Phase Transitions, Local Structure and Anomalous Hall Effect in Ni-Mn-based Magnetic Shape Memory Alloys and Related Systems

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by

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Chapter 8: Summary and Suggestions for Future Work

In this chapter, a brief overview of key findings of the present study and suggestions for future work has been given.

8.1 Summary

In the present thesis, phase transitions, the local as well as global crystal structure, and anomalous Hall effect of two technologically important Ni-Mn-based magnetic shape memory alloys (MSMAs) (Ni_2MnGa and $Ni_{50}Mn_{34}In_{16-x}Al_x$ (x = 0.5, 0.8)) and a related hexagonal NiMnGa system with giant potentiality in the magnetic sensing, actuating, solid-state cooling and memory application, etc., has been extensively investigated. The present thesis involved the study on the polycrystalline samples, which were prepared using the standard arc-melting furnace followed by vacuum annealing as per the requirements. The investigation employed several experimental methods like laboratory-based x-ray diffraction (XRD), differential scanning calorimeter, scanning electron microscope, dc magnetization, ac-susceptibility, and anomalous transport measurements (resistivity, magnetoresistance, and Hall) using in-house experimental facilities. In addition, the advanced synchrotron-based light source was also utilized to carry out synchrotron XRD measurements using the large-scale experiment facility at the P02.1 beamline of PETRA-III, DESY, Hamburg, Germany, as well as Xpress beamline of ELETTRA, Trieste, Italy. For the diffraction measurements, well-characterized high-quality powder samples were used. The key findings of the present study are summarized below:

(1) The combined study of temperature dependent dc, as well as ac magnetization and high-Q synchrotron x-ray powder diffraction (SXRPD) data, revealed the evidence for the short-range

ordered precursor state of the 3*M* modulated premartensite phase at temperatures well above the actual premartensite phase transition temperature (T_{PM}) and even above the ferromagnetic (FM) transition temperature (T_C) in Ni_2MnGa MSMA. This is the first investigation that provided direct structural evidence for the precursor state of the premartensite phase in Ni_2MnGa MSMA. The strain associated with the precursor state coupled with magnetization (i.e., magnetoelastic coupling discussed in the framework of Landau theory) and conveys first-order character to the paramagnetic-to FM phase transition, as revealed by the thermal hysteresis across FM T_C in the heating and cooling magnetization cycles.

(2) A detailed analysis of the magnetotransport data unleashed the evidence of intrinsic anomalous Hall conductivity (AHC) and topological Hall effect (THE) in the austenite, premartensite, and martensite phases of Ni_2MnGa MSMA. A detailed study of AHC revealed that Berry curvature induced intrinsic contribution dominates over the skew scattering and side jump contribution to anomalous Hall effect. The analysis of topological Hall resistivity suggested that THE arose due to the real-space Berry curvature induced by topologically protected skyrmion textures in the martensite and premartensite phases.

(3) The magnetic susceptibility and SXRPD studies provided evidence for chemical pressure-induced suppression of the martensite phase and stabilization of the premartensite phase in $Ni_{50}Mn_{34}In_{16}$ MSMA. The robust evidence for the stable premartensite phase over a wide temperature range from 300 K to 5 K was observed in $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA. The results revealed that the substitution by a smaller size atom, like Al, at In site in $Ni_{50}Mn_{34}In_{16}$ MSMA can stabilize the premartensite phase. The SXRPD pattern under magnetic field conveyed the direct evidence for the magnetoelastic coupling in $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA.

(4) The magnetic measurements provided the first evidence for the first-order paramagnetic to FM phase transition and magnetoelastic coupling in the hexagonal NiMnGa. The SXRPD studies revealed the anomalies in the structural parameters at FM T_C and spin reorientation transition temperature (T_{SRT}) temperature without any symmetry breaking. Within the framework of the Landau theory, quadratic spin-coupling coupling imparts the weakly first-order paramagnetic to FM phase transition. The results also indicate the precursor effect of the spin reorientation transition above actual T_{SRT}. In addition, the high-pressure SXRPD data revealed the observation of pressure-induced isostructural phase transition in the hexagonal NiMnGa.

(5) Magnetic field-dependent ac-susceptibility data revealed the signature of skyrmions stable down to 5 K with hysteric character in the hexagonal NiMnGa. The pair distribution function study using high-*Q* SXRPD data provided the evidence for the local (short-range ordered) noncentrosymmetric trigonal crystal structure with $P3m1$ space group within the global (long-range ordered) average centrosymmetric hexagonal structure ($P6_3/mmc$) in NiMnGa. The result of the local trigonal structure with noncentrosymmetric space group can be ascertained to the origin of the formation of biskyrmions in the hexagonal NiMnGa compound.

8.2 Suggestions for Future Work

A detailed study of local as well as global crystal structure, magnetic and anomalous transport properties in the Ni-Mn-based MSMAs, and related NiMnGa system have been carried out during the present work. The results open several possibilities for future experimental and theoretical investigations. We outline a few of them given below:

(1) In the present thesis, the evidence of precursor state of the premartensite phase in Ni_2MnGa MSMA is an interesting result, which opens a new pathway to investigate the precursor related phenomena in the MSMAs. In general, the Ni-Mn-based MSMAs exhibit modulated martensite

and premartensite phases, wherein the origin of modulation has been a topic of extensive debate to the researcher. Since the cubic austenite phase symmetry remains preserved in the premartensite phase, the premartensite phase turns out to be a perfect platform for studying modulation physics. We believe that the precursor state of the premartensite phase would encourage the researchers to investigate the modulation physics in this precursor state. Based on this result of the precursor state, a future investigation is required to explore the strain-glass-related physics in shape memory alloys and MSMAs. In addition, the possible connection between skyrmions and the local precursor phase needs to be investigated in other systems to enhance the understanding of skyrmions physics and improve its functionality.

(2) The anomalous Hall effect induced by momentum space Berry curvature in the modulated martensite and premartensite phase of Ni_2MnGa has been proposed in this work. It would be of great interest to perform theoretical calculations to generate Berry curvature for the materials with modulated crystal structures like Ni_2MnGa. This would provide a bunch of information and help to understand the connection between anomalous Hall effect and modulation physics, both of which are related to the electronic structure.

(3) It has been proposed that skyrmions are directly related to premartensite phase in Ni-Mn-In MSMA. Our robust evidence for the stabilization of the premartensite phase over a wide temperature range (~300 to 5 K) in $Ni_{50}Mn_{34}In_{15.2}Al_{0.8}$ MSMA induced by chemical pressure tuning demands for the investigation to explore the possibility of the existence of skyrmions and topological Hall effect in Al-substituted (in place of In-site) Ni-Mn-In MSMA having stabilized premartensite phase. The stable premartensite phase provides a new platform to perform a detailed study on the modulation physics and investigation of magnetic domain evolution of the premartensite phase. The possibility of strain-glass with increasing Al-content on In-site in

$Ni_{50}Mn_{34}In_{16}$ MSMA is also an open subject for future investigation. In addition, our results open a new pathway to explore the possibility of stabilization of premartensite phase in Ni-Mn-Sn MSMAs by chemical pressure tuning to improve their different functional properties.

(4) The first-order character of paramagnetic to FM phase transition and magnetoelastic coupling in biskyrmion host NiMnGa is of particular interest and requires further study of the magnetic phase transition in other skyrmion host systems to enhance the understanding of the impact of spin-lattice coupling on the stability of skyrmion textures. The ac magnetization behavior at low temperature, along with the competing FM and antiferromagnetic interactions in the hexagonal NiMnGa, are the indication of the spin-glass, which is an open matter for future investigation. In addition, since the high-pressure SXRPD indicate the isostructural phase transition and reversibility with pressure in NiMnGa, it would be interesting to see the behavior of biskyrmionic textures with external pressure, i.e., the possibility of manipulation of biskyrmionic textures with the application of strain to enhance its applicability.

(5) However, the origin of skyrmions in the materials having the center of inversion symmetry has been proposed to be related with competing interactions between magnetic anisotropy energy and dipolar interactions energy, evidence for the local noncentrosymmetric structure in the centrosymmetric hexagonal NiMnGa investigated in the present work is a major breakthrough and calls for reinvestigation of origin of skyrmions in the systems having a centrosymmetric crystal structure. We believe that our results of the local noncentrosymmetric structure are interesting enough to encourage the theoreticians also to relook at the stabilization of skyrmions and local noncentrosymmetric structure as well as related physics in centrosymmetric materials.