Chapter 8

Summary and Suggestions for future work

8.1 Summary

In this thesis, the magnetocaloric effect (MCE), magnetic states, and transport properties (including anomalous and topological Hall effects) have been investigated in the magnetic shape memory alloys (MSMAs) $Ni_{1.9}Pt_{0.1}Mn_{1.4}In_{0.6}$, $Ni_2Mn_{1.4}In_{0.6}$, and $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$. A prototype and a measurement setup for the direct measurement of the MCE have also been developed in our laboratory. Additionally, pressure-induced structural phase transition and the effect of pressure on the stability of Néel skyrmions near room temperature have been studied in the related PtMnGa hexagonal system.

The present thesis focuses on the study of polycrystalline samples prepared using a standard arc-melting furnace, followed by vacuum annealing as required. Various experimental methods were employed, including laboratory-based X-ray diffraction (XRD) and anomalous transport measurements (resistivity, magnetoresistance, and Hall effect) conducted using in-house facilities. Furthermore, advanced synchrotron radiation sources were utilized for synchrotron XRD measurements at large-scale facilities such as the P02.1 beamline of PETRA-III, DESY, Hamburg, Germany (for temperature-dependent studies), and the Xpress beamline of Elettra, Trieste, Italy (for pressure-dependent studies). Muon spin relaxation (μSR) studies were also performed using the EMU instrument at the ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory. High-quality, well-characterized powder samples were used for these measurements. Micromagnetic simulations for skyrmions were performed using Object-Oriented Micromagnetic Framework (OOMMF) software. The key findings of this study are summarized below:

In **Chapter 3**, the development of a prototype utilizing a permanent magnet and a sophisticated measurement setup with an electromagnet is presented for the direct measurement of adiabatic temperature change in magnetocaloric materials. The prototype operates exclusively at room temperature, while the measurement setup functions within the temperature range of 300 K to 400 K. A comprehensive explanation of the instrumentation, including details about the sensors and magnet, is provided. The accuracy of both setups is validated through experiments conducted with standard gadolinium (Gd) materials. These setups play a critical role in the search for magnetocaloric materials for future solid-state cooling technologies.

In **Chapter 4**, we demonstrated enhanced crystallographic/geometric compatibility and improved magnetocaloric reversibility by analyzing the isothermal entropy change (ΔS_{iso}) using different measurement protocols in a 10% Pt-substituted $\mathrm{Ni_2Mn_{1.4}In_{0.6}}$ magnetic shape memory Heusler alloy. The substitution of Pt decreases the thermal hysteresis by $\sim$ 50% in $\mathrm{Ni_2Mn_{1.4}In_{0.6}}$. The underlying cause of this reduction is explored through an analysis of the crystallographic compatibility between the austenite and martensite phases. The calculated middle eigenvalue of the transformation matrix is 0.9982, deviating by only 0.18% from 1, indicating strong crystallographic compatibility between the austenite and martensite phases in $\mathrm{Ni_{1.9}Pt_{0.1}Mn_{1.4}In_{0.6}}$. The combination of minimal thermal hysteresis and crystallographic compatibility suggests a stress-free transition layer between these phases, which is expected to facilitate a reversible martensite phase transition and, consequently, a reversible MCE. ΔS_{iso} values were calculated from the magnetization curves using three different measurement protocols: isothermal, loop, and isofield. The results were found to be nearly identical, indicating a reversible MCE in the current alloy system. Our study offers insights into the design of new magnetic shape memory Heusler alloys for magnetic refrigeration and suggests that any of the aforementioned measurement protocols can be applied to calculate ΔS_{iso} for materials that satisfy the geometrical compatibility condition.

In **Chapter 5**, We examined the magnetic state of $\mathrm{Ni_2Mn_{1.4}In_{0.6}}$ MSMA within the so-called paramagnetic (PM) gap of the martensite phase using the μSR technique. Muon spin polarization experiences a notable decoupling at $\sim$395 K, accompanied by a sharp decrease in asymmetry. Above this temperature, the temperature-independent nature and large asymmetry value indicate the PM nature of the high-temperature phase. The decline in asymmetry with decreasing temperature points to a transition from disorder (PM) to an ordered magnetic state (either ferromagnetic or antiferromagnetic). The asymmetry remains at lower values until the second magnetic transition ($T_C^M \sim$ 190 K) in the martensite phase, indicating that the magnetic state in the so-called PM gap regime cannot be a disordered (PM) phase. The transition temperature observed in the asymmetry versus temperature plot is higher than the Curie temperature of the $Ni_2Mn_{1.4}In_{0.6}$ MSMA. Temperature-dependent pair distribution function (PDF) analysis reveals the presence of a local martensite phase (with a finite magnetic moment) within the high-temperature austenite phase, which accounts for the reduced asymmetry observed even above the Curie temperature.

In **Chapter 6**, we explored the anomalous Hall effect (AHE) and topological Hall effect (THE) in the $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA, focusing on their correlation with phase transitions. By analyzing the temperature and magnetic field dependence of Hall resistivity, this study reveals that the observed AHE is driven by momentum-space Berry curvature. Notably, the maximum THE value is observed at the boundary between the austenite and premartensite phases (PM-phase). These findings enhance the understanding of the interplay between phase transitions and topological effects in MSMAs, paving the way for potential device applications.

In **Chapter 7**, we investigated pressure-induced iso-structural phase transitions in hexagonal MnPtGa, a promising material for hosting Néel skyrmions. This chapter explores how external pressure affects the structure of material and magnetic properties, inducing phase transitions without altering its crystal structure. These pressure-driven changes have profound implications for the stability and behavior of Néel skyrmions, which are topologically protected spin configurations. The findings demonstrate that pressure serves as an effective tuning parameter for controlling skyrmion stability in MnPtGa near room temperature. The study emphasizes the importance of understanding the interplay between pressure and skyrmion formation, as this insight will guide the design of devices that leverage skyrmion-based phenomena.

8.2 Suggestions for future work

This thesis presents a detailed study of the phase transition, the effect of chemical pressure on the reversibility of the MCE, crystallographic compatibility, the effect of physical pressure on the stabilization of skyrmions, and the transport properties of Ni-Mn-In-based MS-

MAs and the related hexagonal MnPtGa. However, there remain opportunities to further enhance these properties. The findings pave the way for numerous future experimental and theoretical investigations. A few of these possibilities are outlined below:

- So far, a measurement setup using an electromagnet has been designed to measure the direct MCE. The standard sample, Gd, is used as the magnetocaloric material. Its operational range spans from room temperature to 400 K. The system can be upgraded to extend the temperature range, allowing the measurement setup to operate from 200 to 450 K.

- $Ni_2Mn_{1.4}In_{0.6}$ MSMA undergoes a magnetostructural phase transition at the martensite transition temperature. The high-temperature phase adopts a cubic structure, while the low-temperature phase is monoclinic. The material exhibits a thermal hysteresis of $\sim$8 K. Substituting 10% Pt in the parent compound $Ni_2Mn_{1.4}In_{0.6}$ reduces the thermal hysteresis by $\sim$ 50% and satisfies the geometric compatibility condition. Le Bail refinement of 10% Pt doped $Ni_2Mn_{1.4}In_{0.6}$ (i.e. $Ni_{1.9}Pt_{0.1}Mn_{1.4}In_{0.6}$) reveals that the monoclinic phase is 3M modulated with a space group of $P_{2/m}$. For a detailed study of the crystal structure in the low-temperature phase, (3+1)D crystallography (superspace group crystallography) is necessary, which can be performed using JANA software.

- As chemical pressure reduces the hysteresis in $Ni_2Mn_{1.4}In_{0.6}$ MSMA, it has also been suggested in the literature that external pressure can further reduce the hysteresis. Pressure-dependent magnetization measurements are required to assess the effect of pressure on hysteresis. Temperature-dependent SXRPD data (at the required pressure) are necessary to determine the geometric compatibility condition in $Ni_{1.9}Pt_{0.1}Mn_{1.4}In_{0.6}$ MSMA. Materials with lower thermal hysteresis are beneficial for magnetocaloric applications.

- $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA exhibits a stable PM-phase in the temperature range of 300–13 K. Recently, it has been reported that in $Ni_2Mn_{1.4}In_{0.6}$ MSMA, the PM-phase facilitates the formation of a stable zero-field skyrmion. In the present thesis, THE is calculated, and we found that it reaches a maximum value at the boundary between the austenite and PM-phases. Skyrmions are one source of the THE, and therefore, a stable skyrmion phase could exist in $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA. Skyrmion can be investigated using micromagnetic simulations with OOMMF software or direct imaging.