

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 MSMA 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 MSMA.

Some important Ni-Mn-based MSMA (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 MSMA. The results presented in the literature for the Hall effect are, however, controversial and calls for a detailed investigation of these MSMA. 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 Ni₂MnGa 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 exist 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 Ni₂MnGa, Ni₅₀Mn₃₄In_{16-x}Al_x ($x = 0.5, 0.8$) MSMA, 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 MSMA 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 Ni₂MnGa 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 Ni₂MnGa 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 Ni₂MnGa 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 Ni₂MnGa 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 Ni₅₀Mn₃₄In₁₆ 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 Ni₅₀Mn₃₄In_{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 Ni₅₀Mn₃₄In₁₆ 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 Ni₅₀Mn₃₄In₁₆ 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.