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## Multifunctional Properties Related to Magnetostructural Transitions in Ternary and Quaternary Heusler alloys

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### Abstract

In this report, the results of a study on the effects of compositional variations induced by the small changes in concentrations of the parent components and/or by the substitution of Ni, Mn, or In by an extra element Z, on the phase transitions, and phenomena related to the magnetostructural transitions in off-stoichiometric Ni-Mn-In based Heusler alloys are summarized. The crystal structures, phase transitions temperatures, and magnetic and magnetocaloric properties were analyzed for representative samples of the following systems (all near 15 at.% indium concentration): Ni-Mn-In, Ni-Mn-In-Si, Ni-Mn-In-B, Ni-Mn-In-Cu, Ni-Mn-In-Cu-B, Ni-Mn-In-Fe, Ni-Mn-In-Ag, and Ni-Mn-In-Al.

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Keywords: Heusler alloys; MCE; Magnetoresistance; Multifunctional materials

### 1. Introduction

In spite of the significant progress made in recent years in understanding the multifunctional properties related to magnetostructural transitions (MSTs) in Ni-Mn-In based Heusler alloys, the detailed mechanisms responsible for the MSTs are far from

being well understood. A MST is a structural martensitic transition that results in a change of the magnetic state of the material. Magnetic states of high temperature austenitic (AP) and low temperature martensitic (MP) phases in magnetic, off-stoichiometric Heusler alloys can be quite different and inhomogeneous. As a result, MSTs are

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responsible, not only for large magnetocaloric effects (normal and inverse), but also for a slew of other pronounced physical properties including magnetoelasticity, large Hall effect, giant magnetoresistance, high spin polarization, magnetic shape memory effects, and exchange bias [1-5]. These multi-properties are all a consequence of a magnetostructural phase transition, and are therefore related to each other. Identifying the connections between these properties, and their relationships to the phase transitions, is an important issue in condensed matter physics, as such advances will help in better understanding the origins of MSTs, and to develop new materials for multifunctional applications.

In-based Heusler alloys with nearly 15 at. % concentration of In undergo MSTs near room temperature that result in sharp changes in the magnetization and related magnetoresponsive phenomena. Due to the delicate balance between electronic, ionic, vibrational, and magnetic energies in the vicinity of the MST, the properties of these alloys are extremely sensitive to any changes in intrinsic parameters, such as chemical composition, type of crystal structure, as well as on extrinsic parameters, such as fabrication techniques and conditions, annealing temperature, applied magnetic field, pressure, rate of heating and cooling, sequence of measurements, and cycling. It is widely believed (see, for example [6]) that the specific features of electronic band structure of the Heusler alloys are responsible for the MST. Therefore the alloy composition, the concentration of valence electrons per atom ( $e/a$ ), interatomic distances, and crystal structure homogeneity are interconnected major factors affecting the phase transitions and the related phenomena. Following these consideration, the multi-component alloys with even a small volume fraction of the extra elements, Z, present an opportunity to search for desirable properties at ambient temperatures and at accessible magnetic fields.

The changes in  $e/a$  ratio and in structural parameters (cell parameters and volume) are commonly considered to be the factors affecting the electronic structure, and therefore the phase stability and MST temperature in solid solutions based on Heusler alloys. However, in the multi-component Ni-Mn-In-Z systems with a small volume fraction of the extra element Z, these approaches are not always applicable [see 7, 8].

In this report, we summarize the results of our studies on the effects of small changes in concentration of the parent components, and/or by the substitution of Ni, Mn, or In by an extra element Z on the phase transitions and phenomena related to the MSTs in off-stoichiometric Ni-Mn-In based Heusler alloys.

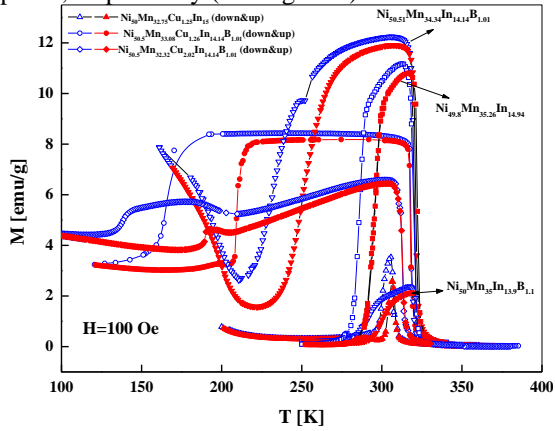
## 2. Experimental procedure

Polycrystalline samples of  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{12}\text{Si}_3$ ,  $\text{Ni}_{50.5}\text{Mn}_{32.32}\text{Cu}_{2.02}\text{In}_{14.14}\text{B}_{1.01}$ ,  $\text{Ni}_{50}\text{Mn}_{1-x}\text{Cu}_x\text{In}_{14}\text{B}$ ,  $\text{Ni}_{50.5}\text{Mn}_{33.08}\text{Cu}_{1.26}\text{In}_{14.14}\text{B}_{1.01}$ ,  $\text{Ni}_{50.51}\text{Mn}_{34.34}\text{In}_{14.14}\text{B}_{1.01}$ ,  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{13.5}\text{Al}_{1.5}$ ,  $\text{Ni}_{50}\text{Mn}_{33.75}\text{Cu}_{1.25}\text{In}_{15}$ ,  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{11}\text{Si}_4$ ,  $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ ,  $\text{Ni}_{49.9}\text{Mn}_{34.9}\text{In}_{15}\text{Ag}_{0.2}$ ,  $\text{Ni}_{49.8}\text{Mn}_{35.26}\text{In}_{14.94}$ ,  $\text{Ni}_{49.9}\text{Mn}_{35.1}\text{In}_{15}$ ,  $\text{Ni}_{49.8}\text{Mn}_{34.9}\text{In}_{15.3}$ ,  $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{15}$ ,  $\text{Ni}_{49.9}\text{Mn}_{34.7}\text{In}_{15.4}$ ,  $\text{Ni}_{49.6}\text{Mn}_{34.8}\text{In}_{15.2}$ ,  $\text{Ni}_{49.8}\text{Mn}_{34.7}\text{In}_{15.5}$ ,  $\text{Ni}_{49.6}\text{Mn}_{34.5}\text{In}_{15.9}$ ,  $\text{Ni}_{49.7}\text{Mn}_{34.8}\text{In}_{15.5}$  and,  $\text{Ni}_{46.7}\text{Fe}_3\text{Mn}_{34.8}\text{In}_{15.5}$ ,  $\text{Ni}_{50}\text{Mn}_{34.8}\text{In}_{15.2}$  have been prepared using 4N purity metals in an Ar atmosphere by arc-melting methods, and annealed in high vacuum ( $\approx 10^{-5}$  torr) for 24 hours at a temperature of 850 °C. The crystal structures were determined by powder X-ray diffraction methods using  $\text{Cu K}\alpha$  radiation. Thermomagnetic curves  $M(H,T)$  have been acquire using a superconducting quantum interference device magnetometer (Quantum Design) in the temperature interval 5–400 K and in magnetic fields up to 50 kOe. The measurements have been carried out during heating after the samples were cooled from 400 K to the starting temperature at zero magnetic field in the zero-field-cooled (ZFC) measurements. Some of magnetization data were collected during the field cooling cycle (FCC). Magnetotransport measurements have been carried out using the standard four-probe method, in the temperature interval 5-400 K at magnetic fields up to 50 kOe. All magnetotransport measurements have been carried out in ZFC conditions. Direct measurements of the adiabatic change of temperature,  $\Delta T_{\text{AD}}$ , under an applied magnetic field have been done using an adiabatic magnetocalorimeter (MagEq MMS 801) in a temperature range of 250-350 K, and in magnetic fields up to 1.8 T. The external magnetic fields have been ramped at a rate of up to 20 kOe/sec during  $\Delta T_{\text{AD}}$  measurements. A differential scanning calorimeter (DSC 8000) has been used to obtain heat flow curves (with a ramp rate of 20 K/min during heating and cooling) in the temperature range of 103-573 K. In the measurements under hydrostatic pressure, Daphne (7373) oil was used as the pressure

transmitting medium. The value of the applied pressure was calibrated by measuring the shift of the superconducting transition temperature of Pb used as reference manometer ( $T_C \sim 7.2$  K at ambient pressure) [9].

### 3. Results and discussion

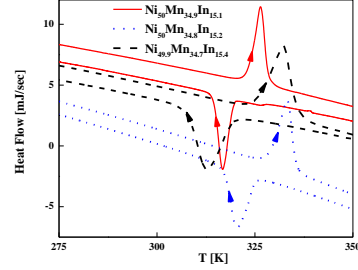
The phase composition of the compounds have been identified based on the XRD results mostly as a mixture of austenitic cubic ( $L2_1$  or B2) and the martensitic crystal structure modifications at 300 K. The behavior reflects the presence of temperature austenitic/martensitic hysteresis in the vicinity of the room temperature. All samples show ferromagnetic type magnetization curves in high magnetic fields ( $H > 1000$  Oe) at 5K. The phase transitions of the systems were found to be similar to that of “parent”  $Ni_{50}Mn_{35}In_{15}$  compound (see Refs. 1 and 2, for example). The samples show three transition temperatures:  $T_{CM}$ ,  $T_A/T_M$ , and  $T_C$ , where  $T_{CM}$  is the Curie temperature of martensitic phase,  $T_A/T_M$  and  $T_C$  are the temperatures of the direct/inverse martensitic transition (MST) and Curie temperature of austenitic phase, respectively (see Figure 1).



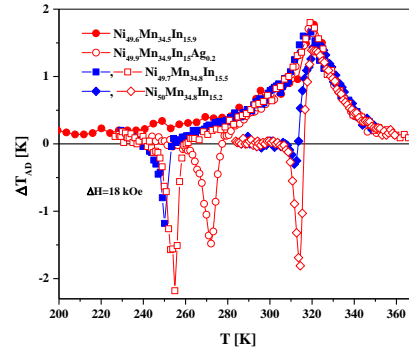
**Fig. 1.**  $M(H)$  curves obtained at  $H=100$  Oe for some compounds based on  $Ni_{50}Mn_{35}In_{15}$ .

The heat flow (HF) and  $\Delta T_{AD}$  curves with respect to temperature demonstrate endothermic peaks and negative values, in the vicinity of the MST, respectively (see Figures 2 and 3). The behavior is a signature of first order transitions. The positive reversible changes in  $\Delta T_{AD}$  are clearly seen in the vicinity of  $T_C$  (see Figure 3). It is necessary to note that several compounds show an irreversibility in the value of  $\Delta T_{AD}$  for direct and inverse MSTs (see

Figure 3). The sample compositions, transition temperatures  $T_A/T_M$ , and  $T_C$  (determined from  $M(T)$  curves at low magnetic field  $H=100$  Oe), along with maximum values of  $\Delta T_{AD}$ , are collected in Table 1.



**Fig. 2.** Heat flow for some samples based on  $Ni_{50}Mn_{35}In_{15}$ .



**Fig. 3.** Temperature dependencies of adiabatic temperature changes obtained at  $\Delta H=18$  kOe for Heusler alloys based on  $Ni_{50}Mn_{35}In_{15}$ .

Some of the compounds based on  $Ni_{50}Mn_{35}In_{15}$  demonstrate puzzling and interesting behaviors of magnetoresistance (MR) in close vicinity and below the MST (see Figure 4, showing a part of the full hysteresis of  $MR(H)$  of  $Ni_{50}Mn_{35}In_{14}B$ . For a more detailed consideration see Ref. [8]). The asymmetry in the MR relative to the applied magnetic field can be clearly seen in Figure 4. Such behavior, as well as the irreversibility of  $\Delta T_{AD}$ , is most likely related to the presence of the metastable “arrested” austenitic state induced by the external magnetic field in close vicinity of the MST. The thermomagnetic curves under different applied pressures ( $P$ ) of  $Ni_{50.51}Mn_{34.34}In_{14.14}B_{1.01}$  compound is shown in Figure 5. As one can see, the MST temperature is extremely sensitive to the pressure, and increases with a rate of  $\sim 96$  K/GPa from 237K at  $P=0.92$  GPa.

A small variation in composition (0.1-2) mol% relative to  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$  results in a variation in  $T_C$  (from 272 K to 326 K, see Table 1) and in significant changes in  $T_M$  (from 140 K to 317 K). Such small compositional changes do not strongly affect the  $e/a$  ratio (particularly in the case of isoelectronic substitution), nor the crystal cell parameters. However, such variations can change the electron wave function distribution and therefore the electron localization function, providing a change in the covalent bonding that is largely responsible for the stabilization of the high-temperature austenite phase [10]. Obviously, this effect depends on the metallic radius of constituent metals. Therefore, the change in the average metallic radius resulting from the difference of the radii of parent and extra metals ( $\Delta R$ ) in different atomic sites is a parameter that can be considered to affect the transitions temperatures. The change in effective radius ( $\Delta R_{\text{eff}}$ ), calculated as a sum of the  $\Delta R$  in the atomic sites of  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$  is introduced in the Table 1. For example, the deficiency of 0.2 at% of Ni was counted as  $\Delta R = (-0.2) \times R_{\text{Ni}}$ .

Table 1. Samples composition in Mol. %, Curie and MST transition temperatures obtained at magnetic field  $H=100$  Oe, adiabatic temperature change in the vicinity of the transition temperatures, for  $\Delta H=18$  kOe, and effective metallic radii changes ( $\Delta R_{\text{eff}}$ ) calculated using the metallic radii from Ref. [11]

composition	$\Delta R_{\text{eff}}$ [Å]	$T_C$ [K]	$T_A$ [K]	$\Delta T_{\text{AD}}$ [K], $T_A$	$\Delta T_{\text{AD}}$ [K], $T_C$
$\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}\text{Si}_4$	-1.38	272	236	-1	0.8
$\text{Ni}_{50}\text{Mn}_{35}\text{In}_{12}\text{Si}_3$	-1.03	274	252	-1.5	0.9
$\text{Ni}_{50.5}\text{Mn}_{32.32}\text{Cu}_{2.02}\text{In}_{14.14}\text{B}_{1.01}$	-0.74	310	190	--	--
$\text{Ni}_{50.5}\text{Mn}_{33.08}\text{Cu}_{1.26}\text{In}_{14.14}\text{B}_{1.01}$	-0.72	318	210	--	--
$\text{Ni}_{50.51}\text{Mn}_{34.34}\text{In}_{14.14}\text{B}_{1.01}$	-0.64	320	256	--	--
$\text{Ni}_{50}\text{Mn}_{35}\text{In}_{13.5}\text{Al}_{1.5}$	-0.34	318	296	-0.5	1.4
$\text{Ni}_{50}\text{Mn}_{33.75}\text{Cu}_{1.25}\text{In}_{15}$	-0.01	307	304	--	--
$\text{Ni}_{49.8}\text{Mn}_{35.26}\text{In}_{14.94}$	-0.09	323	300	--	--
$\text{Ni}_{50}\text{Mn}_{34}\text{In}_{15}$	0	313	314	--	--
$\text{Ni}_{50}\text{Mn}_{34.8}\text{In}_{15.2}$	0.072	320	319	-1.8	1.5
$\text{Ni}_{49.9}\text{Mn}_{34.9}\text{In}_{15}\text{Ag}_{0.2}$	0.12	320	275	--	--
$\text{Ni}_{49.9}\text{Mn}_{35.1}\text{In}_{15}$	0.130	317	305	-2.1	1.6
$\text{Ni}_{49.8}\text{Mn}_{34.9}\text{In}_{15.3}$	0.134	316	308	--	--
$\text{Ni}_{49.9}\text{Mn}_{34.7}\text{In}_{15.4}$	0.139	315	315	-1.3	1.7
$\text{Ni}_{49.6}\text{Mn}_{34.8}\text{In}_{15.2}$	0.2	320	270	--	--
$\text{Ni}_{49.8}\text{Mn}_{34.7}\text{In}_{15.5}$	0.208	320	269	-1.1	1.7
$\text{Ni}_{49.7}\text{Mn}_{34.8}\text{In}_{15.5}$	0.21	319	262	-1.6	1.5
$\text{Ni}_{46.7}\text{Fe}_3\text{Mn}_{34.8}\text{In}_{15.5}$	0.28	320	--	--	--
$\text{Ni}_{49.6}\text{Mn}_{34.5}\text{In}_{15.9}$	0.316	321	--	--	--
$\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$	0.359	326	140	--	--

The ( $T$  vs.  $\Delta R_{\text{eff}}$ ) phase diagram of the systems based on  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$  is shown in Fig.6. Both critical temperatures  $T_C$  and  $T_M$  show a monotonic

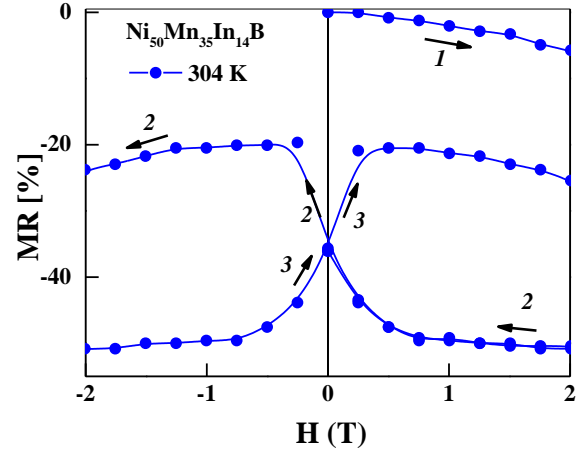


Fig. 4. Part of the magnetic hysteresis of magnetoresistance obtained in close vicinity and below the martensitic transition temperature. Numbers and arrows indicate the magnetization cycles and changes in magnetic field direction.

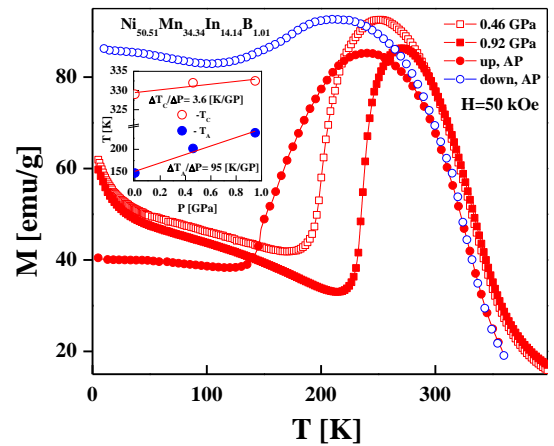
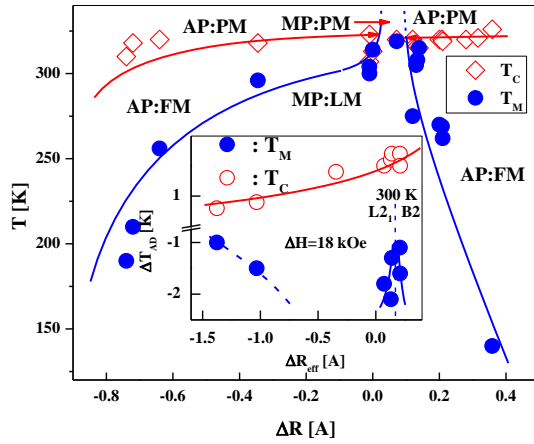


Fig. 5 ZFC and FCC  $M(H)$  curves of  $\text{Ni}_{50.51}\text{Mn}_{34.34}\text{In}_{14.14}\text{B}_{1.01}$  obtained at  $H=50$  kOe and at different applied hydrostatic pressures. Inset: Variation of the transition temperatures  $T_C$  and  $T_M$ , open and closed symbol, respectively, with applied pressure.



**Fig. 6** ( $T$ - $\Delta R_{\text{eff}}$ )-phase diagram of the systems based on  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ . AP and MP, PM, FM, and LM are austenitic and martensitic, paramagnetic, ferromagnetic, and low magnetic phases, respectively. Open and closed symbols are  $T_C$  and  $T_M$ , respectively. Inset: The changes in  $\Delta T_{\text{AD}}$  with effective radius ( $\Delta R_{\text{eff}}$ ) for Heusler alloys based on  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ .  $\Delta T_{\text{AD}}$  in the vicinity of  $T_C$  and  $T_M$  are shown by the open and closed symbols, respectively. The vertical dash line indicates  $\Delta R_{\text{eff}}$ , where a change of the type of cubic structure has been observed at 300K [1].

type of behavior with respect to  $\Delta R_{\text{eff}}$ :  $T_C$  slightly increases and remains nearly constant in  $(-0.74$ - $0.0018)$  and  $(0.202$ - $0.37)$  intervals of  $\Delta R_{\text{eff}}$  changes,  $T_M$  sharply increases/decreases in  $(-1.93$ - $0.0018)$  and  $(0.202$ - $0.37)$  intervals of  $\Delta R_{\text{eff}}$ , respectively. In the vicinity of and above  $\Delta R_{\text{eff}}=0$  (i.e. “parent” compound) in the interval:  $0.08 \leq \Delta R_{\text{eff}} \leq 0.16$ , the  $T_M$  are found to be equal or larger than  $T_C$ , and only the transitions from the strongly correlated PM to the low magnetic state are observed. The  $|\Delta T_{\text{AD}}|$  related to the MST passes through a minimum near  $\Delta R_{\text{eff}} = -0.17$ , and shows a behavior suggesting the existence of two maxima for  $-1.03 < \Delta R_{\text{eff}} < 0.18$  and  $0.205 \leq \Delta R_{\text{eff}} \leq 0.29$  intervals.  $\Delta T_{\text{AD}}$  in the vicinity of  $T_C$  monotonically increases up to 1.8 K for  $\Delta R_{\text{eff}} = 0.4$ . It is interesting to note that the minimum of  $|\Delta T_{\text{AD}}|$  at the MST is consistent with the changes of the structural type of austenitic phase (B2-L2<sub>1</sub>) observed in Ref. [1] at room temperature.

#### 4. Conclusion

The obtained results show that the local distortion in electron structure induced by small variations in

atomic compositions through “local” inhomogeneity can be considered as one of the key factors in temperature stabilization of the martensitic and austenitic phases. The possible presence of the two maxima in  $\Delta T_{\text{AD}}$  near the Heusler alloy with composition  $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$  is an interesting subject for future studies. Thus the multifunctional properties of Ni-Mn-In based Heusler alloys may be enhanced, tuned, and adjusted to required technical parameters using small compositional changes. Though the adiabatic temperature change in Heusler alloys is smaller than that of Gd, it seems to be large enough to be useful for magnetic refrigeration purposes.

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