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Effect of Bi substitution on the magnetic and magnetocaloric properties of $Ni_{50}Mn_{35}In_{15-x}Bi_x$ Heusler alloys

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The structural, magnetic, magnetocaloric, and transport properties of $Ni_{50}Mn_{35}In_{15-x}$-Bi_x (x = 0, 0.25, 0.5, 1, 1.5) compounds has been studied through X-ray diffraction (XRD), differential scanning calorimetry, and magnetization measurements. A mixture of high temperature austenite phase (AP) and low temperature martensitic phase (MP) was observed from the XRD at room temperature. The saturation magnetization M_S at 10 K was found to decrease with increasing Bi content. A shift in the martensitic transition temperature (T_M) relative to the parent compound was observed with a maximum shift of ~ 36 K for x = 1.5. Abnormal shifts in T_C and T_M to higher temperatures were observed at high field for x ≥ 0.5. Large magnetic entropy changes (ΔS_M) of about 40 J/kg K (x = 0) and 34 J/kg K (x = 0.25) were observed at T_M with H = 5 T, which reduced significantly for higher Bi concentrations. The doping of small amounts of Bi in the In sites increased the peak width of the ΔS_M curves at the second order transition, leading to larger values of relative cooling power. A significant magnetoresistance (-30%) was observed near T_M with ΔH = 5T for x = 0.5. https://doi.org/10.1063/1.5004694

I. INTRODUCTION

The magnetocaloric effect (MCE) is an adiabatic temperature change (ΔT_A) or isothermal magnetic entropy change (ΔS_M) in a magnetic material, induced by an applied magnetic field. The effect has been a subject of intense investigation due to its potential application in magnetic refrigeration. Such cooling technology is considered to be eco-friendly and more energy efficient than the conventional vapor cycle refrigeration.[1,2]

Recently, off-stoichiometric Ni-Mn-In based Heusler alloys that undergo first order magnetostructural transitions (MST) near room temperature have attracted interest due to their remarkable magnetoresponsive properties such as magnetic shape memory, exchange bias, large magnetoresistance, Hall effects, and large normal and inverse magnetocaloric effects.[3–10] The off-stoichiometric Ni-Mn-In based alloys undergo a martensitic structural transition from a high temperature austenitic phase (AP) (cubic $L2_1$) to a low temperature martensitic phase (MP) with lower symmetry (tetragonal, orthorhombic, or monoclinic) near room temperature. The compound undergoes several temperature induced magnetic phase transitions: (a) from a ferromagnetic to a low magnetic (antiferromagnetic or paramagnetic) state at the Curie temperature of martensitic phase (T_{CM}); (b) from a low magnetic phase (LMP) of the MP to a ferromagnetic phase of the AP at the MST (T_M); and (c) from a

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ferromagnetic AP to a paramagnetic AP associated with the Curie temperature of the AP (T_C). A coincidence of magnetic and structural phase transitions (known as a MST) from a low magnetic state of the MP to a ferromagnetic state of the AP at T_M has been observed in these compounds.[7,8,11] Such MSTs result in a large jump in magnetization that is necessary for large MCEs. As reported in Ref. 11, changing the stoichiometry or chemical composition, or doping an extra element in the Ni-Mn-In based Heusler alloys changes the conduction electron concentration (e/a), interatomic Mn-Mn distance, and the Ni(3*d*)-Mn(3*d*) hybridization. These factors can modify the electronic band structure and affect the phase transitions and the associated phenomena.[12] However, the exact mechanisms responsible for the unique behaviors of off-stoichiometric Ni-Mn-In based Heusler alloys are not clear. Previous results show that magnetic and structural properties of the ternary Heusler alloys Ni-Mn-In-X are extremely sensitive to type and concentration of the doped elements X.[11–13] Thus, the study of quaternary system is important to understand the mechanisms responsible for unique behavior of these compounds. In $Ni_{50}Mn_{35}In_{15-x}Bi_x$ compounds, the change of the properties due to larger radius and different electronic structure of Bi compared to that of In can be expected. In this work we report the effects of the partial substitution of Bi for In on the magnetic, structural, and magnetocaloric properties of $Ni_{50}Mn_{35}In_{15-x}Bi_x$ (x = 0, 0.25, 0.5, 1, 1.5).

II. EXPERIMENT

Polycrystalline samples of $Ni_{50}Mn_{35}In_{15-x}Bi_x$ (x = 0, 0.25, 0.5, 1.0, 1.5) of nominal compositions were fabricated by arc-melting high purity elements (99.99%) in an ultra-high purity argon atmosphere. The ingots were annealed in high vacuum ($\sim 10^5$ Torr) at 850^0C for 48 hr. The structural characterization was done using powder X-ray diffraction (XRD) using CuKα radiation at room temperature. The magnetization and resistivity (four probe method) were measured using a SQUID magnetometer (Quantum Design) in the temperature interval 10 - 380 K in applied magnetic fields up to 5 T. Differential scanning calorimetry (DSC) measurements were carried out using a DSC 8000 instrument (with a ramp rate of 30 K/min during heating and cooling) in the temperature range 123 - 423 K. The relative cooling power (RCP) was estimated as: RCP = $-\Delta S_M$ (max) $\times$ δT_{FWHM}, where $\Delta\delta_{FWHM}$ is the full-width-at-half-maximum of the $-\Delta S_M$ curve.

III. RESULTS AND DISCUSSIONS

The room temperature XRD patterns for $Ni_{50}Mn_{35}In_{15-x}Bi_x$ are shown in Fig.1 (a). A mixture of high temperature austenite (cubic $L2_1$) and low temperature martensite (tetragonal) phase was observed. Such a mixed phase is typical in Ni-Mn-In-based compounds when the martensitic transition occurs near room temperature.[13,14] The XRD peaks of the AP and MP have been indexed for x = 0 (see in Fig.1). A relative shift in the XRD peaks towards lower two theta angles with respect to the parent compound was observed for the AP, which indicates an increase in the lattice parameters since the metallic radius of Bi (1.70 Å) is greater than that of In (1.663 Å).[15] The lattice parameter for the cubic AP was found to increase linearly with Bi concentration (see Fig 1(a)), as expected.

The field dependence of the magnetization M(H) at T = 10 K is shown in Fig. 1 (b). The M(H) curves at low temperature show the ferromagnetic behavior in the ground state. The values of the saturation magnetization (M_S) were found to decrease linearly relative to that of the parent compound with Bi substitution (see inset of Fig. 1 (b)).

Fig. 2 shows the temperature dependence of the magnetization M(T) during heating and cooling in applied fields of 100 Oe and 50 kOe respectively. The thermal hysteresis observed during heating and cooling cycles in the M(T) curves clearly indicates the temperature induced structural FOT. Sharp changes in the magnetization at T_M and T_C were observed that correspond to magnetic transitions from low a magnetic phase (AFM or PM) to a FM phase and then to a PM phase, for x= 0, 0.25, and 0.5, respectively. However, the jump in magnetization observed as a result of MST at 50 kOe drastically decreases from about 80 emu/g to 20 emu/g for x = 0 and x = 1.0, respectively. Such behavior can result from a non-collinear ferromagnetic structure of austenitic phase induced by the Bi-doping. Thus, the increase in Bi concentration induces a decrease in T_M with a maximum shift

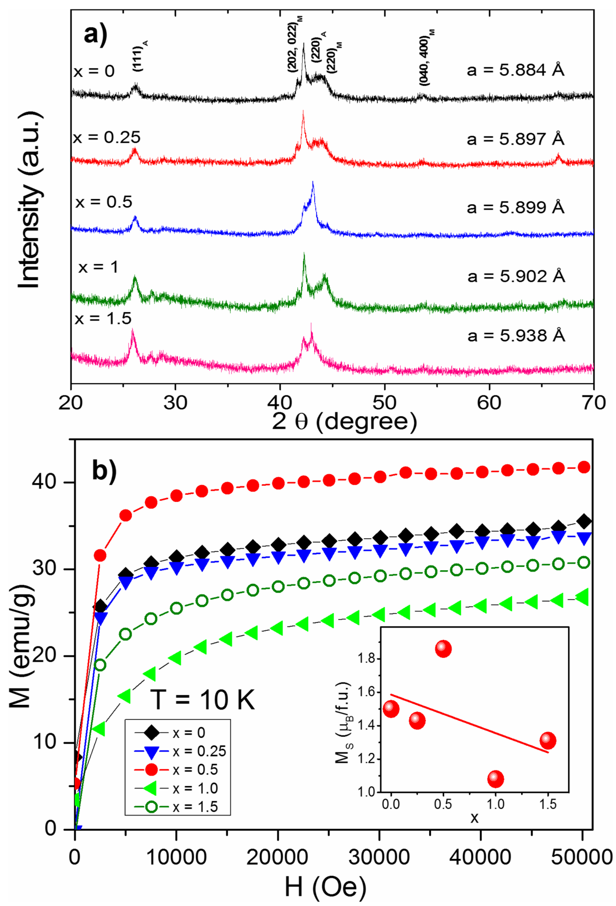

FIG. 1. a) Room temperature XRD patterns of $Ni_{50}Mn_{35}In_{15-x}Bi_x$ ($0 \leq x \leq 1.5$) with nominal compositions. The XRD peaks for $Ni_{50}Mn_{35}In_{15}$ (x = 0) are indexed (b) Field dependence of the magnetization M(H) at T = 10 K. Inset: The saturation magnetization (M_S) as a function of Bi concentration (x) at T = 10 K.

of ΔT = 36 K for x = 1.5 at H=100 Oe, and an increase in the AF component of the AP (see inset of Fig 2(d)). The M(T) curves of samples with a significant AF component (with x≥ 0.5) show an abnormal shift in T_C to higher temperature by more than 50 K (see Figure for x=1.0) and a ~15 K shift of T_M. Such a shift is uncommon since, in $Ni_{50}Mn_{35}In_{15}$, T_M depends on the field according to $T_M(H) \sim H^{-2}$.[10] The shift in T_C can be related to the field-induced FM component in the AP. The collective Jahn-Teller effect and, therefore, the density of electronic states at the Fermi level (N_F), is considered as one possible reason for the martensitic transition.[12] Thus, the increase in N_F due to applied magnetic fields may result in an increase in the temperature of the MST. However, the exact mechanism responsible for such strange behavior is unclear and needs further study.

The occurrence of the structural transition was examined using DSC measurements as shown in Fig. 3. Large endothermic/exothermic peaks with thermal hysteresis were observed in the heat flow curves in heating/cooling cycles, which confirm the first order nature of the structural transition. The observed peaks arise from the latent heat of the transition. The latent heat (L) values associated with structural transition were estimated as discussed in Ref. 14 and given in Fig. 3. The values of the martensitic transition temperature agree well with the M(T) measurements for x = 0, 0.25, 0.5. However, for x = 1 and 1.5, the transition temperatures observed in the M(T) measurements were about 55 K and 36 K below those obtained from DSC measurements, respectively. Such an inconsistency in values of T_M between the M(T) and DSC measurements was also reported in $Ni_{50}Mn_{35}In_{13.9}B_{1.1}$, and has been explained based on the changes in magnetic structure by the application of magnetic field.[16]

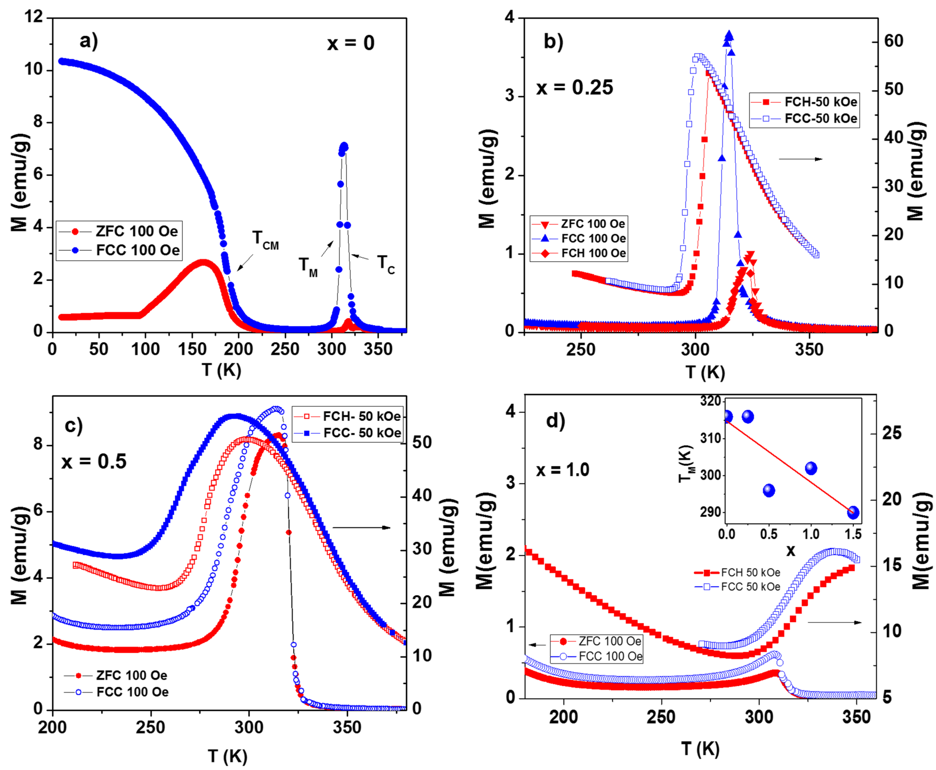

FIG. 2. (a)-(d) The temperature dependence of the magnetization M(T) for $Ni_{50}Mn_{35}In_{15-x}Bi_x$ ($0 \le x \le 1.5$) on heating and cooling in applied magnetic fields of 100 Oe and 50 kOe. Inset of (d): Dependence of T_M on Bi concentration (x) at H = 100 Oe.

Isothermal magnetization M(H) curves typical for $Ni_{50}Mn_{35}In_{15}$ compounds at selected temperatures are shown in the inset of Fig 4 (a). A jump like change in magnetization at the critical field (H_C) was observed indicating the existence of an AFM-FM-like metamagnetic transition near T_M. With increasing temperature, the H_C of the metamagnetic transition decreased. A smooth transition from the FM-like phase to the PM phase was observed near T_C. The compounds with x = 0.25 and 0.5

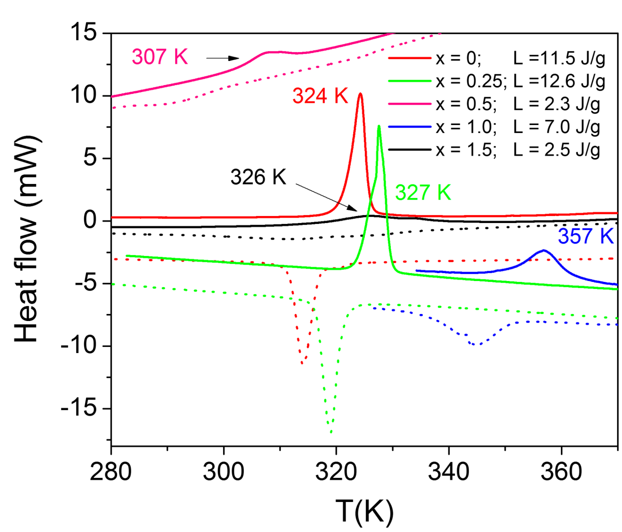

FIG. 3. DSC heat flow curves as a function of temperature. The solid and dotted lines indicate the heating and cooling cycles, respectively.

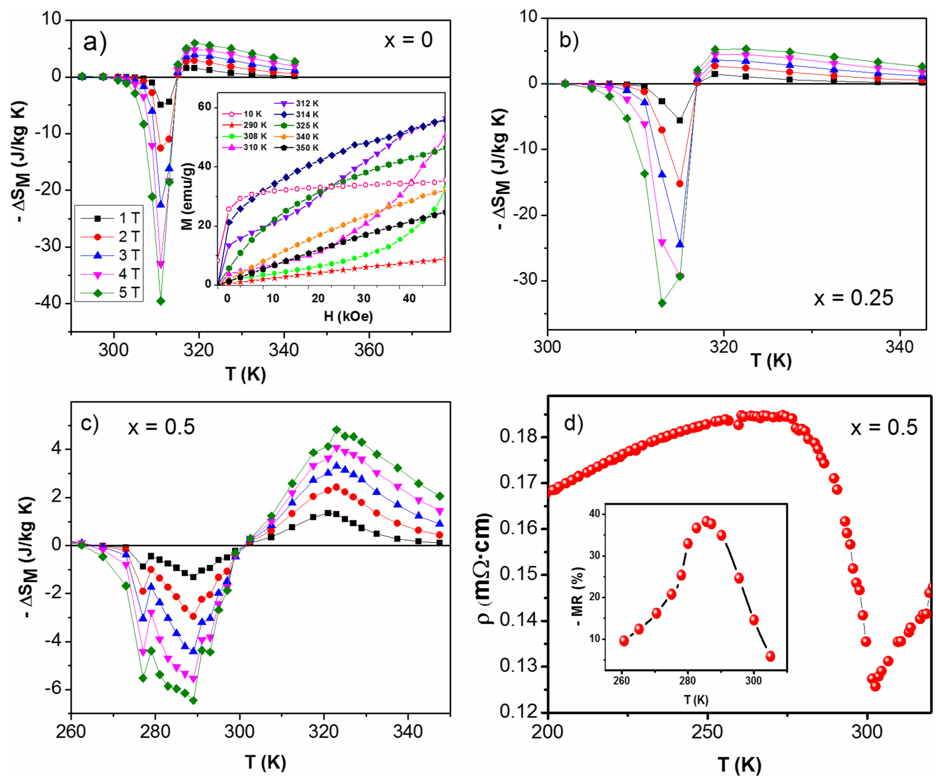

FIG. 4. (a)-(c) Magnetic entropy changes ($-\Delta S_M$) as a function of temperature with a magnetic field change of $\Delta H = 5$T. Inset of (a): Isothermal magnetization M(H) curves at selected temperatures for x = 0. (d) Resistivity (ρ) as a function of temperature (T) at $\Delta H = 5$ T. Inset of (d): the magnetoresistance (MR) as a function of T.

exhibited similar behavior. However, no such field-induced metamagnetic transition was observed in the M(H) curves for the compounds with x = 1.0 and 1.5.

The magnetic entropy change (ΔS_M) calculated from the isothermal M(H) curves near the FOT and SOT are shown in Fig. 4(a)–(c). The ΔS_M values were calculated using the Maxwell relation, $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$.[1,2] The validity of the Maxwell relation to calculate ΔS_M at a FOT has been discussed by Gschneidner et. al in Ref. 17. Both direct (negative ΔS_M) and inverse (positive ΔS_M) magnetic entropy changes were observed near T_C and T_M, respectively. Maximum entropy changes of about 40 J/kg K (x = 0) and 34 J/kg K (x = 0.25) were observed at T_M with H = 5 T. The magnitude of ΔS_M reduced significantly to 6.5 J/kg K (x = 0.5), 0.5 J/kg K (x = 1), and 0.2 J/kg K (x = 1.5), which is related to the small change in magnetization near T_M. Even though ΔS_M is small, the width of peak broadens for x = 0.5, which is beneficial for RCP. Particularly, doping a small amount of Bi in the In site increases the full-width-at-half-maximum (ΔT_{FWHM}) of the $-\Delta S_M$ curve at the SOT, which improves the RCP. The maximum estimated value of the RCP at the SOT was found to be 165 J/kg for x = 0.5 at 5T which is interesting for magnetic refrigeration applications.

The temperature dependence of the resistivity ρ(T) for the compound with x = 0.5 is shown in Fig. 4(d). A high resistivity in the MP followed by a sharp drop at T_M, and a much smaller resistivity in the AP, was observed in ρ(T) curves. The existence of such behavior of ρ(T) has been explained by $\rho \sim [N(E_F)]^{-2}$, where $N(E_F)$ is the density of electronic states at the Fermi energy.[11] Since $N(E_F)$ in the MP is lower than that of the AP, the resistivity is higher in the MP. The magnetoresistance (MR) is defined as: MR(%) = $(\Delta\rho/\rho_o)\times$ 100%, where $\Delta\rho = [\rho(H, T) - \rho_o]$ and $\rho_o = \rho(H = 0, T)$. The (MR) as a function of T with ΔH =5 T is shown in inset of Fig. 4(d). An MR value of -38% was found near T_M, which can be related to the metamagnetic transition as seen from the M(H) curves.

IV. CONCLUSION

In conclusion, the influence of Bi substitution on the magnetic, magnetocaloric, and transport properties of $Ni_{50}Mn_{35}In_{15-x}Bi_x$ has been studied. It was found that T_M shifted by 36 K towards lower temperature with increasing Bi concentration at low field (H = 100 Oe). An abnormal shift in T_C and T_M to higher temperatures was observed at high field (H = 5T) for x ≥ 0.5. The saturation magnetization at 10 K was also found to decrease with Bi content. Large values of ΔS_M ~ 40 J/kg K and 38 J/Kg K were obtained for x = 0 and 0.25 respectively. The magnitude of magnetization change at the FOT decreased dramatically for higher Bi concentrations, resulting in lower values of ΔS_M. In particular, substitution of a small amount of Bi in the In sites increased the peak width of ΔS_M curve near the SOT and enhanced RCP (165 J/Kg for x =0.5 at 5T) which is important for magnetic refrigeration applications. A large MR value of -38 % was observed for the compound with x = 0.5 at MST for ΔH = 5T.

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