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Structural, transport, magnetic, magnetocaloric properties and critical analysis of Ni-Co-Mn-Ga Heusler alloys

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ABSTRACT

In this work, we have investigated structural, transport, magnetic, magnetocaloric (MC) properties and critical exponents analysis of the $(Ni_{2.1-x}Co_x)Mn_{0.9}Ga$ ($x = 0$, 0.04, 0.12 and 0.2) Heusler alloys. For all compositions, cubic austenite (A) phase with metallic character is observed at room temperature (RT). With increasing of Co content, magnitude of resistivity decreases, whereas residual resistivity (ρ_0) and electron scattering factor (A) increases linearly. Magnetic measurements exhibit that ferromagnetic (FM) Curie temperature (T_C^A) increases towards RT by increasing Co concentration. All samples show conventional MC and maximum magnetic entropy change (ΔS_M^{peak}) of -2.8 Jkg^{-1} K^{-1} is observed for $x = 0.12$ at 147 K under 5 T. Further, hysteresis is observed between cooling and warming cycles around FM-PM (T_C^A) transition in $x = 0$, 0.04 samples, which suggests that first order nature of transition. However, there is no hysteresis across T_C^A for $x = 0.12$ and 0.2 samples suggesting second-order nature of the transition. The critical exponents are calculated for $x = 0.12$ sample around T_C^A using Arrott plot and Kouvel-Fisher method, the estimated critical exponents are found closer to the mean-field model reveals the long range ferromagnetic ordering in this composition.

1. Introduction

The family of Ni-Mn based Heusler alloys afford an extensive playground of interesting physical properties. The novel properties of Ni-Mn-Ga alloys have attracted a lot of attention in magneto-strain owing to their prospective applications in sensors and actuators [1,2]. The phase transformation [3] displayed in these alloys give rise to thermos-elasticity, shape memory effect (SME) [4–6], magneto resistance (MR) [7–10] and magnetocaloric (MC) [11–16].

Heusler alloys exhibits two transformations. A pure magnetic transition from paramagnetic (PM) to ferromagnetic (FM) within the cubic austensite phase and a structural transition from cubic austenite to low symmetry martensite phase. The martensite phase can be FM (or) antiferromagnetic (AFM)/PM depending on the alloy composition [4,6,17–19]. In the recent decade, the effect of compositional changes in Ni-Mn-Ga alloys by doping different elements have been studied intensively by experiment and theory [20–25]. Doping of magnetic elements in Heusler alloys exhibit trivial changes in physical properties. Curie and martensitic transitions (T_C and T_M) are altered by replacing various elements in X site of Ni-Mn-X (X = Al, Ga, In, Sn and Sb) system [26], T_C can be controlled by substitution of Co at Ni site of $(Ni_{53.25-x}Co_x)Mn_{21}Ga_{25}$ ($x = 0.75$, 1.5, 2.25) alloys [27].

We discuss about doping of magnetic elements at different sites of Ni-Mn-Ga system as follows: Doping of Co element at Ni site affects the critical temperatures and exchange interactions of martensite and austenite phases in $Ni_{50}Mn_{30}Ga_{20}$ alloy [28]. Fe doping at Mn site of $Ni_{48.7}Mn_{28.1}Fe_2Ga_{21.2}$ improves the magnetostriction and fracture toughness without change in its magnetic and thermos-elastic properties [29,30]. Doping of magnetic elements in Ni-Mn-Ga system at Ni site is expected to give more interesting phenomenon than other sites.

Inter-martensitic transformation is absent by substituting Co at Ni site in $Ni_{46.9}Co_{3.3}Mn_{28.8}Ga_{21}$ system due to local spins inversion of Co [31]. The structural stability and alteration of transformation

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temperatures (T_M and T_C) causes the change in electron density at Fermi level by interchanging of Co at Ni site of $(Ni_{2.16-x}Co_x)Mn_{0.84}$ Ga (x = 0.03–0.09) system [32]. In the $Ni_{50-x}Co_xMn_{50-y}Ga_y$ ($7 \leq x \leq 13$, $18 \leq y \leq 20$) system, Yu et al. [33] reports that partial substitution of Co for Ni atoms tuned the magnetic ordering of parent phase from AFM to FM and decreases T_M while increases T_C. The phase diagram of T_M and T_C in the $(Ni_{2.19-x}Fe_x)Mn_{0.81}$ Ga (x = 0–0.04) system reveals that T_M decreases gradually whereas T_C increase with Fe concentration [34]. Soto-parra et al. [21] clearly pointed out the electron per atom ratio (e/a) variation of T_M and T_C with Co content at Ni site of $(Ni_{50.8-x}Co_x)Mn_{24.8}Ga_{24.4}$ (x = 0–5.2) and Fe doped at Ni site of $(Ni_{52.7-x}Fe_x)Mn_{21.9}Ga_{25.4}$ (x = 0–5.3). The doping of both Co and Fe in these system reveals that T_M decreases whereas T_C increases with e/a. The magnetic field induced reverse phase transformations from AFM (or PM) martensite to FM austenite phase appear near RT in $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ [4]. A steep increase (decrease) of thermal expansion is observed in $Ni_{41}Co_9Mn_{31.5}Ga_{18.5}$ due to martensitic (reverse martensitic) transition [35].

On the other hand, Co substitution at Mn site of $Ni_{47}Mn_{31}X_1$-Ga_{21} (X = Co, Fe) has strong effect on T_C and T_M, while for substitution of Fe at Mn site shows opposite effect in the same system [36]. The change in transformations temperatures (T_M and T_C) causes the change in electron density at the Fermi level by interchanging Mn site in $Ni_{2.16}(Mn_{0.84-y}Co_y)Ga$ (y = 0.04–0.14) system [32]. When the Co is doped in Ga site of $(Ni_{50.26}Mn_{27.30}Ga_{22.44})_{100-x}Co_x$ (x = 0–6), the phase transformation temperatures and crystal structures of martensitic phase is altered and Curie temperature of martensitic phase is lower than that of austenitic phase [37].

From the structural measurements, Satish Kumar et al. [31] observed that Co doped in Ni site of $Ni_{46.9}Mn_{28.8}Ga_{21}Co_{3.3}$ stabilizes cubic austenite structure at RT and martensite at low temperatures (230 and 180 K). On the other hand doping in Mn site of $Ni_{49.8}$-$Mn_{27.2}Ga_{21.2}Co_{1.8}$ non-modulated tetragonal and *7M* orthorhombic phase observed at 290 and 200 K, respectively. When Fe replaces Ga in $Ni_{50}Mn_{27}(Ga_{23-x}Fe_x)$ (x = 1,2) orthogonal structure is observed [36]. Cubic $L2_1$ structure is shown for Co doping in Ga and Mn site of $Ni_{48}Mn_{27}(Ga_{25-x}Co_x)$ (x = 1–4) and $Ni_{48}(Mn_{26-x}Co_x)$ Ga_{26} (x = 1–5) respectively [38]. X-ray diffraction patterns for the $Ni_{52.5}Mn_{20.1}Ga_{25.1}Fe_{2.3}$ [21] sample reveals martensite monoclinic *14M* and *10M* modulated structure at 145 and 270 K, respectively. X-ray diffraction patterns for $Ni_{48.7}(Mn_{30.1-x}Fe_x)Ga_{21.2}$ (x = 0–11) [39] depict that cubic austenite and tetragonal martensite phase coexist in x = 0 and 2, whereas only the cubic parent phase exists for remaining x = 5, 8 and 11 alloys. Martensite transformations are identified clearly from transport measurements for Co doped in Ga and Mn site of $Ni_{48}Mn_{27}(Ga_{25-x}Co_x)$ (x = 1–4) and $Ni_{48}(Mn_{26-x}Co_x)Ga_{26}$ (x = 1–5) alloys [38].

For some of the compositions change in magnetic entropy (ΔS_M) has been reported as follows: The melt spun ribbons of $Ni_{52}Mn_{26}$-Ga_{26} shows magneto-structural transition around 354 K with the increasing trend of MC (−15 to −30.3 $Jkg^{-1}K^{-1}$) for 2 and 5 Tesla fields [40]. Rama Rao et al. [41] reported near RT-MC (~309 K) for $Ni_{55}Mn_{20.6}Ga_{24.4}$ (−9.5 $Jkg^{-1}K^{-1}$) and $Ni_{55}Mn_{19.6}Ga_{25.4}$ (−10.4 $Jkg^{-1}K^{-1}$) ribbons. The $Ni_{2.15}Mn_{0.85}$ Ga and $Ni_{2.19}Mn_{0.81}$ Ga alloys shows an increasing trend of MC (−7.2 to −28 $JKg^{-1}K^{-1}$) [42]. All these literature survey reports suggest an importance of doping (especially Co) in various Heusler alloy system.

The first and second order phase transitions of Ni-Mn-In-Si alloys have been correlated through magnetic entropy and magnetoresistance [43]. Critical exponents are analysed near T_C in manganites [44] re-entrant metallic alloys like $Au_{0.81}Fe_{0.19}$, $Ni_{0.78}Mn_{0.22}$, $Ni_{0.79}Mn_{0.21}$, amorphous $Fe_{0.98}Zr_{0.08}$ [45] and Heusler alloys $Ni_{50}Mn_{35}In_{14}Si_1$ [46], $Mn_4Fe(Ge_{3-x}Si_x)$ [47], $Ni_{50}(Mn_{50-x}Sn_x)$ (x = 13,14) [48], Hence, the same analysis has been carried out to find the magnetism model theory. Moreover, Co addition in NiMnGa alloys provides an opportunity to control the Curie temperature of transforming phases (FM-Austenite to AFM/PM-Martensite).

The purpose of this work is to show how the doping of Co effectively improves structure, electron scattering, T_C, MC and critical behavior. To the best of our knowledge, no experimental study of the critical phenomena is reported in literature for the Co substitution in $(Ni_{2.1-x}Co_x)Mn_{0.9}$ Ga (x = 0–0.2) based system. However, the effect of Co doping increases the ΔS_M, Curie and martensitic temperatures due to effective magnetic moment (Co) ions at Ni site of Ni-Mn-Ga system. Among all samples, the x = 0.12 composition shows conventional MC with maximum ΔS_M of −2.8 $Jkg^{-1}K^{-1}$ near T_M region. Austenite structures are stabilized by varying Co (0–0.2) substitution and lowering the structural transition temperature. Further, critical behavior of x = 0.12 composition has been also studied, in which second order nature of FM-PM transition exists during magnetization measurement.

2. Experimental details

Ingots of $(Ni_{2.1-x}Co_x)Mn_{0.9}$ Ga (x = 0, 0.04, 0.12 and 0.2) alloys are prepared by melting the high purity starting elements (99.9% pure) in a vacuum arc melting furnace (procured from M/S. Vacuum Techniques Pvt. Ltd, Bangalore) under partial Argon atmosphere. The samples are re-melted four times to ensure homogeneity. These alloys are sealed and annealed under high vacuum at 1175 K for 24 h and then quenched. Elemental compositions are determined using scanning electron microscope (SEM, Leo 440*i*) attached with an X-ray energy dispersive spectroscope (EDS) setup. The structural analysis is carried out at RT using a Philips 3121 X-ray diffractometer with Cu-K_α radiation. The transport studies are carried out between 300–4 K using Closed Cycle Refrigerator with Variable Temperature Insert (CCR-VTI) from M/S.Cryo Industries of America, USA. The magnetization measurements are performed by means of a physical property measurement system (PPMS-9T) using vibrating sample magnetometer (VSM) module (Quantum Design, USA). The data are collected for all samples during field cooling and warming modes and isothermal magnetization data are measured at different temperatures around T_M and T_C regions. The transition temperatures such as T_C and T_M are obtained from deep point of corresponding derivative plots.

3. Results and discussion

The powder X-ray diffraction patterns are recorded at RT in $(Ni_{2.1-x}Co_x)Mn_{0.9}$ Ga (x = 0, 0.04, 0.12 and 0.2) which are shown in Fig. 1. The Bragg peaks for all samples indexed with cubic cell $L2_1$ structure with lattice parameter a = 5.8729, 5.8691, 5.8637 and 5.8618 Å for x = 0, 0.04, 0.12 and 0.2 samples, respectively. Only x = 0.12 composition has mixed martensite and austensite (M + A) phase at room temperature although the martensite transition temperature is below room temperature (147 K, Fig. 2a). The martensite phase at room temperature is stabilized due to the residual strains generated *via* grinding the ingot into powder. [49,50]. However, x = 0, 0.04 and 0.20 samples are retained in austensite phase at room temperature.

Fig. 2(a) shows the temperature dependent resistivity $\rho(T)$ curves for $(Ni_{2.1-x}Co_x)Mn_{0.9}$ Ga (x = 0–0.2) alloys. The small hump in resistivity is observed around 147 K and 165 K for x = 0.12 and 0.2 respectively which shows clear indication of martensite transition (T_M). The resistivity of all samples decreased with decreasing temperature. In general, resistivity of Heusler alloys can be influenced by electron-electron, electron-phonon and electron-magnon scattering mechanisms. However, the electron-phonon scattering contribution is relatively small in Heulser alloys at low