text{Mn}_{\text{at}\%} + \text{Ga}_{\text{at}\%})} \quad (3.1)$$

Where:

- $\text{Ni}_{\text{at}\%}$, $\text{Mn}_{\text{at}\%}$, and $\text{Ga}_{\text{at}\%}$ represent the atomic percentages of nickel, manganese, and gallium, respectively.
- The coefficients (10, 7, 3) correspond to the number of valence electrons (electrons in the outermost shell) contributed by each element.

without any addition to the percentage of each atom. The e/a ratio can be changed either by making the alloy Ni-rich or Mn-rich. Ni-rich alloys can be obtained by replacing Mn by Ni, which is represented as $(\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga})$, or by adding Ni in place of Ga, which is written as $(\text{Ni}_{2+x}\text{MnGa}_{1-x})$. Mn-rich compositions with higher e/a ratio are obtained by replacing Ga by Mn in Ni_2MnGa as $(\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x})$. Independent of the approach used to increase the valence electron concentration (e/a), T_M has a linear relation with the e/a ratio; T_M always increases with the e/a ratio. Concerning the aim to improve the relative concentration of Ni-Mn-Z ($Z = \text{Ga, In, Sn, Sb}$) in ternary Heusler alloys, researchers have explored introducing fourth and fifth elements (such as Fe, Co, Cu, or Pt) to enhance the martensitic transformation temperature T_M . These alloying additions alter the valence electron concentration (e/a) and modify the electronic structure, thereby affecting the transformation characteristics [10–15]. The apparent dependence of T_M on e/a ratio in Ni-Mn-based Heusler alloys created the preliminary assumption that the e/a ratio only parameter which can control the martensitic transformation temperature T_M in these alloys.

The relationship between martensitic transformation and e/a ratio is absent in Ni-Mn-Z ($Z = \text{In, Sn, Sb}$). These alloys are not martensitic even though their e/a ratio is equal to or more than Ni_2MnGa ($e/a = 7.5$). This gave motivation to the researchers to identify and understand the other factors that could affect the relation between the martensite transformation and e/a . Studies have reported a correlation between martensitic transformation and the volume of the unit cell at the austenite phase $L2_1$ [16]. Martensitic transformation is systematically observed across all alloy compositions that maintain a cubic crystal structure ($L2_1$ space group $\text{Fm}\bar{3}\text{m}$), with a cubic lattice parameter (a) in the range of 5.80–5.95 Å. This universal behavior suggests that the cubic symmetry—rather than minor deviations in stoichiometry or elemental substitution serves as the primary structural prerequisite for the martensitic transition in these systems [17]. Through EX-AFS studies the local structural disorder between the atoms was identified as the responsible factors of martensitic transformation in these alloys [18]. In all Mn-rich alloys ($\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$) ($Z = \text{In, Sn, Sb}$), the bond distance between Ni-Mn atoms is shorter than that between Ni-Z atoms [19]. In the case of Ni-Mn-Ga alloys also the local structural distortion appears, but in a different way, as the bond distance between Ni-Ga atoms is shorter than between Ni-Mn atoms [20]. For ($\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$) the martensitic transformation occurs at a specific concentration of Mn because of the strain in unit cell which is created by the exchange the larger In by the smaller Mn in the unit cell $L2_1$ austenitic phase [21]. Recent studies have demonstrated that Mn-rich Ni-Mn-Z Heusler alloys are thermally metastable and undergo phase separation upon annealing, forming a mixture of stoichiometric Heusler phase $L2_1$ and tetragonal $L1_0$ phases [22]. In these $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ alloys, the observed martensitic transformation has been attributed to the presence of localised NiMn martensitic phases which are randomly packed within the Heusler matrix [23]. The theoretical studies suggest this transformation behaviour arises from a weakening of covalent hybridisation between atoms due to the additional Mn atom content, which consequently increases the martensitic transformation temperature T_M [24]. In contrast, ab initio calculations indicate that transformations between different marten-

sitic structures (such as modulated and non-modulated phases) are driven primarily by thermodynamic factors [25].

Despite extensive investigations, fundamental questions persist regarding the underlying mechanisms governing martensitic transformations in Ni-Mn-Z ($Z = \text{Ga, In, Sn, and Sb}$) Heusler alloys. Although Ni-Mn-Ga systems exhibit martensitic transformations across both Mn-rich ($\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$) and Ni-rich ($\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$) or ($\text{Ni}_{2+x}\text{MnGa}_{1-x}$) compositional ranges, this behavior displays remarkable dependence of the system. In particular, among other Ni-Mn-Z alloys ($Z = \text{In, Sn, Sb}$), martensitic transformations have been observed in Mn-rich compositions only [26]. The conspicuous absence of such transformations in Ni-rich variants of these systems remains poorly understood and represents a significant gap in the current understanding of shape memory alloys. To elucidate this phenomenon, we have undertaken a comprehensive comparative investigation of local atomic structures in Ni-rich and Mn-rich compositions across two representative systems (Ni-Mn-Ga) and (Ni-Mn-Sn). This study was designed with careful control of the valence electron concentration (e/a), maintaining identical ratios of approximately (≈ 7.7 and 8.1) for both alloy systems, respectively. The selection of these specific values of e/a was motivated by several critical considerations: For Mn-rich Ni-Mn-Sn alloys, previous work has established ($e/a = 8.0$) as the threshold value for the onset of martensitic transformation. However, in the case of the Ni-Mn-Ga system at comparable e/a ratios, the martensitic transformation temperature T_M becomes prohibitively high, exceeding the measurable range of conventional laboratory instrumentation. Consequently, the slightly reduced Ni-Mn-Ga ($e/a = 7.7$) was selected to allow practical experimental characterization while maintaining a meaningful comparison. The investigations in this chapter provide a new view of the complex relationship between local structural disorder, electronic structure, and the martensitic transformability in Heusler alloys. The results suggest that the presence of martensitic structures modifies in the bulk composition, works as a critical factor for the presence of martensitic transformation, and this will help to design new shape memory alloys with specific transformation characteristics.

3.2 Results:

Three compositions each, $\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$, $\text{Ni}_{2.1}\text{MnGa}_{0.9}$, $\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$ ($e/a = 7.7$) and $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$, $\text{Ni}_{2.2}\text{MnSn}_{0.8}$, $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$ ($e/a = 8.1$) were studied here. To check the concentration of each element in all Ni-Mn-Ga and Ni-Mn-Sn alloys after preparation, energy dispersive spectroscopy (SEM/EDAX) was employed to determine the variation in the compositions. The Heusler alloys were determined by averaging the elemental content 100 μm with respect to a check at four different points within this area for each sample. Through EDAX analysis, the compositions obtained were within 2% of the actual samples. The average elemental composition has been used to determine the e/a ratio for all alloys after the preparation procedure. Table 3.1 shows a comparison between the nominal and EDAX compositions. The values of the e/a ratio also have been tabulated along with a martensitic transformation T_M and the magnetic ordering temperature T_C for all alloys.

Table 3.1: EDAX composition, e/a ratio, martensitic transformation temperature (T_M) and magnetic ordering temperature (T_C) for the Ni-Mn-Ga and Ni-Mn-Sn alloys.

Alloy	EDAX composition	e/a	T_M (K)	T_C (K)
$\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$	$\text{Ni}_2\text{Mn}_{1.2}\text{Ga}_{0.8}$	7.7	316	365
$\text{Ni}_{2.1}\text{MnGa}_{0.9}$	$\text{Ni}_{2.04}\text{Mn}_{1.1}\text{Ga}_{0.86}$	7.67	341	350
$\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$	$\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$	7.7	390	382
$\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$	$\text{Ni}_2\text{Mn}_{1.42}\text{Sn}_{0.58}$	8.07	276	310
$\text{Ni}_{2.2}\text{MnSn}_{0.8}$	$\text{Ni}_{2.2}\text{Mn}_{1.03}\text{Sn}_{0.77}$	8.07		275
$\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$	$\text{Ni}_{2.43}\text{Mn}_{0.62}\text{Sn}_{0.95}$	8.1		180

X-ray diffraction measurements were performed at room temperature to study the crystal structure behavior of these alloys within the range of 20° to 100°. Le Bail refined diffraction patterns of the six alloys are shown in figures 3.1 and 3.2

The results obtained from the analysis of the X-ray pattern for all alloys are shown in Table 3.2. Ni-Mn-Ga alloys show different types of martensitic crystal structures at room temperature, which are either modulated or non-modulated. The Mn-rich alloy $\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$ displays a modulated martensitic 5M structure that agrees with the lit-

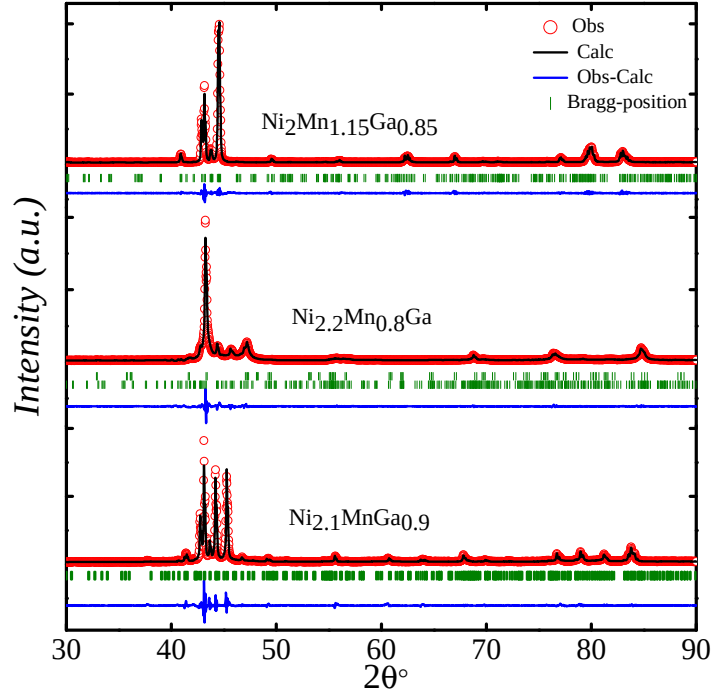


Figure 3.1: Le-Bail refined x-ray diffraction patterns for Ni-Mn-Ga alloys recorded at room temperature.

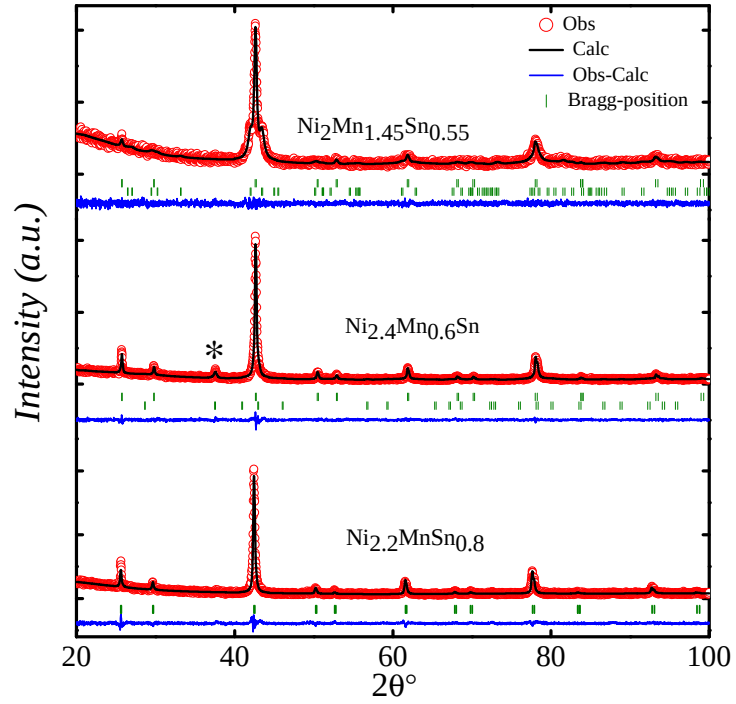


Figure 3.2: Le-Bail refined x-ray diffraction patterns for Ni-Mn-Sn alloys recorded at room temperature.

erature [27]. Second, in the case of Ni-rich alloys, $\text{Ni}_{2.1}\text{MnGa}_{0.9}$ exhibits a 7M incommensurate modulated martensitic structure, while $\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$ alloy has a non-modulated (NM) $L1_0$ tetragonal martensitic structure along with the presence of a minor phase related to the 7M modulated monoclinic martensitic structure [28, 29]. The presence of a dual phase structure in Ni-rich Heusler alloys can be fundamentally understood by exploring the thermodynamic and crystallographic phase diagram, which indicate the presence of intermartensitic transformations [30, 31]. Specifically, the compositions within the e/a ratio range 7.68 to 7.73 exhibit intermartensitic transformation close to room temperature (293 K-298 K) [30].

Table 3.2: Structural phases and the respective lattice parameters for alloys.

Alloy	Structure	Lattice parameters
$\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$	5M	$a = 4.22807(9) \text{ \AA}$, $b = 5.59321(11) \text{ \AA}$, $c = 4.20248(9) \text{ \AA}$ $q = 0.4003$, $\beta = 90.25$
$\text{Ni}_{2.2}\text{Mn}_{0.8}\text{Ga}$	NM	$a = 3.85268(24) \text{ \AA}$, $c = 6.517999(64) \text{ \AA}$
	7M	$a = 4.22436(27) \text{ \AA}$, $b = 5.50576(71) \text{ \AA}$, $c = 4.23147(25) \text{ \AA}$ $q = 0.309$, $\beta = 91.76$
$\text{Ni}_{2.1}\text{MnGa}_{0.9}$	7M	$a = 4.19775(6) \text{ \AA}$, $b = 5.52133(13) \text{ \AA}$, $c = 4.23124(9) \text{ \AA}$ $q = 0.304$, $\beta = 92.75$
$\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$	cubic	$a = 5.99691(2) \text{ \AA}$
	modulated	$a = 4.31141(71) \text{ \AA}$, $b = 5.73264(147) \text{ \AA}$, $c = 4.24090(119) \text{ \AA}$
$\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$	cubic	$a = 5.99431(2) \text{ \AA}$
$\text{Ni}_{2.2}\text{MnSn}_{0.8}$	cubic	$a = 6.01820(7) \text{ \AA}$

In the case of Ni-Mn-Sn alloys (see Figure 3.2) the Mn-rich alloy $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$ exhibits a largely austenitic phase $L2_1$ with a space group $Fm-3m$ with a minor martensitic phase related to the 7M structure at room temperature, which is related to the martensitic transformation at $T_M = 276\text{K}$ [32]. The Ni-rich alloys $\text{Ni}_{2.2}\text{MnSn}_{0.8}$ and $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$ show both a $L2_1$ structure at room temperature within MnO phase, which is less than 2%.

To determine the martensitic transformation temperature T_M for all alloys, DSC measurements were performed in the temperature range of 300 to 500 K. Through the DSC curves, the Ni-Mn-Ga alloys exhibit first-order transformation above room temperature,

whereas Ni-Mn-Sn alloys exhibit no transformation above room temperature. The calculation of the martensitic transformation temperature was performed taking the average of the martensitic/austenitic start and finish temperatures during warming and cooling cycles, see Figure 3.3. The DSC thermograms exhibited well-defined endothermic and exothermic peaks corresponding to the forward and reverse martensitic transformations, which occur due to the change of alloy structure at a specific temperature.

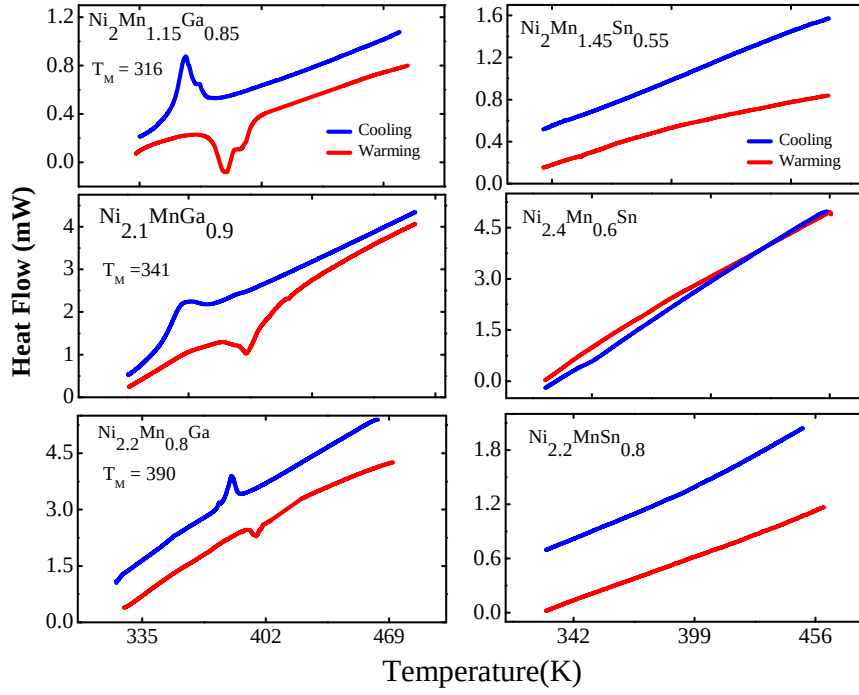


Figure 3.3: DSC measurement of Ni-Mn-Ga and Ni-Mn-Sn alloys showing the thermal transition behavior.

The magnetic ordering temperature of all alloys was characterized by analyzing their magnetic behavior under an applied magnetic field of 100 Oe. Figure 3.4 presents the magnetization as a function of temperature carried out in the temperature range of 5 K to 400 K.

Each alloy exhibits a paramagnetic to ferromagnetic phase transition, while decreasing the temperature, the value of magnetization starts to increase through the Curie temperature T_C . The precise determination T_C for each composition was accomplished through careful analysis of the minimum point in the first derivative of the magnetization curves

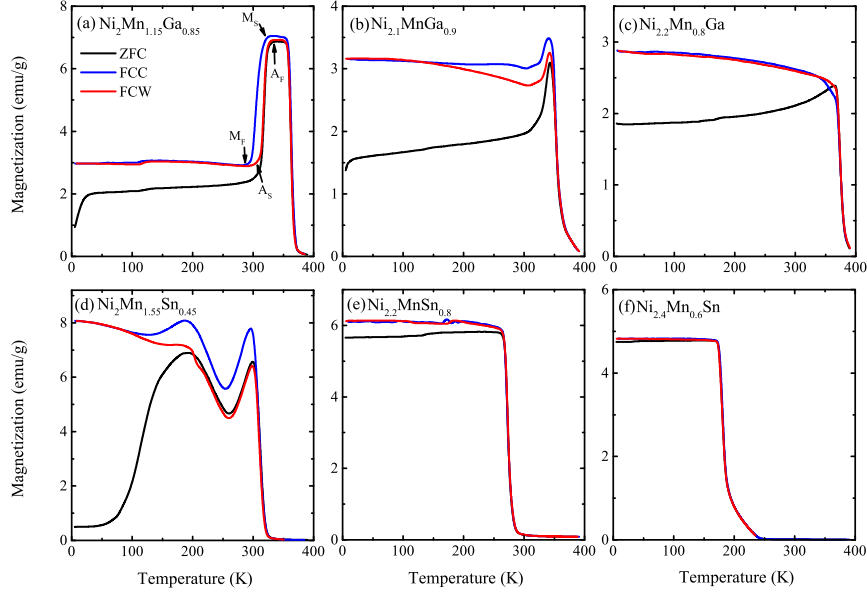


Figure 3.4: Magnetization as a function of temperature under an applied field of 100 Oe during ZFC, FCC and FCW cycles for Ni–Mn–Ga and Ni–Mn–Sn alloys.

see Table 3.1. The hysteresis between the field-cooled cooling (FCC) and field-cooled warming (FCW) magnetization curves provides conclusive evidence for the first-order martensitic transformation in these alloys.

Thus far, it is established that martensitic transformation is present in all the Ni-rich and Mn-rich Ni-Mn-Ga alloys while, only the Mn-rich Ni-Mn-Sn alloy exhibits martensitic transformation. Both the Ni-rich Ni-Mn-Sn alloys do not undergo any martensitic transformation down to 5 K as seen from their magnetization curves. To understand this difference in the behaviour of Ni-Mn-Sn alloys, extended x-ray absorption fine structure (EXAFS) spectra recorded at the Ni K and Mn K edges in the respective alloys were analysed. The previous analysis of EXAFS spectra in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys [19, 33] and on $\text{Ni}_2\text{Mn}_{1.4}\text{Sn}_{0.6}$ [17] and $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ [34, 35] alloys were used as guides to fit the present data. To develop a structural model for fitting the EXAFS spectra at Mn K and Ni K edges, the austenitic $L2_1$ structure was considered as the base structure. In the austenitic $L2_1$ phase of a Ni-Mn-Z (Z = Ga or Sn) Heusler alloy, Ni is surrounded by four each of Mn and Z atoms in its first coordination and by six Ni atoms in its second

coordination. On the other hand, Mn has eight Ni and six Z atoms as its first and second nearest neighbors. With the addition of Ni in place of Mn or Z atom (Ni-rich alloys) and Mn in place of Z atom (Mn-rich alloys) additional atoms are introduced in the first and second coordination of the absorbing atoms. These changes in the near neighbour environment of Ni and Mn are listed in Table 3.3.

Table 3.3: Expected near neighbour environment, as per their austenitic crystal structure, around Mn and Ni atoms in the Mn-rich and Ni-rich Ni-Mn-Z alloys.

Edge	Near Neighbour	$\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$	$\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Z}$	$\text{Ni}_{2+x}\text{MnZ}_{1-x}$
Ni edge	1st	Ni-Mn	Ni-Mn	Ni-Mn
		Ni-Z	Ni-Ni(Mn)	Ni-Z
			Ni-Z	Ni-Ni(Z)
	2nd	Ni-Ni	Ni-Ni	Ni-Ni
			Ni(Mn)-Sn	Ni(Z)-Mn
Mn edge	1st	Mn-Ni	Mn-Ni	Mn-Ni
	2nd	Mn-Z	Mn-Z	Mn-Z
		Mn-Mn(Z)		Mn-Ni(Z)
	3rd	Mn-Mn	Mn-Mn	Mn-Mn

As the scattering of the photoelectron generated in the process of x-ray absorption is from the electron density around a scattering atom, there is a need for a Z contrast (Z - Z') of at least five atomic numbers between two scatters at an identical distance from the absorbing atom. Hence it will be difficult to distinguish between equidistant Ni and Ga or Ni and Mn scattering atoms. Hence, in the analysis of Ni-Mn-Ga alloys, we have not differentiated between Ni-Mn and Ni-Ni(Mn) scattering correlations in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ in our analysis. Here Ni-Ni(Mn) refers to Ni occupying Mn sites. Similarly, Ni-Ga and Ni-Ni(Ga) and Mn-Ga and Mn-Mn(Ga) correlations are also indistinguishable in $\text{Ni}_{2+x}\text{MnGa}_{1-x}$ and $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ alloys respectively. These problems does not arise in Ni-Mn-Sn alloys, except for indistinguishability of Ni-Mn and Ni-Ni(Mn) correlations in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Sn}$ alloys. The changes in the near neighbour environment of the constituent atoms upon the alloy transforming to the martensitic state will be discussed on a case to case basis in the following paragraphs. All the three Ni-Mn-Ga alloys have their M_f well above the

temperature (300 K) at which EXAFS spectra are recorded. In the martensitic state, the previous EXAFS studies show that the degeneracy of second neighbour correlations changes from six in the austenitic state to four and two in the martensitic state. Similarly, the third neighbour degeneracy also changes from twelve in the austenitic state to eight and four in the martensitic state [19,33]. Due to indistinguishability between Mn, Ni and Ga as scatterers, the same structural model was used to fit the Mn and Ni EXAFS data in all the three Ni-Mn-Ga alloys. Further, to improve the reliability of parameters by increasing the number of degrees of freedom, both Mn and Ni EXAFS data were fitted together using common parameters wherever possible. EXAFS data in the k-space data from 3 to 14 $\text{\AA}^{-1}$ was used for fitting and the fits were performed in the R-space from 1 to 4 $\text{\AA}$. The values of amplitude reduction factor, $S0^2$, for the respective EXAFS data were obtained from fitting the EXAFS data in standard metal foil. The values of $S0^2$ for Mn and Ni respectively were 0.7 and 0.8. The fits to the Mn and Ni K edge EXAFS data in R-space, for the three Ni-Mn-Ga alloys are presented in Figure 3.5 and the parameters obtained from fitting are listed in Table 3.4. As reported earlier, the Ni-Ga bond distance is shorter by about 0.02 $\text{\AA}$ than Ni-Mn bond distance in all the three alloys. Further, the second neighbour 6-fold degenerate Ni-Ni and Mn-Ga bond distances split into two distances, one long and one short. A similar splitting is noted in the third neighbour distance as well and such splitting are in agreement with earlier reports [19,33]. In the 5M modulated ground state, the c -parameter of the equivalent cubic cell is shorter than a while the 7M modulated ground state has $c/a > 1$ [36]. These changes can also be noted in the EXAFS analysis. In $\text{Ni}_2\text{Mn}_{1.15}\text{Ga}_{0.85}$, the shorter Ni-Ni and Mn-Ga bonds are two-fold degenerate while in the other two Ni-rich alloys, the shorter Ni-Ni and Mn-Ga bonds have a degeneracy of four.

The situation is different in the case of Ni-Mn-Sn alloys. In $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$, the nearest neighbour Ni-Mn distance is shorter than Ni-Sn even though the fractional content of the cubic phase at room temperature is in majority. Further, the second neighbour Mn-Sn and Mn-Mn(Z) (where Mn(Z) represents Mn occupying the Sn sub-lattice) distances are

not equal in contrast to them being identical as per the cubic lattice symmetry of the alloy. Such differences in near neighbour environment of Mn and Ni has been observed earlier in similar Ni-Mn-Sn alloys [17]. Recently, it was shown that such Mn-rich alloys possess local structural environments corresponding to stoichiometric Heusler alloy, for instance, Ni_2MnIn and $L1_0$ tetragonal phase of NiMn [23]. These alloys phase separate into the respective Heusler and $L1_0$ phases upon temper annealing. Such a phase separated model [23] was used to fit the Mn and Ni EXAFS in $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$. Good fits were obtained to both the EXAFS data and the parameters obtained are listed in Table 3.4. These parameters match very well with the bond distances obtained from the reported crystal structure for the two end members.

In the case of Ni-rich Ni-Mn-Sn alloys, a model based on their respective crystal structures was used to simultaneously fit the Mn and Ni EXAFS. The near neighbour environments of Mn and Ni are given in Table 3.3. Accordingly, in $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$, the nearest neighbour environment of Ni consists of equidistant, Ni-Mn, Ni-Sn and Ni-Ni(Mn) correlations, while Mn is surrounded by eight Ni atoms in its nearest neighbour environment. Using the constraints imposed by the crystal structure, a good fit could not be obtained for both Mn and Ni EXAFS data. Upon relaxing constraints, good fits were obtained but some of the distances were far off from the model values obtained from the crystallographic data of the alloy. For instance, the Ni-Ni(Mn) distance was about 2.75 Å instead of the expected value of 2.58 Å. Such large distance indicate presence of local structural disorder and cannot be explained using only a $L2_1$ structure. Therefore, a new model was conceived based on phase separated local structure as in the case of Mn-rich alloy described above. $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$ alloy was thought to consist of (0.6)[Ni_2MnSn] and (0.4)[Ni_3Sn]. Ni_3Sn is hexagonal with $P6_3/mmc$ space group [37]. Using the two structures in proportionate amounts stated above, a model was stitched with Mn and Ni as absorbing atoms and the EXAFS data at the two K edges was fitted simultaneously. The fits obtained are described in Figure 3.6 and the parameters obtained are given in Table 3.4. The obtained distances agree well with the crystallographic distances of the respective struc-

tural phases, Ni_2MnSn and Ni_3Sn . A similar model, consisting of Ni_2MnSn and Ni_3Mn in a 80:20 ratio, successfully described the EXAFS at Mn and Ni K edge in $\text{Ni}_{2.2}\text{MnSn}_{0.8}$. The bond distances obtained from fitting agree well with those expected in Ni_2MnSn and disordered cubic Ni_3Mn (ICDD: 01-071-9645) [38]. Thus, EXAFS studies indicate that both Mn-rich and Ni-rich Ni-Mn-Sn alloys consist of a random distribution of two types of structural units. One of the structural unit is stoichiometric Heusler composition and the other depends on the composition of the alloy. These structural units are randomly packed in the cubic $L2_1$ structure. It is quite well known that such non-stoichiometric alloys, especially $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ phase separate into cubic Ni_2MnSn and $L1_0$ tetragonal NiMn [39].

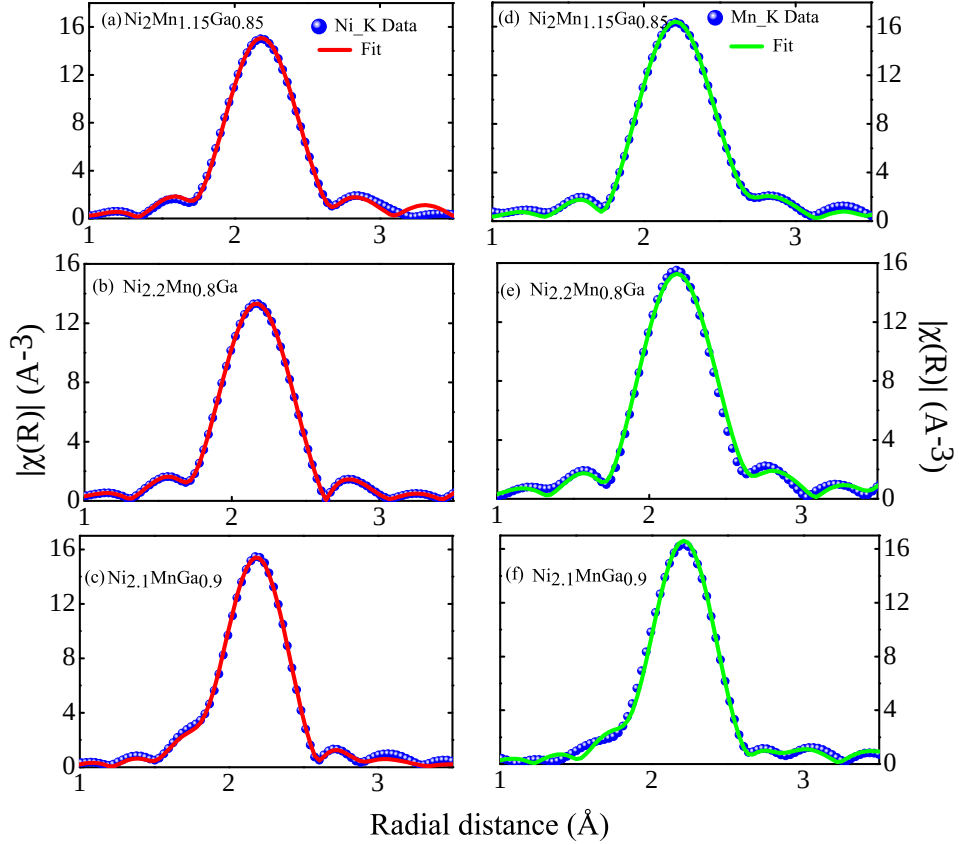


Figure 3.5: Magnitude of Fourier transforms of EXAFS (filled circles) along with the best fits (line) at the Mn and Ni K edges for Ni–Mn–Ga alloys.

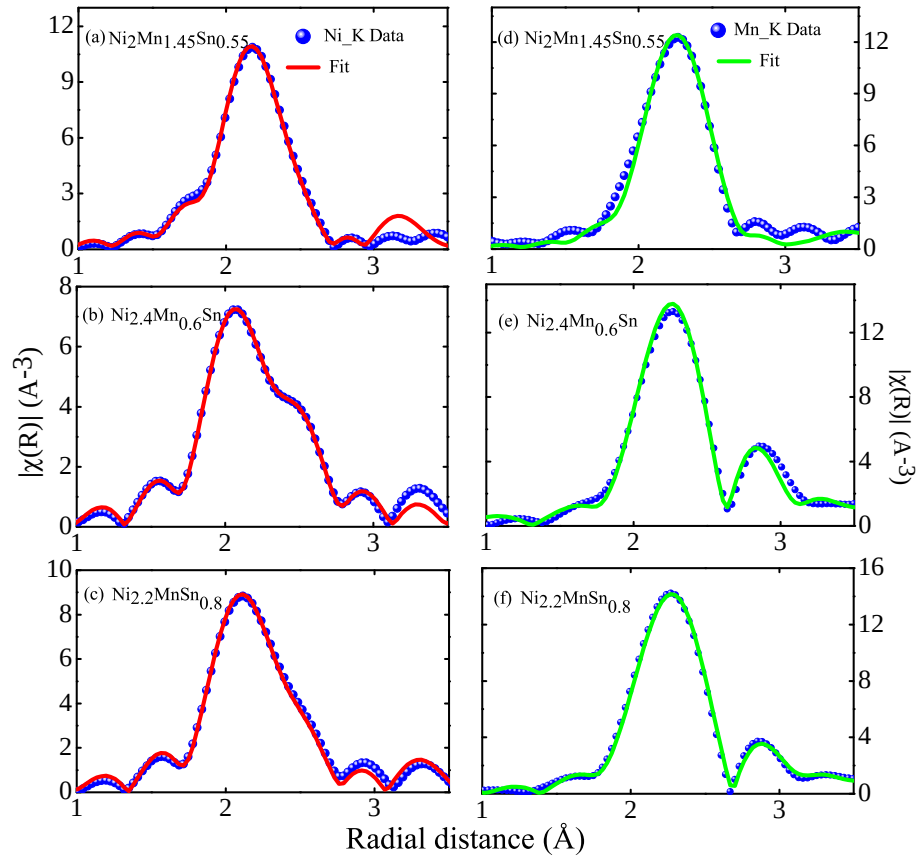


Figure 3.6: Magnitude of Fourier transforms of EXAFS (filled circles) along with the best fits (line) at the Mn and Ni K edges for Ni-Mn-Sn alloys.

Table 3.4: Local structural parameters like the type of bond, coordination number (C.N.), bond length (R), mean square disorder in bond distance (σ^2) obtained from Mn and Ni K EXAFS analysis in Ni–Mn–Ga and Ni–Mn–Sn alloys. C.N. was kept fixed at the crystal structure allowed value throughout the analysis. Bond distances belonging to the two phases in Ni–Mn–Sn alloys are separated by a horizontal line.

Alloys	Bonds	C.N.	R (Å)	σ^2 (Å ²)	Alloys	Bonds	C.N.	R (Å)	σ^2 (Å ²)
Ni ₂ Mn _{1.15} Ga _{0.85}	Ni–Mn	4	2.516(5)	0.005(1)	Ni ₂ Mn _{1.45} Sn _{0.55}	Ni–Mn	4	2.548(93)	0.025(6)
	Ni–Ga	4	2.498(11)	0.009(1)		Ni–Sn	4	2.605(18)	0.004(1)
	Ni–Ni	8	3.107(12)	0.007(1)		Ni–Ni	4	3.022(97)	0.005(4)
	Ni–Ni	4	2.889(21)	0.016(2)		Ni–Ni	4	2.660(38)	0.002(1)
	Mn–Ga	2	3.152(20)	0.007(2)		Mn–Sn	4	3.525(97)	0.005(4)
	Mn–Ga	2	2.932(2)	0.023(2)		Mn–Sn	4	3.482(1)	0.004(2)
	Mn–Mn	8	4.232(17)	0.014(2)		Mn–Mn	6	3.762(58)	0.003(2)
Ni _{2.2} Mn _{0.8} Ga	Ni–Mn	4	2.520(5)	0.006(1)	Ni _{2.4} Mn _{0.6} Sn	Ni–Mn	4	2.581(6)	0.011(1)
	Ni–Ga	4	2.502(5)	0.008(1)		Ni–Sn	4	2.581(6)	0.010(2)
	Ni–Ni	8	2.716(18)	0.008(1)		Ni–Ni	4	2.993(15)	0.014(2)
	Mn–Ga	2	3.063(21)	0.014(2)		Mn–Sn	4	3.001(20)	0.005(2)
	Mn–Ga	2	2.716(18)	0.008(1)		Mn–Sn	6	3.241(16)	0.015(2)
	Mn–Mn	12	4.262(14)	0.016(1)		Mn–Mn	6	2.477(16)	0.010(3)
Ni ₂ MnGa _{0.9}	Ni–Mn	4	2.518(4)	0.006(1)	Ni ₂ MnSn _{0.8}	Ni–Mn	4	2.585(4)	0.008(1)
	Ni–Ga	4	2.492(4)	0.008(1)		Ni–Sn	4	2.585(4)	0.004(1)
	Ni–Ni	8	3.092(17)	0.009(1)		Ni–Ni	4	2.993(17)	0.006(2)
	Mn–Ga	2	3.143(20)	0.006(2)		Mn–Sn	4	3.001(20)	0.004(2)
	Mn–Ga	2	2.919(60)	0.015(2)		Mn–Mn	6	2.464(20)	0.014(2)
	Mn–Mn	4	2.919(60)	0.039(12)		Ni–Mn/Ni	12	2.549(10)	0.012(2)
	Mn–Mn	8	4.236(17)	0.015(2)				3.586(25)	0.023(3)

3.3 Discussion:

In this work, the cause of the lack of martensitic transition in Ni-rich Ni-Mn-Sn alloys is examined. A comparison of Mn-rich ($\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$) and Ni-rich ($\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Z}$ and $\text{Ni}_{2+x}\text{MnZ}_{1-x}$) alloys ($\text{Z} = \text{Ga}$ and Sn) reveals that only the Mn-rich Ni-Mn-Sn alloy experiences martensitic transition. Although their e/a ratios are almost identical to those of the Mn-rich alloy, neither of the Ni-rich Ni-Mn-Sn alloys exhibits any first-order transformation. However, all three of the Ni-Mn-Ga alloys undergo a martensitic state transition from the austenitic state. Although they have a similar ratio e/a , the Ni-Mn-Ga alloys differ in their crystal structure at T_C , T_M and martensitic state. Of the three alloys, the Mn-rich Ni-Mn-Ga alloy has the lowest T_C and T_M . Additionally, at room temperature, it exhibits a 5M modulated structure as opposed to the Ni-rich alloys 7M structure. At room temperature, the $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Z}$ alloy exhibits a mixed 7M and non-modulated crystal structure, with the highest T_M of approximately 390K. The T_C of Ni-Mn-Sn alloys scales with the Mn content, even though martensitic transformation is only observed in Mn-rich alloys. The highest T_C is found in the alloy with the highest Mn content. EXAFS is used to solve the riddle of the lack of martensitic transition in both Ni-rich alloys. Significant local structural distortion surrounding the Mn and Ni atoms is indicated by EXAFS at the Mn and Ni K edges in these alloys. Similar to $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ alloys [23], all three Ni-Mn-Sn alloys exhibit a phase-separated local structure around Mn and Ni. The case of $\text{Ni}_2\text{Mn}_{1.45}\text{Sn}_{0.55}$ is made up of Ni_2MnSn and NiMn , whereas the local structure of Mn and Ni in $\text{Ni}_{2.4}\text{Mn}_{0.6}\text{Sn}$ is made up of Ni_2MnSn and Ni_3Sn , and the Mn and Ni local structure in $\text{Ni}_{2.2}\text{MnSn}_{0.8}$ is contributed by Ni_2MnSn and Ni_3Mn . Only NiMn is known to undergo martensitic transformation from the $B2$ structure to the $L1_0$ structure among all of these contributors to the local structure around Mn and Ni. This may be the main cause of the lack of martensitic transformation in Ni-rich Ni-Mn-Sn alloys. Ni-Mn-Ga alloys do not exhibit such a phase-separated local structure. The comparable electronic densities surrounding the constituent atoms, Mn, Ni, and Ga, may be the cause. Even if

we assume a phase separated local structure in Ni-Mn-Ga alloys as in the case of Ni-Mn-Sn alloys, one of the constituents in all three alloys would be Ni_2MnGa which is martensitic. Hence, both Ni-rich and Mn-rich Ni-Mn-Ga alloys undergo martensitic transformation..

3.4 Conclusion:

In conclusion, to understand why martensitic transformation is absent in Ni-rich Ni-Mn-Sn alloys, we examined Ni-rich Ni-Mn-Ga and Ni-Mn-Sn alloys. Both Ni-rich Ni-Mn-Sn alloys do not experience a structural phase transition, even though their e/a ratios are identical to Mn-rich Ni-Mn-Sn alloy. The existence of phase-separated local structures surrounding Ni and Mn in all three varieties of Ni-Mn-Sn alloys is the main cause of this behavior. Of the phase-separated entities only NiMn nucleated in Mn-rich undergoes martensitic transformation. Hence, the absence of such a phase-separated local structure in Ni-Mn-Ga alloys may be because the phases and photoelectron scattering amplitudes of Mn, Ni, and Ga are almost identical. However, it is not surprising that all three Ni-Mn-Ga alloys are martensitic because they would all have martensitic Ni_2MnGa even if local structures separated by phase were present.

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Chapter 4

Effect of Rapid Quenching and Temper Annealing on Phase Stability and Physical Properties of Ni-Mn-Z ($Z = \text{Ga, In}$)

4.1 Introduction:

Multifunctional properties of Ni-Mn-Z ($Z = \text{Ga, Sn, In, Sb}$) type Heusler alloys around room temperature emerge from the strong magnetostructural coupling present in them [1–3]. Continuous efforts are being made to improve the multifunctional properties of these alloys as well as to understand the underlying mechanism [4, 5]. Recent, studies have highlighted the metastable nature of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$, wherein they break down into a dual-phase composite alloy made up of the Heusler $L2_1$ and tetragonal $L1_0$ phases after temper annealing [5–8]. The phenomenon of shell ferromagnetism, which is seen when these alloys are annealed in an external magnetic field, is one effect of this metastable structure. The structural and magnetic properties are strongly dependent on the chemical composition of the alloys, often described by the e/a ratio [9]. The Heusler alloys in

the stoichiometric state have a ferromagnetic ground state, and the magnetic moment is located at Mn atom sites. The antiferromagnetic interactions occur due to the occupation of other sub-lattices by Mn atoms in a non-stoichiometric Heusler alloy. The presence of strong AF interactions lead to a positive change in entropy resulting in the inverse magnetocaloric effect [10]. EXAFS studies at the Mn and Ni K edges in these Ni-Mn-Z Heusler alloys have brought out a compelling evidence for the presence of local structural distortions within the cubic austenite phase of the off-stoichiometric $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$. These distortions play a decisive role in the behavior of the materials under thermal treatment processing. Temper annealing at specific temperature and for duration leads to segregation of local structural defects into $L2_1$ and $L1_0$ phases, suggesting a connection between local disorder at the atomic level and bulk phase instability [11]. Furthermore, the presence of significant localised structural disorder and metastable crystal structure in these alloys poses a complex scientific problem. Although presence of defects are often associated with the emergence of irreducible states—such as strain glass, where frozen dislocations persist under thermal cycling—these alloys do not exhibit this behavior. Despite the apparent structural requirements, the lack of a strain glass phase poses crucial questions concerning the fundamental processes controlling the kinetic arrest and metastability in these alloys. Whether competing interactions, kinetic barriers, or alternative relaxation pathways inhibit the formation of a non-ergodic state, needs more research. Therefore, to understand clearly the behavior of the alloys in Chapter 3, we employed temper annealing treatment for Ni-rich and Mn-rich, Ni-Mn-Ga, and Ni-Mn-In alloys, and these results are described in Chapter 4. The alloys chosen to this study are $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$, $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$, $\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.46}\text{MnIn}_{0.54}$, $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$, with taking care to ensure that all the alloys had the same e/a ratio. All alloys were first annealed at (750°C) for 48 h followed by rapid quenching in ice water (RQ) then a part from the same alloys were temper annealed for 96 h at (400°C) followed by furnace cooling to room temperature (TA). Both, (RQ) and (TA) alloys were characterized by the EDAX, DSC, Resistivity, XRD and Magnetization to study the properties of them under the conditions of Rapid quenched and temper

annealing. The results of this study will be explained in the following section.

4.2 Results:

Energy-dispersive X-ray spectroscopy (SEM-EDAX) was employed to obtain constituent atom composition and the e/a ratio of the alloys. The measurements were performed on four different spots within an area at room temperature and the results are tabulated in Table 4.1 along with the transformation temperature of the alloys.

Table 4.1: Nominal and EDAX-measured compositions of Ni-Mn-Ga and Ni-Mn-In alloys along with their e/a ratios and martensitic transformation temperatures.

Alloy	EDAX composition	e/a	T_M (K)
$\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$	$\text{Ni}_{2.04}\text{Mn}_{1.76}\text{Ga}_{0.2}$	8.33	868
$\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$	$\text{Ni}_{2.01}\text{Mn}_{1.81}\text{In}_{0.19}$	8.34	788
$\text{Ni}_{2.46}\text{MnGa}_{0.54}$	$\text{Ni}_{2.44}\text{Mn}_{1.01}\text{Ga}_{0.55}$	8.28	740
$\text{Ni}_{2.46}\text{MnIn}_{0.54}$	$\text{Ni}_{2.44}\text{Mn}_{1.02}\text{In}_{0.54}$	8.29	
$\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$	$\text{Ni}_{2.93}\text{Mn}_{0.1}\text{Ga}_{0.97}$	8.23	

To understand the effect of temper annealing on the alloy compositions, XRD measurements were performed on all the RQ and TA alloys at room temperature. In case of Mn rich $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$ and $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ Le Bail refinement of X-ray diffraction plots revealed tetragonal $L1_0$ type structures for both the RQ alloys. Following temper annealing, a secondary $L2_1$ phase was noted in the two alloys (see insets of Figure 4.1).

In the case of other three Ni-rich alloys, $\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.46}\text{MnIn}_{0.54}$ and $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$. X-ray diffraction data of (RQ) and (TA) alloys showed no change in the phase after temper annealing. $\text{Ni}_{2.46}\text{MnGa}_{0.54}$ alloy displays a tetragonal structure along with an extra phase, identified as γ phase [12] which is a martensitic with transformation temperature = 747 K. The other Ni rich alloy $\text{Ni}_{2.46}\text{MnIn}_{0.54}$ has three structural phases in its x-ray diffraction pattern, which are cubic $L2_1$, Ni_3Mn , and a hexagonal phase. Lastly, $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$ displays cubic $L1_2$ type crystal structure in both RQ and TA states. Figure 4.2 shows the Le Bail refined X-ray diffraction patterns for Ni-rich alloys. The alloy structures

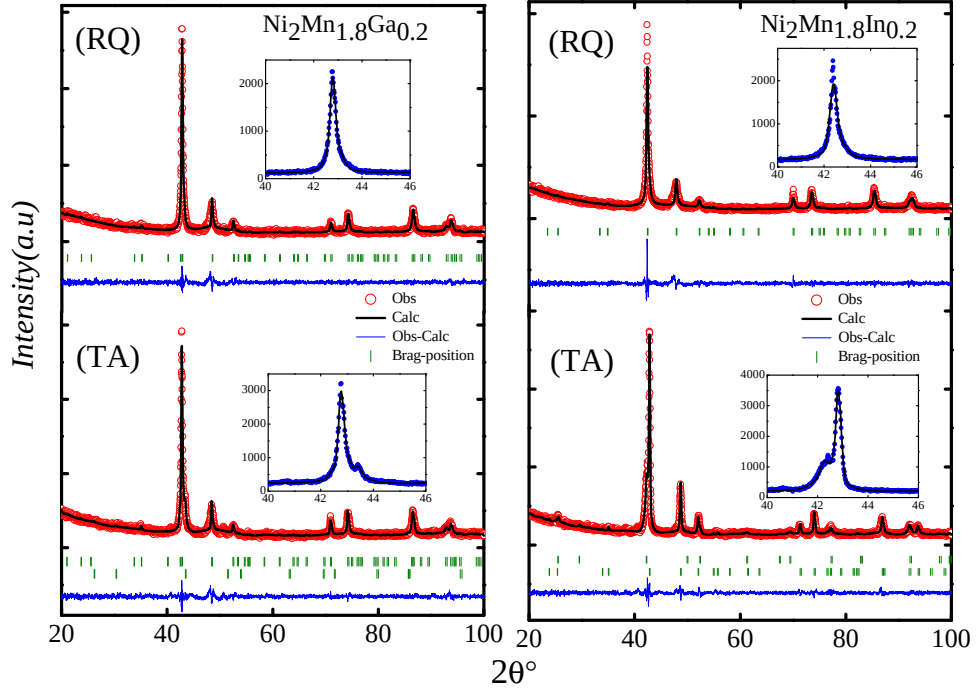


Figure 4.1: X-ray diffraction data for the alloys $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$ and $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ in rapid quenched (RQ) and Temper annealing (TA).

and their lattice parameters, obtained from the X-ray patterns of rapidly quenched and temper annealed samples, are listed in Table 4.2.

The martensitic transformation temperature T_M for the alloys was determined by using differential scanning calorimetry (DSC) from room temperature to 1000 K in both rapid quenching (RQ) and tempering annealing (TA). The results are listed above; see Table 4.1. The DSC showed that only $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$, $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ and $\text{Ni}_{2.46}\text{MnGa}_{0.54}$ exhibit a first-order structural transition at high temperature, but in the case of $\text{Ni}_{2.46}\text{MnIn}_{0.54}$, $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$, it does not exhibit any structural transformation which is in agreement with the XRD results; Figure 4.3 shows the DSC measurements for the alloys, in the case of temper annealing alloys, there was no numerical change in the martensitic transformation temperature [13].

Figure 4.4, shows magnetization as a function of temperature for RQ and TA alloys of $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$ and $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ recorded in an applied field of 100 Oe during ZFC, FCC and FCW protocols. Both RQ alloys show magnetization typical of an antiferromagnetic

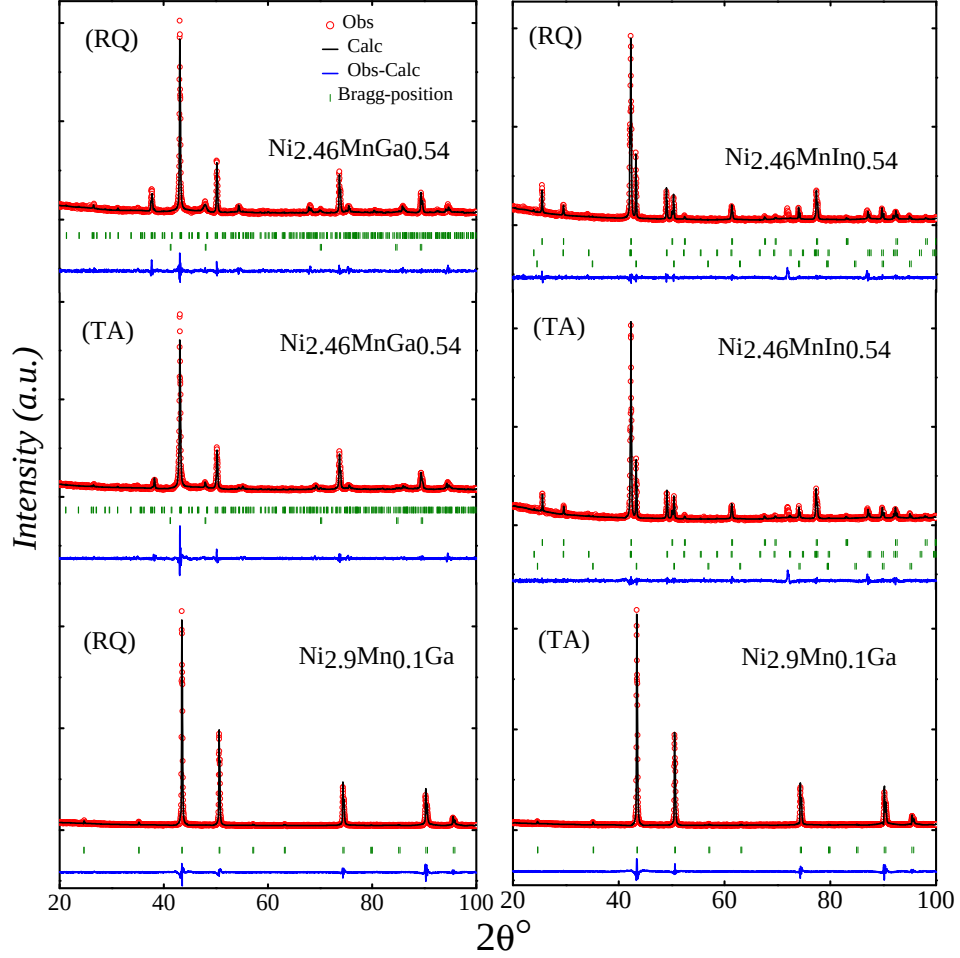


Figure 4.2: X-ray diffraction data for the alloys $\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.46}\text{MnIn}_{0.54}$ and $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$, in rapid quenched (*RQ*) and Temper annealing (*TA*).

material with Neel Temperature > 400 K. Upon temper annealing, a significant change in magnetic moment is noted. In the case of $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$, magnetic moment increases about 3 times and with a large separation between ZFC and FC curves indicating strong frustration effects. The TA alloy of $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$, on the other hand, displays a clear para to ferro transition at about 320 K which corresponds to the T_C of Ni_2MnIn . This agrees well with the observed phase separation of the alloy composition into $L2_1$ and $L1_0$ phases.

$M(T)$ curves of $\text{Ni}_{2.46}\text{MnGa}_{0.54}$ in Figure 4.5 show very little deviations between RQ and TA states. Compared to RQ alloy, a slight decrease in magnetic moment is noted in the TA alloy composition. This change could be attributed to induces atomic disorder

Table 4.2: Phase structures and corresponding lattice parameters of Ni-Mn-Ga and Ni-Mn-In alloys obtained by X-ray diffraction after rapid quenching and temper annealing, (NM) refers to non modulated tetragonal and (Hex) refers to hexagonal phase.

Alloy	RQ		TA	
	Structure	Lattice parameter	Structure	Lattice parameter
$\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$	NM	$a=5.30867(0)\text{\AA}$ $c=6.96389(0)\text{\AA}$	NM $L2_1$	$a=5.31001(4)\text{\AA}$ $c=6.96771(61)\text{\AA}$ $a=5.88487(74)\text{\AA}$
$\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$	NM	$a=3.80340(15)\text{\AA}$ $c=3.50552(14)\text{\AA}$	NM $L2_1$	$a=3.74196(67)\text{\AA}$ $c=3.51353(61)\text{\AA}$ $a=6.06187(13)\text{\AA}$
$\text{Ni}_{2.46}\text{MnGa}_{0.54}$	NM $L2_1$	$a=7.56901(11)\text{\AA}$ $c=6.84715(95)\text{\AA}$ $a=3.80759(14)\text{\AA}$	NM $L2_1$	$a=7.51405(17)\text{\AA}$ $c=6.86073(22)\text{\AA}$ $a=3.63276(14)\text{\AA}$
$\text{Ni}_{2.46}\text{MnIn}_{0.54}$	$L2_1$ $L1_2$ Hex	$a=6.03876(25)\text{\AA}$ $a=3.62073(9)\text{\AA}$ $a=4.28743(12)\text{\AA}$ $c=5.21959(17)\text{\AA}$	$L2_1$ $L1_2$ Hex	$a=6.03805(12)\text{\AA}$ $a=3.61596(53)\text{\AA}$ $a=4.28117(63)\text{\AA}$ $c=5.22156(16)\text{\AA}$
$\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$	$L1_2$	$a=3.60134(16)\text{\AA}$	$L1_2$	$a=3.60652(28)\text{\AA}$

due to annealing, changes in exchange interaction due to changes in bond distances and redistribution of defects. Additionally, a step like feature just below 300 K is also noted in the TA alloy. Changes in the lattice parameters may be noted in the RQ and TA alloys of $\text{Ni}_{2.46}\text{MnGa}_{0.54}$ in Table 4.2. The $M(T)$ curves in both, RQ and TA states of $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$ are very similar to each other, in agreement with the invariant structures of the two alloy compositions noted from x-ray diffraction.

Magnetization and resistivity measurements have been recorded for RQ and TA alloy compositions of $\text{Ni}_{2.46}\text{MnIn}_{0.54}$. The $M(T)$ curves for this alloy do not show any difference between the (RQ) and (TA) data, as can be seen in Figure 4.6. Resistivity curves of both alloys are also very similar to each other.

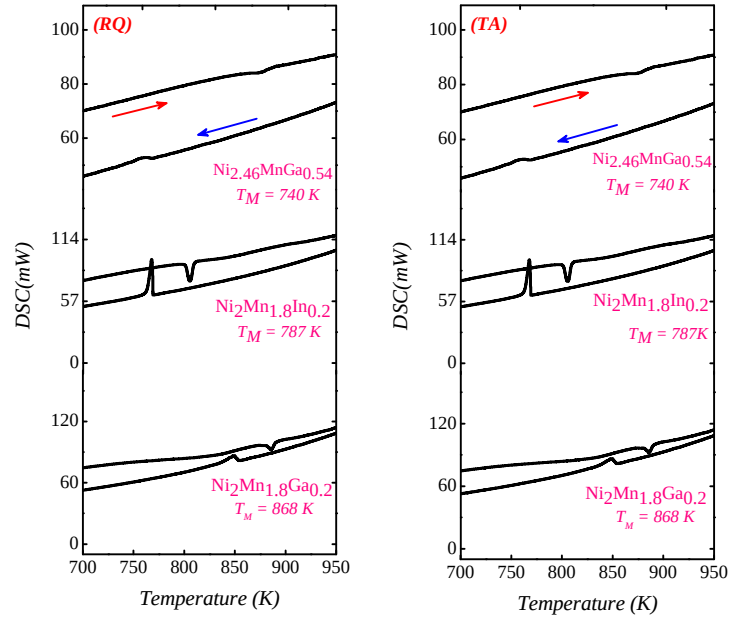


Figure 4.3: DSC thermogram showing the martensitic transformation behavior of alloys during heating and cooling cycles in both RQ and TA.

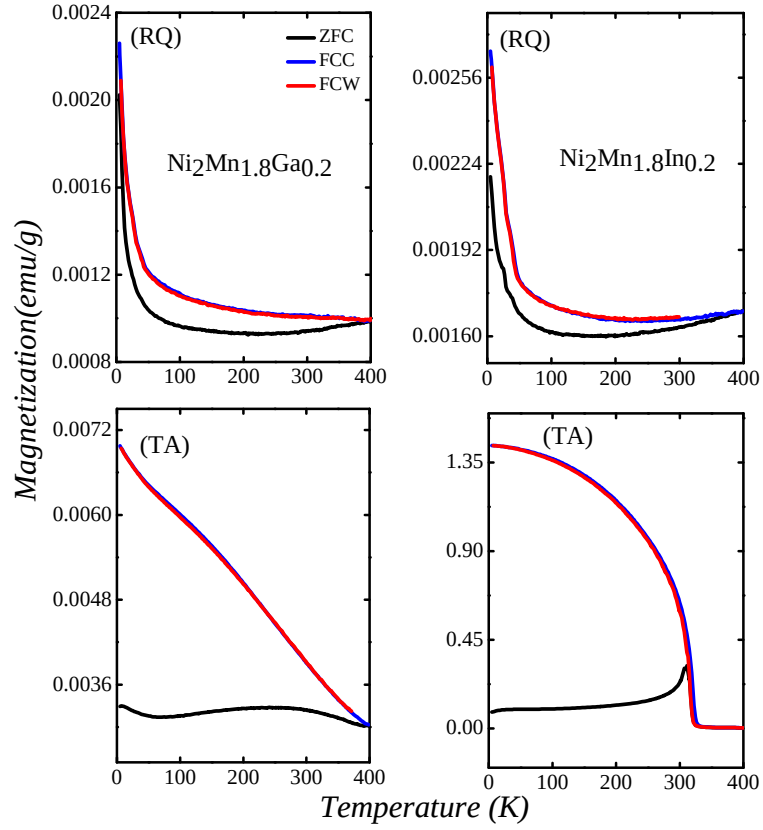


Figure 4.4: ZFC, FCC and FCW curves for $\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$, $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$ in (RQ) and (TA).

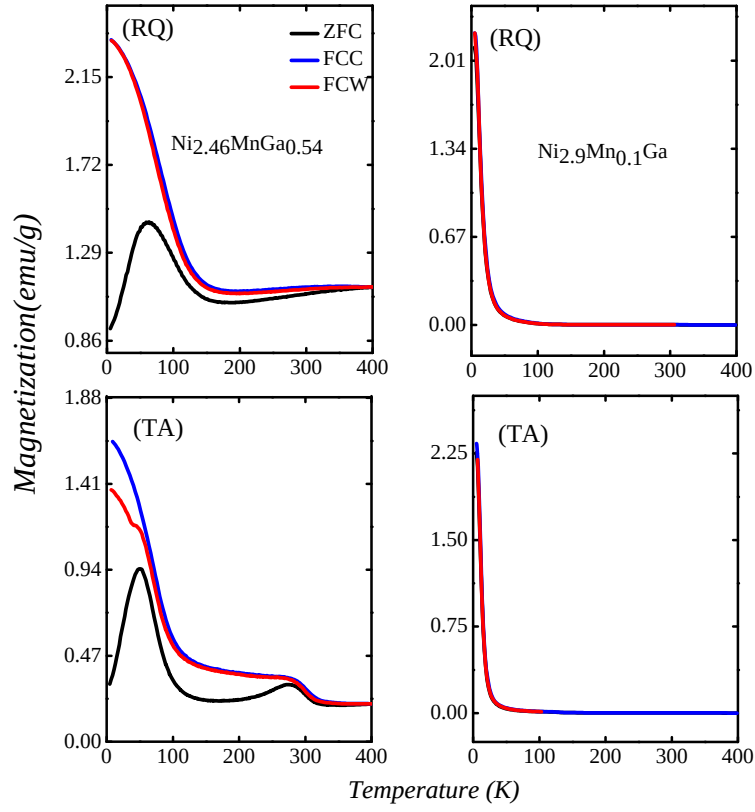


Figure 4.5: ZFC, FCC and FCW curves for $\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$ in (RQ) and (TA) .

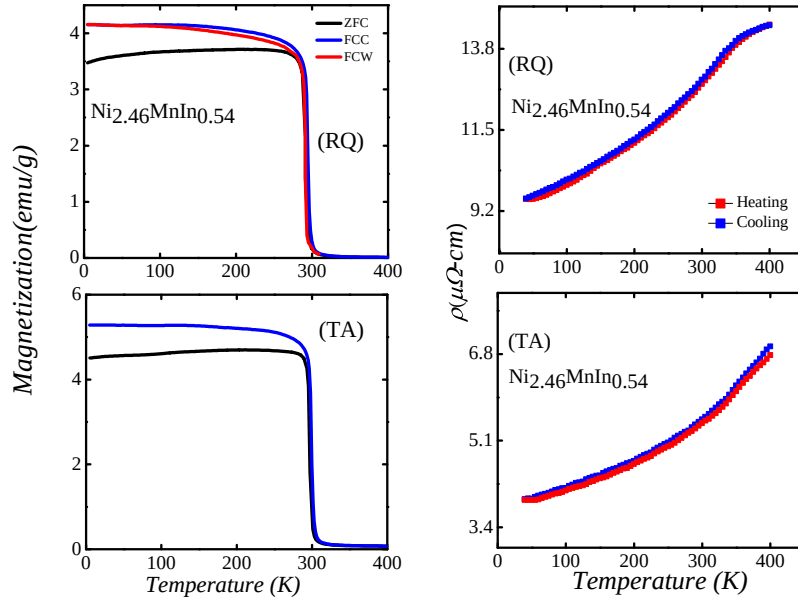


Figure 4.6: ZFC, FCC and FCW and Resistivity curves in both sequence warming and cooling in (RQ) and (TA) .

4.3 Discussion:

In this study, the effect of temper annealing on the phase stability of Heusler alloys and defect evaluation in Ni-Mn-Ga and Ni-Mn-In Heusler alloys. To ensure the purpose of this study, we carefully chosen the alloys maintaining nearly identical valence electron ratio e/a . Every alloy underwent two sets of heat treatment protocol. One half of the alloys were quenched from a high temperature and the other halves were further subjected to temper annealing at a lower temperature and furnace cooling to room temperature. This path revealed a fundamental difference in structural stability of Mn and Ni rich in Heusler alloys. The Mn-rich alloys ($\text{Ni}_2\text{Mn}_{1.8}\text{Ga}_{0.2}$ and $\text{Ni}_2\text{Mn}_{1.8}\text{In}_{0.2}$) exhibited a clear phase separation into $L2_1$ and $L1_0$ by temper annealing, which is in agreement with previous studies [14, 15]. This behavior of Mn-rich alloys can be understood by several interrelated mechanisms, firstly, high-Mn-content alloys exhibit high magnetic interactions and localized lattice distortions due to the Jahn-Teller effect which will decrease the energy barrier for phase decomposition [16]. Secondly, larger Mn atoms compared to the size of the Ni atom will introduce a significant local strain field, leading to rearrangement of atomic positions during prolonged period annealing [17]. Lastly, the behavior of Mn to form antiferromagnetic couplings in concentrated alloys creates additional driving forces for phase separation [18]. These factors collectively explain why Mn-rich compositions are particularly susceptible to microstructural changes under temper annealing conditions. The Ni rich alloys ($\text{Ni}_{2.46}\text{MnGa}_{0.54}$, $\text{Ni}_{2.46}\text{MnIn}_{0.54}$ and $\text{Ni}_{2.9}\text{Mn}_{0.1}\text{Ga}$) exhibit remarkable resistance to phase separation, maintaining the main phase structure without any detectable decomposition after temper annealing. The stability of these alloys aligns with the theoretical predictions of stronger hybridization and higher configurational entropy in Ni-rich systems [19, 20]. The notable changes in the magnetic properties of these alloys despite the structural stability suggest the possibility of defect redistribution processes. As reported, Ni-rich alloys resort to form antisite defects in Ni atoms that acquire Mn sites rather than undergo complete phase separation [21], which are in agreement

with our magnetic measurements, indicating that temper annealing likely induces local rearrangement of these defects without large-scale compositional changes. The absence of phase separation within the martensitic transformation of Ni-rich alloys has important features for applications requiring thermal stability; these results suggest that Ni-rich systems may be more suitable for devices operating under temper annealing exposure [22]. The Mn-rich systems are sensitive to temper annealing which could limit their usefulness for specific functional properties [23]. So, this study bridges an important gap in understanding the stoichiometry-dependent phase stability in Heusler alloys.

4.4 Conclusion:

Nonstoichiometric Heusler alloys are prone to defect formation and phase separation within a structure under this process, even when the alloy is in a homogeneous composition. The chemical composition of the alloy, which is a deviation from the main stoichiometric composition, undergoes these microstructural changes, which will lead to reduced free energy levels by rearrangement of the atomic positions. Mn-rich alloys show a greater tendency for phase separation compared to the Ni-rich alloys. This difference is likely due to increased strain energy and additional magnetic interactions resulting due to larger Mn concentration promoting clustering and decomposition in Mn rich alloys.

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Chapter 5

Role of local structural distortions in the variation of martensitic transformation temperature with e/a ratio in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn or Sb}$) alloys

5.1 Introduction:

The abundance of valence electron atom (e/a) ratio is a key parameter used to understand and identify the structural and magnetic properties of the Heusler alloys, Specifically, in the relation between magnetic behavior and potential applications in spintronics. The e/a ratio plays a crucial role in determining the electronic structure of Heusler alloys, thereby affecting their magnetic behavior, thermodynamic stability, and functional applications. Furthermore, this ratio has a pronounced influence on the martensitic transformation temperature in these alloys. Previous studies frequently observe a linear correlation between the martensitic transformation temperature and the e/a ratio, highlighting its importance

in tailoring phase transition properties [1]. Ni_2MnZ ($Z = \text{In, Sn, Sb}$) Heusler alloys exhibit a stable ferromagnetic with $L2_1$ structure even if their e/a ratio is equal or more than Ni_2MnGa [2]. Ni_2MnZ ($Z = \text{In, Sn, Sb}$) display a martensitic transition with increasing of e/a ratio obtained through the replacement of Z atoms by Mn, resulting in Mn-rich $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$. In addition, the Mn substitution modifies the magnetic ground state and exhibits a strong correlation between the structural and magnetic degrees of freedom, giving rise to variety of effects such as the magnetic shape memory effect [3,4], giant magnetoresistance [5] and exchange bias [6]. The off-stoichiometric Ni-Mn-Z alloys undergo a phase transformation from a high temperature austenitic phase to a low temperature martensitic phase with ($L2_1$ or $B2$ structure to martensitic structure). The martensite structure is found to be either tetragonal, $L1_0$, non modulated (NM) structure or a modulated structure such as 7M and 5M, depending on the content of Mn substantiated in the Z sites. Transformation usually occurs via one or more intermediate transformations, with the structure continuously evolving from one type of modulation to another [7]. In case of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ where ($Z = \text{In, Sn, Sb}$), the alloys undergo martensitic transition at a specific value of x dependent on the type of Z atom. The value of $x \approx 0.35$, $x \approx 0.4$ and $x \approx 0.45$ for In, Sn, and Sb, respectively [8]. As full replacement of Z atoms with Mn results in a binary NiMn alloy, the rate at which T_M increases with the electron-to-atom ratio (e/a) also depends on the Z element. This rate is highest for $Z = \text{Sb}$ and progressively lowers for $Z = \text{Sn}$ and In. Due to the martensitic transition in these alloys the magnetic ground state will be change from ferromagnetic ($x = 0$) to antiferromagnetic ($x = 1$), with the intermediate alloy compositions displaying a complex magnetic state with competing ferromagnetic and antiferromagnetic interactions which is often results in a glassy magnetic state [3,9]. Recently, alot of studies have examined the relation between the first order transition and the magnetic properties in Ni-Mn-Z ($Z = \text{Ga, In, Sn and Sb}$) Heusler alloys [1,10,11]. Based on the experimental studies of theses alloys it is suggested that the martensitic transition occurs in alloys with lattice parameter of the parent is $\leq 6 \text{ \AA}$ [12]. Extended x-ray absorption fine structure studies in such $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ alloys

have highlighted the role of the structural distortions in the nearest neighbor environment in inducing martensitic transformation and the associated magnetic interactions in these systems [13–15]. As mentioned in chapter 4 the metastable structure of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ phase separates into $L1_0$ and $L2_1$ upon temper annealing depending on the annealing conditions and temperatures which reinforce the local structural modifications in the phase transformation [16]. As reported above, the critical value of x increases with change of Z atom from In to Sn and Sb respectively [1]. Therefor, To determine the factors which are responsible for the variation in the martensitic transformation temperature T_M as a function of electron-to-atom ratio (e/a), depending on the specific Z atom eight compositions were chosen as below :

- Fixed Z element (In) with variable e/a ratio:

1. $\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$ ($e/a = 7.8$)
2. $\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$ ($e/a = 7.85$)
3. $\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$ ($e/a = 7.9$)
4. $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ ($e/a = 8.0$)

- Fixed e/a ratio (8.0) with variable Z element:

1. $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$
2. $\text{Ni}_2\text{Mn}_{1.34}\text{Sn}_{0.66}$
3. Ni_2MnSb

- Comparable T_M ($\approx 400\text{K}$) with varying Z element and e/a ratio:

1. $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ (e/a = 8.0)
2. $\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$ (e/a = 8.2)
3. $\text{Ni}_2\text{Mn}_{65}\text{Sb}_{0.35}$ (e/a = 8.3)

5.2 Results:

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDAX) was used to determine the chemical compositions of the alloys $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ (Z= In, Sn, Sb), the measurements were performed in an average sample area of ($100\mu\text{m}^2$) to ensure the precision of the results. The comprehensive data presented in Table 5.1 includes both nominal and measured compositions, the martensitic transformation temperature T_M which have been calculated from the DSC measurements and performed in the temperature range of (300 K to 550 K).

Table 5.1: EDAX composition, e/a ratio, and the martensitic transformation temperature for $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In}, \text{Sn}$ and Sb) alloys.

Alloy	EDAX composition	e/a	T_M (K)
$\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$	$\text{Ni}_{1.99}\text{Mn}_{1.26}\text{In}_{0.75}$	7.74	
$\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$	$\text{Ni}_{2.02}\text{Mn}_{1.34}\text{In}_{0.64}$	7.88	200
$\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$	$\text{Ni}_{2.04}\text{Mn}_{1.36}\text{In}_{0.60}$	7.93	335
$\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$	$\text{Ni}_{2.08}\text{Mn}_{1.46}\text{In}_{0.46}$	8.10	436
$\text{Ni}_2\text{Mn}_{1.34}\text{Sn}_{0.66}$	$\text{Ni}_{2.03}\text{Mn}_{1.32}\text{Sn}_{0.65}$	8.03	
Ni_2MnSb	$\text{Ni}_{2.06}\text{Mn}_{1.01}\text{Sb}_{0.93}$	8.08	
$\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$	$\text{Ni}_{2.07}\text{Mn}_{1.56}\text{Sn}_{0.37}$	8.26	434
$\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$	$\text{Ni}_{2.05}\text{Mn}_{1.68}\text{Sb}_{0.27}$	8.40	439

Figure 5.1 shows the characteristic thermal signatures of the phase transformation obtained from DSC measurements during heating and cooling cycles.

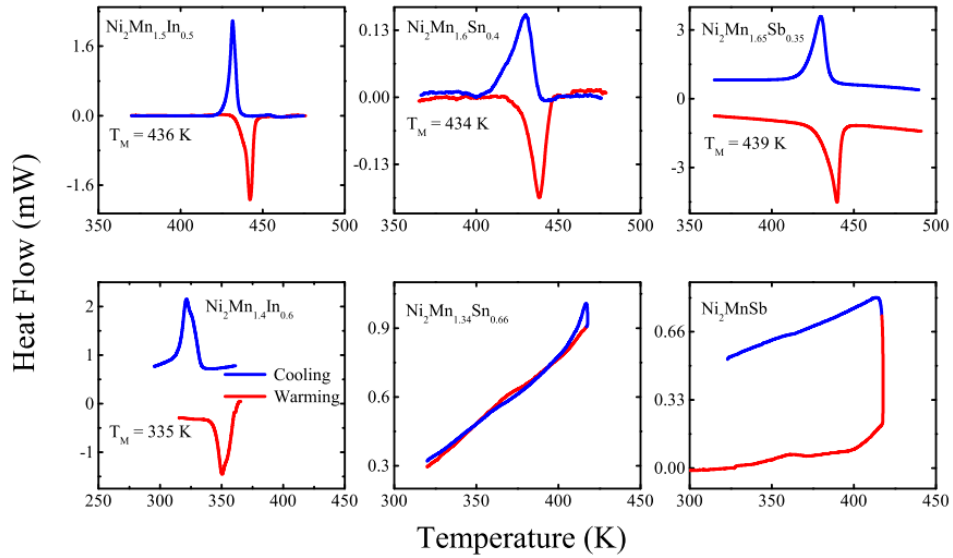


Figure 5.1: DSC thermograms of $\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$ $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ $\text{Ni}_2\text{Mn}_{1.34}\text{Sn}_{0.66}$ Ni_2MnSb $\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$ $\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$.

To identify structural phases for all alloys, X-ray diffraction measurements were performed at room temperature with respect to the $2\theta^\circ$ range between (20° and 100°), the data were analyzed using Jana2020 software. As shown in Figures 5.2 and 5.3 all compo-

sitions have a pure phase without impurity phases. Table 5.2 shows the rietveld refined structures and the lattice parameters of the alloys. The alloys have been classified into three different groups depending on the X-ray diffraction patterns of the alloys see Figure 5.4. The first group of alloys is represented as the same Z atom with a change in the e/a ratio, (see Figure 5.4 (a)). The structure of these alloys transforms from the austenite structure $L2_1$ to a martensite structure 7M with increasing e/a ratio (Mn content). Such a change in the martensitic transformation temperature with the e/a ratio will lead to a change in the crystal structure of the alloy, as can be seen in Ni-Mn-In alloys [3,4].

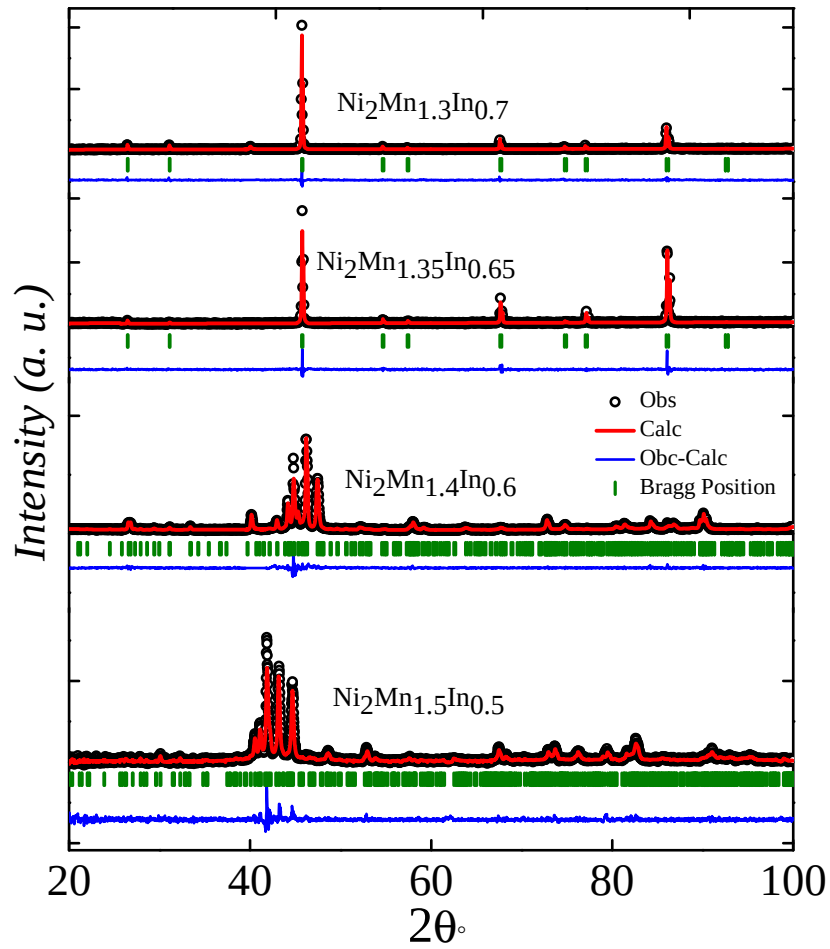


Figure 5.2: Rietveld-refined XRD patterns of $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ ($x = 0.3-0.5$) recorded at room temperature.

With the change of the Z atom ($Z = \text{In}, \text{Sn}, \text{Sb}$) but with a similar e/a ratio (see Figure 5.4 (b)) the alloys $\text{Ni}_2\text{Mn}_{1.34}\text{Sn}_{0.66}$, Ni_2MnSb exhibit austenite structure $L2_1$, but in the case of $\text{Ni}_2\text{Mn}_{0.5}\text{In}_{0.5}$ is a martensitic alloy as mentioned above. As reported, the critical value of the e/a ratio for $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ and $\text{Ni}_2\text{Mn}_{1+x}\text{Sb}_{1-x}$ at which alloys undergo martensitic transformation is (8.15 and 8.20), respectively [8].

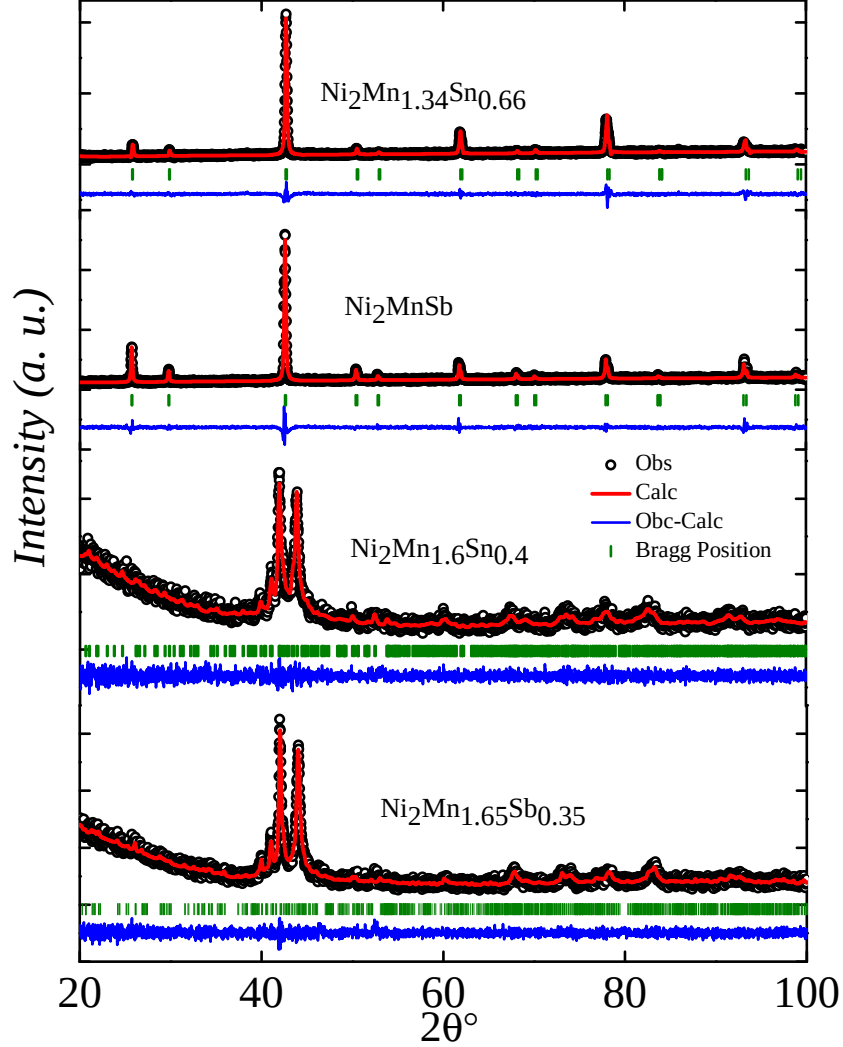


Figure 5.3: Rietveld-refined XRD patterns of the alloys with same $e/a \approx 8.0$ recorded at room temperature.

Figure 5.4(c) shows the last group of alloys with the same $T_M \approx 400K$ and different e/a and Z atoms, the XRD pattern shows that all the alloys in this case are martensite alloys within an incommensurately 7M modulated structure [17,18] at room temperature due to the higher e/a ratio (Mn content).

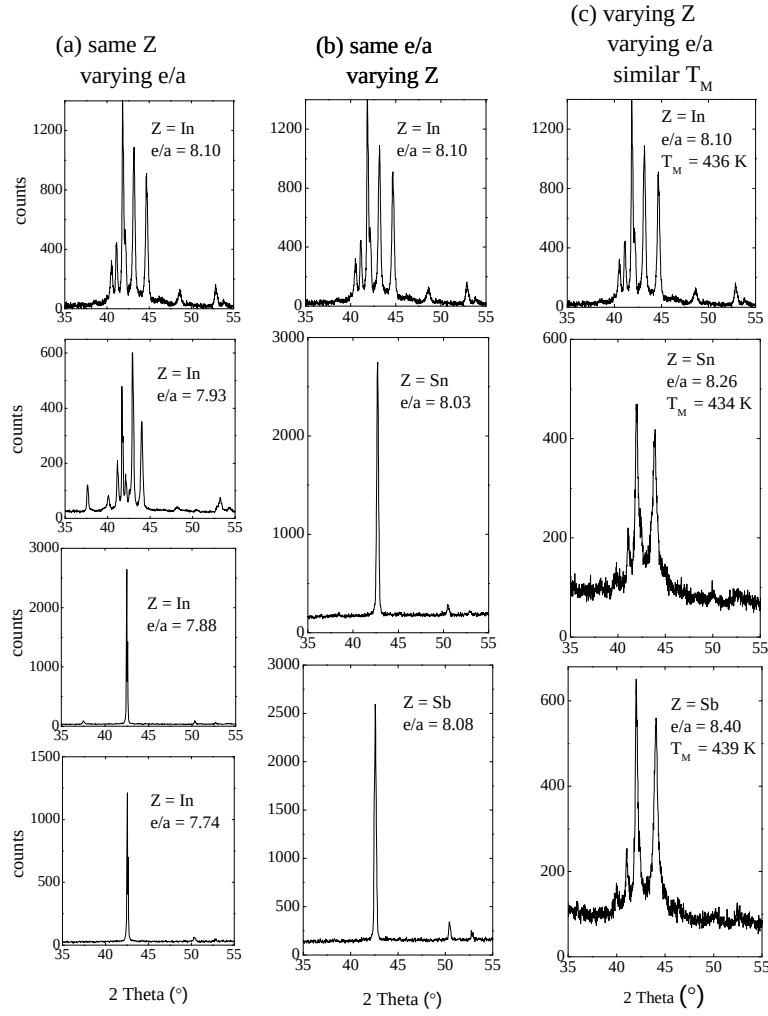


Figure 5.4: Room-temperature X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn, and Sb}$) alloys are presented, arranged according to their respective e/a ratios for comparative analysis.

It may be noted that when the alloys with a fixed e/a ratio but with different Z atom are considered, the martensitic transformation temperature varies depending on the Z atom of the Ni-Mn-Z Heusler alloys. However, if the transformation temperature is maintained same for alloys with different Z ($\text{Z} = \text{In, Sn, Sb}$) atom the e/a ratio increases from In to Sn and Sb. Considering the end member composition achieved after a complete replacement of Z atom, is NiMn in all the three cases, the above variation of crystal structure at room temperature and the relative concentration of the Z atom for In, Sn and Sb clearly indicate that the critical value of e/a ratio at which the alloys display martensitic instability and

the slope of T_M vs. e/a curve increases from $Z = \text{In}$ to $Z = \text{Sb}$.

Table 5.2: Lattice parameters obtained from Rietveld fitting for the X-ray diffraction patterns of all the alloys.

Alloy	Structure	Lattice parameters
$\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$	L2_1	$a = 6.01278(5) \text{ \AA}$
$\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$	L2_1	$a = 6.00701(5) \text{ \AA}$
$\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$	7M	$a = 4.3892(2) \text{ \AA}, b = 5.6424(2) \text{ \AA}, c = 4.3337(1) \text{ \AA}$ $\beta = 94.23(1)^\circ, q = 0.3321(4)c^*$
$\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$	7M	$a = 4.4024(3) \text{ \AA}, b = 5.5470(4) \text{ \AA}, c = 4.3240(2) \text{ \AA}$ $\beta = 94.23(1)^\circ, q = 0.3101(3)c^*$
$\text{Ni}_2\text{Mn}_{1.33}\text{Sn}_{0.67}$	L2_1	$a = 6.01203(8) \text{ \AA}$
Ni_2MnSb	L2_1	$a = 6.00053(4) \text{ \AA}$
$\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$	7M	$a = 4.3003(12) \text{ \AA}, b = 5.6202(19) \text{ \AA}, c = 4.3110(12) \text{ \AA}$ $\beta = 90.33(5)^\circ, q = 0.2874(45)c^*$
$\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$	7M	$a = 4.2997(18) \text{ \AA}, b = 5.6089(22) \text{ \AA}, c = 4.2916(35) \text{ \AA}$ $\beta = 90.54(1)^\circ, q = 0.3055(54)c^*$

Magnetization studies were conducted to identify magnetic transitions and characterize the magnetic phases in the alloys as shown in Figure 5.5. The measurements were recorded in the temperature range of 5 K to 400 K in the ZFC, FCC and FCW mode within an applied field of 100 Oe of all alloys. Four of these alloys $\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$, $\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$, $\text{Ni}_2\text{Mn}_{1.33}\text{Sn}_{0.67}$, Ni_2MnSb , exhibit paramagnetic to ferromagnetic transi-

tion with decreasing temperature at $T_C = 307$ K, 305 K, 325 K and 347 K, respectively. On the other hand the remaining four alloys exhibit a low magnetic moment at 5 K in their ZFC state and large bifurcation between ZFC and FC magnetization curves indicating a complex magnetic order due to competing ferro and antiferromagnetic interactions. As reported, the antiferromagnetic interaction can arise from an indirect interaction between the Mn atoms in the Y sublattice and those in the Z sublattice of X_2YZ Heusler structure [19]. However, both theoretical models and experimental studies have identified additional exchange mechanisms that contribute to the observed antiferromagnetic coupling [20,21]. First-principles calculations discover that the key exchange pathways in these materials originate from structural distortions that disrupt symmetry at Mn sites in non-stoichiometric Ni-Mn-Z alloys [15, 20]. Temperature-dependent magnetization $M(T)$ curves for the Ni-Mn-In alloys, which are presented in Figure 5.5, show that the onset of martensitic transformation is first observed near 200 K in $Ni_2Mn_{1.35}In_{0.65}$ ($e/a = 7.88$), which remains ferromagnetic below its Curie temperature ($T_C = 305$ K). In contrast, $Ni_2Mn_{1.3}In_{0.7}$ ($e/a = 7.74$) shows no martensitic transition within the measured temperature range. As the e/a ratio increases, the martensitic transition temperature (T_M) increases systematically, reaching to 420 K in $Ni_2Mn_{1.5}In_{0.5}$ ($e/a = 8.10$). In particular, for $Ni_2Mn_{1.4}In_{0.6}$ with ($T_M = 330$ K, marked by an arrow in Fig. 4) and $Ni_2Mn_{1.5}In_{0.5}$, the transformation occurs in the paramagnetic regime. While, alloys with $e/a \approx 8.0$ but different Z elements ($Z = Sn, In$), we find that Sn and In based compositions exhibit no martensitic transition down to 5 K. To achieve a martensitic transformation comparable to $Ni_2Mn_{1.5}In_{0.5}$ ($e/a = 8.10$), higher e/a ratios of 8.26 ($Z = Sn$) and 8.35 ($Z = Sb$) are required. These observations support two key findings: (1) a threshold e/a ratio is necessary to trigger the martensitic transformation, and (2) T_M *vs.* e/a slope steepens for Sn and Sb substitutions compared to In.

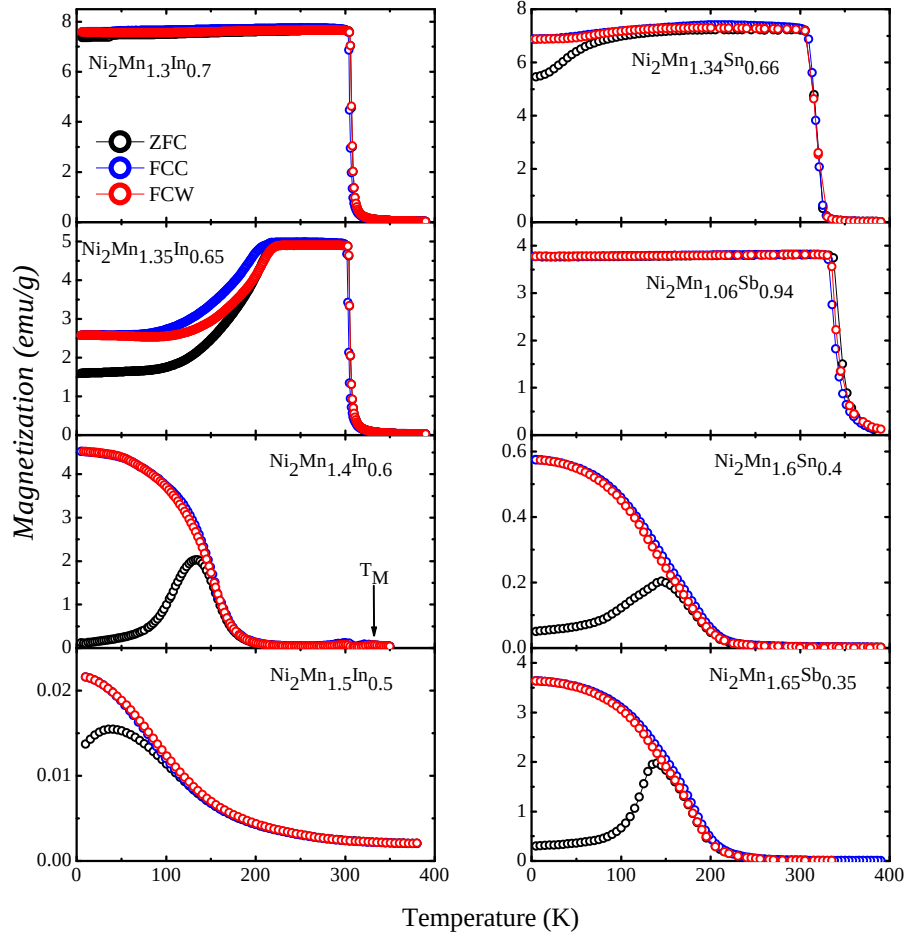


Figure 5.5: Temperature-dependent magnetization (M - T) curves measured under 100 Oe applied field, showing zero-field-cooled (ZFC), field-cooled cooling (FCC), and field-cooled warming (FCW) protocols across 5 - 400 K.

To investigate the origin of the different relationships T_M versus e/a for ($Z = \text{In}$, Sn , and Sb alloys), EXAFS studies were performed at the Ni and Mn K edges in the eight compositions. The previous study of EXAFS on such alloys has demonstrated the presence of local structural distortion in the near-neighbor environment of the absorber atom Mn and Ni [13–15]. In particular, the EXAFS analysis showed a consistent deviation from ideal $L2_1$ symmetry across all non-stoichiometric Ni-Mn-Z alloys, manifested through systematically shorter Ni-Mn bond lengths compared to Ni-Z distances. Remarkably, this local structural disorder is present even in the compositions that remain austenitic down

to 5 K. First principle calculations and spectroscopic studies suggest that these atomic scale distortions strengthen the hybridization of Ni-3d and Mn-3d, creating favorable electronic conditions for martensitic transformation [20, 22]. The universal presence of this bond length asymmetry implies that the local distortion is necessary for martensitic transformation. Figure 5.6 shows the Fourier transform magnitudes of $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ alloys at the edges of Ni and Mn, and Figure 5.7 gives the magnitudes of the Fourier transform EXAFS at the Ni and Mn K edges of $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$, $\text{Ni}_2\text{Mn}_{1+x}\text{Sb}_{1-x}$ alloys. The data were fitted with respect to EXAFS parameters which have been mentioned in chapter 3 in the K and R spaces in the range of 3 to 14 $\text{\AA}^{-1}$ and 1 to 4 $\text{\AA}$, respectively. The EXAFS fitting results are listed in Table 5.3.

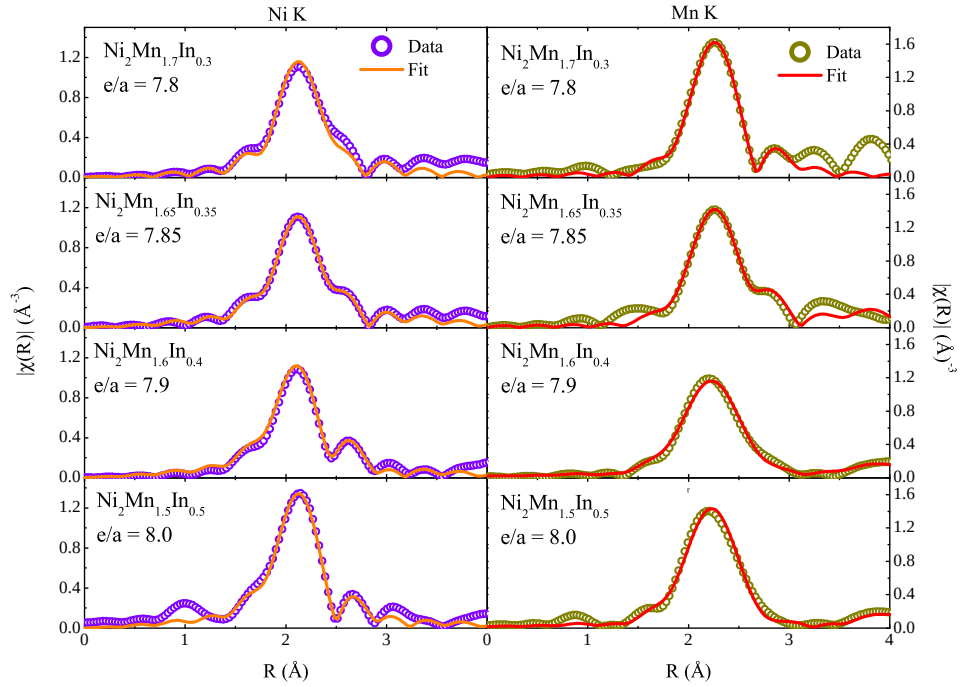


Figure 5.6: Fourier transform magnitudes of EXAFS spectra (open circles) with theoretical fits (solid lines) for Ni and Mn K edges in Ni-Mn-In alloys.

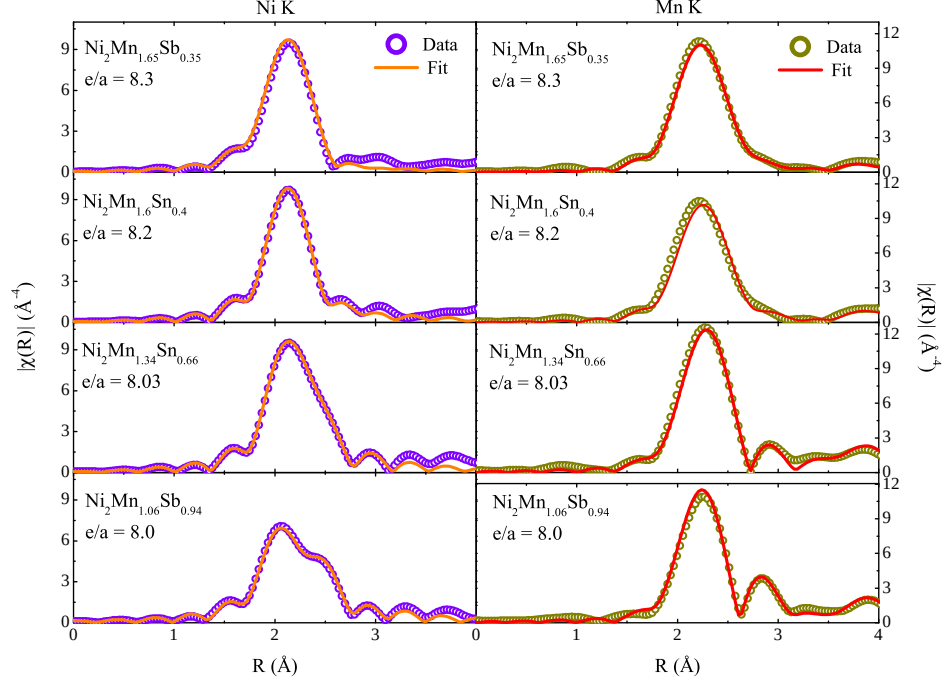


Figure 5.7: Fourier transform magnitudes of EXAFS spectra (open circles) with theoretical fits (solid lines) for Ni and Mn K edges in Ni-Mn-Sn and Ni-Mn-Sb alloys.

By comparing the results of the EXAFS analysis for all alloys concerning the Z atom and the ground state of the alloys, the bond distance of the nearest neighbour Ni-Mn is shorter than the Ni-Z atoms; furthermore, the second nearest neighbor bond distances Mn-Z and Mn-Mn_Z are almost equal in austenite alloys. while in alloys that undergo a martensitic phase transformation the bond distance of Mn-Mn_Z is greater than Mn-Z. In the case of ferromagnetic alloys, the third closest neighbor Mn-Mn bond distance is around ≈ 4.2 Å while in alloys that dominant antiferromagnetic interaction is 4.3 Å. These findings align with previous reports on Ni₂Mn_{1+x}In_{1-x} systems [13, 15, 21] and are further supported by studies of Ni₂Mn_{1.4}Sn_{0.6} [14].

Table 5.3: Bond length (R) and mean square radial disorder (σ^2) of the near neighbor correlations around Mn and Ni in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ (Z = In, Sn, Sb) alloys.

Alloy	Bonds									
	Ni-Mn		Ni-Z		Mn-Z		Mn-Mn _Z		Mn-Mn	
	R Å	σ^2 Å ²	R Å	σ^2 Å ²	R Å	σ^2 Å ²	R Å	σ^2 Å ²	R Å	σ^2 Å ²
$\text{Ni}_2\text{Mn}_{1.3}\text{In}_{0.7}$	2.589(10)	0.010(1)	2.627(10)	0.006(1)	2.930(20)	0.005(2)	2.935(20)	0.005(2)	4.254(20)	0.015(2)
$\text{Ni}_2\text{Mn}_{1.35}\text{In}_{0.65}$	2.585(6)	0.013(1)	2.640(6)	0.005(1)	2.916(20)	0.003(2)	2.941(10)	0.006(3)	4.245(30)	0.016(2)
$\text{Ni}_2\text{Mn}_{1.4}\text{In}_{0.6}$	2.582(8)	0.012(1)	2.625(10)	0.006(1)	2.894(61)	0.043(14)	2.981(26)	0.022(8)	4.341(35)	0.025(3)
$\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$	2.571(8)	0.009(1)	2.620(8)	0.004(1)	2.880(100)	0.035(15)	2.999(80)	0.021(7)	4.341(35)	0.028(3)
$\text{Ni}_2\text{Mn}_{1.33}\text{Sn}_{0.67}$	2.572(4)	0.010(1)	2.603(4)	0.006(1)	2.940(20)	0.008(1)	2.950(10)	0.007(2)	4.210(20)	0.013(2)
Ni_2MnSb	2.567(3)	0.010(1)	2.585(3)	0.008(1)	2.959(17)	0.013(2)	2.959(17)	0.013(2)	4.233(20)	0.012(2)
$\text{Ni}_2\text{Mn}_{1.6}\text{Sn}_{0.4}$	2.572(7)	0.010(1)	2.593(5)	0.005(1)	2.890(100)	0.032(16)	3.070(40)	0.023(6)	4.330(40)	0.024(3)
$\text{Ni}_2\text{Mn}_{1.65}\text{Sb}_{0.35}$	2.561(6)	0.010(1)	2.591(9)	0.007(1)	2.870(70)	0.029(10)	3.040(30)	0.023(4)	4.310(40)	0.025(3)

5.3 Discussion:

Substitution of Mn at the Z atom sites in Ni_2MnZ ($Z = \text{In, Sn or Sb}$) or, conversely, replacing Mn by Z atoms in the binary $\text{Ni}_{50}\text{Mn}_{50}$ has a significant effect on the martensitic as well as magnetic ground states of these alloys. There have been several experimental and theoretical studies on the evolution of structure, magnetic and martensitic properties that have paved way for design of better alloys for several applications [7, 23–26]. However, a detailed analysis on the role of different Z atoms in inducing these properties are missing. It has been argued in the literature that the Heusler structure of $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ can accommodate the strain caused by the size difference between the Z atom and Mn. The strain accommodation is up to a critical doping content beyond which the nonstoichiometric alloy undergoes a martensitic transformation. The structural strain due to size difference between the Mn and Z atoms can be estimated by the difference in Mn–Z and Mn–Mn_Z bond distances. Figure 5.8 shows a plot of difference between Mn–Mn_Z and Mn–Z bond distances as a function of the e/a ratio. In the case of austenitic alloys, irrespective of the Z atom, the difference between the two bond distances is nearly zero. On the other hand, a difference of $\sim 10\%$ between Mn–Mn_Z and Mn–Z bond distances is noted for the martensitic alloys, and it increases further with increasing e/a ratio of the alloys.

Another intriguing aspect of these Mn-rich alloys is that they undergo a phase separation into a Heusler and a L1_0 phase upon temper annealing [16, 27, 28]. The shorter Ni–Mn bond distance could result from the segregation of NiMn type structural entities in these Mn-rich alloys [29]. Figure 5.9 compares Ni–Mn and Ni–Z bond distances as a function of the e/a ratio for the alloys with different Z atoms. Regardless of the type of Z atom, the Ni–Mn bond distance seems to decrease linearly with increasing e/a ratio. In contrast, the Ni–Z bond distance displays a completely different behavior. Although their specific trends remain unclear, the Ni–In bond distances are larger than the Ni–Sn which are larger than Ni–Sb bond lengths.

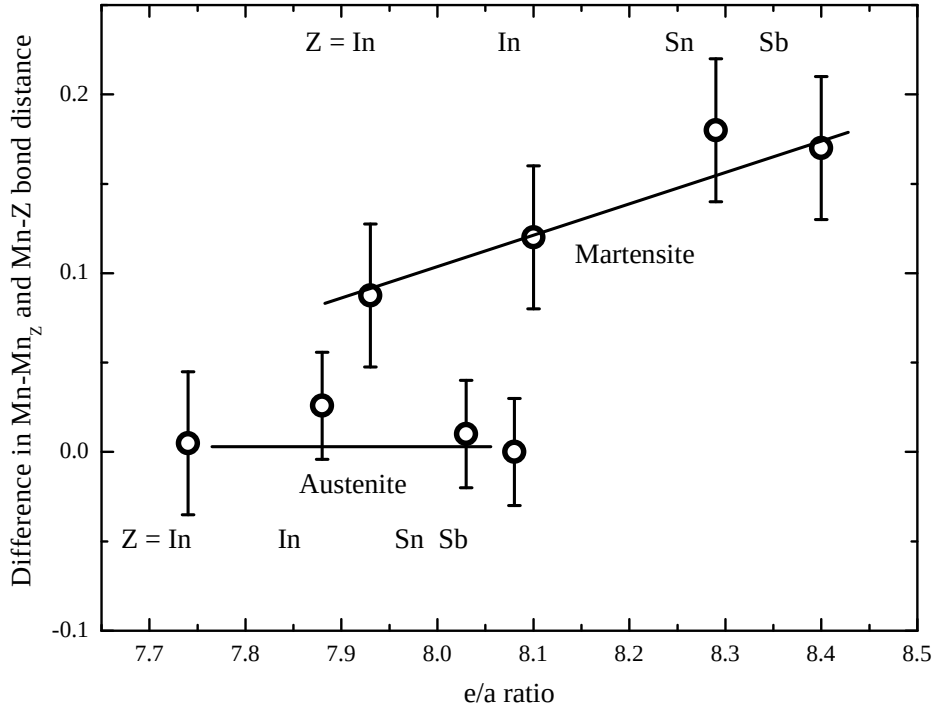


Figure 5.8: Difference in the second nearest neighbor Mn-Z and Mn-Mn_z as a function of e/a ratio in the Ni-Mn-Z alloys.

The behavior of the nearest neighbor distances reveals the reason for the higher critical values of e/a at which martensitic transformation occurs in $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ and $\text{Ni}_2\text{Mn}_{1+x}\text{Sb}_{1-x}$. Figure 5.9 shows that the difference between Ni-Mn and Ni-Z bond distances progressively decrease as Z changes from In to Sn to Sb. Ideally, in $L2_1$ symmetry, the two nearest neighbor bond distances, Ni-Mn and Ni-Z, should be equal. However, disparities are seen between these two bond distances in the cubic and martensitic phases of such Mn-rich alloys.

Replacement of Z atoms by Mn also segregates NiMn type structural units in a Heusler matrix [27]. The nearest neighbor Ni-Mn bond distance in the $B2$ or $L1_0$ phase of NiMn is shorter than the Ni-Mn bond distance in the Heusler phase, producing a local strain. It has been recently shown that this strain drives the martensitic instability in Ni-Mn-In alloys [29]. Therefore, the difference between Ni-Mn and Ni-Z bond distances in

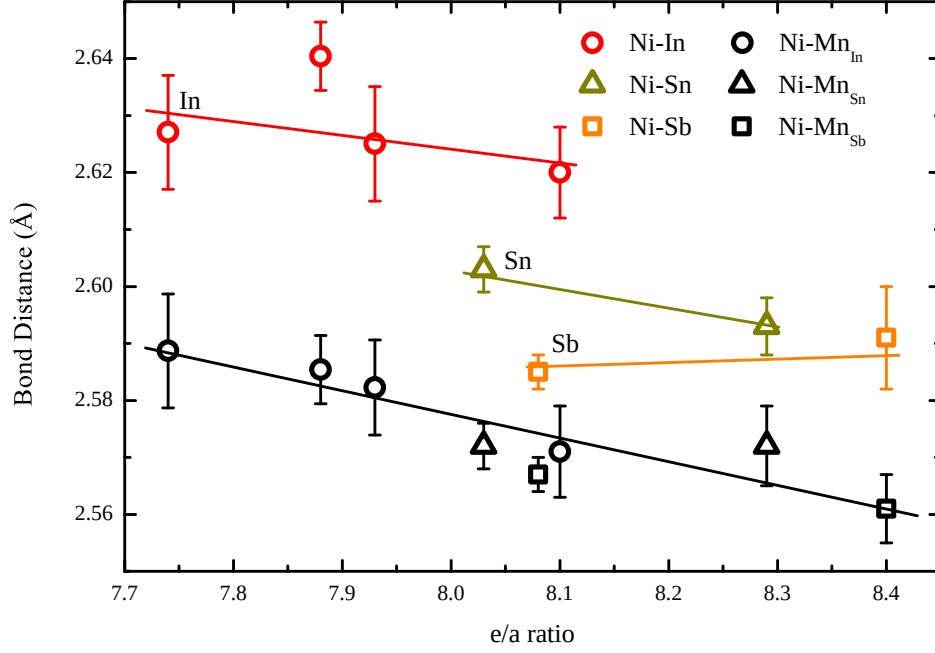


Figure 5.9: Variation of the nearest neighbor Ni-Mn and Ni-Z bond distances in the Ni-Mn-Z alloys as a function of e/a ratio.

$\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ alloys indicates presence of local strain produced by the replacement of the Z atom by Mn in these alloys. A smaller difference between the two distances implies lower strain or better compatibility between NiMn and Ni_2MnZ structural units which are formed locally in these off-stoichiometric alloys. A lower strain will also accommodate a larger amount of Mn at the Z atom site before the structure transforms from the cubic structure to a lower symmetry martensitic structure. Therefore, the critical concentration of Mn at which martensitic transformation occurs, progressively increases from In to Sn to Sb. Since the end member achieved after a complete replacement of Z atom is NiMn for all the three Z members considered here, the slope of variation of T_M vs. e/a ratio also progressively increases from In to Sb. The locally segregated NiMn type structural units also affect the magnetic ground state of these alloys. Presence of antiferromagnetic NiMn structural units weaken the long range ferromagnetic interactions leading to disappearance of austenitic T_C . Increasing Mn content leads to the growth of antiferromagnetic

clusters and shrinking of ferromagnetic Ni_2MnZ type ferromagnetic clusters. The strong competition between these ferromagnetic and antiferromagnetic clusters gives rise to a spin glass state. This is aptly clear from the similarities of the magnetization behaviour of all Ni-Mn-Z alloys with same T_M in Figure 5.5.

5.4 Conclusion:

In summary, several $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn and Sb}$) alloys were investigated to understand the cause of different slopes of T_M vs. e/a curves for different Z atoms. In the case of alloys with the same Z atom and increasing e/a ratio, the difference between the nearest neighbor Ni-Mn and Ni-Z bond distances remains nearly constant irrespective of the state of the alloy. A distortion in the second nearest neighbor distances, Mn-Z and Mn-Mn_Z appears in the martensitic alloys. Such first and second neighbor distortion can be conceived as a strain developing in the $L2_1$ structure due to the different atomic sizes of Mn and Z atoms. This strain is accommodated up to a critical concentration of Mn, and beyond which the alloy transforms martensitically to a lower symmetry structure.

A change in the Z atom from In to Sn and Sb in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ while keeping their e/a ratio similar shows that the critical value of x at which the martensitic transformation appears depends on the type of Z atom. In the present case, the alloys with $\text{Z} = \text{Sn and Sb}$ with $e/a \sim 8$ are ferromagnetic austenitic down to the lowest temperature investigated. Martensitic transformation at the same temperature as $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ ($e/a \sim 8$) can be achieved in alloys with $\text{Z} = \text{Sn and Sb}$ at an e/a ratio of 8.3 and 8.4, respectively. While the second neighbor distortions appear only in the martensitic compositions of Ni-Mn-Sn and Ni-Mn-Sb alloys, the nearest neighbor distortion decreases progressively from $\text{Z} = \text{In}$ to Sn to Sb. The lower first neighbor distortion allows for accommodation of higher content of Mn at the Z atom site as the Z atom changes from In to Sb, and hence the martensitic transformation appears at a higher value of Mn content. Since the end member alloy in all three cases is NiMn, the increasingly higher values of Mn content at the Z atom site

implies a steeper slope for the T_M *vs.* e/a ratio curves as the Z atoms change from In to Sn to Sb.

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Chapter 6

Effects of In doping in the martensitic alloy $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5}$

6.1 Introduction:

So far we have seen the role of local structural distortions in martensitic transformation of Mn-rich Ni-Mn-Z ($Z = \text{In}, \text{Sn}$ and Sb) alloys [1]. Ni-Mn-Ga alloys are distinctly different from the above Ni-Mn-Z alloys. Firstly, Ni_2MnGa is martensitic [2], while other Ni_2MnZ alloys are not [3–5]. Secondly, only Mn-rich Ni-Mn-Z alloys display martensitic transformation [6, 7] while, stoichiometric, Ni-rich and Mn-rich, Ni-Mn-Ga alloys undergo martensitic transformation [8–11]. The transformation temperature in Ni-Mn-Ga alloys also scales with e/a ratio [12, 13]. Further our previous EXAFS studies showed that in the martensitic state of Ni-Mn-Ga alloys, Ni-Ga bond distance is less than Ni-Mn bond distance, while, in case of other Ni-Mn-Z alloys, the non-stoichiometric compositions have Ni-Mn distance is shorter than Ni-Z bond distance even in the austenite phase. To understand these differences in local structural distortions and their role in the martensitic transformation of these alloys, we have undertaken a study involving the substitution of In for Ga in $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) while maintaining their e/a ratio constant at 8.

6.2 Results:

The alloy compositions were determined by using Energy Dispersive X-ray Spectroscopy (SEM-EDAX). To ensure a representative analysis, we acquired spectra from four distinct spots on each surface of the sample. The measured values exhibited a 2% discrepancy relative to the original samples, Table 6.1 shows the difference between the actual samples and EDAX within the transformation temperatures determined by DSC in both the warming and cooling sequences.

Table 6.1: EDAX composition, e/a ratio, and the martensitic transformation temperature for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.

Alloy	EDAX composition	e/a	T_M (K)
$\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5}$	$\text{Ni}_2\text{Mn}_{1.52}\text{Ga}_{0.48}$	8.02	679
$\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.4}\text{In}_{0.1}$	$\text{Ni}_{2.01}\text{Mn}_{1.49}\text{Ga}_{0.41}\text{In}_{0.09}$	8.01	549
$\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.3}\text{In}_{0.2}$	$\text{Ni}_{1.99}\text{Mn}_{1.53}\text{Ga}_{0.29}\text{In}_{0.19}$	8.013	473
$\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.2}\text{In}_{0.3}$	$\text{Ni}_{2.01}\text{Mn}_{1.53}\text{Ga}_{0.21}\text{In}_{0.25}$	8.05	482
$\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.1}\text{In}_{0.4}$	$\text{Ni}_{2.01}\text{Mn}_{1.4}\text{Ga}_{0.12}\text{In}_{0.38}$	8.08	421
$\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$	$\text{Ni}_{2.09}\text{Mn}_{1.45}\text{In}_{0.46}$	8.11	436

The DSC measurements were performed in the temperature range of (300-800 K), as can be seen in Figure 6.1, the martensitic transformation for the alloy $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5}$ is equal to 679 K, but with an increase of the x content from 0.0 to 0.5 the martensitic transformation decreases linearly with this variation in the x content, Figure 6.2 shows the variation of expected e/a ratio and actual e/a ratio determined from EDAX and the martensitic transformation temperature as a function of In content (x). The black dash line is represented the e/a ratio for actual samples, the red squares show the e/a ratio which calculated from the EDAX data, and the blue circles denote the martensitic transformation temperature for all alloys.

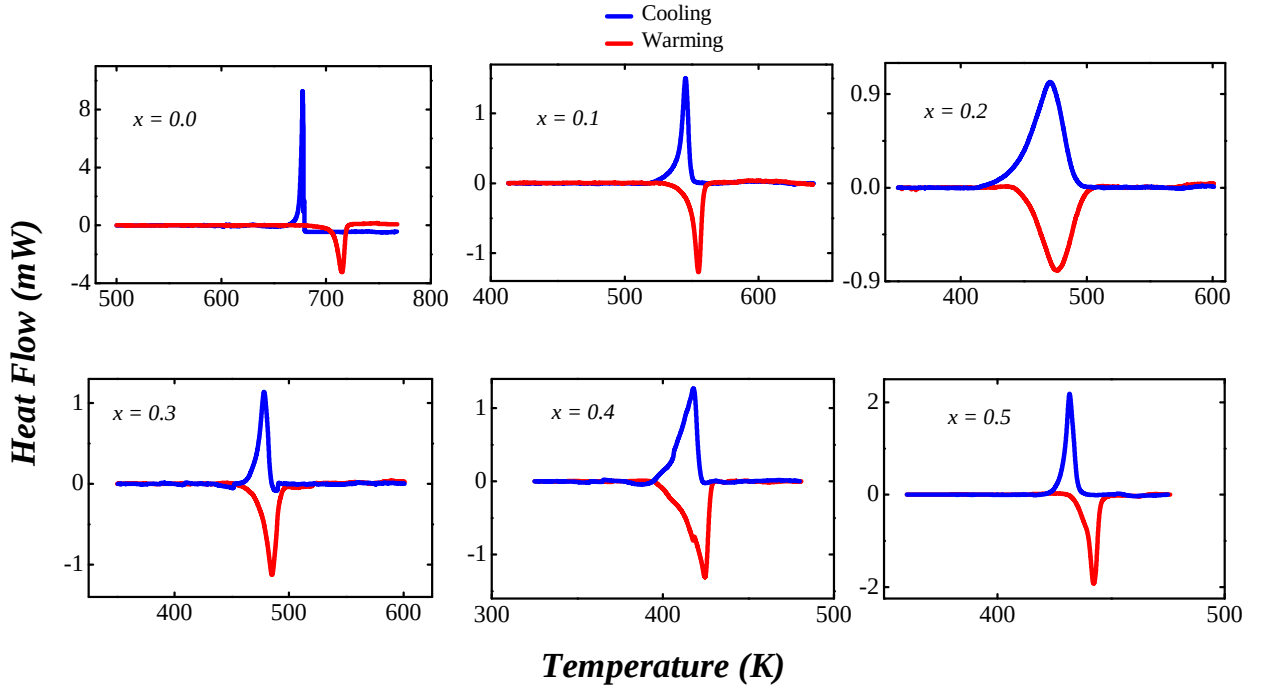


Figure 6.1: Differential Scanning Calorimetry (DSC) curves for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), showing the martensitic and reverse transformations during heating and cooling.

Figures 6.3 and 6.4 show X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), recorded at room temperature. With an increase in the x content from 0.0 to 0.4, the microstructure is transferred from the non-modulated structure to the 7M structure with a decrease in the martensitic transformation temperature [14]. At

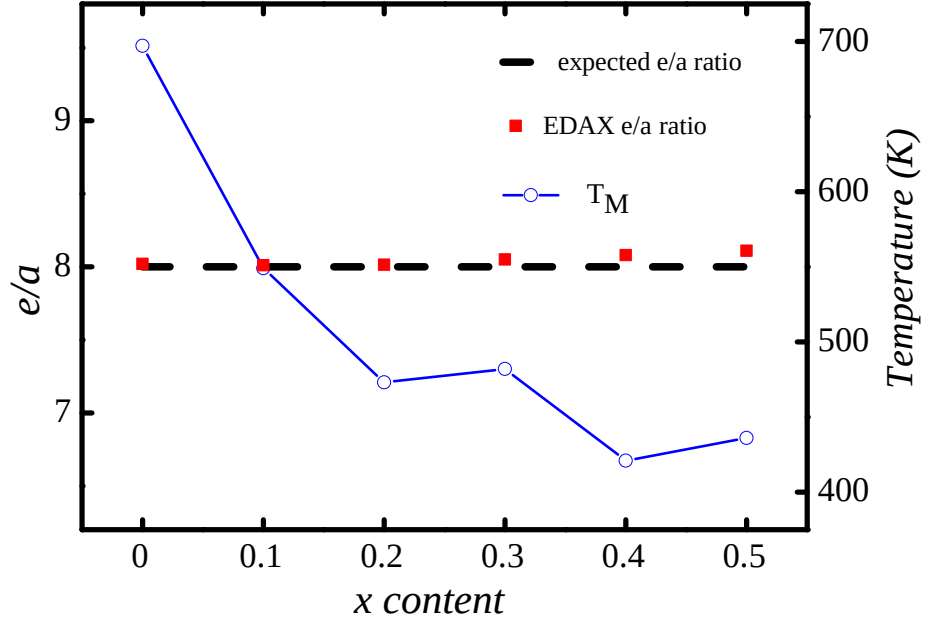


Figure 6.2: the relation between x contents and martensitic transformation temperature T_M .

$x = 0.4$, the alloy structure is largely non-modulated with small fraction of 7M phase. but in the case of $x = 0.5$ it is a pure phase 7M martensitic structure. X-ray parameters are listed in Table 6.2

Figure 6.5 shows the correlation between the unit cell volume and the progression of martensitic transformation in $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys. Its found that with substitution of In for Ga, the unit cell volume increased accompanied by a decrease in the martensitic transformation temperature. The observed relationship suggests that changes in unit cell volume during the martensitic transformation will lead to alterations in the crystal structure due to the larger radius of the In atom compared to the Ga atom. Table 6.3 shows the variation of the unit cell volume.

Figure 6.6 displays the $M(T)$ as a function to the temperature for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) in the temperature range of 5 K to 400 K, during ZFC, FCC and FCW sequences. All alloys exhibit antiferromagnetic behavior with $T_N > 400$ K. ZFC magnetization increases with increasing temperature and culminates into a broad

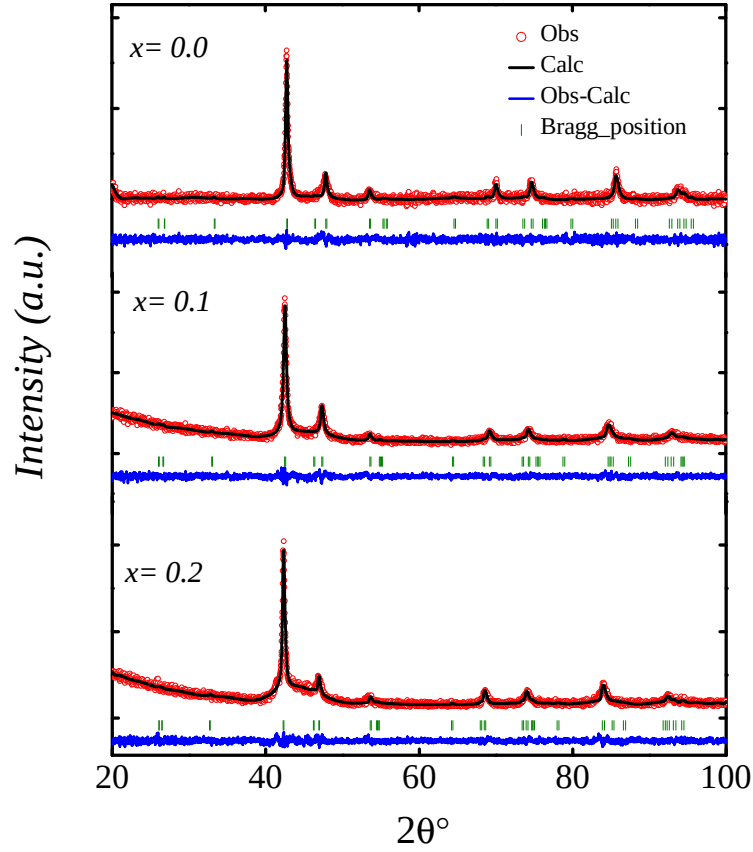


Figure 6.3: XRD pattern of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2$) with Rietveld refinement. The observed data are shown as black points, the calculated profile as a red line, and the difference between them as a blue line. Bragg reflection positions are marked below the pattern.

peak at a characteristic temperature T_P before decreasing to an even lower value at 400 K. This broad peak in ZFC magnetization is indicative of the coexistence of ferro and antiferromagnetic interactions. Sometimes, it is also referred as the ferromagnetic ordering temperature of the martensitic phase. The value of T_P decreases with increasing In content and hints at weakening ferromagnetic interactions. The large splitting between the ZFC and FC curves indicates presence of competing magnetic interactions. These competing interactions arise due to formation of spatial configuration fluctuations. The stoichiometric Ni_2MnZ alloy is ferromagnetic. Here, the Ni atoms occupy A (0,0,0) and C (0.5,0.5,0.5) sites, while Mn atoms occupy the B sites (0.25,0.25,0.25) and the Z atoms occupy the D sites (0.75, 0.75, 0.75). The ferromagnetism arises due to RKKY interaction

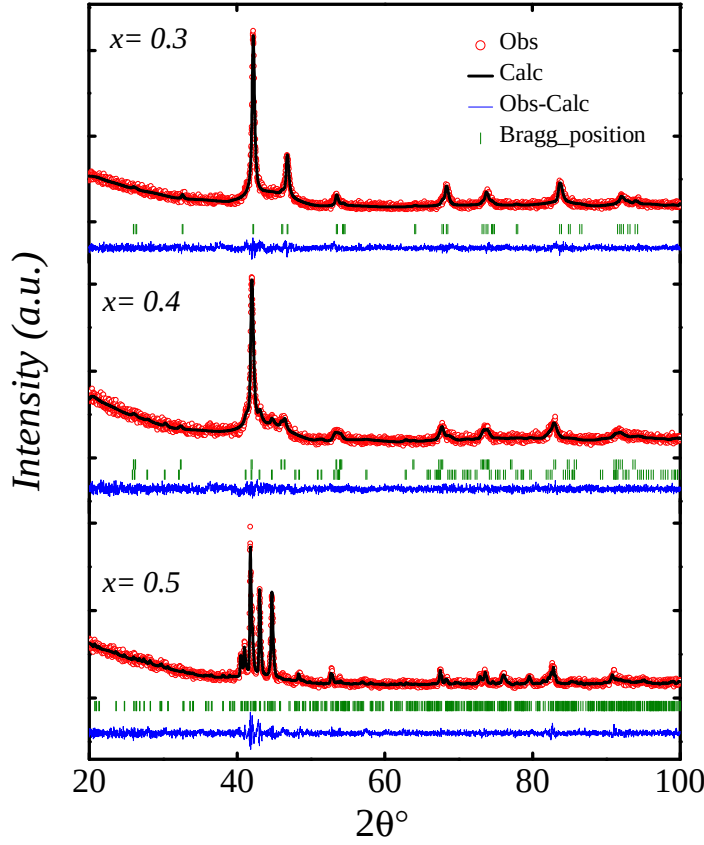


Figure 6.4: XRD pattern of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.3, 0.4, 0.5$) with Rietveld refinement. The observed data are shown as black points, the calculated profile as a red line, and the difference between them as a blue line. Bragg reflection positions are marked below the pattern.

between Mn atoms at the B sites. When Mn atoms occupy the D sites in the Mn-rich Ni-Mn-Z alloys, additional antiferromagnetic interactions are introduced between Mn(B) and Mn(D) atoms. Further, the compositional fluctuation can result in antiferromagnetically dominated Mn-rich (Ni-Mn-Ni-Mn) regions and ferromagnetically dominated Z-rich regions (Ni-Mn-Ni-Z). Presence of such regions [15].

EXAFS spectroscopy was used to study the local structural distortion and the chemical ordering of the $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys. This method was chosen because it offers element-specific details about the local coordination environment, such as the order should be reversed. interatomic distances, coordination numbers and thermal and static disorder. To understand how the substitution of indium for gallium

Table 6.2: Lattice parameters obtained from Rietveld fitting for the X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.

X	Structure	Lattice parameters
0.0	NM	$a = 3.79712(54) \text{ \AA}, c = 6.38602(12) \text{ \AA}$
0.1	NM	$a = 3.83810(67) \text{ \AA}, c = 6.38788(14) \text{ \AA}$
0.2	NM	$a = 3.87754(42) \text{ \AA}, c = 6.35354(10) \text{ \AA}$
0.3	NM	$a = 3.87927(42) \text{ \AA}, c = 6.35055(9) \text{ \AA}$
0.4	NM+7M	$a = 3.91922(40) \text{ \AA}, c = 6.36163(9) \text{ \AA},$ $a = 4.1023(26) \text{ \AA}, b = 5.5177(18) \text{ \AA}, c = 4.32264(9) \text{ \AA},$ $\beta = 94.5872(58)^\circ$
0.5	7M	$a = 4.102(3) \text{ \AA}, b = 5.5470(4) \text{ \AA}, c = 4.32210(2) \text{ \AA},$ $\beta = 90.54(10)^\circ, q = 0.3055(54)c^*$

affects the electronic structure and phase stability of these materials, it is essential to know how the substitution alters the local structure surrounding the constituent atoms. To this end, EXAFS analysis was conducted at the Ni and Mn edges. The EXAFS data at the Ni and Mn edges were analyzed using the model derived from the XRD studies on these alloys, the analysis was carried out using 14 independent parameters, The amplitude of the reduction factor S_0^2 were obtained by analyzing the corresponding metal foils. These values were fixed constant throughout the analysis of the experimental samples Figures 6.7 and 6.8 show the magnitude of the Fourier transform of $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), for $x = 0.0 - 0.3$ the model which was used to fit the data is a non-modulated structure, but for $x = 0.4$ and 0.5 the structure has changes to the modulated structure 7M.

In the case of $x = 0$ and 0.1 alloys, Ni-Ga distance is shorter than Ni-Mn bond distance, in agreement with earlier results on Ni-Mn-Ga alloys [16]. The Ni-In distance present in $x = 0.1$ alloy is not considered because of its relatively minor contribution to the EXAFS

Table 6.3: Expansion of the unit cell volume with respect to x content.

In content (x)	Unit cell volume ($\text{\AA}^3$)
0.0	92.07
0.1	94.1
0.2	95.53
0.3	95.57
0.4	97.72
0.5	98.34

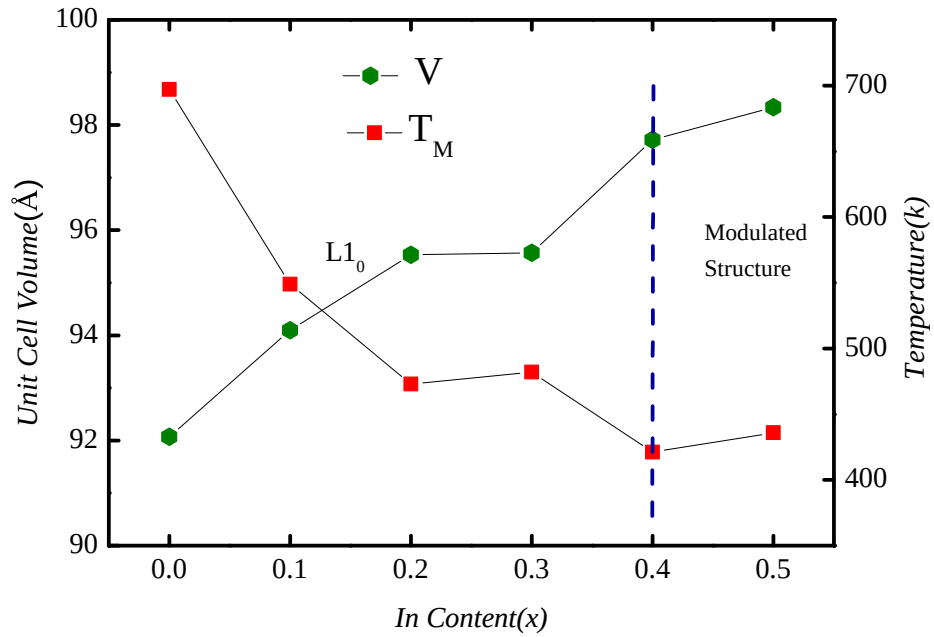


Figure 6.5: The relationship between unit cell volume and the martensitic transformation, showing that an increase in unit cell volume is associated with changes in the crystal structure.

spectra. However, in the case of $x = 0.2 - 0.5$ Ni-In bond distance is present in the alloys. Ni-Ga and Ni-In bond distances can be estimated in $x = 0.2$ and $x = 0.3$ while only Ni-In distance can be measured in $x = 0.4$, as can be seen in Table 6.4. From the table, it

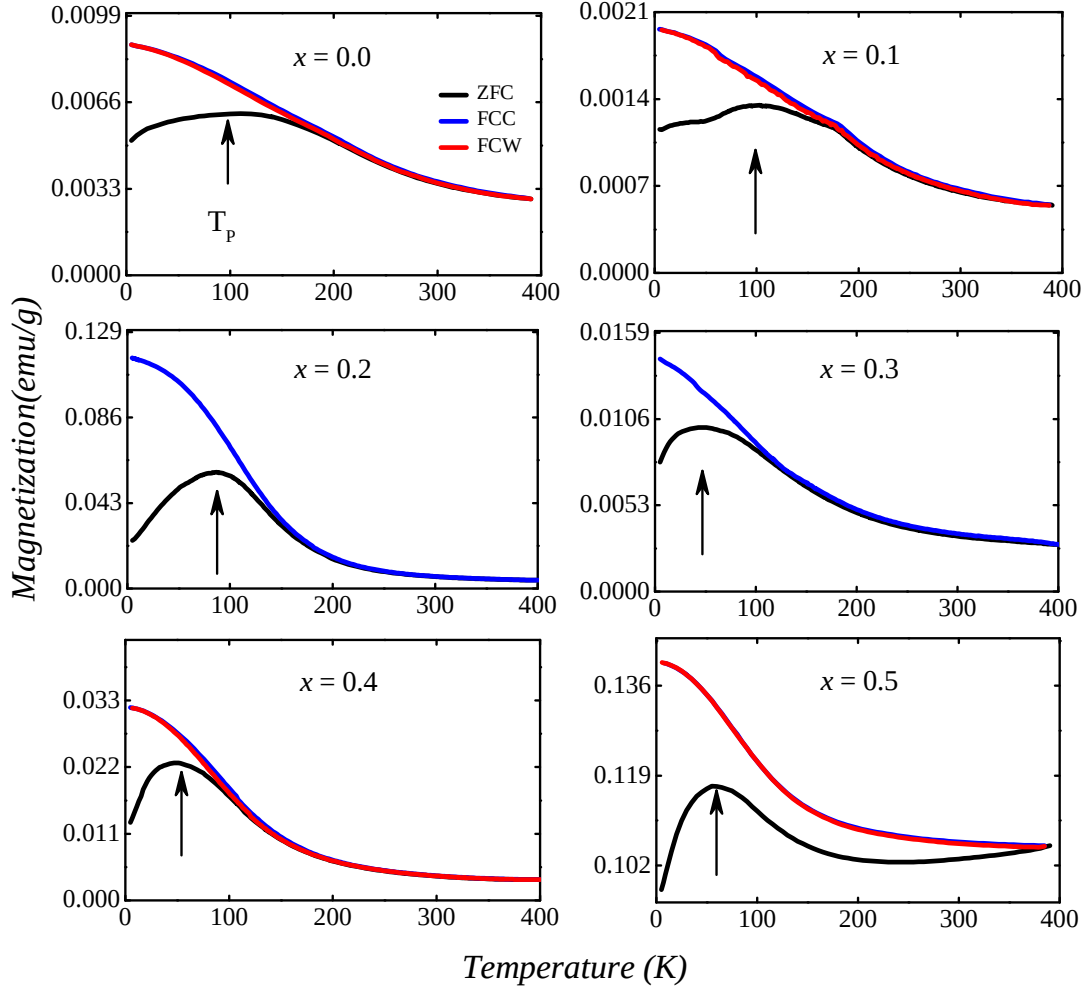


Figure 6.6: the ZFC and FC $M(T)$ curves for $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys in a magnetic field of 100 Oe.

is observed that, irrespective of the dopant concentration Ni-Ga bond distance is always shorter than Ni-Mn while Ni-In is always larger than Ni-Mn bond distance. It should be noted that in all Ni-Mn-Ga martensitic compositions, Ni-Ga is shorter than Ni-Mn while in all Ni-Mn-In martensitic alloys, Ni-Mn is shorter than Ni-In and this is preserved even in their solid solutions. Further, the second nearest neighbour distances are as per the respective crystal structure of the alloys. In tetragonal (NM) alloys, the second nearest neighbour distances are distinctly split into two while in the modulated structures, the average bond distance is close to cubic state. Here too, as per earlier reports, in the 7M structured alloys, the Mn(B)-Mn(D) distance is shorter than Mn-In distance.

Table 6.4: Bond length (R) and mean square radial disorder ($\sigma^2(\text{\AA}^2)$) of the near neighbor correlations around Mn and Ni in $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.

	Ni K edge										Mn K edge									
	Bonds										Bonds									
	Ni-Mn	$\sigma^2(\text{\AA}^2)$	Ni-Ga	$\sigma^2(\text{\AA}^2)$	Ni-In	$\sigma^2(\text{\AA}^2)$	Ni-Ni	$\sigma^2(\text{\AA}^2)$	Ni-Ni	$\sigma^2(\text{\AA}^2)$	Mn-Mn	$\sigma^2(\text{\AA}^2)$	Mn-Ga	$\sigma^2(\text{\AA}^2)$	Mn-Ga	$\sigma^2(\text{\AA}^2)$	Mn-Ga	$\sigma^2(\text{\AA}^2)$	Mn-In	$\sigma^2(\text{\AA}^2)$
0.0	2.539(91)	0.006(12)	2.523(12)	0.010(20)			2.644(14)	0.007(21)	3.443(14)	0.008(18)	2.644(14)	0.007(21)	3.443(14)	0.008(18)						
0.1	2.555(14)	0.008(13)	2.515(26)	0.003(33)			2.602(34)	0.009(70)	3.460(39)	0.016(59)	2.602(34)	0.009(70)	3.460(39)	0.016(59)						
0.2	2.564(11)	0.009(13)	2.457(40)	0.005(40)	2.623(17)	0.004(27)	2.622(20)	0.009(52)	3.451(27)	0.017(39)	2.622(20)	0.009(52)	3.451(27)	0.017(39)			2.799(44)	0.007(43)	3.016(54)	0.007(52)
0.3	2.563(92)	0.009(12)	2.477(72)	0.006(31)	2.632(32)	0.005(49)	2.634(27)	0.014(93)	3.447(25)	0.014(33)	2.634(27)	0.014(93)	3.447(25)	0.014(33)			3.104(18)	0.017(39)	2.935(11)	0.013(19)
0.4	2.582(74)	0.011(41)			2.636(69)	0.008(85)			3.101(30)	0.027(37)	2.879(65)	0.026(11)							2.782(11)	0.033(13)
0.5	2.571(8)	0.009(1)			2.620(8)	0.004(1)			3.011(7)	0.031(4)	2.999(80)	0.021(7)							2.880(100)	0.035(15)

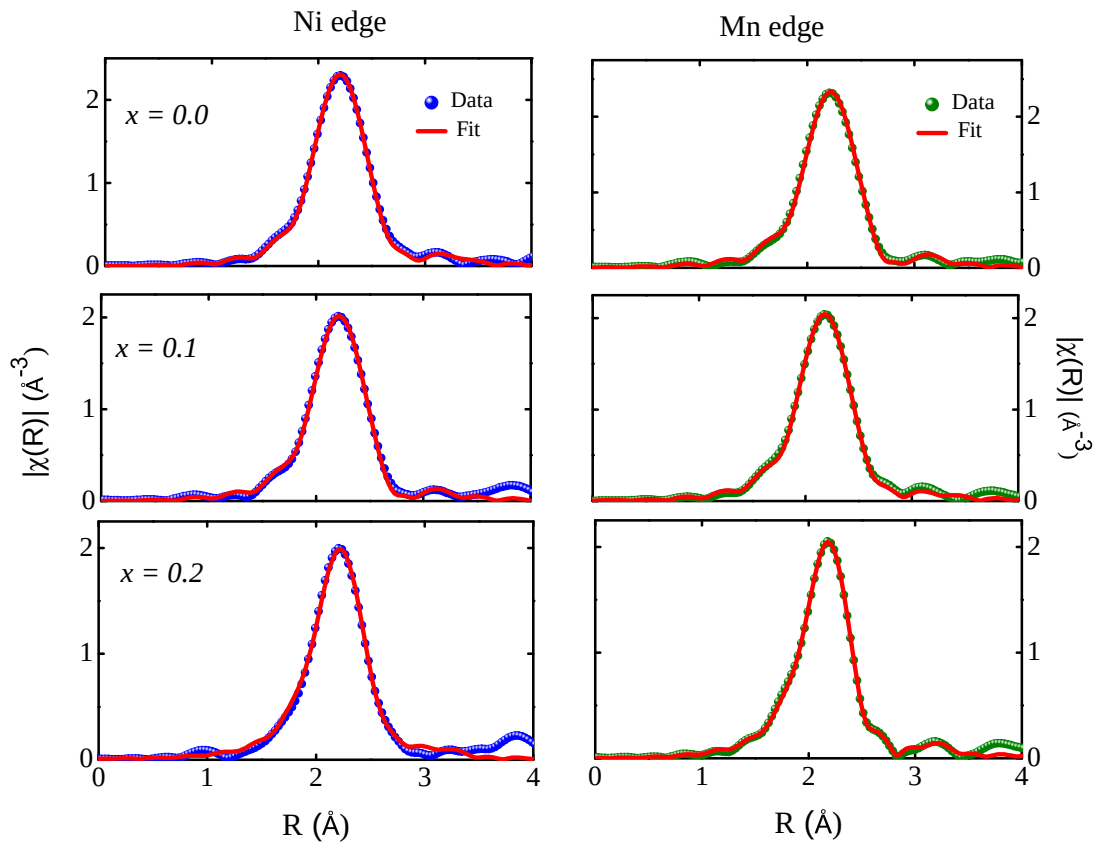


Figure 6.7: The magnitude of Fourier transform of the EXAFS spectra recorded at 300 K at the Ni K and Mn K edges for the alloys $x = 0.0$, $x = 0.1$ and $x = 0.2$ in the series $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$.

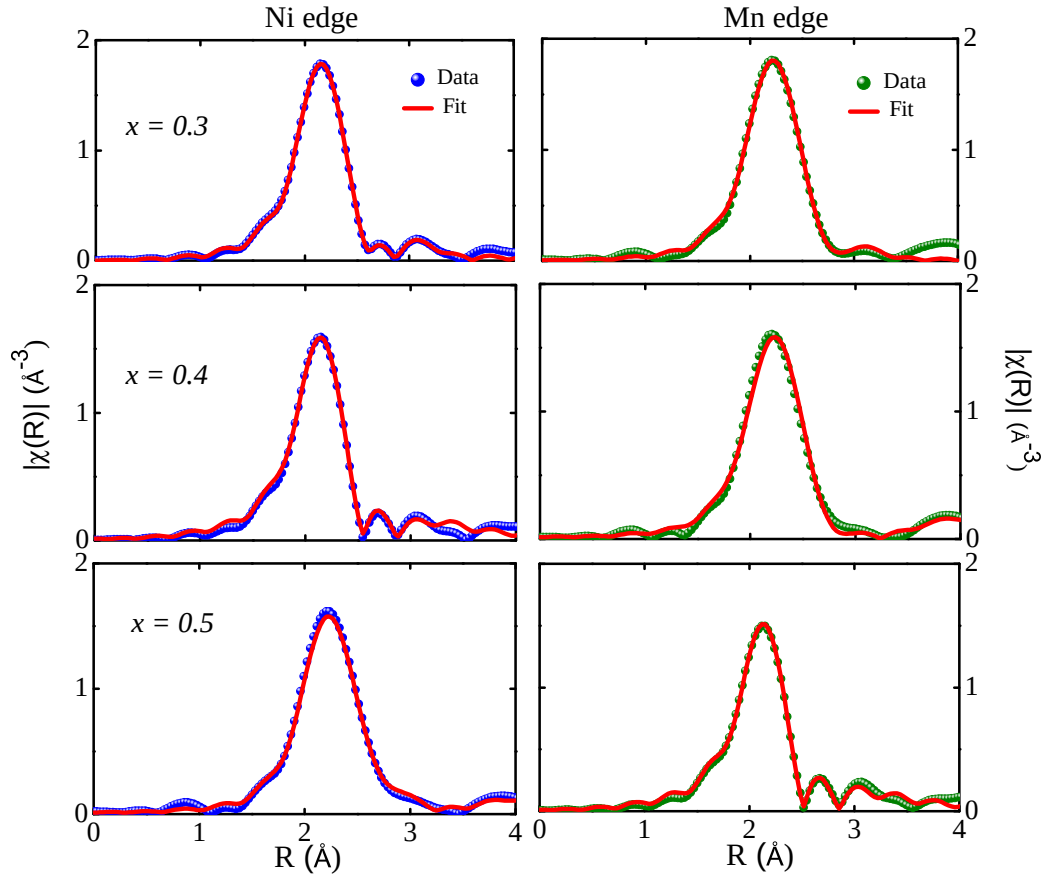


Figure 6.8: The magnitude of Fourier transform of the EXAFS spectra recorded at 300 K at the Ni K and Mn K edges for the alloys $x = 0.3$, $x = 0.4$ and $x = 0.5$ in the series $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$.

6.3 Discussion:

The analysis of X-ray diffraction data confirms that the alloy structure changes from the tetragonal (NM) structure to the (7M) structure. Differential scanning calorimetry (DSC) reveals a systematic decrease in the martensitic transformation temperature T_M with increasing In content. Magnetization measurements show that all alloys exhibit a complex magnetic behavior with dominant antiferromagnetic interactions with a decrease in T_P .

Figure 6.9, shows the relationship between the martensitic transition temperature and the nearest neighbour distortion. The analysis of the first coordination shell from EXAFS reveals a definitive hierarchy in bond lengths: the Ni-Ga bond is the shortest, the Ni-Mn bond is intermediate, and the Ni-In bond is the longest. This hierarchy is a direct manifestation of the atomic size difference, where the large ionic radius of In elongates its bonds relative to Ga. Concurrently, the Mn-In bond is found to be shorter than the average Mn-Mn bond. In these local distortions, the short Ni-In bonds and the shortened Mn-In bonds collectively generate significant internal strain within the lattice. The system alleviates this strain through a macroscopic expansion of the unit cell. This dilation provides greater geometric freedom, better accommodating the size mismatch between the constituent atoms (In and Ga on the Z-sublattice). We therefore conclude that this strain accommodation mechanism, mediated by unit cell expansion, is the primary factor responsible for the suppression of the martensitic transformation temperature.

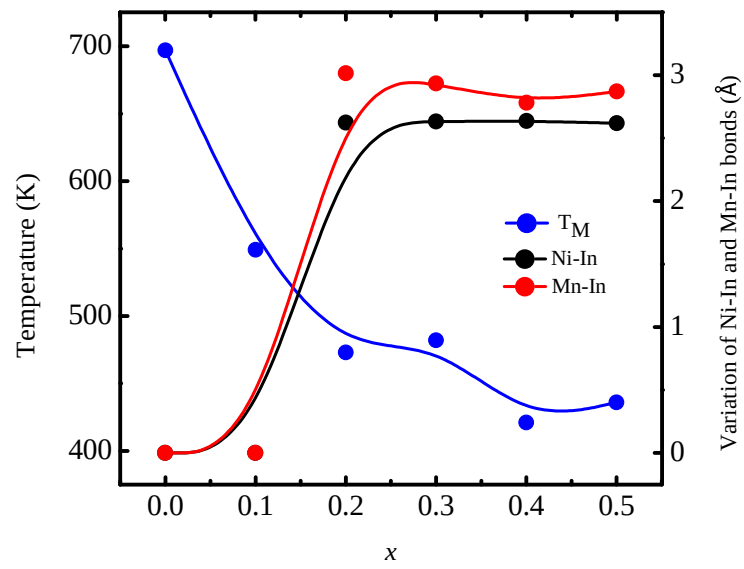


Figure 6.9: The variation of Ni-In and Mn-In bond distances with x contents.

6.4 Conclusion:

In summary, this chapter focused on the relation between the temperature of the martensitic transformation and the Z atom, as obtained from XRD and EXAFS measurements where the temperature of the martensitic transformation T_M decreases with increasing indium content (x). This happens along with an increase in the alloy's unit cell volume. The reason for this inverse relationship can be explained by lattice strain accommodation. In Ni-Mn-based Heusler alloys, the martensitic transformation is very sensitive to crystallographic strain, which is caused by size mismatches between the different atoms occupying the lattice sites which will lead to strain being better accommodated because of the different sizes between In and Ga atoms. The larger atoms such as indium create substantial internal strain because of the size mismatch with the other atoms. First, this strain energy destabilizes the high-symmetry austenite phase, providing a driving force for the transformation to the lower-symmetry martensite, often appearing as an increase in T_M for small substitutions. However, as the concentration of the larger solute atoms increases $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{In}_x$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$), a point is reached when the unit cell expands significantly and gradually. This volume expansion serves as a compensation mechanism; by expanding the crystal lattice, the bond distance of Ni-Mn also increased with increasing In. As a result, the main driving force for the martensitic transformation is reduced. With the strain already relieved by the increased lattice parameters, the thermodynamic driving force for the system to shear cooperatively into martensite is lessened. This leads to the transfer of the alloy structure from the NM structure to the modulated structure followed by the stabilization of the austenite phase, which is experimentally seen as a systematic decrease in the temperatures of the start M_s and finish M_f . Thus, the reduction in transformation temperature with increasing 'x' is not simply a compositional effect but is mediated by the accompanying unit cell expansion, which accommodates the larger constituent atoms, reducing the austenite strain energy and inhibiting the martensitic transformation.

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Chapter 7

Summary and Future Work

7.1 Summary:

Ni₂MnZ stoichiometric alloy has a substantial influence on the functional properties of Ni-Mn-based Heusler alloys, especially the martensitic transformation temperature T_M that underlies their shape memory and magnetocaloric effects. Hence, the way to control the martensitic transformation temperature is by adjusting the valence electron concentration electron-to-atom (e/a) ratio. However, the non-stoichiometry of the substances, whether from too much Ni or too much Mn, does not just change the electron cloud uniformly. Rather, it sets off intricate microstructural evolution processes that ultimately decide whether the martensitic transformation occurs macroscopically or not. This investigation explores the different behaviors of Ni-rich and Mn-rich Ni-Mn-Z alloys, contending that the martensitic transformation is enabled by the type of secondary phase that forms during phase separation rather than just the e/a ratio.

Since Ni contributes more valence electrons than Mn or Z elements (In, Sn, Sb), the introduction of Ni nonstoichiometry - creating Ni-rich alloys such as Ni_{2+x}Mn_{1-x}Z or Ni_{2+x}MnZ_{1-x} directly increases the ratio e/a. Traditionally, a higher martensitic transformation temperature is associated with a higher e/a ratio. However, experimental observations consistently show a paradox: Ni-rich alloys often show suppression or ab-

sence of the martensitic transformation after a certain threshold. The intrinsic instability of the off-stoichiometric Heusler structure is the cause of this phenomenon. A random distribution of extra atoms cannot be sustained indefinitely by the crystal lattice. As a result, to reduce the free energy, the system goes through a local phase separation process in which excess atoms and structural flaws are separated into discrete nanoscale chemical domains inside the matrix.

The phase separation in Ni-rich alloys, as Ni_2MnZ and Ni_3Z phase (such as Ni_3In , Ni_3Sn , and Ni_3Sb) and the Ni_3Mn phase is resistant to the diffusionless shear-dominated mechanism of a martensitic transformation due to their complex crystal structures, which are hexagonal $DO19$ or cubic $L2_2$. These stable precipitates function as strong barriers in the composite microstructure they form. They physically demarcate the limits of possible martensitic variations and interfere with the phonon softening and long-range strain fields required to initiate and spread the change. The widespread presence of these non-transforming phases mechanically and thermodynamically stabilizes the high-temperature austenite phase, preventing the collective atomic shear from occurring throughout the entire sample volume, even in the case of a theoretically favorable e/a ratio for martensite formation in the surrounding Heusler matrix. Therefore, both phases in Ni-rich alloys are not a martensitic phase. But in the case of Ni-Mn-Ga alloys even with a considerable phase separation in Ni-rich alloys, the stoichiometric Ni_2MnGa is a martensitic phase at 220 K.

However, Mn-rich alloys such as $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ exhibit a distinct and frequently more noticeable propensity to phase separation. Because the positive enthalpy of mixing between Mn and Z elements is higher than that between Ni and Mn or Ni and Z, the driving force for segregation in these alloys is usually stronger. In compositions rich in Mn, phase separation is feasible and is also very likely due to this increased thermodynamic impetus. The phase separation in Mn-rich alloys are Ni_2MnZ and NiMn , which is a martensitic phase with a structure of $\beta - \text{Mn}$ or (it can be ordered as $B2 / L1_0$). The slope of a martensitic transformation T_M in Ni-Mn-based Heusler alloys is not solely a function of

global parameters such as electron concentration (e/a), but is deeply affected by local atomic distortion and the resulting lattice strain. A critical insight into this behavior comes from examining the nearest neighbor bond distances within the crystal structure, specially the length of Ni-Mn and Ni-Z bond distances. In Mn-rich alloys (where $Z = \text{In, Sn, or Sb}$), a consistent and crucial structural feature is observed that the Ni-Mn is shorter than the Ni-Z, which is not a minor detail but a fundamental factor controlling the alloy's stability and transformation behavior.

The difference in the bond distance directly influences the crystal lattice ability to accommodate extra Mn atoms, and when the differences in bond distance are small, the lattice deformation will be less. This small deformation will allow the crystal structure to combine a high concentration of Mn atoms with the maintenance of the $L2_1$ structure. Therefore, the system can easily expand to accommodate the atomic mismatch up to the system became unstable system and which will transfer to the lower energy level martensitic transformation. The smaller bond distribution differences are related to the high concentration of Mn, which is required to destabilize the parent phase and set up to start the martensitic transformation phase. In the process of transformation, the bond length differential behaves as a volumetric strain gauge within the lattice; a smaller differential means the system can tolerate more compositional tuning (more Mn) before the accumulated strain triggers the structural collapse into martensite. Additionally, in the case of comparing two different alloys such as Ni-Mn-Ga and Ni-Mn-In the transformation becomes more illustrative. The difference between the Ni-Z and Ni-Mn bond distances changes from the negative region to the positive region because the Ga atom is smaller than the Mn atom, which is typically shown in the Ni-Ga atom and is shorter than that in Ni-Mn. In the case of the substance the Ga atom by In atom this difference in the radial size will force the unit cell to expand substantially to accommodate the strain which will lead to increase in the unit cell volume. This process has a dramatic effect on the bond distance, the larger Z atom pushes the surrounding atoms apart, causing the Ni-Z bond to elongate. Consequently, the Ni-Z bond length surpasses that of the Ni-Mn bond,

flipping the difference from negative to positive. This volumetric expansion is a critical mechanism for strain accommodation. This accommodation also fundamentally alters the bonding environment and the stability of the phase. Therefore, the driving force of the martensitic transformation temperature in Heusler alloys is a complex common between electronic effects (e/a) and elastic or volumetric effects (lattice strain). The structure of unit cell does not simply scale uniformly; the specific geometry of unit cell depends on how different atoms are fit together in the positions of the unit cell, and resulting in a strain accommodation because of the size difference in the atoms, which will lead to a unique condition for the unit cell stability for each specific Z atom necessitates consideration of these local bond characteristics and the alloy's capacity for strain accommodation, which are ultimately determined by the specific chemistry of the Z element.

7.2 Future work:

This study identifies the factors that influence the martensitic transformation in Heusler alloys, Ni-Mn-Z alloys (where Z = Ga, In, Sn, and Sb) and elucidates how the martensitic transformation varies with changes in the Z atoms. Future work will systematically explore microstructure-property relationships in Heusler alloys through a structured approach. First, a baseline series of Mn-rich $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) will be prepared to evaluate the isolated effect of excess Mn on phase separation and martensitic transformation. Second, a novel high-entropy system $\text{Ni}_2\text{Mn}(\text{Al}_{0.25}\text{Ge}_{0.25}\text{Si}_{0.25}\text{Ti}_{0.25})$ will be synthesized with a fixed e/a ratio matching the Mn-rich baseline, enabling a direct comparison of how configurational entropy alters phase stability and transformation behavior. Third, individual elements of the high-entropy system (e.g. Ge) will be doped into selected Mn-rich baseline alloys (e.g., $\text{Ni}_2\text{Mn}_{1.5}\text{Ga}_{0.5-x}\text{Ge}_x$ to isolate the specific role of each dopant. The objectives of this work are the following.

- To quantify the influence of Mn-rich stoichiometry (x) in $\text{Ni}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$ on martensitic transformation temperature, hysteresis and phase separation mechanisms.

- To determine how high-entropy design (in quaternary Z-site systems) suppresses long-range phase separation and modifies transformation behavior compared to conventional binaries at constant e/a .
- Individual effects of specific dopants (e.g., Ge) on local structure, precipitation, and functional properties in Mn-rich Ni-Mn-Ga alloys.

List of Publications:

1. N. Manea, E. Welter, K. R. Priolkar, Factors influencing the martensitic transformation in Ni-Mn-Z ($Z = \text{Ga, Sn}$) Heusler alloys, J. Phys. D: Appl. Phys. 57 145304 (2024).
2. N. Manea, E. Welter, K. R. Priolkar, Role of local structural distortions in the variation of martensitic transformation temperature with e/ a ratio in $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($Z = \text{In, Sn or Sb}$) alloys, PCCP, 27,2528 (2025).

Conference Presentations and Participation:

1. Participated in "Two days workshop on Material Science between University of Porto, University of Coimbra and Goa University" held at Goa University from 18 - 19th November, 2019.
2. Participated in "Three days workshop X-ray Crystallography" Organized by SCS and SPAS held at Goa University from 21 - 23th July, 2022.
3. Participated in "ICCD workshop on Materials Characterization using powder X-ray diffraction" under Goa University Crystallography workshop 2023 - guew-j, Organized by SCS and SPAS held at Goa University from 7 - 8th December, 2023.
4. Participated in "Two days workshop on Raman spectroscopy" Organized by SCS and SPAS at Goa University from 26 - 27th February, 2024.
5. Presented a poster on "Is e/a Ratio the driving factor for the scaling of martensitic transition temperature in heusler alloys" in the 65 th DAE Solid State Physics Symposium, organized by BARC, BRNS, and DAE held at Bhabha Atomic Research Center, Mumbai, during 15 - 19th Dec,2021.
6. Presented a poster on Presented a poster on "Role of the local atomic distortion on the Z atom dependence of martensitic transition temperature in Ni-Mn-Z ($Z= \text{Ga,}$

In, Sn, Sb) Heusler alloys” in National Conference on Electronic Structure held at Gao University, Goa, from November 14 - 16th, 2022.

7. Presented poster on Presented a poster on ”Role of the local atomic distortion on the Z atom dependence of martensitic transition temperature in Ni-Mn-Z (Z= Ga, In, Sn, Sb) Heusler alloys” in the International Conference on Advanced Materials: Properties and Applications held at Goa University, Goa, India during 20 - 24th Feb, 2023.