Dedicated to the nation, teachers, family and friends

CERTIFICATE

It is certified that the work contained in the thesis titled *"PHASE TRANSITIONS, LOCAL STRUCTURE AND ANOMALOUS HALL EFFECT IN Ni-Mn-BASED MAGNETIC SHAPE MEMORY ALLOYS AND RELATED SYSTEMS"* by *"ANUPAM KUMAR SINGH"* has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive, Candidacy and SOTA for the award of the Ph.D. degree.

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DECLARATION BY THE CANDIDATE

I, *ANUPAM KUMAR SINGH*, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **Dr. SANJAY SINGH** for a period from **JULY 2016** to **FEBRUARY 2022** at the **SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY**, Indian Institute of Technology (Banaras Hindu University), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, thesis, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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Title of the Thesis: *"Phase Transitions, Local Structure and Anomalous Hall Effect in Ni-Mn-based Magnetic Shape Memory Alloys and Related Systems"*

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Copyright Transfer

Acknowledgements

i

Table of Contents

List of Figures

List of Tables

List of Abbreviations

Anisotropic Atomic Displace Parameters	AADP
Alternating Current	ac
Atomic Displace Parameters	ADP
Antiferromagnetic	AFM
Anomalous Hall Conductivity	AHC
Anomalous Hall Effect	AHE
Anomalous Thermal Expansion	ATE
Austenite and Premartensite	A+PM
Body Centered Cubic	BCT
Birch–Murnagan Equation-of-State	B-M EoS
Backscattered Electrons	BSE
Cryogenic Free Measurement System	CFMS
Diamond Anvil Cell	DAC
Direct Current	dc
Dzyaloshinskii-Moriya Interactions	DMI
Density of States	DOS
Differential Scanning Calorimetry	DSC
Energy Dispersive Analysis of X-rays	EDAX
Energy Dispersive Spectroscopy	EDS
Electrical Transport Option	ETO
Field Cooling	FC

Face Centered Cubic	FCC
Field Cooled Warming	FCW
Ferromagnetic	FM
Formula Unit	f. u.
Full-Width at Half-Maxima	FWHM
Hour	h
High-Resolution Transmission Electron Microscope	HRTEM
Inelastic Neutron Scattering	INS
Lattice Parameters	LP
Long-Range	LR
Long-Range Ordered	LRO
Lorentz Transmission Electron Microscopy	L-TEM
Magnetocrystalline Anisotropy	MCA
Magnetic Field Induced Strain	MFIS
Minute	min
Magnetoresistance	MR
Magnetic Properties Measurement System	MPMS
Magnetic Shape Memory Alloy	MSMA
Magnetic Shape Memory Effect	MSME
Martensite Phase Transition	MPT
Ordinary Hall Effect	OHE
Pair Distribution Function	PDF
Premartensite	PM

Premartensite Phase Transition	PMT
Physical Properties Measurement System	PPMS
Positive Thermal Expansion	PTR
Sample to Detector Distance	SDD
Secondary Electrons	SE
Scanning Electron Microscope	SEM
Shape Memory Alloy	SMA
Shape Memory Effect	SME
Superconducting Quantum Interference Device	SQUID
Short-Range	SR
Short-Range Ordered	SRO
Spin Reorientation Transition	SRT
Synchrotron X-ray Powder Diffraction	SXRPD
Thermal Expansion Coefficient	TEC
Topological Hall Effect	THE
Vibrating Sample Magnetometer	VSM
X-ray Diffraction	XRD
Zero-Field Cooled Warming	ZFCW
Zero Thermal Expansion	ZTE
Two Dimensional	2D
Second-Order	2nd O

List of Symbols

Area	A
Austenite Finish Temperature	A_f
Austenite Start Temperature	A_s
Thermal Factor	B
Bulk Modulus	B
Pressure Derivative of Bulk Modulus	B'
Fermi Energy	E_F
Reduced Structure Function	$F(Q)$
Gibbs Free Energy	G
Pair Distribution Function	$G(r)$
Calculated Pair Distribution Function	Gcal
Difference Pair Distribution Function	Gdiff
Experimental Pair Distribution Function	Gexp
Magnetic Field	H
Current	I
Intensity	I(Q)
Measured Intensity	I$_m(Q)$
Boltzmann Constant	k_B
Incident Wave Vector	$\boldsymbol{k_i}$
Reflected Wave Vector	$\boldsymbol{k_f}$
Magnetic Anisotropy Constant	K_u

Length	L
Magnetization	M
Spontaneous Magnetization	M_S
Martensite Start Temperature	M_s
Martensite Finish Temperature	M_f
Magnetic Field Dependent Magnetization	$M(H)$
Temperature Dependent Magnetization	$M(T)$
Pressure	P
Magnitude of Scattering Vector	Q
Maximum Value of Scattering Vector	Q_{max}
Maximum Instrumental Q-value	$Q_{maxinst}$
Minimum Value of Scattering Vector	Q_{min}
Distance	r
Resistance	R
Ordinary Hall Coefficient	R_0
Anomalous Hall Coefficient	R_S
Scaling Coefficient	S_H
Total Scattering Structure Function	$S(Q)$
Time	t
Temperature	T
Curie Temperature	T_C
Curie Temperature of the Martensite Phase	T_C^M
Martensite Transition Temperature	T_M

Onset of Curie Temperature	T_{onset}
Premartensite Transition Temperature	T_{PM}
Spin Reorientation Transition Temperature	T_{SRT}
Isotropic Atomic Displacement Parameter	U_{iso}
Unit Cell Volume	V
Valence Electron Concentration Per Atom	e/a
Isothermal Entropy Change	ΔS_{iso}
Peak Value of Isothermal Entropy Change	ΔS_{pk}
Change in Temperature	ΔT
Change in Volume	ΔV
Wavelength	λ
Angstrom	Å
Grüneisen Parameter	γ
Magnetic Flux	ϕ
Phase Shift	Φ
Resistivity	ρ
Magnetic Permeability of Free Space	μ_0
Anomalous Hall Resistivity at Zero-field	ρ_{AH}
Anomalous Hall Resistivity	ρ_{AHE}
Longitudinal Resistivity	ρ_{xx}
Hall Resistivity	ρ_{xy}
Calculated Hall Resistivity	ρ_{xy}^{cal}

Experimental Hall Resistivity	ρ_{xy}^{exp}
Topological Hall Resistivity	ρ_{xy}^{T}
Maxima of Topological Hall Resistivity	ρ_{xy}^{Tmax}
Anomalous Hall Conductivity	σ_{AH}
Intrinsic Anomalous Hall Conductivity	σ_{AH}^{in}
Longitudinal Conductivity	σ_{xx}
Hall Conductivity	σ_{xy}
Twinning Stress	σ_{tw}
External Stress	σ_{ext}
AC-susceptibility	χ
Real Part of AC-susceptibility	χ'
Temperature Dependent AC-susceptibility	$\chi(T)$
Magnetic Field Dependent AC-susceptibility	$\chi(H)$
Correlation length	ξ
Debye Temperature	Θ_D
Bohr Magneton	μ_B
Maximal Strain	ε_0
Correlation Parameter	δ_2
Rescaled Temperature	θ
Bragg Angle	2θ
Spin-Orbit Interaction Energy	ϵ_{SO}

Preface

Shape memory alloys (SMAs) are a special class of materials that remember their shape with the application of temperature and (or) stress. The shape change in these materials, which can be manipulated by both temperature and stress, is directly related to a structural (martensite) phase transition. These alloys have received tremendous interest due to their extensive technological applications ranging from automobiles, aerospace, marine structures, biomedical devices to energy conversion devices. Recently, another kind of SMAs gained huge interest, where shape change can be manipulated, and a large strain can be generated with the application of external magnetic field. These materials are termed magnetic shape memory alloys (MSMAs). The MSMAs have the advantage over the conventional SMAs as large strain can be generated within the martensite phase with magnetic field, which provides faster switching. Thus, the discovery of MSMAs offers potential for developing novel sensors and actuators based on the application/removal of the magnetic field with or without external stress at a fixed temperature. Among the several MSMAs, the Ni-Mn-based MSMAs are of current interest as, besides a large magnetic field induced strain (MFIS), they also exhibit several exotic physical properties/phenomena, e.g., giant magnetocaloric effect, large magnetoresistance, anomalous Nernst effect, strain glass transition, skyrmionic textures etc. These exotic properties/phenomena of Ni-Mn-based MSMAs make these materials very important for solid-state cooling and information storage technology applications also.

The origin of the above-mentioned properties of Ni-Mn-based MSMAs is closely related to their interesting phase transition behavior. These alloys exhibit a paramagnetic to ferromagnetic (FM) phase transition and sometimes include FM to antiferromagnetic and (or) ferrimagnetic phase transition. Besides the magnetic phase transitions, they also show a structural phase transition from the high temperature cubic austenite to a low-temperature lower-symmetry martensite phase. In

general, the martensite phase of Ni-Mn-based MSMAs exhibits structural modulation, which plays a vital role in the appearance of huge strains in these alloys. Therefore, it is important to understand the phase transitions and crystal structure of different phases in order to explore the different physical properties of Ni-Mn-based MSMAs.

Some important Ni-Mn-based MSMAs (e.g., Ni_2MnGa) show an interesting precursor (or premartensite) phase, which precedes the martensite phase, with preserved cubic symmetry of the austenite phase. As premartensite phase is directly related to the martensite phase, it also affects the related physical properties (e.g., strain glass behavior and skyrmionics textures) observed in these alloys. Therefore, a detailed understanding of the premartensite phase is necessary to tune the related physical properties of the martensite phase. Although the precursor have been observed in the austenite phase also in terms of the appearance of diffuse scattering and softening of 1/3 (110) transverse acoustic (TA_2) phonon mode in Ni_2MnGa due to the development of local short-range correlations, it is still unclear whether these precursor effects are related to the martensite or the premartensite phase. This calls for a systematic study of the local structure of these alloys. In addition, since the premartensite phase usually appears in a rather narrow temperature range with weak signatures in the bulk physical property measurements, a premartensite phase stable over a wider temperature window is desirable for a proper understanding of this state. The results presented in this thesis provide evidence for a precursor state of the premartensite phase as local structure in the austenite phase of Ni_2MnGa MSMA, where the stability of the premartensite phase is narrow and robust evidence for the stabilization of the premartensite phase as ground state of the Ni-Mn-In MSMA via chemical pressure tuning using magnetization and high-resolution, high-flux as well as high-Q synchrotron x-ray diffraction data analysis.

In recent years, additional contributions (anomalous and topological) to the conventional Hall effect have been reported in Ni-Mn-based MSMAs. The results presented in the literature for the Hall effect are, however, controversial and calls for a detailed investigation of these MSMAs. The existing literature also suggests that the topological Hall effect associated with skyrmions may be influenced by the premartensite phase. Therefore, it is essential to investigate the role of the premartensite phase on the topological Hall effect in these alloys. In the present thesis, results of a comprehensive study on the origin of the anomalous and topological Hall effect in Ni_2MnGa MSMA is presented using analysis of magnetotransport data.

The hexagonal compound NiMnGa, which comes under another class of related materials, has received vast attention due to the observation of stable biskyrmionic textures, which can be utilized in the skyrmion-based spintronic devices at higher temperatures. Although temperature dependent structural and magnetic studies have been performed in the past, a detailed investigation of the correlation between the structural and magnetic behavior is still unclear in this compound. Interestingly, the stability of skyrmionic textures in some of the materials is found to be very sensitive to external uniaxial stress or pressure. This suggests that the stability of the skyrmionic spin textures can be manipulated through spin-lattice/magnetoelastic coupling. The manipulation of skyrmions with external pressure provides an additional tool for manipulating the functionality of such compounds. Thus, a detailed study of the hexagonal compound NiMnGa with external hydrostatic pressure may provide important information, which can be useful for the applications in spintronic devices. The present thesis provides results of a comprehensive study of phase transitions on NiMnGa using magnetization as well as temperature and pressure dependent synchrotron x-ray diffraction data. In general, the stabilization of skyrmions have been proposed to exit in noncentrosymmetric materials due to the presence of Dzyaloshinskii–Moriya interaction.

However, the NiMnGa has a hexagonal structure with a centrosymmetric space group ($P6_3mmc$) and yet it hosts biskyrmionic textures. To understand the origin of biskyrmions in this compound, the results of a local structure study of the NiMnGa using high-Q synchrotron x-ray diffraction data analysis are also presented in this thesis.

In this thesis, a detailed study of the phase transition, local as well as global crystal structure, and anomalous Hall effect are performed in Ni_2MnGa, $Ni_{50}Mn_{34}In_{16-x}Al_x$ ($x = 0.5, 0.8$) MSMAs, and a related hexagonal NiMnGa system. The present thesis is divided into eight chapters.

Chapter 1 provides definition and a detailed description of martensite transition, shape memory alloys, magnetic shape memory alloys and related terms used in this work, followed by a review of literature related to the Ni-Mn-based MSMAs and hexagonal NiMnGa.

Chapter 2 contains the details of the synthesis process, including a detailed discussion of various components, several characterization techniques employed, e.g., laboratory source x-ray diffraction measurements for checking the phase purity, energy dispersive analysis of x-rays for composition determination, differential scanning calorimetry for the phase transition temperatures. In addition, the details of the magnetic and magnetotransport measurements using physical properties, magnetic properties, and cryogenic free measurement systems are provided. The details of the synchrotron x-ray powder diffraction (SXRPD) measurements carried out at the P02.1 beamline of PETRA-III and Xpress beamline of ELETTRA at different temperatures and pressures, respectively, are also presented in this chapter.

Chapter 3 provides evidence for the precursor state of the premartensite phase in Ni_2MnGa MSMA using atomic pair distribution function analysis of the high-Q SXRPD data and magnetization studies. This precursor state is present in the short-range only with a crystal structure similar to the premartensite phase. The Arrott plot, critical isotherms and universal curve analysis

confirm the first-order character of paramagnetic to FM phase transition in Ni_2MnGa MSMA, while the analysis of the high-resolution SXRPD data reveals the presence of magnetoelastic coupling. The role of such a coupling in inducing first-order FM phase transition is rationalized using the Landau theory considerations.

Chapter 4 presents evidence for intrinsic anomalous Hall conductivity as well topological Hall effect in Ni_2MnGa MSMA. A detailed analysis of Hall conductivity reveals that intrinsic Berry curvature contribution dominates over skew scattering and side jump in the austenite, premartensite and martensite phases of Ni_2MnGa MSMA. The presence of skyrmions is indicated in the martensite as well as the premartensite phases by the observation of characteristic temperature-independent behavior of the peak value of the topological Hall resistivity.

Chapter 5 describes the results of a detailed structural and magnetic investigation of the effect of Al-substitution in $Ni_{50}Mn_{34}In_{16}$ MSMA using SXRPD and magnetization data. The combined analysis of magnetization and SXRPD data reveal that the premartensite phase is stabilized over a wide temperature range in $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA. This robust evidence for the stabilization of the premartensite phase is shown to result by tuning of the chemical pressure via substitution with a smaller size atom (Al) at the In site in $Ni_{50}Mn_{34}In_{16}$ MSMA. The structure of stabilized premartensite phase is shown to be $3M$ modulated monoclinic in the $P2/m$ space group. The analysis of the SXRPD data measured under the magnetic field provides evidence for the presence of magnetoelastic coupling, which plays a crucial role in the stabilization of the PM phase in $Ni_{50}Mn_{34}In_{16}$ MSMA by Al substitution.

Chapter 6 presents the results of magnetization data and a detailed crystal structure investigation using SXRPD on the biskyrmion host hexagonal NiMnGa compound. The Arrott plots analysis and presence of small thermal hysteresis around FM T_C in the magnetization data reveal first-order

character of the paramagnetic to FM phase transition in this compound. We also presented evidence for magnetoelastic coupling at the FM as well as the spin reorientation transitions (SRT). It is argued that the Ni-Mn and Ni-Ga mediated exchange interactions dominate the paramagnetic to the FM phase transition, while the Mn-Mn mediated exchange interactions dominate the SRT. In addition, the evidence for an isostructural phase transition driven by hydrostatic pressure at a pressure around 4 GPa in the hexagonal NiMnGa using pressure dependent SXRPD data analysis is also presented in this chapter.

Chapter 7 provides the signature of biskyrmionic states in NiMnGa using magnetic field-dependent ac-susceptibility measurements and a detailed analysis of the local structure of NiMnGa using the pair distribution function method. A high-Q SXRPD data reveals the presence of noncentrosymmetric trigonal structure with space group $P3m1$ in the short-range, which may be responsible for the presence of the biskyrmionic state. On the other hand, the long-range structure of NiMnGa remains centrosymmetric hexagonal with $P6_3/mmc$ space group.

Chapter 8 summarizes the key findings of the present thesis and proposes a few suggestions for future work in the field related to this study.