Exchange Bias and Magnetoresistance Effects in

Ni$_{50}$Mn$_{50-y}$X$_y$ ($X = \text{In, Sn}$) Alloys

by

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Abstract

Recently, a kind of new ferromagnetic shape memory alloys (FSMAs) has been discovered in Ni$_{50}$Mn$_{50-y}$X$_y$ (NiMnX, X = In, Sn, Sb) systems, in which the magnetization in the martensite phase is very low in comparison to that of the austenite phase. This kind of alloys is termed metamagnetic shape memory alloys (MSMAs) to distinguish them from previously discovered FMSAs. Beside producing magnetic-field-induced strain (MFIS) with large stresses of over 100 MPa caused by magnetic field-induced phase transformation, the MSMAs also exhibit several other important sensor capabilities, such as large magnetoresistance effect, large inverse magnetocaloric effect, and exchange bias effect. These properties have attracted much interest in recent years. However, to date, the magnetic properties in the martensitic state of these alloys are not clear and the sensor capabilities of MSMAs are needed to be further explored.

In the present work, the magnetic properties in the martensitic state and magnetoresistance effect of NiMnX (X = In, Sn) have been studied. Exchange bias effect is observed in the martensitic state of NiMnX (X = In, Sn) alloys after zero-field cooling from an unmagnetized state, which cannot be expected in the previous exchange bias systems. We propose that this is related to the newly formed interface between different magnetic phases during the initial magnetization process. The magnetic unidirectional anisotropy, which is the origin of EB effect, can be created isothermally below the blocking temperature. Both the value of exchange bias field and its sign can be tuned isothermally or by the amplitude of remanent magnetization
after zero-field cooling. This tunability is strongly dependent on the direction of the initial magnetization field for the hysteresis loop measurements. In addition, the value of exchange bias field can also be tuned by the amplitude of the cooling field during field cooling.

The magnetoresistance effect in MSMA Ni_{49.5}Mn_{34.5}In_{16} has also been studied in detail. The large negative magnetoresistance is observed within the transformation regime across the first-order magnetic transition, which is correlated to the magnetic-field-induced phase transformation from antiferromagnetic martensite to ferromagnetic austenite. The irreversibility and “overshooting” behaviors in isothermal magnetoresistance of Ni_{49.5}Mn_{34.5}In_{16} are observed at temperatures reached by heating and cooling processes, respectively. The strong thermal-history-dependent (THD) magnetoresistance behavior in MSMA Ni_{49.5}Mn_{34.5}In_{16} is discussed in terms of phase coexistence, strain-induced THD energy diagram and the competition of instable and THD metastable phases.
1. “Exchange bias obtainable through zero-field cooling from an unmagnetized state in Ni-Mn-Sn alloys”
   
   B. M. Wang, Y. Liu, B. Xia, P. Ren, and L. Wang


2. “Large exchange bias after zero-field cooling from an unmagnetized state”
   
   B. M. Wang, Y. Liu, P. Ren, B. Xia, K. B. Ruan, J. B. Yi, J. Ding, X. G. Li, and L. Wang


3. “Enhanced magnetoresistance through magnetic-field-induced phase transition in Ni$_2$MnGa co-doped with Co and Mn”
   
   B. M. Wang, P. Ren, Y. Liu, and L. Wang


4. “Strong thermal-history-dependent magnetoresistance behavior in Ni$_{49.5}$Mn$_{34.5}$In$_{16}$”
   
   B. M. Wang, L. Wang, Y. Liu, B. C. Zhao, Y. Zhao, Y. Yang, and H. Zhang

5. “A second-order ferromagnetic transition in the martensitic state of 
Ni_{49.5}Mn_{32.5}Cu_{4}Sn_{14}: A critical behavior study”

   **B. M. Wang**, L. Wang, Y. Liu, and B. C. Zhao


6. “Exchange bias and its training effect in the martensitic state of bulk 
polycrystalline Ni_{49.5}Mn_{34.5}In_{16}”

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## List of Abbreviations and Symbols

### Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>CEB</td>
<td>Conventional exchange bias</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EB</td>
<td>Exchange bias</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectrometry</td>
</tr>
<tr>
<td>FC</td>
<td>Field cooling</td>
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<tr>
<td>FCC</td>
<td>Field cooled cooling</td>
</tr>
<tr>
<td>FCH</td>
<td>Field cooled heating</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>FMTM</td>
<td>Ferromagnetic transition in the martensite</td>
</tr>
<tr>
<td>FSMA</td>
<td>Ferromagnetic shape memory alloy</td>
</tr>
<tr>
<td>MCE</td>
<td>Magnetocaloric effect</td>
</tr>
<tr>
<td>MFIS</td>
<td>Magnetic-field-induced strain</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistance</td>
</tr>
<tr>
<td>MSMA</td>
<td>Metamagnetic shape memory alloy</td>
</tr>
<tr>
<td>MT</td>
<td>Martensitic transformation</td>
</tr>
<tr>
<td>NiMnX</td>
<td>Ni$<em>{50}$Mn$</em>{50-y}$X$_y$</td>
</tr>
<tr>
<td>PM</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical properties measurement system</td>
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<td>RM</td>
<td>Remanent magnetization</td>
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XXIV
<table>
<thead>
<tr>
<th>Acronym</th>
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</tr>
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<tbody>
<tr>
<td>RMT</td>
<td>Reverse martensitic transformation</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFM</td>
<td>Superferromagnetic</td>
</tr>
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<td>SMA</td>
<td>Shape memory alloy</td>
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<td>SME</td>
<td>Shape memory effect</td>
</tr>
<tr>
<td>SME</td>
<td>Shape memory effect</td>
</tr>
<tr>
<td>SPM</td>
<td>Superparamagnetic</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device</td>
</tr>
<tr>
<td>SSG</td>
<td>Superspin glass</td>
</tr>
<tr>
<td>THD</td>
<td>Thermal-history-dependent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero-field cooling</td>
</tr>
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</table>

**Symbols**

- $A_f$: Austenitic transformation finish temperature
- $A_s$: Austenitic transformation start temperature
- $H$: Magnetic field intensity
- $H_{m}^{\text{max}}$: Maximum measurement field
- $H_c$: Coercivity
- $H_{EB}$: Exchange bias field
- $H_L$: Left coercive field
- $H_R$: Right coercive field
- $H_{\text{applied}}$: Applied field
- $H_{FC}$: Cooling field
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$M(H)$</td>
<td>Magnetic hysteresis loop</td>
</tr>
<tr>
<td>$M_{sat}$</td>
<td>Saturation magnetization</td>
</tr>
<tr>
<td>$M_{mi}$</td>
<td>Initial magnetization</td>
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<tr>
<td>$M^p$</td>
<td>Positive magnetization</td>
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<tr>
<td>$M^N$</td>
<td>Negative magnetization</td>
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<tr>
<td>$M_f$</td>
<td>Martensitic transformation finish temperature</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Martensitic transformation start temperature</td>
</tr>
<tr>
<td>$T_B$</td>
<td>Blocking temperature</td>
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<tr>
<td>$T_c$</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>$T_c^M$</td>
<td>Curie temperature of the martensite</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Néel temperature</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$\rho(T)$</td>
<td>Temperature dependence of resistivity</td>
</tr>
<tr>
<td>$\rho(H)$</td>
<td>Magnetic field dependence of resistivity</td>
</tr>
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Chapter 1 Introduction

1.1 Background

Shape memory effect was first observed in Au–Cd alloys in 1951 and became well known with its discovery in Ti–Ni alloys in 1963 [1]. Ti–Ni alloys are the most popular shape memory alloys (SMAs) with applications in various fields. Because the strain and stress generated by the shape memory effect are extremely large as compared to those generated in piezoelectric and magnetostrictive materials, SMAs have been used for actuators such as motors and supersonic oscillators extensively. However, since the output actuation in SMAs occurs through temperature change for an input signal, it is not easy to obtain a rapid response to the input signal at frequencies greater than 5 Hz because the thermal conductivity of the alloys is a rate determining factor of the response [2]. This fatal drawback restricts the application of SMAs as high-speed repeatable actuators. Magnetic shape memory alloys in which a rapid output strain is achieved through the application of a magnetic field have been developed to overcome this obstacle.

Magnetic field-induced strains (MFIS) have been observed first in Heusler alloys Ni$_2$MnGa in 1996 [3]. These materials have attracted considerable attention as potential magnetic actuator materials and current studies have reported large MFIS
values up to 9.5% [4]. MFIS obtained in the ferromagnetic Ni$_2$MnGa single crystal is explained by the rearrangement of martensite variants due to an external field. When the crystalline magnetic anisotropy energy is greater than the energy driving the variant boundaries, the angle between the magnetization and the applied magnetic field directions is lowered by not only the independent rotation of magnetization but also the variant rearrangement in order that the magnetic easy axis is aligned parallel to the magnetic field direction. Thus, the variant rearrangement yields the MFIS, which is comparable to the strain induced by the uniaxial stress applied to the martensitic phase. Although large output strain and rapid response can be confirmed in Ni$_2$MnGa alloys, the output stress is principally lower than 5 MPa [5]. Furthermore, the significant brittleness of Ni$_2$MnGa single crystals is a serious problem that prevents the application of this material. On the other hand, magnetic-field-induced phase transformation is a useful method for obtaining an output stress larger than that resulting from the variant rearrangement in the martensitic phase, which has been studied in Ni-Mn-Ga alloy [6, 7]. The transformation temperature change ($\Delta T$) induced by magnetic field change ($\Delta H$) is approximately given by the Clausius-Clapeyron relation in the magnetic phase diagram: $\Delta T = (\Delta M/\Delta S) \Delta H$. The $\Delta M$ and $\Delta S$ are the differences in magnetization and entropy between austenite and martensite phases, respectively. In Ni$_2$MnGa alloys, a huge magnetic field is required to obtain
magnetic-field-induced transformation because both the austenite and martensite
phases exhibit ferromagnetism and the saturated magnetization of the martensite
phase is comparable to that of the austenite phase.

Very recently, a kind of new ferromagnetic SMAs (FSMAs) has been discovered
in NiMn$X$ ($X$=In, Sn, Sb) systems, in which the magnetization in the martensite phase
is very low in comparison to that of the austenite phase [8]. This kind of alloys is
termed metamagnetic shape memory alloys (MSMAs) to distinguish them from
previous FMSAs without metamagnetic transition accompanying with MT [9]. Beside
producing MFIS with large stresses of over 100 MPa caused by magnetic field-
induced phase transformation [10-17], the MSMAs also exhibit several other
important sensor capabilities, such as large magnetoresistance effect for
magnetoresistive reading heads [17-30], large inverse magnetocaloric effect for room
temperature refrigerator [23-25, 27, 29, 31-65], and exchange bias effect [66-71].
These properties have attracted much interest in recent years.

1.2 Objective and Scope

To date, the magnetic properties in the martensitic state of these alloys are not
clear and the sensor capabilities of MSMAs need to be further explored. The purpose
of the present research is to investigate and understand the magnetic and electrical transport properties of NiMnX (X = In, Sn), and to optimize its sensor capabilities for potential applications, including exchange bias (EB) effect and magnetoresistance effect.

The scope of the present study is listed as follows:

(a) EB after zero-field cooling from an unmagnetized state

EB effect is usually observed in systems with interface between different magnetic phases after field cooling. We observe an unusual phenomenon in which a large EB exists in Ni-Mn-In bulk alloys after zero-field cooling from an unmagnetized state. Namely, the magnetic unidirectional anisotropy, which is the origin of EB effect, can be created isothermally below the blocking temperature. A model to explain such unusual phenomenon is proposed and has been successfully verified with various experimental observations.

(b) Giant tunable EB effect in Ni<sub>50</sub>Mn<sub>37</sub>In<sub>13</sub>

Both the value of EB field and its sign can be tuned isothermally or by the amplitude of remanent magnetization after zero-field cooling. This tunability is strongly dependent on the direction of the initial magnetization field for the hysteresis
loop measurements. In addition, the value of EB field can also be tuned by the amplitude of the cooling field during field cooling.

(c) Magnetoresistance effect in MSMA Ni_{49.5}Mn_{34.5}In_{16} alloy

Temperature- and magnetic-field-dependent resistivities have been measured in MSMAs Ni_{49.5}Mn_{34.5}In_{16}. The large negative magnetoresistance is observed within the transformation regime across the first-order magnetic transition, which is correlated to the magnetic-field-induced phase transformation from antiferromagnetic martensite to ferromagnetic austenite. The irreversibility and “overshooting” phenomena in isothermal magnetoresistance of Ni_{49.5}Mn_{34.5}In_{16} are observed at temperatures reached by heating and cooling processes, respectively. The strong thermal-history-dependent (THD) magnetoresistance behavior is discussed in terms of phase coexistence, strain-induced THD energy diagram and the competition of instable and THD metastable phases.

1.3 Organization of the thesis

In Chapter 2, a literature survey of the magnetic properties of MSMAs NiMnX (X=In, Sn, and Sb) alloys, including MFIS induced by magnetic field-induced phase
transition, large magnetoresistance, and magnetocaloric effect, exchange bias are presented.

In Chapter 3, the experimental procedures and analysis methods are presented. These include alloy production using vacuum arc melting, chemical analysis, and characterization of magnetic properties.

In Chapter 4, the phenomenon of EB in the NiMnX (X = In, Sn) alloys after zero-field cooling from an unmagnetized state and its origin are discussed.

In Chapter 5, giant tunable EB effect in Ni50Mn37In13 and its origin are discussed.

In Chapter 6, strong thermal-history-dependent magnetoresistance effect in MSMA Ni49.5Mn34.5In16 has been studied in detail.

Finally, conclusions are given in Chapter 7, followed by some suggestions on future work.
Chapter 2 Literature review

In this chapter, a literature survey of the magnetic and electrical properties of MSMA\textsubscript{s} NiMn\textit{X} (\textit{X}=In, Sn, Sb) alloys, including crystal structure, magnetic-field-induced reverse martensitic transformation, shape memory effect, magnetoresistance, magnetocaloric effect, and exchange bias, is presented.

\textbf{2.1 Crystal structure of NiMn\textit{X} (\textit{X}= In, Sn)}

The austenite phase of stoichiometric Ni\textsubscript{50}Mn\textsubscript{25}X\textsubscript{25} (\textit{X}= In, Sn) alloys is a body centered cubic (bcc) structure with Fm \textit{\bar{3}} m space group (\textit{L}2\textsubscript{1} Heusler atomic order), as shown in Figure 2-1(a). The martensitic transformation (MT) in these stoichiometric Ni\textsubscript{2}Mn\textit{X} (\textit{X}=In, Sn, Sb) has not yet been observed. However, researchers observed that MT from the Heusler-type austenite phase to the monoclinic or orthorhombic martensite phase occurs in the Mn rich Ni-Mn-\textit{X} (\textit{X}=Sn, In, Sb) alloys [8]. Neutron diffraction study in Ni\textsubscript{50}Mn\textsubscript{36}Sn\textsubscript{14} shows that the excess of Mn atoms in this off-stoichiometric alloy occupy a number of 4(b) sites (Sn sites in the stoichiometric compound) in the \textit{L}2\textsubscript{1} structure [72]. The structure of martensite has a superlattice...
structure derived from the Cubic Heusler structure by a periodic displacement of the atoms in successive (110) planes along the [1\overline{1}0] direction. They are characterized as five-layered (10M), seven layered (14M), and non-modulated (L10) modulated martensites, depending on the Mn concentration [11, 73]. The martensite with stacking orders (3\overline{2}) and (5\overline{2}) for the (110) basal planes of the auternite phase, as demonstrated in Figure 2-1(b).
Figure 2-1. The crystal structure models for (a) austenite L2\(_1\) phase, (b) (220) L\(_{21}\) basal plane, 10 M and 14 M martensite phases.

2.2 Magnetic-field-induced reverse martensitic transformation
MT is a kind of diffusionless first-order phase transformation. This first-order phase transformation allows the martensite to grow in the austenite without creating long-range stress fields or excess interfacial energy (no atomic migration is required) [74]. There are four characteristic temperatures defining the thermoelastic phase transformations: $M_s$ (martensite start temperature), at which martensite first appears in the austenite; $M_f$ (martensite finish temperature), below which the entire body is in the martensitic phase; $A_s$ (austenite start temperature), at which austenite first appears in the martensite; $A_f$ (austenite finish temperature), Above which the specimen is in the original undistorted state. A typical DSC curve of a Ni$_{49.8}$Mn$_{28.9}$Ga$_{21.6}$ single crystal demonstrating all of these temperatures is shown in Figure 2-2 [75]. FSMAs are a class of SMAs showing shape memory effect and magnetism simultaneously. In the previous FSMAs, such as NiMnGa [3], FePd [76, 77], FePt [78], NiCoGa [79], NiCoAl [80, 81], and NiFeGa [82], the change of magnetization between austenite and martensite is so small due to the combination of FM or PM austenite and FM martensite phases. However, in Mn rich NiMn$_X$ ($X=$Sn, In, and Sb) alloys, the magnetization in the martensitic phase is very low in comparison to that of the austenite phase, as shown in Figure 2-3 [15].
Figure 2-2. DSC curve of a Ni$_{49.8}$Mn$_{28.9}$Ga$_{21.6}$ single crystal [75].

Figure 2-3. Temperature dependence of the magnetization with applied field $H=0.9$ T after a zero field cooling (left y scale) and DSC curves (right y scale) of Ni$_{48.3}$Mn$_{37.5}$Sn$_{14.2}$ alloy [15].
Figure 2-4 shows the thermomagnetization curves for magnetic fields of 0.5 kOe, 20 kOe, and 70 kOe for a Ni$_{45}$Co$_3$Mn$_{36.6}$In$_{13.4}$ alloy [10]. It is observed that the difference in the saturated magnetization between the austenite and martensite phases is approximately 100 emu/g and the temperatures $M_s$, $M_f$, $A_s$ and $A_f$ decrease about 30 K due to the increase in the magnetic field from 0.5 kOe to 70 kOe. This result suggests that the martensite phase can be transformed to the austenite phase by application of the magnetic field. This behavior, i.e., the magnetic-field-induced reverse martensitic transformation, was also confirmed in the isothermal magnetization curves at 270 and 290 K, as shown in Figure 2-5 [10]. It is observed that the curves at 320 K and 200 K that correspond to the autenitic and martensitic phases exhibit simple ferromagnetic and weakmagnetic behavior, respectively. However, those at 270 and 290 K show drastic variations in magnetization due to the magnetic-field-induced reverse martensitic transformation at approximately 60 and 30 kOe, respectively. The transformation temperature change ($\Delta T$) induced by magnetic field change ($\Delta H$) is approximately given by the Clausius-Clapeyron relation in the magnetic phase diagram:

$$\Delta T = (\Delta M/\Delta S) \Delta H$$

(2.1)

where $\Delta M$ and $\Delta S$ are the differences in magnetization and entropy between austenite and martensite phases, respectively. So the decrease in the MT temperatures can be
attributed to the magnetically induced stabilization of the austenite phase, which is mainly caused by the difference in the saturated magnetization between the austenite and martensitic phases.

Figure 2-4. Thermomagnetization curves of the Ni\textsubscript{45}Co\textsubscript{5}Mn\textsubscript{36.6}In\textsubscript{13.4} alloy measured in several magnetic fields [10].

Figure 2-5. Magnetization versus magnetic field curves for the Ni\textsubscript{45}Co\textsubscript{5}Mn\textsubscript{36.6}In\textsubscript{13.4} alloy between 200 K and 320 K. The curves at 270K and 290K show metamagnetic transition behaviour [10].
2.3 Shape memory effect

2.3.1 Conventional shape memory effect

Assuming a single crystal SMA is cooled from the austenite phase to a temperature below $M_s$, martensite variants forms in a self-accommodating manner to minimize the elastic energy. During this process, the shape of the specimen has not changed macroscopically, but there are twin-related martensite variants in the body and the boundaries between the corresponding twin variants are quite mobile. If an external load is applied, the twin boundaries need to move to accommodate it and deformation consequently occurs. When the stress is high enough, the martensite will become a single variant which is stable under the stress. Now, with the specimen heated to a temperature above $A_s$, reverse transformation happens and if this transformation is crystallographically reversible, the original shape is regained after $T > A_f$. It is worth noted that the multiple martensite variants formed within a single crystal are crystallographically equivalent but the orientations are different, resulting in a strain incompatibility at the variant boundaries. To minimize strain energy without loss of coherence at the variant boundaries (i.e. without degradation by fracture), the variants have to be deformed. The multi-variant state can be transformed
into a nearly single variant of martensitic phase by appropriate mechanical treatment.

Such a complete process is illustrated in Fig 2-6.

Figure 2-6. Primary mechanism of the shape memory effect under load and heating cycle.

Figure 2-7(a) and (b) show the stress–strain curves of the Ni$_{45}$Co$_5$Mn$_{36.7}$In$_{13.3}$ ($A_s$ =307 K, $A_f$ =315 K) and Ni$_{45}$Co$_5$Mn$_{36.5}$In$_{13.5}$ ($A_s$ =253 K, $A_f$ =315 K) single crystals, respectively, to which were applied a compressive strain of approximately 7% at 298 K [9]. The stress–strain characteristics at the testing temperature of $T_t$ =298 K are dependent on the $A_s$ and $A_f$ temperatures of the specimens, that is, when $A_f < T_t$, 

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typical pseudoelastic behavior with a closed loop appeared, as shown in Figure 2-7(b), and when \( A_s > T_t \), the deformed strain remained even after the stress was removed, as shown in Figure 2-7(a). An almost perfect SME in the as-deformed specimen in Figure 2-7(a) was confirmed by dilatometric examination whilst heating to 373 K. These results confirm that the MSMAs are generally shape-memory and pseudoelastic materials.

![Compressive stress–strain curves](image)

**Figure 2-7.** Compressive stress–strain curves for (a) Ni\(_{45}\)Co\(_5\)Mn\(_{36.7}\)In\(_{13.3}\), and (b) Ni\(_{45}\)Co\(_5\)Mn\(_{36.5}\)In\(_{13.5}\) single crystals at \( T_t =298 \) K [9].
2.3.2 Magnetic shape memory effect

In FSMAs, the shape recovery can also be induced by an external magnetic field [3, 10]. The large MFIS, on the order of 5–10%, has been studied extensively since 1996 [3-6], which is based on the field-induced reorientation of martensite twins. In this case, the magnetic field triggers the motion of martensite twin interfaces such that twins with a favorably oriented easy axis of magnetization, relative to the external magnetic field, grow at the expense of other twins leading to an external shape change [Figure 2-8(a)] [6]. This mechanism requires simultaneous application of external stress and a magnetic field to obtain reversible shape change. The field-induced martensite twin reorientation is possible in materials with high magnetocrystalline anisotropy energy and low energy of twin boundary motion. But the output stress resulting from the variant rearrangement in the martensite is restricted to only a few MPa [83], which limits the practical application of these FSMAs.

In addition to field-induced reorientation of martensitic twins, magnetic-field-induced phase transformation is a second possible mechanism for inducing large MFIS [Figure 2-8(b)] [6]. Very recently, MFIS produced by magnetic-field-induced reverse martensitic transformation from martensite to austenite has been found in NiMn-based Heusler alloys NiMnX (X=In, Sn, Sb) [10, 84]. Figure 2-9 shows the recovery strain induced by the magnetic field at 298 K at which a compressive pre-
strain of approximately 3% was applied along the direction plotted with a filled circle in the stereographic triangle, and the magnetic field was applied vertically to the compressive axis of the specimen [9]. The recovery strain started to increase at approximately 2 T and rose sharply at approximately 3.6 T and then gradually increased to 8 T with the magnetic field. A recovery strain of approximately 2.9%, almost equal to the pre-strain of 3%, was obtained with a magnetic field of 8 T. However, only a slight change in length was observed from approximately 3 T when the magnetic field was removed. This behavior induced by the magnetic field is comparable to the general shape memory effect due to the reverse transformation induced by heating. In contrast with the FMSMs such as Ni$_2$MnGa and FePd, the MSMA system has many advantages for practical applications. The most important advantage may be that the present MFIS can yield a high output stress, which is 50 times larger than that generated in pervious FSMAs [10]. The Clausius–Clapeyron relation on the critical stress for the stress-induced MT is given by

$$\frac{d\sigma_c}{dT} = \frac{\Delta S}{\varepsilon \cdot V_m}$$

(2.2)

where $\varepsilon$ denotes the difference in the lattice strain between the austenite and martensite phases in a corresponding direction and $V_m$ denotes the molar volume of the alloy. The magnetic field-induced change in the critical stress corresponds to the output stress obtained by the combination with Eq. (2.1), as follows:
This equation shows that the output stress yielded by the MSMA is proportional to the magnetic field.

Figure 2-8. Effect of applied magnetic field, $H$, on the reorientation of the martensite twin variants (a), and phase transformation (b) in ferromagnetic shape memory alloys [6].
Figure 2-9. Recovery strain at 298 K induced by a magnetic field for the Ni$_{45}$Co$_5$Mn$_{36.7}$In$_{13.3}$ single crystal [9].

2.4 Giant magnetoresistance effect

Giant magnetoresistance (GMR) is a quantum mechanical effect, a type of MR effect, observed in thin film structures composed of alternating ferromagnetic and nonmagnetic metal layers [85, 86]. The effect manifests itself as a significant decrease in electrical resistance in the presence of a magnetic field as shown in Fig. 2-10 [87]. In the absence of an applied magnetic field the direction of magnetization of adjacent ferromagnetic layers is anti-parallel due to a weak anti-ferromagnetic coupling between layers, and it decreases to a lower level of resistance when the magnetization...
of the adjacent layers align due to an applied external field. The spins of the electrons of the nonmagnetic metal align parallel or anti-parallel with an applied magnetic field in equal numbers, and therefore suffer less magnetic scattering when the magnetizations of the ferromagnetic layers are parallel. The magnitude of MR is defined by \([ (R_H - R_0)/R_0 ] \times 100\%\), where \(R_H\) and \(R_0\) are resistance under magnetic field and zero field, respectively. This effect is exploited commercially by manufacturers of hard disk drives. The 2007 Nobel Prize in physics was awarded to Albert Fert and Peter Grünberg for the discovery of GMR.

Figure 2-10. Schematic representation of the GMR effect in a trilayer film with two FM layers F1 and F2 sandwiching a non-magnetic metal spacer layer M [87].
It is noticeable that large MR effect also occurs in bulk intermetallic compounds, particularly in those alloys that undergo first-order phase transition, such as SmMn$_2$Ge$_2$ \cite{88}, FeRh \cite{89}, GdSiGe \cite{90}, and MnAs \cite{91}. MR has also been measured in a few FSMAs NiMnGa alloys, which undergo a first-order phase transition to a martensitic phase of low symmetry \cite{92,93}. In NiMnGa systems, only 5% negative MR has been reported at 8 T \cite{92}. For Fe-doped NiMnGa, the MR can reach 9% at 5 T \cite{93}. The maximum MR appears at MT due to the redistribution of electrons and the increase of phase boundary scattering. The values of MR in these materials are not enough for application. Recently, in MSMAs NiMn$X$ ($X=$In, Sn, and Sb), a large MR effect associated with the magnetic-field-induced metamagnetic reverse MT has been reported extensively \cite{17-30}. Figure 2-11(a) shows resistivity versus temperature behavior of the sample measured at $H = 0$ and $H = 50$ kOe for both heating and cooling cycles in Ni$_{50}$Mn$_{35}$Sn$_{15}$ alloy \cite{22}. The clear thermal hysteresis around the first-order MT is present for both zero field and 50 kOe runs. However, the MT is shifted to lower T in the presence of $H$. In the cooling run, the martensite develops between temperatures $M_s$ and $M_f$, while austenite develops between $A_s$ and $A_f$ during heating. In the $H$-$T$ phase diagram of the sample [inset of Figure 2-11(a)], the white and black shadings, respectively, denote the region of phase coexistence for cooling and heating legs. The average estimated shift of $M_s$ for 50 kOe
of magnetic field is about 12 K. This produces large negative MR in the sample.

Figure 2-11(b) shows the plot of MR at 50 kOe versus temperature for both heating and cooling legs. MR of about −16% is observed in the sample for the heating leg, while on the cooling leg, MR is found to be around −19%.

Figure 2-11. (a) Resistivity as a function of temperature for both heating and cooling cycles for Ni₅₀Mn₃₅Sn₁₅. (b) MR as a function of temperature for heating and cooling cycles for 50 kOe of field [22].
Figure 2-12. Variation of MR vs field strength at various temperatures for (a) Ni$_{50}$Mn$_{34}$In$_{16}$ and (b) Ni$_{50}$Mn$_{35}$In$_{15}$. In (c) plotted are the corresponding saturated magnetoresistances [18].

The MR can also be measured as a function of field at a constant temperature.

Figure 2-12(a) and (b) displays the MR versus field for Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ single crystals, respectively. The values for 100 and 150 K peak at over
80%, and in a wide range from 100 to 180 K the MR can exceed 70% in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16}.

A saturated value of ~60% was attained at only about 3.5 T at 289 K in Ni\textsubscript{50}Mn\textsubscript{35}In\textsubscript{15}.

The saturated MR can exceed 70% in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16}. A saturated value of ~60% was attained at only about 3.5 T at 289 K in Ni\textsubscript{50}Mn\textsubscript{35}In\textsubscript{15}. The saturated MR is depicted in Figure 2-12(c). Noticeably, in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16}, the saturated MR displays a marked increase when the temperature falls from 200 to 100 K; it becomes smaller below 100 K because under such circumstances the largest field available to us can only induce an incomplete transformation. The larger MR effect in MSMAs NiMn\textsubscript{X} (\textsubscript{X}=In, Sn, and Sb) indicates possibility of practical applications of them as magnetic sensor in the future.

### 2.5 Inverse magnetocaloric effect

The magnetocaloric effect (MCE) is a temperature change that occurs when a magnetic field is applied under adiabatic conditions. Figure 2-13 shows the working principal of magnetic refrigerator using MCE. An isothermal application of a magnetic field decreases the entropy of the spin structure. A subsequent adiabatic demagnetization allows the spins to become disordered again, by means of the thermal energy provided by the phonon bath of the isolated sample. This causes cooling.
The MCE effect in paramagnetic materials has been widely used for attaining very low temperatures (mK) by applying a magnetic field isothermally and removing it adiabatically. Moreover, the effect can also be exploited for room-temperature refrigeration by using giant MCE materials [94-96]. As opposed to cooling by adiabatic demagnetization, cooling by adiabatic magnetization (inverse MCE) requires an increase of entropy on applying a magnetic field. The inverse MCE is observed in systems, such as Fe$_{40}$Rh$_{51}$ [97], Mn$_3$Si$_3$ [98], Mn$_{1.95}$Cr$_{0.05}$Sb [98], and Mn$_{1.82}$V$_{0.18}$Sb [99], where magnetically inhomogeneous states exist near the first-order magnetic transformations. Because of the presence of mixed magnetic exchange...
interactions, it is thought that the application of an external magnetic field leads to further spin disorder in these systems giving rise to an increase in the entropy. The field-induced entropy change $\Delta S$ can be estimated from magnetization measurements using Maxwell relation:

$$\Delta S(T, H) = \mu_0 \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH$$

(2.4)

Another interesting group of alloys in relation to the MCE is the ferromagnetic Heusler alloys based on Ni–Mn, of which Ni–Mn–Ga is the most studied series (also because of the presence of the magnetic shape-memory effect). Across a broad composition range, these alloys transform from an austenitic state to a martensitic state. In each of the states, the magnetic coupling is ferromagnetic, but with different ferromagnetic exchange. The MT in Ni–Mn–Ga is first order with a narrow thermal hysteresis, and the application of a magnetic field at temperatures close to this transition leads to a large MCE [100-103]. The maximum MCE is obtained when structural and magnetic transition temperatures lie close to each other [101]. For samples with compositions close to Ni$_2$MnGa stoichiometry, an inverse MCE has been reported [102]. This effect, however, vanishes as the magnetic field increases, and the standard MCE is observed at high fields. Such an inverse MCE is an extrinsic effect arising from the coupling at the mesoscale between the martensitic and
magnetic domains. Very recently, the giant inverse MCE has been observed in
MSMAs NiMnX (X=In, Sn, and Sb) [23-25, 27, 29, 31-65].

Figure 2-14 shows the isothermal magnetization curves measured near the
martensitic transition temperature in Ni\textsubscript{50}Mn\textsubscript{35.3}In\textsubscript{14.7} [42]. The interesting feature is
the sharp changes in the magnetization at the different critical fields in both the
magnetizing and demagnetizing processes. These critical fields strongly depend on
the temperature at which the isothermals were measured. These features strongly
suggest the metamagnetic nature of the material. Based on the Maxwell relations Eq.
2.4, the magnetic entropy change can be calculated from the isothermal data as shown
in Figure 2-14 [42]. The most striking feature of the entropy change is the giant,
inverse entropy change in the range of 295–315 K with magnitudes of 28.6 and 28.2 J
K\textsuperscript{−1} kg\textsuperscript{−1} for the respective magnetizing and demagnetizing processes at 5 T. These
values are comparable to those of the Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{2} [94], MnAsSb [104] and La(Fe, Si)\textsubscript{13}
[105] alloys, known as magnetocaloric materials, in which the absolute value |ΔS| in
the field of 50 kOe is 18 J kg\textsuperscript{−1} K\textsuperscript{−1} at 276 K, 40 J kg\textsuperscript{−1} K\textsuperscript{−1} at 317 K and 30 J kg\textsuperscript{−1} K\textsuperscript{−1} at
184 K, respectively.
Figure 2-14. Isothermal magnetization curves measured near the martensitic transition temperature [42].

Figure 2-15. The entropy change as a function of the temperature under different magnetic field variations ($\Delta H$) Calculated entropy change using (a) the magnetizing curves and (b) the demagnetizing curves [42].
2.6 Magnetic hysteresis loop

2.6.1 After field cooling (conventional exchange bias effect)

In 1956, Meiklejohn and Bean discovered a type of magnetic anisotropy in fine particles of FM cobalt coated with AFM cobalt oxide [106]. In their discovery, they found a shift in the zero field cooled (ZFC) and field cooled (FC) hysteresis loops of the oxide coated particles as shown in Figure 2-16. Since then it was observed in many different systems containing FM/AFM interfaces, such as small particles [107], inhomogeneous materials [108] FM films on AFM single crystals [109], and thin films [110]. It is well known that when a sample with FM/AFM interfaces is cooled through the Neel temperature ($T_N$) of the antiferromagnet, with the FM Curie temperature ($T_C$) greater than $T_N$, exchange bias (EB) is induced in the system. EB can be qualitatively understood by assuming an exchange interaction at the AFM/FM interface as shown in Figure 2-17[111]. When a field is applied in the temperature range $T_N < T < T_C$, the FM spins line up with the field, while the AFM spins remain random [Figure 2-17(i)]. When cooling to $T < T_N$, in the presence of the field, due to the interaction at the interface, the AFM spins next to the FM align ferromagnetically to those of the FM (assuming ferromagnetic interaction). The other spin planes in the AFM “follow” the AFM order so as to produce zero net magnetization [Figure 2-17
(ii)]. When the field is reversed, the FM spins start to rotate. However, for sufficiently large AFM anisotropy, the AFM spins remain unchanged [Figure 2-17 (iii)]. Therefore, the interfacial interaction between the FM/AFM spins at the interface, tries to align ferromagnetically the FM spins with the AFM spins at the interface. In other words, the AFM spins at the interface exert a microscopic torque on the FM spins, to keep them in their original position (ferromagnetically aligned at the interface) [Figure 2-17 (iv)]. Therefore, the FM spins have one single stable configuration, i.e. the anisotropy is unidirectional. Thus, the field needed to reverse completely an FM layer will be larger if it is in contact with an AFM, because an extra field is needed to overcome the microscopic torque. However, once the field is rotated back to its original direction, the FM spins will start to rotate at a smaller field, due to the interaction with the AFM spins (which now exert a torque in the same direction as the field) [Figure 2-17 (v)]. The material behaves as if there was an extra (internal) biasing field. Therefore, the FM hysteresis loop is shifted in the field axis, i.e. EB. Over the years, materials possessing EB properties have been utilized significantly in many technological devices including permanent magnets, magnetic recording media, sensors, read heads, and many other devices [111, 112].
Figure 2-16. Hysteresis loops at 77 K of oxide-coated cobalt particles. The solid line results from cooling the material in a 10 kOe field. The dash line shows the loop when cooled in zero field [106].

The EB behavior have also been observed in the martensitic state of MSMAs NiMnSb and NiMnSn [66, 67, 69], which is attributed to the coexistence of FM and AFM exchange interactions in the system. Figure 2-18 shows magnetization hysteresis loops of Ni$_{50}$Mn$_{36}$Sn$_{14}$ at different temperatures measured after field cooling in the 10 kOe field [67]. It is clear to see that the magnetic hysteresis loops significantly shift to the negative field at the region of measured temperatures
indicating that the EB phenomena indeed exists in the MSMA Ni_{50}Mn_{36}Sn_{14}. Such behavior is an addition to the multifunctional properties of the MSMAs.

Figure 2-17. Schematic diagram of the spin configuration of an FM/AFM bilayer at different stages (i)-(v) of an exchange biased hysteresis loop[111].
Figure 2-18. Magnetization hysteresis loops of Ni₅₀Mn₃₆Sn₁₄ alloy measured at (a)\(T=2\) K, (b) \(T=30\) K, (c) \(T=70\) K, and (d) \(T=100\) K. Inset: enlarged (b) view of the central region of the loops [67].

2.6.2 After zero-field cooling from an unmagnetized state

The interface between FM and AFM is fixed in the conventional EB (CEB) systems after fabrication. When the system is zero-field cooled from an unmagnetized FM state to \(T < T_B\) (\(T_B\) is blocking temperature, above which AFM is no longer hind the rotation of FM spins), the FM domains are in random orientations and the net magnetization is zero. Here, we simplify it as two FM domains with opposite
directions parallel to the direction of the magnetic field [Figure 2-19(1)]. Note that the spin configurations are a simple cartoon to illustrate the effect of the coupling. The AFM spins next to the FM align ferromagnetically due to the interaction at the interface assuming FM interaction between FM and AFM (it can be AFM interaction [113]). The total net magnetization is zero in the initial state in the system [Figure 2-19(1)]. When a positive field (right direction) is applied, the FM spins with left direction start to rotate. If AFM anisotropy is sufficiently large, the AFM spins remain unchanged. The rotated FM spins are exerted a microscopic torque, due to FM interaction between FM and AFM at the interface, to keep them in their original position (left direction) [Figure 2-19(2)]. After removal of the position field, there is a remanent magnetization due to magnetic interaction among FM domains [Figure 2-19(3)]. When the negative field is applied and removed, the same process occurs for FM spins with right direction. Although the local FM-AFM interaction is unidirectional in the CEB systems after ZFC from an unmagnetized state, the hysteresis loop representing a collective effect of whole FM-AFM interaction is centrally symmetric (no EB effect). If the AFM anisotropy is not very large, the AFM spins near the interface will rotate when the FM spins are rotated by the magnetic field [114, 115]. However, the rotated AFM spins will return to their initial positions due to AFM anisotropy energy after removal of the external magnetic field. Then,
they will still exert a microscopic torque on the FM spins due to FM interaction between FM and AFM at the interface, which is similar to the case of AFM spins remain unchanged during FM rotation resulting in a symmetric hysteresis loop (no EB effect).

Figure 2-19. Hysteresis loop of the CEB systems (FM-AFM) with a fixed interface after ZFC from an unmagnetized state (right) and schematic diagram of the spin configuration at different stages (left).
2.7 Summary

MSMAs NiMnX (X = In, Sn) showing SME, MR, MCE, EB etc, is a kind of multifunctional materials. However, the magnetic properties in the martensitic state of these alloys and the sensor capabilities of MSMAs are not clear. In this work, we propose to investigate and understand the magnetic and electrical transport properties of these alloys.
Chapter 3 Experiment methods

3.1 Alloy fabrication

The polycrystalline Ni-Mn-In and Ni-Mn-Sn alloys were prepared under argon atmosphere using Ni, Mn, In, and Sn of 99.9% purity in an Emund Buhler mini arc melting system. Since the high vapor pressure of Mn, it is very easy to lose Mn during arc melting. So we added about 4% more Mn in all nominal compositions during alloys production. The sample was remelted several times and subsequently annealed at 1000ºC for 24 hours and slowly cooled to room temperature to ensure homogeneity.

3.2 Composition measurement

For semi-quantitative analysis of elements in the alloy specimens, energy dispersive spectroscopy (EDS) was carried out on five different regions of the specimens polished to a mirror-finish surface. A JEOL JSM-5600LN scanning electron microscope (SEM), operated at the accelerating voltage of 20 keV, was used.

Figure 3-1 & 2 show the energy dispersive x-ray (EDX) spectrums of the nominal compositions Ni$_{50}$Mn$_{50-x}$In$_x$ (NiMnIn$_x$, $x = 11, 12, 13, 14,$ and 15) and Ni$_{50}$Mn$_{50-y}$Sn$_y$ NiMnSn$_y$, $y = 8, 9, 10, 11,$ and 12) alloys, respectively. The final compositions were obtained by averaging 5 different areas with similar composition in each sample and
are summarized in Table 3-1 and 2. The actual Ni content in all samples is lower than nominal one due to the loss in the melting process. We used the nominal compositions to represent the samples in the whole text.

Table 3-1. Compositions of NiMnIn\textsubscript{x} determined by EDX analysis

<table>
<thead>
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<th>(x) (nominal)</th>
<th>Ni</th>
<th>Mn</th>
<th>In</th>
</tr>
</thead>
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<tr>
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<td>49.2</td>
<td>39.4</td>
<td>11.4</td>
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<td>49.6</td>
<td>38.4</td>
<td>12.0</td>
</tr>
<tr>
<td>13</td>
<td>49.0</td>
<td>37.5</td>
<td>13.5</td>
</tr>
<tr>
<td>14</td>
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<td>35.5</td>
<td>15.5</td>
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</table>

Table 3-2. Compositions of NiMnSn\textsubscript{y} determined by EDX analysis.

<table>
<thead>
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<th>(y) (nominal)</th>
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<th>Mn</th>
<th>Sn</th>
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<td>42.3</td>
<td>8.4</td>
</tr>
<tr>
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</tr>
<tr>
<td>11</td>
<td>49.4</td>
<td>39.3</td>
<td>11.3</td>
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<tr>
<td>12</td>
<td>49.1</td>
<td>38.5</td>
<td>12.4</td>
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</table>
Figure 3-1. The EDX spectrums of NiMnIn\textsubscript{x} (x = 11, 12, 13, 14, and 15). The insets show the scanning electron microscopic pictures. The little rectangles mark the positions where we took the EDX spectrums.
Figure 3-2. The EDX spectrums of NiMnSn_y (y = 8, 9, 10, 11, and 12). The insets show the scanning electron microscopic pictures. The little rectangles mark the positions where we took the EDX spectrums.
3.3 Powder X-ray diffraction measurement

The crystal structure was analyzed by powder X-ray diffraction (XRD) using a Bruker D8 advanced X-ray diffractometer with accelerating voltage of 40 kV, tube current of 40 mA, Cu-Kα radiation, and normal 0/20 scanning mode. The scan step was 0.01°, the time per step is 5 s and the scan range was from 20° to 80°. All experiments were performed at room temperature. Before performing powder XRD, all samples were annealed at 600-700 °C under high vacuum (~2 × 10⁻⁶ Torr) for 5-10 hours to remove the residual stress induced during grinding. All the XRD peaks can be indexed for a monoclinic crystal structure, which is consistent with the result observed by Krenke et al. [11, 73] for a same nominal composition sample. The lattice parameters decrease with increasing the Mn content due to the smaller atomic radius of Mn (Table 3-1 & 2).
Figure 3-3. Powder X-ray diffraction patterns at room temperature for NiMnIn\textsubscript{x} alloys ($x = 11, 12, 13, 14,$ and $15$). The inset shows details in the range $40^\circ \leq 2\theta \leq 44.5^\circ$.

Table 3-3. Lattice parameters of NiMnIn\textsubscript{x} ($x = 11, 12, 13, 14,$ and $15$) at room temperature.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
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</tr>
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<td>87.87</td>
</tr>
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<td>5.844</td>
<td>21.312</td>
<td>88.32</td>
</tr>
</tbody>
</table>
Figure 3-4. Powder X-ray diffraction patterns at room temperature for NiMnSny alloys ($y = 8, 9, 10, 11,$ and $12$). The inset shows details in the range $40^\circ \leq 2\theta \leq 46^\circ$.

Table 3-4. Lattice parameters of NiMnSny ($y = 8, 9, 10, 11,$ and $12$) at room temperature.

<table>
<thead>
<tr>
<th>$y$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.532</td>
<td>30.404</td>
<td>94.11</td>
</tr>
<tr>
<td>9</td>
<td>4.333</td>
<td>5.583</td>
<td>30.057</td>
<td>94.09</td>
</tr>
<tr>
<td>10</td>
<td>4.339</td>
<td>5.611</td>
<td>29.864</td>
<td>93.51</td>
</tr>
<tr>
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<td>5.620</td>
<td>29.888</td>
<td>93.32</td>
</tr>
<tr>
<td>12</td>
<td>4.348</td>
<td>5.619</td>
<td>29.863</td>
<td>92.98</td>
</tr>
</tbody>
</table>
3.4 Martensitic phase transformation measurement

The martensitic transformation behavior was measured using differential scanning calorimeter (DSC) (TA Instruments, MDSC 2920), and the transformation temperatures were determined using slope line extension method. A heating and cooling rate of 10°C/min was used. In NiMnX (X = In, Sn, Sb, Ga et al.) alloys, the magnetic transition always accompany with the first-order martensitic transformation. First-order AFM transition has been confirmed by recent neutron polarization analysis in Ni50Mn40Sn10 with higher Mn content [116]. Furthermore, first-order ferromagnetic-antiferromagnetic transition has been observed in Ni50Mn37Sn13 with lower Mn content [116], and first-order paramagnetic-ferromagnetic transition in Ni2.19Mn0.81Ga [101]. Thus, we can use DSC, a technique which is sensitive to the first-order phase transition, to determine the AFM transition of NiMnX (X = In, Sn) alloy with higher Mn content [Figure 3-5]. The martensite transformation temperature ($T_m$, peak temperature from DSC) or AFM transition temperature increases continuously with decreasing X content [Figure 3-5(c)].
Figure 3-5. DSC curves of NiMnIn$_x$ (a) and NiMnSn$_y$ (b). The arrows show the heating and cooling directions. (c) $T_m$ as a function of In and Sn content.
3.5 Magnetic and electronic properties measurements

The magnetic properties were measured using physical properties measurement system (PPMS) (Quantum Design, temperature range from 1.9 K to 400 K, magnetic field up to 9 Tesla) platform with a vibrating sample magnetometer (VSM) module. The alternative current (ac) susceptibility was measured using a superconducting quantum interface device (SQUID, Quantum Design). The resistivity was measured by a standard four-probe method in PPMS using an ac technique.
Chapter 4 Exchange bias after ZFC in NiMnX alloys

4.1 Background

When a system consisting of ferromagnetic (FM)-antiferromagnetic (AFM) [106], FM-spin glass (SG) [117], AFM-ferrimagnetic (FI) [118], and FM-FI [119] interface is cooled with field through the Néel temperature ($T_N$) of the AFM or glass temperature ($T_{SG}$) of the SG, exchange bias (EB) is induced showing a shift of hysteresis loop [$M(H)$] along the magnetic field axis. Since its discovery by Meiklejohn and Bean in 1956 [106], EB has been extensively studied during the past fifty years, partly because of its applications in ultrahigh-density magnetic recording, giant magnetoresistance and spin valve devices [111, 112]. The EB effect is attributed to an FM unidirectional anisotropy formed at the interface between different magnetic phases [111]. Generally, the process of field cooling (FC) from higher temperature is used to obtain FM unidirectional anisotropy in different EB systems [106, 117-119]. The FM unidirectional anisotropy can also be realized by depositing the AFM layer onto a saturated FM layer [111], by ion irradiation in an external magnetic field [120], by zero-field cooling (ZFC) with remnant magnetization [121, 122]. In a word, the FM unidirectional anisotropy in these EB systems is formed by reconfiguring the FM spins at the interface between different magnetic phases. Here, we named the previous
EB generally observed after FC as the conventional EB (CEB). Furthermore, Saha et al. [123] argued that a small spontaneous EB observed after ZFC without remnant magnetization, which has been ignored or attributed to the experimental artifact, can be explained theoretically in an otherwise isotropic EB system. The CEB effect after FC has also been observed in NiMn-based Heusler bulk alloys, such as NiMnSn [67], NiMnSb [66], and NiMnIn [70], coexisting of AFM and FM phases. In this Chapter, we report a large EB effect after ZFC from an unmagnetized state in NiMnX (X = In, Sn) bulk alloys. Namely, a large FM unidirectional anisotropy can be produced isothermally, which has never been reported to date and cannot be expected in the CEB systems. In order to explain this remarkable result, we propose a model related to the newly formed interface between different magnetic phases during the initial magnetization process.

4.2 Results and analysis

4.2.1 $M(T)$, $RM(T)$ and $M(H)$ at 300 K in NiMnX (X = In, Sn)

Figures 4-1& 2 show the M(T), RM(T) and M(H) at 300 K of NiMnInx (x =11, 12, 13, 14, and 15) and NiMnSny (y =8, 9, 10, 11, and 12), respectively. The M(T) curves were measured under $H =100$ Oe after ZFC and FC. The remanent magnetization (RM) as a function of temperature in NiMnX (X = In, Sn) was
measured at zero field on heating after the samples were field-cooled under 10 kOe from 300 to 10 K. The RMs decrease with increasing temperature and become zero before reaching 300 K in NiMnX (X = In, Sn). The M(H) curves at 300 K in NiMnInx are straight lines without any SPM/FM feature, which indicates that their Tcs are at lower temperatures. These results make sure that unmagnetized initial states at lower temperatures in these samples can be obtained after ZFC from 300 K.

Figure 4-1. $M(T)$ measured in $H=100$ Oe under ZFC and FC in NiMnInx (a) $x=14$, 15. (b) $x=11, 12, 13$. (b) RM as a function of temperature for NiMnInx. (c) $M(H)$ curves for NiMnInx at 300 K.
Figure 4-2. $M(T)$ measured in $H = 100$ Oe under ZFC and FC in NiMnSny (a) $y = 12, 11$. (b) $y = 10, 9, 8$. (b) RM as a function of temperature for NiMnSny. (c) $M(H)$ curves for NiMnSny at 300 K.

4.2.2 CEB effect after FC in NiMnInx

The CEB effect after FC has also been observed in NiMnInx ($x = 11, 12, 13, 14,$ and 15) as shown in Figure 4-3, which is due to the coexistence of AFM and FM phases and interaction at the interface below $T_B$ [66, 67, 70].
Figure 4-3. (a) Hysteresis loops of NiMnInx at 10 K after FC ($H = 40$ kOe) from 300 K. The larger scale at low field curves are shown in (b) $x = 11, 12$, (c) $x = 13, 14, 15$. The $M(H)$ curves shifted along the field axis show the EB effect.

4.2.3 Hysteresis loops after ZFC from an unmagnetized state in NiMnIn13 and NiMnSn10

Two measurement processes can be used to obtain a closed $M(H)$ loop after ZFC (only consider $|+H| = |-H|$):
(1) P type, $0 \rightarrow (+H) \rightarrow 0 \rightarrow (-H) \rightarrow 0 \rightarrow (+H)$,

(2) N type, $0 \rightarrow (-H) \rightarrow 0 \rightarrow (+H) \rightarrow 0 \rightarrow (-H)$.

The first $0 \rightarrow (+H)/(-H)$ curve is called as an initial magnetization curve. Generally, these two kinds of measurement will obtain the same loop except for the initial magnetization curve. Thus, only one of them has been used to obtain $M(H)$ loop in the previous studies. We denoted these two measurements as P and N types, respectively, because they will give the different results in the present study.

An unmagnetized state at 10 K can be obtained after ZFC (the remanent field of magnet is zero) from an unmagnetized state (ZFC starts from an unmagnetized state of the samples). Before each ZFC $M(H)$ loop measurement in the present case, there are two methods/conditions have been used: (1) Before each ZFC, the superconductor magnet was demagnetized by oscillating fields at 300 K (in PPMS) or heated up to its superconductor transition temperature (in SQUID, magnet reset) to remove the pinned magnetic flux. (2) The samples were zero-field cooled from 300 K. Since the $T_c$s of all samples are lower than 300 K, the ZFC starts from an unmagnetized state. The magnetization at the starting point of the initial magnetization curve ($H = 0$) is zero, indicating the initial state at 10 K is an unmagnetized state. That is, the shifted $M(H)$ curves (EB effect) are obtained isothermally from an unmagnetized initial state. Furthermore, the shift direction of $M(H)$ loop is strongly dependent on the direction of
the initial magnetizing field, further indicating the isothermal formation of magnetic unidirectional anisotropy (the origin of EB effect) during the initial magnetization process.

### 4.2.3.1 P type $M(H)$ loops measured under different $|H_{m}^{\text{max}}|$ at 10 K after ZFC

Figure 4-4 & 6 show the P type $M(H)$ of NiMnIn13 and NiMnSn10 at 10 K after ZFC from 300 K with different maximum measurement fields ($|H_{m}^{\text{max}}| = |+H|=|-H|$) at 10 K after ZFC from 300 K. The magnetization at the starting point of the initial magnetization curve ($H = 0$) is zero, indicating the initial state at 10 K is an unmagnetized state (Fig 4-5 &7). It is worth noting that the ZFC $M(H)$ loop shows a large shift along the magnetic field axis, which has never been observed in any previous CEB systems. The equal magnetization values in the highest positive and negative magnetic fields indicate the shifted loop is not a nonsymmetrical minor hysteresis loop.
Figure 4-4. P type $M(H)$ loops $[0 \rightarrow (+H) \rightarrow 0 \rightarrow (-H) \rightarrow 0 \rightarrow (+H)]$ measured under different $|H_m^{\text{max}}|$s at 10 K after ZFC from 300 K in NiMnIn13. The initial magnetization curves $[0 \rightarrow (+H)]$ are shown in the next figure.
Figure 4-5. (a) Initial magnetization curves $[0 \rightarrow (+H)]$ for different $|H_{m}^{\text{max}}|$s at 10 K after ZFC from 300 K in NiMnIn13. (b) The magnetization values in the highest positive ($M^p$) and negative ($|M^N|$) magnetic fields for different $|H_{m}^{\text{max}}|$s.
Figure 4-6. P type $M(H)$ loops $[0 \rightarrow (+H) \rightarrow 0 \rightarrow (-H) \rightarrow 0 \rightarrow (+H)]$ measured under different $|H_m^{\text{max}}|$s at 10 K after ZFC from 300 K in NiMnSn10. The initial magnetization curves $[0 \rightarrow (+H)]$ are shown in the next figure.
Figure 4-7. (a) Initial magnetization curves \([0 \rightarrow (+H)]\) for different \(|H_m^{\text{max}}|\)s at 10 K after ZFC from 300 K in NiMnSn10. (b) The magnetization values in the highest positive \((M^p)\) and negative \((|M^N|)\) magnetic fields for different \(|H_m^{\text{max}}|\)s.
4.2.3.2 Strong initial magnetization field direction dependence of EB effect after ZFC

We also measured the N type $M(H)$ loops with opposite direction of the initial magnetization field at 10 K after ZFC (Figure 4-8 &9), which shift to the positive magnetic field axis showing a centrally symmetric image of the P type $M(H)$ loops. This result cannot be expected from the effect of remanent field of superconductor magnet/remanent magnetization of the samples, in which the shift direction of $M(H)$ loop is independent on the direction of the initial magnetization field. Furthermore, both the EB field ($H_{EB}$) and coercivity ($H_c$) after ZFC can be larger than those after FC [Figure 4-8(b)], which indicates that the EB after ZFC in the present case is not a spontaneous EB [123]. The $H_{EB}$ and $H_c$ are defined as $H_{EB} = - (H_L+H_R)/2$ and $H_c = -(H_L - H_R)/2$, respectively, where $H_L$ and $H_R$ are the left and right coercive fields.
Figure 4-8. (a) The low field part of P type $M(H)$ loops for different $|H_{m}^{\text{max}}|$s at 10 K after ZFC from 300 K in NiMnIn13. (b) The low field part of N type $M(H)$ loops for different $|H_{m}^{\text{max}}|$s at 10 K after ZFC from 300 K. The $H_{EB}$ (c) and $H_{c}$ (d) as a function of $|H_{m}^{\text{max}}|$ for P an N types $M(H)$ loops.
Figure 4-9. (a) The low field part of P type $M(H)$ loops for different $|H_{m}^{\max}|$s at 10 K after ZFC from 300 K in NiMnSn10. (b) The low field part of N type $M(H)$ loops for different $|H_{m}^{\max}|$s at 10 K after ZFC from 300 K. The $H_{EB}$ (c) and $H_c$ (d) as a function of $|H_{m}^{\max}|$ for P an N types $M(H)$ loops.
In order to compare results from ZFC with that from FC, we measured the $M(H)$ loops after FC under P and N types. Before each measurement, the cooling field at 10 K was removed after FC. Then we can $M(H)$ loops under P and N types. As expected from the CEB effect after FC, the $M(H)$ curve is only dependent on the direction of cooling field [Figure 4-10(d)], and it is independent on the direction of the initial magnetization field [Figure 4-10(c)].

Figure 4-10. $M(H)$ loops measured at 10 K with $|H_m^{\text{max}}| = 40$ kOe after FC (a) P and N types under the same cooling field (both direction and magnitude), (b) P type under the opposite directions of the same magnitude of the cooling field. (c) and (d) are the larger scale at low field for (a) and (b), respectively.
4.2.3.3 P and N type $M(H)$ loops after ZFC measured by using SQUID

To further rule out the effect from remanent field of superconductor magnet, we measured the $M(H)$ loops after ZFC by using SQUID with magnet reset function. Before each ZFC, the superconductor magnet was heated up to its superconductor transition temperature to remove the pinned magnetic flux (magnet reset). Figure 4-11 shows the P and N types $M(H)$ loops after ZFC, which are the same as the results obtained by PPMS.

Figure 4-11. (a) P and (b) N types $M(H)$ loops at 10 K after ZFC measured by using SQUID. The insets give the larger scale at the low field.
4.2.3.4 Temperature dependence of EB after ZFC

To further confirm this phenomenon after ZFC, we measured the temperature dependence of $H_{EB}$ and $H_c$ for $|H_{m}^{\text{max}}| = 40$ kOe as shown in Figure 4-12 &13 in NiMnIn13 and NiMnSn10, respectively. The $H_{EB}$ approximately linearly decreases with increasing temperature at low temperatures and gradually disappears around the blocking temperature ($T_B$), at which the $H_c$ reaches its maximum value. These relationships are similar to those in the CEB systems obtained after FC [111]. The AFM anisotropy decreases with the increasing of temperature. Thus, the FM rotation can drag more AFM spins, giving rise to the increase in $H_c$; whereas the AFM can no longer hinder the FM rotation above $T_B$. As a result, the $H_c$ reaches its maximum value and $H_{EB}$ reduces to zero at higher temperatures.
Figure 4-12. (a) Temperature dependence of P type $M(H)$ loops with $|H_m^{\text{max}}| = 40$ kOe after ZFC from 300 K in NiMnIn13. (b) The low field part of $M(H)$ loops. (c) Temperature dependence of $H_{EB}$ and $H_c$ after ZFC for $|H_m^{\text{max}}| = 40$ kOe.
Figure 4-13. (a) P type $M(H)$ loops with $|H_{m}^{\text{max}}| = 40$ kOe at different temperatures after ZFC from 300 K in NiMnSn10. (b) The low field part of $M(H)$ loops. (c) Temperature dependence of $H_{EB}$ and $H_{c}$ after ZFC for $|H_{m}^{\text{max}}| = 40$ kOe.
4.2.3.5 Training effect of EB at 10 K after ZFC

Figure 4-14 (a)-(e) show P type $M (H)$ loops measured for 10 consecutive cycles at 10 K after ZFC from 300 K with several selected $|H_{m}^{\text{max}}|$s, and (f) the $H_{\text{EB}}$ as a function of number of cycles at 10 K after ZFC for $|H_{m}^{\text{max}}| = 15, 25, 35, 45, 55$ kOe. There is a large decrease in $H_{\text{EB}}$ occurs between $n = 1$ and $n = 2$, followed by a more gradual decrease for subsequent loops. The training effect in NiMnIn13 after ZFC is also similar to that in the conventional EB obtained after FC, which composes two distinct mechanisms [124]. One is due to the biaxial anisotropy of the AFM resulting in abrupt single cycle training, while the other is related to the depinning of uncompensated AFM spins resulting in a gradual decrease for subsequent loops.
Figure 4-14. (a)-(e) P type $M$ ($H$) loops measured for 10 consecutive cycles at 10 K after ZFC from 300 K with several selected $|H_m^{\text{max}}|$s. (f) $H_{EB}$ as a function of number of cycles at 10 K after ZFC for $|H_m^{\text{max}}| = 15, 25, 35, 45, \text{ and } 55 \text{kOe}$. 

(a) $|H_m^{\text{max}}| = 15 \text{kOe}$

(b) $|H_m^{\text{max}}| = 25 \text{kOe}$

(c) $|H_m^{\text{max}}| = 35 \text{kOe}$

(d) $|H_m^{\text{max}}| = 45 \text{kOe}$

(e) $|H_m^{\text{max}}| = 55 \text{kOe}$

(f) $H_{EB}$ as a function of number of cycles at 10 K after ZFC for $|H_m^{\text{max}}|$ = 15, 25, 35, 45, and 55 kOe.
4.2.4 Hysteresis loops after ZFC from an unmagnetized state in NiMnIn$_x$ ($x = 11, 12, 14, \text{ and } 15$) and NiMnSn$_y$ ($y = 8, 9, 11, \text{ and } 12$)

Finally, we have further verified this large EB effect observed after ZFC by changing the content of $X$ ($X=\text{In, Sn}$). The saturation magnetization of NiMn$X$ ($X=\text{In, Sn}$) increases with increasing $X$ content [11, 73]. Thus, the size of the initial domains can be changed by $X$ content, which may affect the EB effect. The reasons for $X$ content dependence of EB effect after ZFC in NiMn$X$ alloys will be discussed in the Discussion part and it will help to find out the origin of this new interesting result.
Figure 4.15. (a) P type $M(H)$ loops measured under different $|H_m^{\text{max}}|$s in NiMnIn11 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_m^{\text{max}}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{\text{max}}|$. 

a. NiMnIn11
Figure 4-16. (a) Initial magnetization curves \([0 \to (+H)]\) for different \(|H_{m}^{\text{max}}|\)s in NiMnIn11 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different \(|H_{m}^{\text{max}}|\)s.
Figure 4-17. (a) P type $M(H)$ loops measured under different $|H_m^{\text{max}}|$s in NiMnIn12 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_m^{\text{max}}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{\text{max}}|$. 

b. NiMnIn12
Figure 4-18. (a) Initial magnetization curves $[0 \rightarrow (+H)]$ for different $|H_{m}^{\text{max}}|$ in NiMnIn12 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different $|H_{m}^{\text{max}}|$s.
c. NiMnIn14

Figure 4-19. (a) P type $M(H)$ loops measured under different $|H_{m}^{\text{max}}|$s in NiMnIn14 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_{m}^{\text{max}}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_{m}^{\text{max}}|$.
Figure 4-20. (a) Initial magnetization curves $[0 \rightarrow (+H)]$ for different $|H_m^{\text{max}}|$s in NiMnIn14 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different $|H_m^{\text{max}}|$s.
d. NiMnIn15

Figure 4-21. (a) P type $M(H)$ loops measured under different $|H_m^{\text{max}}|$s in NiMnIn15 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_m^{\text{max}}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{\text{max}}|$. 

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Figure 4-22. (a) Initial magnetization curves \([0 \rightarrow (+H)]\) for different \(|H_{m}^{\text{max}}|\)s in NiMnIn15 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different \(|H_{m}^{\text{max}}|\)s.
Figure 4-23. (a) P type $M(H)$ loops measured under different $|H_{m}^{\max}|$s in NiMnSn8 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_{m}^{\max}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_{m}^{\max}|$. 

e. NiMnSn8
Figure 4-24. (a) Initial magnetization curves $[0 \rightarrow (+H)]$ for different $|H_{m}^{\text{max}}|$s in NiMnIn11 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different $|H_{m}^{\text{max}}|$s.
Figure 4-25. (a) P type $M(H)$ loops measured under different $|H_m^{max}|$s in NiMnSn9 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_m^{max}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{max}|$. 
Figure 4-26. (a) Initial magnetization curves \([0 \rightarrow (+H)]\) for different \(|H_m^{\text{max}}|s\) in NiMnSn9 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different \(|H_m^{\text{max}}|s\).
g. NiMnSn11

Figure 4-27. (a) P type $M(H)$ loops measured under different $|H_m^{\text{max}}|$s in NiMnSn11 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_m^{\text{max}}|$s. (c) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{\text{max}}|$.
Figure 4-28. (a) Initial magnetization curves \([0 \rightarrow (+H)]\) for different \(|H_{m_{\text{max}}}|\)s in NiMnSn11 at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different \(|H_{m_{\text{max}}}|\)s.
h. NiMnSn12

Figure 4-29. (a) P type $M(H)$ loops measured under different $|H_{m}^{\text{max}}|$s in NiMnSn12 at 10 K after ZFC from 300 K. (b) The low field part of P type $M(H)$ curves for different $|H_{m}^{\text{max}}|$s. (c) The left ($H_{L}$) and right ($H_{R}$) coercive fields as a function of $|H_{m}^{\text{max}}|$. 
Figure 4-30. (a) Initial magnetization curves $[0 \rightarrow (+H)]$ for different $|H_{m}^{\text{max}}|$s in NiMnSn$_{12}$ at 10 K after ZFC from 300 K. (b) The magnetization values in the highest positive and negative magnetic fields for different $|H_{m}^{\text{max}}|$s.
4.3 Discussion

From the above results, we observed a large EB effect after ZFC from an unmagnetized state in NiMnX (X = In, Sn) alloys. Namely, FM unidirectional anisotropy, usually obtained by FC from higher temperature, can be induced isothermally during the initial magnetization process in the present alloys. This phenomenon has never been reported to date and cannot be expected in the CEB systems.

To investigate the origin of the formation of FM unidirectional anisotropy during the initial magnetization process, we consider the evolution of the initial magnetic state of NiMnIn13 after ZFC under the external magnetic field. The $M(T)$ curves of NiMnX (X = In, Sn) exhibits a peak at $T_p$ and an irreversibility between ZFC and FC curves (Figure 4-1 and 2), which is similar to that of NiCoMnSn [125]. The magnetic state of NiMnX (X = In, Sn) at low temperatures is superparamagnetic (SPM) domains embedded in AFM matrix as in NiCoMnSn. The difference between SPM and conventional paramagnetic (PM) is that the atomic spins in the conventional PM are replaced by the superspins including hundreds or thousands of atomic spins with the same direction in SPM. The SPM domains are collectively frozen forming a superspin glass (SSG) state at lower temperatures [125]. To confirm this SSG state, we
measured ac susceptibility at various frequencies ($f_s$) with an ac magnetic field of 2.5 Oe after ZFC from 300 K in NiMnIn13. Figure 4-31 shows the temperature dependence of the real part of ac susceptibility. The $T_p$ increases with increasing frequency, which can be fitted to a critical power law for SSG [126],

$$\tau = 1/2\pi f = \tau^* (T_p/T_g-1)^{z\nu}$$

(4.1)

where $\tau^*$ is the relaxation time of individual particle moment, $T_g$ is the static glass temperature and $z\nu$ is the dynamic critical exponent. Our data can be fitted well by Eq. (4.1) with $\tau^* \approx 10^{-8}$ s, $z\nu \approx 9.7$ and $T_g \approx 52$ K [Figure 4-31(b)]. These values are close to those reported for SSG ($\tau^* \approx 10^{-8}$ s and $z\nu \approx 10.2$) [127].

To further confirm SSG state at low temperature in NiMnIn13 after ZFC, we used the well defined stop-and-wait protocol to measure its memory effect in the ZFC $M(T)$ as shown in Figure 4-32, which is an unequivocal signature of SSG behavior [126]. The sample was first ZFC from 300 K to 10 K and then the $M(T)$ (reference line, curve 1) was measured during heating under $H = 200$ Oe. In the stop-and-wait protocol, the sample was ZFC from 300 K to an intermittent stop temperature $T_w = 32$ K and waited for $10^4$ s followed by further cooling to 10 K. The $M(T)$ (curve 2) was then measured under the same conditions as chosen for the reference line. The inset of Figure 4-32 shows the difference between curve 2 and 1. The dip at $T_w = 32$ K clearly shows the memory effect.
Figure 4-31. (a) Temperature dependence of the real part of the ac susceptibility measured at frequencies $f = 0.1, 1, 10, 100, 1000$ Hz with ac magnetic field of 2.5 Oe after ZFC from 300 K. (b) The plot of $\log_{10} f$ vs $\log_{10} (T_p/T_g-1)$ (open circles) and the best fit to Eq. (4.1) (solid line).
Figure 4-32. Temperature dependence of the reference magnetization (curve 1) and of the magnetization with a stop-and-wait protocol at $T_w = 32$ K with waiting time $t_w = 10^4$ s (curve 2), measured in $H = 200$ Oe. The inset shows the temperature dependence of magnetization difference between curve 2 and 1.

Figure 4-33 shows the possible evolution of the initial magnetic state of NiMnIn13 after ZFC under the external magnetic field. It is a simplified schematic diagram with SPM domains embedded in an AFM single domain (AFM anisotropy axis is parallel to the direction of the applied magnetic field). The initial magnetic state after ZFC is a superspin glass (SSG) state. The white arrows represent the superspin direction of SPM domains. The dashed white circles show the coupling interfaces of SPM-AFM. The dashed blue lines represent the coupling
domains is a glassy coupling, while the solid blue lines represent the coupling of SPM domains is a superferromagnetic (SFM) exchange. The applied magnetic field aligns all the SPM domains along the direction of the external field. When the Zeeman energy of AFM spins ($J_{ZE}$, which is proportional to the magnitude of the magnetic field) near the interface is larger than the coupling energy of SPM-AFM at the interface ($J_{int}$, constant) and their anisotropy energy (constant), the applied field will align these AFM spins along the direction of the external field [128]. Therefore, the SPM domains will grow in size. However, the enlarged SPM domains are at metastable state and the coupling interface of SPM-AFM remains unchanged at this stage [see the dashed white circles in Figure 4-33]. After removal of the external magnetic field, they will shrink and return to their initial sizes due to the AFM anisotropy energy.
Figure 4-33. Simplified schematic diagrams of the evolution of the SPM domains embedded in an AFM single domain (AFM anisotropy axis is parallel to the direction of the applied magnetic field) under the external magnetic field at temperature below $T_B$.

The growth of SPM domain size will decrease the inter-domain distance, thus increases the interaction between SPM domains. This is similar to the process of increasing the concentration of SPM nanoparticles in the conventional SSG systems [126]. When the interaction between SPM domains reaches the critical value, the coupling of SPM domains will become superferromagnetic (SFM) exchange through tunnelling superexchange [126]. The difference between SFM and conventional FM is that the atomic spins in the conventional FM are replaced by the superspins of SPM.
domains. The formation of SFM exchange may change the internal interaction of each enlarged SPM domain (metastable at SSG state) such that they become stable as shown in Figure 4-33. [While in the case of SPM nanoparticles embedded in AFM matrix with a chemical interface (different materials) [112], the SPM nanoparticles cannot grow to form larger stable particles at the expense of AFM matrix]. As a result, a new stable SFM-AFM interface with unidirectional moment of SFM is formed and will pin the SFM superspins below $T_B$, which is similar to an FM-AFM interface with unidirectional FM spins formed after FC in the CEB systems. The difference is that in the present case the SFM-AFM interface is induced isothermally by the external magnetic field. While in the CEB systems it is usually reconfigured under FC. According to this model, the moment of SPM domains increases with increasing size under the external magnetic field. We have only considered AFM domains with anisotropy axis parallel to the external magnetic field in this model. For AFM domains with anisotropy axis non-parallel to the external magnetic field, there is an angle between the direction of the initial magnetization field and the anisotropy axis. This configuration can still result in EB effect, which is similar to the EB effect in the CEB systems with different angles between the direction of the cooling field and the AFM anisotropy axis [129]. Based on the above analyses, we believe that a SFM
unidirectional anisotropy, which is similar to an FM unidirectional anisotropy, can be formed during the initial magnetization process in the present alloys.

Figure 4-34 &35 (a) shows $H_{EB}$ and $H_c$ as a function of $|H_{m_{\text{max}}}^{\text{max}}|$ in NiMnIn13 and NiMnSn10, respectively. There is a critical $|H_{m_{\text{max}}}^{\text{max}}|$ ($H^\text{crit}$, 30 kOe in NiMnIn13 and 35 kOe in NiMnSn10), at which $H_{EB}$ reaches the maximum value and $H_R$ remains almost constant at higher $|H_{m_{\text{max}}}^{\text{max}}|$ [Figure 4-34 &35 (b)]. The maximum $H_{EB}$ means the formation of the maximum FM unidirectional anisotropy [111]. Thus, the meaning of $H^\text{crit}$ is that at which SSG state completely transforms to SFM state, producing maximum SFM unidirectional anisotropy. The decrease of the $H_{EB}$ at higher $|H_{m_{\text{max}}}^{\text{max}}|$ is only due to the decrease of the $H_L$, which may originate from the change of bulk AFM spin structure under large applied magnetic field. The bulk AFM spin structure has been shown to play a crucial role on EB effect in thin film system [130].
Figure 4-34. (a) $H_{EB}$ (left panel) and $H_c$ (right panel) as a function of $|H_{m}^{\text{max}}|$ in NiMnIn13 at 10 K after ZFC. (b) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_{m}^{\text{max}}|$. Inset shows the definition of $H_L$ and $H_R$ in a $M(H)$ loop. The dot line shows the position of $H^{\text{crit}} = 30$ kOe.
Figure 4-35. (a) $H_{EB}$ (left panel) and $H_c$ (right panel) as a function of $|H_m^{max}|$ in NiMnSn10 at 10 K after ZFC. (b) The left ($H_L$) and right ($H_R$) coercive fields as a function of $|H_m^{max}|$. The dot line shows the position of $H^{crit} = 35$ kOe.

When $|H_m^{max}| < H^{crit}$, only part of the SSG state transforms to the SFM state during the initial magnetization process. For SSG state, there is a remnant magnetization and $H_c$ in $M(H)$ loops due to irreversible switching of a collective state [127]. The $H_c$ (both $H_L$ and $H_R$) increases with increasing $|H_m^{max}|$ (a series of minor
hysteresis loops). However, the number of SPM domains at SSG state will decrease
with increasing $|H_{m}^{\text{max}}|$ due to more SSG state transforming to SFM state, which
generates more new interfaces with SFM unidirectional anisotropy. Thus, the $H_{EB}$
increases with increasing $|H_{m}^{\text{max}}|$ at this stage, leading to the increase of coercive field
in one direction ($H_L$) and the decrease in the other ($H_R$). The final coercive fields are
attributed to a combined effect of SPM domains in SSG and SFM states. Due to the
opposite $|H_{m}^{\text{max}}|$ dependence for these two effects, the $H_R$ reaches maximum at a field
smaller than $H_{c}^{\text{crit}}$. For $H_L$, both effects have the same $|H_{m}^{\text{max}}|$ dependences, resulting in
a continuous increase of $H_L$ with $|H_{m}^{\text{max}}|$. As a result, the field, at which $H_c$ reaches
maximum, is smaller than the $H_{EB}^{\text{crit}}$ of $H_{EB}$. Further supports to the model shown in
Figure 4-33 are provided in the Chapter 5 including the anomalous remanent
magnetization dependence of EB effect, the isothermal tuning of EB after ZFC from
an unmagnetized state, and the strong cooling field dependence of CEB effect in
NiMnIn$_{13}$.

Finally, we have further verified the model by changing the size of the initial
domains, which is crucial to the formation of the SFM unidirectional anisotropy. If
the size of the initial domains is larger than the critical value, SFM or FM domains
will form and no EB effect will appear after ZFC [70]. Figure 4-36 and 37 (a) show
the $M(H)$ curves of NiMnIn$_x$ ($x = 11, 12, 13, 14,$ and $15$) and NiMnSn$_y$ ($y = 8, 9, 10,$
alloys at 10 K. The saturation magnetization of NiMnX (X = In, Sn) increases with increasing X content [Fig 4-36 & 37 (b)], which is consistent with the previous results [11, 73]. The $T_c$s of these alloys are lower than 300 K and the $T_N$ decreases continuously with increasing In content. The saturation magnetization of NiMnX at 10 K is very small compared with that of the stoichiometric compound Ni$_{50}$Mn$_{25}$X$_{25}$ (Ni$_{50}$Mn$_{25}$In$_{25}$~80 emu/g, Ni$_{50}$Mn$_{25}$Sn$_{25}$~73 emu/g, pure FM state at low temperatures) [11, 73]. The decrease of saturation magnetization in the off-stoichiometric alloys is due to the excess of Mn atoms occupying a number of In sites, which produces AFM coupling [11, 73]. Take NiMnIn$_x$ alloys as an example, the SFM (may include some SPM or FM domains) volume fraction increases from ~1 % in NiMnIn11 to ~ 35 % in NiMnIn15 at 10 K [Figure 4-36 (b)]. Thus, the average domain size in $x = 14$ alloy is larger than that of NiMnIn13 at the initial state. The larger size of SPM domain makes the $H^\text{crit} = 15$ kOe, at which all of the SSG state transforms to SFM state, being smaller than that of NiMnIn13 [Figure 4-36 (c)]. Furthermore, the SFM volume fraction in $x = 14$ alloy is about 22 % (the total volume fraction of SPM/SFM in the initial state is less than this value), which is close to the threshold concentration for percolation in three dimensional system ($\sim 16 %$) [131]. The SFM domains no longer separate from each other in AFM matrix at larger volume fraction resulting in the formation of FM domains at $x > 14$. For $x = 15$ alloy, there is no SPM domains at the
initial state and the $M(H)$ loops after ZFC shows double-shifted behavior with no EB effect, which is similar to the results of NiMnIn16 [70]. For $x = 11$ and 12, the continuous increase of $H_{EB}$ with $|H_{m}^{\text{max}}|$ up to 80 kOe is due to the smaller size of SPM domain, which is similar to results of NiMnIn13 for $|H_{m}^{\text{max}}| < H^{\text{crit}}$. Large $H_{c}$ has also been observed for $x = 11$ and 12 and the $H_{c}$ of NiMnIn12 shows tendency to maximum value at higher $|H_{m}^{\text{max}}|$ prior to the maximum of $H_{EB}$ [Figure 4-36 (d)]. All of these results are consistent to the discussions in NiMnIn13 within the model as shown in Figure 4-33. All the above discussions are suitable for NiMnSn$_y$ alloys as well with different critical values.
Figure 4-36. (a) Field dependence of magnetization of NiMnIn$_x$ ($x = 11, 12, 13, 14,$ and 15) at 10 K. (b) Saturation magnetization ($M_{\text{sat}}$) (filled squares) and SFM volume fraction (open squares) as a function of In content at 10 K. (c) and (d) $|H_{m_{\text{max}}}|$ dependence of $H_{EB}$ and $H_c$ at 10 K for $x = 11, 12$ (right panel), and 14, 15 (left panel).
Figure 4-37. (a) Field dependence of magnetization of NiMnSn\(_x\) at 10 K. (b) Saturation magnetization \((M_{\text{sat}})\) (filled squares) and SFM volume fraction (open squares) as a function of In content at 10 K. (c) and (d) \(|H_{\text{m}}^{\text{max}}|\) dependence of \(H_{\text{EB}}\) and \(H_c\) at 10 K for \(x = 8, 9\) (right panel), and 11, 12 (left panel).

In order to be understood well, the same simple cartoon has been used to describe the spin configurations of the Figure 4-33. There are two assumptions: (1) FM domains grow in size at the expense of AFM domain during the initial magnetization process and the enlarged FM domains (both size and direction) can be preserved after removal of the field. Namely, the FM-AFM interface can be changed
isothermally; (2) For the subsequently applying field even with the opposite direction, the newly formed FM-AFM interface remains unchanged. Let us see what will happen for hysteresis loop measurements in this case. The initial state after ZFC from an unmagnetized state is the same as Figure 2-17 [Figure 4-38]. When a positive field is applied (initial magnetization process), the FM spins with left direction start to rotate. The AFM spins near the interface will rotate following FM rotation due to the FM interaction between FM and AFM at the interface [114, 115]. If the part of AFM domain with rotated spins become a new part of FM domain and the AFM spins at the new interface is the same as FM spins (Assumption 1), there is no microscopic torque exert on the rotated FM spins (domain on the right side) at this stage [Figure 4-38(2)], which is different from the case in the CEB system [Figure 2-17(2)]. When the field is reversed, the FM spins (both left and right domains) start to rotate. If the newly formed FM-AFM interface remains unchanged at this stage (Assumption 2), the AFM spins at the interface exert a microscopic torque to the rotated FM spins to keep them in their original position [Figure 4-33(4)]. The FM spins in this case have only one stable configuration, which is similar to the case in the CEB systems after FC [111]. That is, if these two assumptions are satisfied, the FM unidirectional anisotropy can be formed isothermally after ZFC from an unmagnetized state.
Figure 4-38. Hysteresis loop in the case with a variable interface after ZFC from an unmagnetized state (right) and schematic diagram of the spin configuration at different stages (left).

4.4 Summary

We have observed a large EB effect after ZFC from an unmagnetized state in NiMnX (X = In, Sn) bulk alloys, exhibiting the same relationship of the temperature dependence of $H_{EB}$ and $H_c$, and the training effect as in the CEB systems observed after FC. Such phenomenon is attributed to a SFM unidirectional anisotropy formed during the initial magnetization process. These results will open a new direction to realize EB effect.
Chapter 5 Giant tunable EB effect in Ni$_{50}$Mn$_{37}$In$_{13}$

5.1 Background

In the previous CEB systems, the value of $H_{\text{EB}}$ obtained after FC can be tuned by the magnitude of cooling field ($H^{\text{FC}}$) [132, 133]. In a lower $H^{\text{FC}}$ range, the $H_{\text{EB}}$ increases with increasing of $H^{\text{FC}}$ due to the saturation of the FM layer magnetization [132]. In a higher $H^{\text{FC}}$ range far above $H_c$, if the coupling at the FM/AF interface is FM, $H_{\text{EB}}$ is not further affected by $H^{\text{FC}}$ [132]. However, if the coupling at the interface is AF, $H_{\text{EB}}$ is tuned in a large field range and even changes its sign under lager $H^{\text{FC}}$, which is ascribed to the competition between the exchange energy and the Zeeman energy [113, 133]. The bulk AFM spin structure has also been shown to play a crucial role on EB effect [130]. Moreover, the value of $H_{\text{EB}}$ can also be tuned by the $H^{\text{FC}}$ through changing the thickness of FM layer in a spontaneous lamellar FM/AFM phase separated material [134].

On the other hand, Miltényi et al. [122] reported that the EB effect can be well tuned by cooling in zero field from different remanent magnetization (RM) states in the CEB systems. The $H_{\text{EB}}$ increases with increasing RM and the sign of $H_{\text{EB}}$ changes when changing the sign of RM. This allows one to select the desired value of $H_{\text{EB}}$.
through a simple cooling procedure after device preparation, which shows a very technological importance.

\( \text{Ni}_{50}\text{Mn}_{37}\text{In}_{13} \) (NiMnIn13) has the maximum EB effect in NiMnIn system, so we chose it for the further investigations on EB tunable effect, including an anomalous remanent magnetization dependence of EB effect, the isothermal tuning of EB after ZFC from an unmagnetized state, and the strong cooling field dependence of CEB effect. These results can be explained well by isothermal field-induced transition from SSG to SFM state as shown in Figure 4-33 in the Chapter 4.

5.2 Results and discussion

5.2.1 Anomalous remanent magnetization dependence of EB effect

To obtain the different magnetization states in NiMnIn13, we applied different positive fields on sample at 35 K (above \( T_B = 30 \) K) and removed them as shown in Figure 5-1 (a). The result shows that this procedure can establishes different RMs by applying different fields. Then, the sample was zero-field cooled to 10 K. After that, the P and N types \( M(H) \) loops were measured, respectively. During the ZFC from 35 K to 10 K, the RM reduces a little. Figure 5-1 (b) shows the RMs at 10 K as a function of applied field at 35 K. The RM at 10 K can be changed continuously by applying different fields at 35 K. The P and N type \( M(H) \) loops were measured with
$|H_m^{\text{max}}| = 40 \text{ kOe}$ for each RM state, respectively. The equal magnetization values in the highest positive and negative magnetic fields indicate the shifted loop is not a nonsymmetrical minor hysteresis loop. It is worth noting that the P and N types $M(H)$ loops shift to the opposite field direction at small RM state [+0.37 emu/g, Figure 5-2 (c)], while shift to the same field direction at large RM state [+1.59 emu/g, Figure 5-2 (d)]. There is a difference between the first cycle of P and N types $M(H)$ loops for larger RM state [Figure 5-2 (d)]. The second cycle of P type $M(H)$ loop is the same as the first cycle of N type $M(H)$ loop. These results may be due to the large training effect in NiMnIn$_{13}$. The first cycle of N type $M(H)$ loop, the direction of the initial magnetization field direction is opposite to the RM direction, is actually obtained after once magnetization reversal. Namely, it should be regarded as a second cycle hysteresis loop.
Figure 5-1. (a) Isothermal magnetic-field dependence of magnetization for different applied fields at 35 K. The inset: a larger scale at low. (b) The RM at 10 K as a function of applied field at 35 K.
Figure 5-2. P and N types $M(H)$ loops ($|H_{m}^{\text{max}}| = 40 \text{ kOe}$) at 10 K measured after cooling in zero field from 35 K with different RM states, (a) RM = + 0.37 emu/g, (b) RM = + 1.59 emu/g. (c) and (d) are the larger scale at low field in (a) and (b), respectively. The magenta solid line in (d) shows the second cycle of P type $M(H)$ loop.

Figure 5-3 shows the RM dependence of $H_{EB}$ at 10 K obtained from first and second cycles of P and N types $M(H)$ loops. The large difference between two cycles of P or N types $M(H)$ loops is due to the large training effect in the system. For N type, not only the value of $H_{EB}$ but also its sign can be tuned by changing the value of RM. For P type, only the value of $H_{EB}$ decreases with increasing RM at the first cycle and...
it is almost a constant at the second cycle. These results are different from the RM dependence of EB effect in the previous CEB systems: the $H_{\text{EB}}$ decreases monotonically with decreasing RM and changes its sign when the sign of RM is changed [122]. Note that there is a large EB effect at zero RM state, which is attributed to the field-induced transition from SSG to SFM states in the Chapter 4.

![Graph of $H_{\text{EB}}$ vs. $M^{\text{rem}}$](image)

Figure 5-3. RM dependence of $H_{\text{EB}}$ at 10 K obtained from first and second cycles of P and N types $M(H)$ loops.

Here, we use the model shown in Figure 4-33 in the Chapter 4 to explain the anomalous RM dependence of EB effect in NiMnIn13 (Figure 5-4). Note that the
diagram of Figure 5-4 only shows the change of SFM volume fraction and magnetization direction at different stages, which is different from the diagram of Figure 4-33 in the Chapter 4 showing the process of isothermal field-induced SSG to SFM transition. The initial magnetic state is SSG state at 35 K after ZFC, which is similar to that at 10K. When a large field $+H_2 > +H_{35K}^{\text{crit}}$ ($H_{35K}^{\text{crit}}$ is a critical field at which SSG state just completely transforms to SFM state at 35 K, which is different from the critical field at 10 K) is applied, all of the SSG state will transform to SFM state. After removal of field, there is a large RM of SFM. This RM persists to lower temperature after ZFC. The white arrows in Figure 5-4 show the net RM parallel to the direction of field at 10K. The non-zero net positive RM is pinned by the around AFM matrix below $T_B$ (= 30 K), which will produce negative EB effect and the EB effect is independent of the direction of the initial magnetization field. This is similar to that observed in the previous CEB systems [122].

When a small field $+H_1 < +H_{35K}^{\text{crit}}$ is applied at 35 K, only part of the SSG state can transform to the SFM state, resulting in a small positive RM of SFM. The mixed SSG and SFM states persist to 10 K after ZFC from 35 K. Note that the larger magnetic field can still transform the remanent SSG to SFM states at 10 K and the induced SFM magnetization direction is determined by the direction of the initial magnetization field. For P type measurement with the positive initial magnetization
field \([+H_3 (+40 \text{ kOe}) > +H_{\text{crit}} (30 \text{ kOe})]\), the SSG state transforms to SFM state with positive RM. That is, the net RM direction is always along the positive field direction for P type \(M(H)\) loops regardless of the initial state (pure SFM or mixed SSG and SFM states). The positive RM will produce negative EB, which is consistent with the experiment results [Figure 5-2 (c)]. While for N type measurement with the negative initial magnetization field \([-H_3| (-40 \text{ kOe}) > +H_{\text{crit}}]\), the remanent SSG state transforms to SFM state with negative RM. Therefore, the net RM along the field direction is dependent on the values of the positive RM of the initial SFM state and negative RM of newly induced SFM state. The magnetometry measures the average coupling over the whole interface area in the sample. The different values of net positive or negative RM at 10 K can be obtained from N type \(M(H)\) loops through applying different magnetic fields at 35 K, which will produce negative or positive EB effect with different value of \(H_{EB}\). In a word, the magnitude of \(H_{EB}\) and its sign can be tuned effectively by the value of RM in the initial state.
Figure 5-4. Schematic diagrams of SSG and SFM states embedded in an AFM matrix at different stages. The white arrows represent the direction of net RM at SFM state parallel to the direction of magnetic field. This diagram only shows the change of SFM volume fraction and magnetization direction at different stages, which is different from the diagram of Figure 4-33 showing the process of isothermal field-induce SSG to SFM transition.

5.2.2 Isothermal tuning of EB after ZFC from an unmagnetized state

Based on the results shown in Figure 5-4, the similar results should be obtained isothermally if the initial state is at 10 K after ZFC from an unmagnetized state. In order to check this point, we applied different positive fields \( H_{\text{applied}} \) and removed them at 10 K after ZFC from an unmagnetized state, then measured the P and N types
$M(H)$ loops with $|H_{m}^{\text{max}}| = 40$ kOe, respectively. As shown in Figure 5-5, the P and N types $M(H)$ loops shift to the opposite direction at small applied field (+10 kOe), while shift to the same direction at larger applied field (+40 kOe). Figure 5-6 shows the $H_{\text{applied}}$ dependence of $H_{\text{EB}}$ at 10 K obtained from P and N types $M(H)$ loops. For N type, not only the value of $H_{\text{EB}}$ but also its sign can be tuned by changing the magnitude of the applied field. While for P type, only the value of $H_{\text{EB}}$ decreases with increasing $H_{\text{applied}}$. These results are similar to the anomalous RM dependence of EB effect, which can be explained within the Figure 5-4. The isothermal tuning of EB after ZFC from an unmagnetized state in the present case is strongly dependent on the direction of the initial magnetization field, which cannot be expected in the previous CEB system with the similar isothermal tuning effect [135, 136].
Figure 5-5. P and N types $M(H)$ loops ($|H_{m_{\text{max}}}^{\text{max}}| = 40 \text{kOe}$) at 10 K measured after different positive fields were applied and removed isothermally (a) $H_{\text{applied}}^{\text{applied}} = + 10 \text{kOe}$, (b) $H_{\text{applied}}^{\text{applied}} = + 40 \text{kOe}$. (c) and (d) are the larger scale at low field in (a) and (b), respectively. The magenta solid line in (d) shows the second cycle of P type $M(H)$ loop.

According to the field-induced transition from SSG to SFM state as shown in Figure 4-33 in the Chapter 4, the different positive applied fields produce the different volume fractions of SFM state with positive direction unidirectional anisotropy. After
that, for the P type $M(H)$ measurement, the positive initial magnetization field $[+40 \text{kOe} > H^{\text{crit}} (30 \text{kOe})$, SSG state will completely transform to SFM state] will transform remanent SSG state to SFM with positive direction unidirectional anisotropy. So the EB is always negative EB for P type measurement. While for N type $M(H)$ measurement, the negative initial magnetization field ($-40 \text{kOe} > H^{\text{crit}}$) will transform remanent SSG state to SFM with negative direction unidirectional anisotropy. The direction of net unidirectional anisotropy is dependent on the magnitude of $H^{\text{applied}}$ before $M(H)$ measurement. That is why the $H_{EB}$ (both value and sign) from N type $M(H)$ is strongly dependent on the magnitude of the positive $H^{\text{applied}}$.

In order to further confirm isothermal field-induced transition from SSG to SFM state, we measured $M(H)$ loops with smaller $|H_m^{\text{max}}| = 10 \text{kOe}$ after isothermally applying different fields at 10 K. The 10 kOe can only transform little SSG to SFM state at 10 K. So we use 10 kOe measurement field to check the magnetic state changed or not after applying different fields. The sample was first zero-field cooled from 300 to 10 K. Then different positive fields were applied and reduced to $+10 \text{kOe}$. After that, $M(H)$ loops were measured following $+10 \text{kOe} \rightarrow 0 \rightarrow -10 \text{kOe} \rightarrow 0 \rightarrow +10 \text{kOe}$ (1ˢᵗ cycle). Other than the phenomenon of EB effect, the shape of $M(H)$ loop was also changed by applying different fields isothermally (Figure 5-7). For $H^{\text{applied}} \geq$
30 kOe, there is an FM-type $M(H)$ loop, which is consistent with the result in the main text that $H^{\text{crit}} = 30$ kOe at 10 K. The difference of magnetization between two cycles, only observed at $+10$ kOe $\rightarrow 0 \rightarrow -10$ kOe branch, may originate from the change of AFM bulk spin structure by larger field and the changed AFM bulk spin structure can recover after field reversal.

![Graph showing $H_{EB}$ dependence on $H_{applied}$ at 10 K.](image)

**Figure 5-6.** $H_{applied}$ dependence of $H_{EB}$ at 10 K obtained from P and N types $M(H)$ loops.
5.2.3 Strong cooling field dependence of the CEB effect in NiMnIn13

We measured the $M(H)$ loops ($|H_{m}^{\text{max}}| = 20$ kOe) at 10 K after FC from 300 K under different $H^{\text{FC}}$s [Figure 5-9 (a)]. The sample was first cooled with $+H$ from 300 to 10 K, then the magnetic field was reduced/increased to $+20$ kOe at 10 K isothermally, after that a closed $M(H)$ loop was measured following $+20$ kOe $\rightarrow$ 0 $\rightarrow$
-20 kOe → 0 → +20 kOe (1st cycle). Figure 5-8 (a) shows the 1st and 2nd cycles $M(H)$ loops measured at 10 K after FC ($H_{FC} = +60$ kOe) from 300 K. $M_{ini}$ is the magnetization under +20 kOe after reducing from +60 kOe. $M_P$ and $M_N$ are the magnetizations under +20 kOe and −20 kOe in the second cycle, respectively. Figure 5-8 (b) shows the $M_{ini}$, $M_P$, and $|M_N|$ as a function of $H_{FC}$ at 10 K. From these curves we can make the following observation: (1) A difference between $M_{ini}$ and $M_P$ at $H_{FC} > 10$ kOe, which is related to the change of AFM bulk spin structure by cooling field, (2) The $M_P (=|M_N|)$ increases with the increasing of $H_{FC}$ up to 40 kOe, then decreases slowly at larger $H_{FC}$. The $H_{EB}$ increases steeply with increasing $H_{FC}$ up to a maximum at $H_{FC} = 1$ kOe, then decreases with increasing $H_{FC}$, which is different from that in the CEB systems [Figure 5-10 (a)] [132]. The $H_{EB}$ can be changed hugely from 1658 Oe for $H_{FC} = 1$ kOe to 288 Oe for $H_{FC} = 80$ kOe. The difference of $H_{EB}$ between two cycles shows the training effect of CEB in NiMnIn13.
Figure 5-8. (a) 1st and 2nd cycles $M(H)$ loops ($|H_m^{\text{max}}| = 20 \text{ kOe}$) measured at 10 K after FC ($H^\text{FC} = +60 \text{ kOe}$) from 300 K. The sample is first cooled with +60 kOe from 300 K to 10 K, then the magnetic field is reduced to +20 kOe at 10 K isothermally, after that a closed $M(H)$ curve is measured following +20 kOe → 0 → -20 kOe → 0 → +20 kOe (1st cycle). (b) $M^{\text{ini}}$, $M^p$ and $|M^N|$ as a function of $H^\text{FC}$ at 10 K.
Figure 5-9. (a) $M(H)$ loops ($1^{\text{st}}$ cycles, $|H_m^{\text{max}}| = 20 \text{ kOe}$) measured at 10 K after FC from 300 K under different $H^{\text{FC}}$s. The sample is first cooled with $+H$ from 300 K to 10 K, then the magnetic field is reduced/increased to $+20$ kOe at 10 K isothermally, after that a closed $M(H)$ curve is measured following $+20 \text{ kOe} \rightarrow 0 \rightarrow -20 \text{ kOe} \rightarrow 0 \rightarrow +20 \text{ kOe}$ ($1^{\text{st}}$ cycle). (b) $H_{EB}$ as a function of $H^{\text{FC}}$ for $1^{\text{st}}$ and $2^{\text{nd}}$ cycles. The inset gives a larger scale at smaller cooling fields.
Considering the large $H^{\text{FC}}$ dependence of $M^p (= |M^N|)$ at $H^{\text{FC}} < 40$ kOe, the decrease of $H_{EB}$ with the increasing of $H^{\text{FC}}$ at this range may partially come from the increase of FM phase volume fraction by cooling field [134]. This result can be obtained from model shown in Figure 4-33 in the Chapter 4. The SPM/FM domain size increases with increasing applied field. If the sample is cooled down under different fields from higher temperature, the SPM/FM domain size is dependent on the magnitude of the applied field. After further cooling, the increase of interaction among domains transforms SSG to SFM state. That is, the saturation of SFM (volume fraction) is strongly dependent on the cooling field. However, the linear relationship of $H_{EB}$ as a function of $1/M^p$ is only satisfied at $1 \text{kOe} < H^{\text{FC}} < 10 \text{kOe}$ range [Figure 5-10 (b)].

The cooling field dependence of $H_{EB}$ in the present case can be divided four zones [Figure 5-10 (c)]: (1) $0 < H^{\text{FC}} < 1 \text{kOe}$, the $H_{EB}$ increases with increasing of $H^{\text{FC}}$ due to the saturation of the FM layer magnetization [132], (2) $1 \text{kOe} < H^{\text{FC}} < 10 \text{kOe}$, the $H_{EB}$ decreases with increasing of $H^{\text{FC}}$ due to the increasing of FM volume fraction [134], (3) $10 \text{kOe} < H^{\text{FC}} < 40 \text{kOe}$, the $H_{EB}$ decreases with increasing of $H^{\text{FC}}$ due to the increasing of FM volume fraction and the change of AFM bulk spin structure, (4) $40 \text{kOe} < H^{\text{FC}} < 80 \text{kOe}$, the $H_{EB}$ decreases with increasing of $H^{\text{FC}}$ due to the change
of AFM bulk spin structure [130]. The $H_{EB}$ obtained after ZFC decreases with increasing $|H_m^{\text{max}}|$ at large field ($|H_m^{\text{max}}| > 30$ kOe) may come from the same reason.

![Figure 5-10.](image)

Figure 5-10. (a) Compare $H_{EB}$ as a function of $H^{FC}$ with that in Ref. [132]. (b) Compare $H_{EB}$ as a function of $1/M^p$ with that in Ref. [134]. (c) The cooling field dependence of $H_{EB}$ in the present case can be divided four zones.

### 5.3 Summary

In summary, we observed an anomalous RM dependence of EB effect in NiMnIn13. Both the value of exchange bias field and its sign can be tuned by the
amplitude of RM without changing its sign. This tunability is strongly dependent on
the direction of the initial magnetization field for the hysteresis loop measurements.
The RM at 10 K in the initial state not only reflects the magnetization state of the
sample, but also reflects the ratio of SSG to SFM state transition at 35 K. Furthermore,
the EB effect after ZFC from an unmagnetized state can be tuned isothermally. The
isothermal tuning of EB is also strongly dependent on the direction of the initial
magnetization field. The strong cooling field dependence of $H_{EB}$ in NiMnIn 13 can be
divided four zones: (1) $0 < H^{FC} < 1$ kOe, the $H_{EB}$ increases with increasing of $H^{FC}$ due
to the saturation of the FM layer magnetization, (2) $1$ kOe $< H^{FC} < 10$ kOe, the $H_{EB}$
decreases with increasing of $H^{FC}$ due to the increasing of FM volume fraction, (3) $10$
kOe $< H^{FC} < 40$ kOe, the $H_{EB}$ decreases with increasing of $H^{FC}$ due to the increasing
of FM volume fraction and the change of AFM bulk spin structure, (4) $40$ kOe $< H^{FC}$
$< 80$ kOe, the $H_{EB}$ decreases with increasing of $H^{FC}$ due to the change of AFM bulk
spin structure. The $H_{EB}$ obtained after ZFC decreases with increasing $|H_{m}^{max}|$ at large
field ($|H_{m}^{max}| > 30$ kOe) may come from the same reason. All these results can be
explained well by field-induced transition from SSG to SFM state as shown in Figure
4-33 in Chapter 4.
Chapter 6 Magnetoresistance effect in NiMnIn16

6.1 Background

Giant magnetoresistance (GMR) effect first discovered in magnetic multilayers attributed to the spin-dependent scattering of conduction electrons [85, 86], is a significant property for use in magnetoresistive read-head technology. So it has attracted much interest in recent years. In addition to the magnetic multilayers, GMR also occurs in some bulk intermetallic materials, such as SmMn$_2$Ge$_2$ [88], FeRh [89], Gd$_5$Si$_{1.8}$Ge$_{2.2}$ [90], and MnAs [91], in which the GMR effect occurs at a magnetic-field-induced first-order phase transition from antiferromagnetic (AFM) to ferromagnetic (FM) states. Moreover, the behavior of MR is also a very important parameter for magnetic sensor technology [137]. Recently, a negative-positive-negative switching behavior of MR with temperature has been reported in FM shape memory alloy Ni$_{1.75}$Mn$_{1.25}$Ga due to $s$-$d$ scattering in the FM austenite and competing of spin fluctuations of partial AFM and decreasing of electron scattering at twin and domain boundaries with the application of external magnetic field in the ferrimagnetic martensite [138].
Very recently, a large MR effect associated with the magnetic-field-induced metamagnetic RMT from AFM martensite to FM austenite in MSMAs has been reported extensively [17-21]. Additionally, a large inverse magnetocaloric effect around this magnetostructural transition was also observed [32, 33, 39]. Furthermore, the initial magnetic state of MSMAs in the regime across the first-order magnetic transition depends on the thermomagnetic history of the sample [139].

In this Chapter, we perform detailed studies of MR behavior of MSMA Ni$_{49.5}$Mn$_{34.5}$In$_{16}$, which shows large MR effect in NiMnIn system. It is found that the MR behavior shows strong thermal-history dependence in the transformation regime across the first-order magnetic transition. This phenomenon can be interpreted by phase coexistence, strain-induced thermal-history-dependent (THD) energy diagram and the competition of unstable and THD metastable phases. Our results not only indicate possibility of practical applications for MSMAs as magnetic sensor, whose response behavior can be tuned by changing the thermal history of the devices, but also provide fundamental insight of the phase coexistence and metastability scenario.

6.2 Results and analysis

Figure 6-1(a) shows the temperature dependence of the resistivity $\rho(T)$ in Ni$_{49.5}$Mn$_{34.5}$In$_{16}$ measured at $H = 0$ and 60 kOe for both heating and cooling cycles,
respectively. The heating and cooling cycles are indicated by the arrows. The superscripts 0 and 60 with $M_s$ (martensite start temperature), $M_f$ (martensite finish temperature), $A_s$ (austenite start temperature), $A_f$ (austenite finish temperature) denote these temperatures determined from zero and 60 kOe field $\rho(T)$ curves, respectively. The thermal hysteresis around the first-order martensitic transformation (MT) is observed in cycles measured at both zero and 60 kOe field. At zero field, with decreasing temperature the $\rho$ shows a decrease at ~310 K, which corresponds to the onset of the FM state in the austenite [70]. The $\rho$ shows an abrupt jump at 267 K, which corresponds to the MT from the FM austenite to AFM martensite. As a result, superzone boundary gaps are formed in the sample, which alters the density of the electronic states near the Fermi surface [140]. The MT and reverse MT (RMT) start and finish temperatures are determined by the end points of the thermal hysteresis observed [Figure 6-1(a)] [141]. When a field of 60 kOe is applied, all of the characteristic temperatures shift to lower temperatures, indicating that external magnetic field can destroy low magnetization AFM martensite phase and stabilize high magnetization FM austenite phase, namely, magnetic field can induce metamagnetic RMT [10]. The shift of $M_s$ for 60 kOe field is about 25 K, which produces large negative MR in the sample. In addition, the $\rho$ around the Curie temperature is reduced by application of magnetic field due to the reduced spin
scattering by the magnetic-field-induced alignment of the local spins, which is similar to the case of manganites [142, 143]. Figure 6-1(b) shows the MR \([\rho(H)-\rho(0)]/\rho(0)\) at \(H = 60\) kOe versus temperature for both heating and cooling cycles. The maximum MR is about -57\% at 264 K on the heating cycle, while on the cooling cycle it is found to be about -62\% at 243 K. The difference of MR in the heating and cooling cycles is likely due to the different fractions of coexistent austenite and martensite phases during the MT and RMT (see next discussion).

Figure 6-1. (a) Resistivity as a function of temperature \(\rho(T)\) for both cooling and heating cycles (indicated by arrows) at zero and 60 kOe field for Ni_{49.5}Mn_{34.5}In_{16}. (b) MR as a function of temperature for cooling and heating cycles for 60 kOe field \([\rho(60)-\rho(0)]/\rho(0)\).
The isothermal ρ(H) curves were measured at several temperatures within the transformation regime reached under the following two protocols (P1 and P2). In P1, the sample is first zero field cooled to 100 K from 350 K to ensure a complete martensite state and then zero field heated to test temperatures; in P2, test temperatures are reached directly by zero field cooling the sample from 350 K. Figure 6-2(a) shows the results of normalized isothermal resistivity versus magnetic field \[\rho(H)/\rho_1(0), \rho_1(0)\text{ is zero-field }\rho\text{ of sequence 1 at the first cycle}\] measured at several temperatures within the RMT regime reached under P1. The sequences of measurement are shown on the curve of temperature at 265 K: first cycle [1 (0 to 60 kOe) → 2 (60 kOe to 0)] → second cycle [3 (0 to -60 kOe) → 4 (-60 kOe to 0)]. The \(\rho\) decreases gradually with increasing magnetic field and the MR reaches saturation at 60 kOe field for \(T \geq 270K\). At the first cycle, with decreasing field the \(\rho\) cannot return back to its initial value even when the magnetic field is reduced to zero. Therefore, the zero-field \(\rho\) before and after the application of the magnetic field shows a large irreversibility and the irreversible ratio \([\rho_1(0)-\rho_2(0)]/\rho_1(0)-\rho_1(60\text{kOe}]\) increases with temperature [Figure 6-2(b)]. But at the second cycle envelope curves are obtained at all test temperatures. It is interesting to note that the sample almost retains its low \(\rho\) when the magnetic field is removed and persists for the second cycle at 275 K. A clear hysteresis observed during the increase and decrease of the magnetic field at a
fixed temperature indicates the first-order nature of this magnetic-field-induced phase transition. The MRs of 60 kOe for the first \[
\frac{\rho_1(0) - \rho_1(60\text{kOe})}{\rho_1(0)}\] and second cycles \[
\frac{\rho_3(0) - \rho_3(60\text{kOe})}{\rho_3(0)}\] are shown in Figure 6-2(b), respectively. The MR increases first and reaches a maximum at 265 K, then decreases gradually with further increasing temperature at the first cycle; while it decreases sharply at T > 265 K at the second cycle. Moreover, the MR of the second cycle is much smaller than that of the first cycle. Figure 6-3(a) shows \(\rho(H)\) measured at several temperatures within MT regime reached under P2. The behavior of the \(\rho(H)\) is quite different from those measured at temperatures reached under P1, even at the same temperatures. An obvious positive MR is observed at low field in some higher temperature curves and a negative MR appears at higher magnetic field in all the curves. Figure 6-3(b) shows the MRs of 60 kOe for the first and second cycles, respectively. At the first cycle, the MR first increases with increasing temperature, reaching a maximum at 260 K, then decreases with further increasing temperature. But the MR shows monotonous decrease with increasing temperature at the second cycle. An unusual observation is that the appearance of what we refer to as “overshooting”: As the H is removed, the \(\rho\) is larger than its original value. Both the overshooting ratios for the first cycle \[
\frac{R_2(0) - R_1(0)}{R_1(0)}\] and the second cycle \[
\frac{R_4(0) - R_3(0)}{R_3(0)}\] increase with temperature.
[Figure 6-3(c)]. This phenomenon demonstrates an interesting relaxation behavior of the sample $\rho$ relating to the magnetic-field-induced phase transition.

Figure 6-2. (a) Normalized field dependence of $\rho$ measured at different constant temperatures under P1. (b) Temperature dependence of MR of 60 kOe for the first $[\rho_1(0) - \rho_1(60\text{ kOe})]/\rho_1(0)$ and second cycles $[\rho_2(0) - \rho_2(60\text{ kOe})]/\rho_2(0)$ (left panel) and irreversible ratio $[R_1(0) - R_2(0)]/[R_1(0) - R_1(60\text{ kOe})]$ for the first cycle (right panel), respectively. The filled (▲) and (■) represent the MR of 60 kOe measured after 5h relaxation for first and second cycles, respectively.
Figure 6-3. (a) Field dependence of $\rho$ measured at different constant temperatures under P2. The arrows at low field show the position where the maximum positive MR appears. (b) Temperature dependence of MR of 60 kOe for the first and second cycles, respectively. The filled (■) and (▲) represent the MR of 60 kOe measured after 5h relaxation for first and second cycles, respectively. (c) Temperature dependence of the overshooting ratios for the first cycle [$R_2(0) - R_1(0)]/R_1(0)$ and the second cycle [$R_4(0) - R_3(0)]/R_3(0)$, respectively.

In order to further understand the above two different THD MR behaviors, we measured the $\rho(H)$ with loading and unloading field following the routes in Figure 6-
4(a) at 265 K (within both MT and RMT regimes) reached under P1 and P2, respectively. The magnetic field is increased from zero to $H_m = 10$ kOe and then removed gradually. This was repeated for increasing values of $H_m$ up to 60 kOe. For temperature is reached under P1, the $\rho$ decreases with increasing magnetic field even at a small field. It is clear to see that magnetic field induces transformation from martensite to austenite phase step by step and only part of them can return back to martensite when the magnetic field is removed. The irreversibility of $\rho$ in the latter measurement (41.6 %) is comparable to the former one with increasing magnetic field to 60 kOe directly (42.8 %) [Figure 6-2(b)]. For temperature is reached under P2, a positive MR exists with loading a low field and an obvious “overshooting” appears when decreasing the magnetic field. The “overshooting” continues with increasing magnetic field step by step until the maximum field 60 kOe is applied and then a small irreversibility appears for removing 60 kOe to zero[Figure 6-4(c)]. In addition, with loading the same maximum magnetic field of 60 kOe at the same temperature, the “overshooting” in the latter measurement (10.71 %) is larger than that of the former one with increasing magnetic field to 60 kOe directly (2.78 %) [Figure 6-3(a)], which means the relaxation depends on not only the value of the maximum magnetic field but also the route of loading magnetic field.
Figure 6-4. (a) The sequence of loading and removing magnetic field for the next measurements. (b), (c) Field dependence of $\rho$ following the sequence showing in Fig 7-4(a) at $T=265$ K reached under P1 and P2, respectively. The arrows show the sequence of loading and unloading magnetic field.

We should keep in mind that the large MR effect in MSMAs is intimately related to the first-order magnetic transition accompanying with MT. In the standard notation of first-order phase transition, the extent of metastability is bound between $T^*$ and $T^{**}$ [141]. Below $T^*$, the supercooled state becomes unstable, and the system completely transforms into low-$T$ phase. Similarly, above $T^{**}$, the superheated state completely
transforms into high-$T$ phase. In case of MT, the $T^*$ and $T^{**}$ are equal to $M_f$ and $A_f$, respectively. In real system, the presence of disorder and/or impurity can locally reduce the free energy barrier, causing the low-$T$ (or high-$T$) phase to nucleate even above $T^*$ while cooling (or below $T^{**}$ while heating) [13]. Therefore, one can have phase coexistence in the regimes across MT and RMT. Minor hysteresis loops measurement is an useful experimental technique to study the phase coexistence during a first-order phase transition [144]. Figure 6-5(a) and (b) show descending and ascending branches of minor hysteresis loops, respectively. For clear visualization, only loops in the transformation regime are shown. In Figure 6-5(a) the first minor loop ($n_m=1$) was obtained by cooling the sample from 350 K to 265 K, and then was heated to 350 K. Loops $n_m=2, 3, 4, 5, 6$ were then measured by interrupting the cooling successively further down the descending branch than the prior minor loop. The full $n=1$ loop (350 K $\rightarrow$ 100 K $\rightarrow$ 350 K) is also shown for the reference. It is clear to see that strong irreversible behaviors for minor loops initiated inside the transformation regime. It is clear to see that strong irreversible behaviors for minor loops initiated inside the transformation regime. To take minor loop $n_m=1$ (initiated on a cooling cycle at 265 K) as an example, the $\rho(T)$ of the heating curve does not come reversibly along that of the cooling curve due to the already transformed AFM martensite phase at 265 K. Moreover, a slight increase in $\rho$ with temperature is
observed due to temperature dependence of transformed martensite phase, which is similar to the $\rho(T)$ behavior of the martensite phase. Upon further heating, the $\rho$ changes to a decreasing behavior due to more and more martensite to austenite transformation. The same process was repeated on the ascending branch by heating the sample from 100 K to several predetermined temperatures in the transformation regime, and then was cooled to 100 K. A similar phenomenon was observed as shown in Figure 6-5(b). The evidence of phase coexistence is clearly obvious from the fact that the $\rho$ of the sample measured at any temperature within the transformation regime is dependent on the thermal history of sample due to different factions of austenite and martensite phases. Furthermore, the reversible behavior of minor hysteresis loops for descending (ascending) branch (not shown here), initiated from temperatures at which MT (RMT) doesn’t take place, further indicates the irreversible behavior originated from martensite and austenite phase coexistence in the regimes across MT and RMT in the present alloy.
Figure 6-5. (a) Minor loops for the descending branch and the full loop. The $\rho$ is normalized to the value of 350 K. (b) Minor loops for the ascending branch and the full loop. The $\rho$ is normalized to the value of 100 K. Refer to the text for more details.
Figure 6-6. Time dependence of isothermal normalized resistivity at 270, 265 K reached under P1 (right panel), and 265, 260 K reached under P2 (left panel). The solid lines are the logarithmic fit to the data.

On the other hand, within the transformation regime, the martensite and austenite coexist in different free energy minima separated by an energy barrier, and part of austenite (martensite) phase becomes supercooled (superheated) phase during cooling (heating) [141, 145]. We now address the question of stabilities of the superheated martensite and superheated austenite phases by performing time-dependent $\rho [\rho(t)]$ for 18000 s at several temperatures within transformation regime of RMT and MT reached under P1 and P2, respectively [Figure 6-6]. It is interesting to note that the relaxation behavior at temperatures reached under P1 is completely
different from that reached under P2. For temperatures reached under P2, a very large relaxation $\sim 20\%$ at $T=265$ K in $\rho$ was observed and it decreases quickly with decreasing temperature (only $\sim 5\%$ at $T=260$ K). Moreover, the relaxation of $\rho$ with time obeys the logarithmic relation: $\rho(t)/\rho(t=0) = 1+S_0\ln(t/t_0)$, where $t_0$ and $S_p$ are the fitting parameters [solid lines in Figure 6-6]. A logarithmic relaxation of physical parameters is well established and it can happen due to the thermal excitation of the system across the distribution of energy barriers. This increase of martensite fraction with time at a constant temperature indicates isothermal nature of the MT [146, 147].

But for temperatures reached under P1, the $\rho$ quickly decreases about 0.3% in a few minutes and recover gradually with time. The absence of time-dependent effect shows an athermal nature of the RMT [146, 147]. One may argue that this phenomenon is simply due to a small overheating of the sample or the relaxation of metastable martensite is very fast like the magnetization response of FM materials to an external magnetic field (That is, no time-scale metastable phase). Here we mention two points again in the present case: (i) the $\rho$ of austenite is smaller than that of martensite [Figure 6-1(a)], so the relaxation phenomenon originated from overheating is only increase of $\rho$ quickly with time; (ii) for a first-order phase transition, the time-scale superheated state (metastable state) is the necessary process during heating [141].

Therefore, we concluded that the superheated martensite is stable with time (in fact, it
reduces a little during relaxation, see next discussion) and becomes unstable state under an external driving, such as temperature, magnetic field and so on.

In order to see how the stabilities of superheated martensite and supercooled austenite phases influence the MR behavior of the present alloy, we measured the isothermal $\rho(H)$ after 5 h relaxation measurements [Figure 6-7]. As can be seen in the Figure 6-7(a), the MR behavior for temperatures reached under P1 is insensitive to the relaxation, except for the low field part ($<10$ kOe) at the first cycle, where the $\rho$ is nearly constant. Compared with the results obtained without relaxation [Figure 6-2(b)], the MR of 60 kOe measured after relaxation reduces at the first cycle and has almost the same value for the second cycle [see the filled rectangles and triangles in the Figure 6-2(b)]. However, the MR measured after relaxation for P2 is quite different from that of the original ones obtained without relaxation: (i) the “overshooting” of $\rho$ for the first and second cycles are replaced by its irreversibility and reversibility, respectively; (ii) the values of MR are quite different from that obtained without relaxation [see the filled rectangles and triangles in the Figure 6-3(b)].
Figure 6-7. (a) Normalized field dependence of $\rho$ measured after 5 h relaxation at 270 and 265 K reached under P1. (b) Normalized field dependence of $\rho$ measured after 5 h relaxation at 265 and 260 K reached under P2. The sequences of measurement showing on the curve of temperature at 265 K are the same as described in the caption of Figure 6-2 (a).
6.3 Discussion

We argue that the value of MR due to magnetic-field-induced RMT at a certain temperature within the transformation regime, at which martensite and austenite coexist in the sample, is dependent on two factors: one is the ratio of the martensite fraction, which is proportional to the MR and decreases with temperature; the other is the instability of the martensite under external magnetic field, which is proportional to the MR and increases with temperature. At low temperature, the martensite is relatively stable so that a magnetic field of 60 kOe can only induces a little part of them to become austenite producing a small MR. With increasing temperature, the martensite becomes more and more instable so that the same field can induces more martensite fraction to transform to austenite resulting in a lager MR. But the ratio of martensite fraction decreases with increasing temperature, which is disadvantageous to produce a large MR. As a result, the maximum MR exists at a temperature at which the maximum magnetic field just can transform all the martensite fraction to austenite.

At a structural phase transition, anisotropically deformed domains of the low-temperature ordered phase emerge in the high-temperature disordered phase, as the temperature is lowered [148]. In this process, elastic strains are induced around the domains, which will store extra elastic energy across transition. Thus, the equilibrium
temperatures at which martensite and austenite have the same free energy for cooling and heating are different from each other [Figure 6-8(a)] [145]. The superscripts martensite and austenite with G denote free energy of martensite and austenite, respectively. The subscripts C and H with G denote free energy for cooling and heating, respectively. They can be calculated by $T_0=(M_s+A_t)$ and $T_1=(A_s+M_t)$ for cooling and heating, respectively [145]. That is, the free energy of martensite is lower than that of austenite during the MT, while it is higher than that of austenite during the RMT, which produces a strain-induced THD energy diagram in the present alloy. Figure 6-8[(b)-8(d)] show the change of instable and metastable phases with loading and unloading magnetic field before and after relaxation at constant temperatures reached under P1 and P2, respectively. The two minima represent the free energy of martensite and austenite phases, respectively, and transformation from one minimum to the other is hindered by the energy barrier.
Figure 6-8. (a) Schematic free energy versus temperature for martensite and austenite during cooling and heating, respectively. [(b)-(d)] Schematic energy diagrams with two local minima corresponding to the austenite and martensite and instable and metastable phases change with loading and unloading magnetic field before and after 5 h relaxation at temperatures reached under P1 (or after 5 h relaxation), before relaxation at temperatures under P2, and after 5 h relaxation at temperatures under P2, respectively. The red, blue empty circles and grey filled circle represent superheated martensite phase, supercooled austenite phase, and instable martensite phase, respectively.
For temperatures reached under P1, the free energy minimum of martensite is higher than that of austenite and the metastable phase is superheated martensite at initial state [Figure 6-8(b)]. With the application of a magnetic field, the martensite minimum increase and the barrier of transforming martensite to austenite become smaller [22]. As a result, the martensite fraction transforms to austenite easily by thermal activation producing a large negative MR. The negative MR due to magnetic-field-induced RMT is observed in the whole process, except for the low field part (<10 kOe) at the first cycle, where the decrease of $\rho$ is only due to the relaxation of superheated martensite phase as suggested by relaxation measurement [Figure 6-6] and the results of $\rho(H)$ measured after relaxation [Figure 6-7(a)]. With reducing magnetic field the transformed superheated martensite will not return back to the initial state showing large irreversibility at the first cycle. In addition, the ratio of metastability to the instability of martensite increases with temperature resulting in the irreversible ratio of the transformed martensite increases with temperature [Fig. 6-2(b)]. The reversible curve of $\rho(H)$ at the second cycle indicates all of the superheated martensite phase transforms to austenite at the first cycle. The reduction of MR of 60 kOe at the second cycle is due to only transformable instable martensite contributes to the MR at this process. After relaxation, the MR reduces for the first cycle and doesn’t change for the second cycle [Figure 6-2(b)] showing the superheated
martensite does exist after relaxation and reduce a little with relaxation. With further increasing temperature to 275 K, since the higher barrier between austenite and martensite and lower free energy at austenite phase, both the superheated and few instable martensite phases cannot return back to the initial state when decreasing the magnetic field to zero, which causes almost completely irreversibility of ρ(H). Noted that there is no hysteresis at the second cycle of ρ(H) for T = 275 K, showing the small MR observed at this stage is not related to the magnetic-field-induced first-order RMT. Furthermore, disorder gives a spatial variation of the free energy profile, as a result, the threshold field for the martensite to austenite transformation varies over the sample and causes a gradual melting of the martensite with increasing magnetic field [Figure 6-4(a)].

For the temperatures reached under P2, the free energy minimum of martensite is less than that of austenite and the metastable phase is supercooled austenite at initial state [Figure 6-8(c)]. Since large relaxation of supercooled austenite in this process [Figure 6-6], there are two completing factors to determine the value of ρ at low field: one is the relaxation of supercooled austenite, the other is the magnetic-field-induced RMT. When magnetic field is not enough to transform martensite to supersaturate austenite state, the MR is dominated by relaxation of supercooled austenite producing positive MR effect. The relaxation of supercooled austenite decreases dramatically
with decreasing temperature, which explained why the positive MR effect is observed only at some higher temperatures in the transformation regime [Figure 6-3(a)]. With further increasing magnetic field, the free energy diagram will change to the middle one in Figure 6-8(c), where martensite minimum lifts up to higher value and the barrier between the martensite and austenite decreases. Thus part of the martensite transforms to austenite and the negative MR due to magnetic-field-induced RMT will become domination. When the field is removed to zero, the free energy diagram changes back to its initial curve. Since the austenite is a supersaturate state (metastable state), the magnetic-field-induced transformed fraction will return back to martensite completely by thermal fluctuation, giving the envelope cycle of the MR. The intriguing “overshooting” of $\rho$ can be understood by the relaxation of supercooled austenite fraction to martensite phase accompanying with the reverse transformation. The “overshooting” increases with the increase of magnetic field step by step showing the relaxation of supercooled austenite is related to the ratio of the transformed martensite. The supercooled austenite fraction may interact with their neighbor transformed martensite fraction and relax to the lower energy martensite state accompanying with the reverse transformation of transformed martensite with unloading the magnetic field. The MR becomes smaller at the second cycle indicating that the relaxation of austenite enhances the stability of the martensite at the same
temperature [Figure 6-3(b)]. Thus, the same magnetic field may not make all of the last transformable martensite transforms to austenite phase again at the second cycle. That is why the MR does not show maximum value at the second cycle due to the 60 kOe field is not enough to make all of the martensite fraction transforms to austenite in our testing temperature range. After relaxation, all of the supercooled austenite phase relax to martensite state resulting in no metastable phase contributing to the subsequent MR measurements as shown in Figure 6-8(d). Meanwhile, the martensite fraction increase after relaxation, which will also influence the subsequent MR measurements. The negative MR due to magnetic-field-induced RMT dominates in the whole process even at low field. With reducing magnetic field, part of transformed martensite can not return back to the initial state due to the energy barrier between austenite and martensite phases. The increase of MR at 265 K and decrease of MR at 260 K after relaxation [Figure 6-3(b)] can be explained by the competing of contributions of increase martensite phase and stabilized martensite to the value of MR, which has been discussed detailed in the first paragraph of discussion part.

6.4 Summary

In conclusion, a strong THD isothermal MR behavior is observed in MSMA Ni_{49.5}Mn_{34.5}In_{16}. The main features of the THD MR behavior, i.e., irreversibility and
“overshooting”, can be well understood in terms of phase coexistence, strain-induced THD energy diagram and the competition of instable and THD metastable phases. The present results not only indicate possibility of practical applications for MSMAs as magnetic sensor, whose response can be tuned by changing the thermal history of the devices, but also provide fundamental insight of the phase coexistence and metastability scenario.
Chapter 7 Conclusions and suggestions for future work

7.1 Conclusions

We have studied the exchange bias and magnetoresistance effects in NiMnX (X = In, Sn) alloys. Exchange bias effect is observed in the martensitic state of NiMnX (X = In, Sn) alloys after zero-field cooling from an unmagnetized state, exhibiting the same relationship of the temperature dependence of $H_{EB}$ and $H_c$, and the training effect as in the previous exchange bias systems observed after field cooling. Such phenomenon has been explained by a proposed model, in which a SFM unidirectional anisotropy is formed during the initial magnetization process.

Both the value of exchange bias field and its sign can be tuned by the amplitude of remanent magnetization without changing its sign. This tunability is strongly dependent on the direction of the initial magnetization field for the hysteresis loop measurements. The isothermal tuning of EB is also strongly dependent on the direction of the initial magnetization field. The strong cooling field dependence of $H_{EB}$ in NiMnIn13 can be divided four zones: (1) $0 < H_{FC}^{C}$ (cooling field) $< 1$ kOe, the $H_{EB}$ increases with increasing of $H_{FC}^{C}$ due to the saturation of the FM layer
magnetization, (2) \(1 \text{kOe} < H^{FC} < 10 \text{kOe}\), the \(H_{EB}\) decreases with increasing of \(H^{FC}\) due to the increasing of FM volume fraction, (3) \(10 \text{kOe} < H^{FC} < 40 \text{kOe}\), the \(H_{EB}\) decreases with increasing of \(H^{FC}\) due to the increasing of FM volume fraction and the change of AFM bulk spin structure, (4) \(40 \text{kOe} < H^{FC} < 80 \text{kOe}\), the \(H_{EB}\) decreases with increasing of \(H^{FC}\) due to the change of AFM bulk spin structure.

The THD isothermal MR behavior of MSMA Ni\(_{49.5}\)Mn\(_{34.5}\)In\(_{16}\) was investigated. Irreversibility in isothermal MR is observed in reverse martensitic transformation temperature range, while an intriguing “overshooting” phenomenon is observed in forward martensitic transformation temperature range, showing a strong thermal-history dependence of MR behavior. Such a THD MR behavior can be explained in terms of phase coexistence, THD metastable phase, and magnetic-field-induced phase transition.

7.2 Suggestions for future work

Although we have conducted various researches on the NiMn\(_X\) \((X = \text{In, Sn})\) bulk alloys, the following studies are important and should be performed in the future.
1. Element replacement effect, which is one of the effective methods to optimize physical properties.

2. Fabricate NiMnX (X = In, Sn) MSMA thin films and study their electrical and magnetic properties, which will give us very important information for their future application in microelectromechanical system (MEMS).

3. Develop a novel metamagnetic shape memory alloy (MSMA)/ferroelectrics heterostructures possessing multiferroic functionality. Such heterostructures which combine the giant piezomagnetic effect of MSMA with the piezoelectric effect of ferroelectrics is expected to demonstrate a giant magnetization change directly controlled by the electric field. The expected giant magnetization change of such novel multiferroic heterostructures through direct application of electric field makes them a promising solution for a new generation of magnetic data storage technologies, sensors and transducers.
References


