Structural, Thermal and Magnetic Properties of Ga Excess Ni-Mn-Ga

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Abstract. The martensitic transition and the ferro- to paramagnetic transition have been studied in a series of Ga excess Ni-Mn-Ga specimens \[\text{Ni}_{2-x}\text{MnGa}_{1+x} (0.4 \leq x \leq 0.9)\] by differential scanning calorimetry and magnetization measurements. The martensitic transition exhibits a hysteresis whose width is similar to Ni\(_2\)MnGa, indicating that the transition is thermoelastic. The latent heat of transformation is comparable with other Ni-Mn-Ga alloys. A substantial increase in the martensitic transition temperature is observed due to Ga doping. Interestingly, the x-ray diffraction pattern of all the compositions studied show a modulated martensitic structure in the martensitic phase.

Introduction

Ferromagnetic shape memory alloy (FSMA) Ni\(_2\)MnGa has a potential for practical applications due to its large magnetic field induced strain (MFIS) [1]. Ni\(_2\)MnGa shows ferromagnetic as well as structural transition from high temperature cubic austenitic phase to low temperature martensitic phase. The modulation observed in the crystal structure of Ni-Mn-Ga in the martensitic phase influences the MFIS, since MFIS has been observed only for the modulated structures [2]. Largest MFIS of 10% at field about 1 Tesla has been reported for Ni\(_{1.95}\)Mn\(_{1.19}\)Ga\(_{0.86}\) that exhibits seven layer modulated structure in the martensitic phase [3]. However, the low structural and magnetic transition temperatures and brittleness of Ni\(_2\)MnGa are shortcomings for its practical high temperature applications. Thus, in last few years a considerable amount of work has been performed to overcome these problems. For example, off-stoichiometric Ni-Mn-Ga and different other ferromagnetic shape memory alloys like Fe-Pt, Fe-Pd, Co-Ni-Al, Mn-Ni-In have been investigated [4-9]. It has been reported that addition of Fe in place of Mn in Ni-Mn-Ga improves the ductility of the alloy [10] and MFIS of 5.5% was obtained [11]. Small MFIS of 0.17% has been reported for Ni-Mn-Al and its martensitic transition temperature is below room temperature [12]. Structural and magnetic properties of non-stoichiometric Ni-Mn-In and Ni-Mn-Sn have been studied [13]. However, these alloys have not turned out to be viable alternatives for Ni-Mn-Ga. Therefore, it is still an important challenge to search for materials having properties that are better than Ni-Mn-Ga. Recently, we have proposed by total energy calculations based on density functional theory, differential scanning calorimetry and x-ray diffraction that Ga\(_2\)MnNi could possibly exhibit ferromagnetic shape memory effect with highest \(T_M\) in Ni-Mn-Ni series [14]. The importance of Ga in making Ni\(_2\)MnGa a FSMA is clear from the fact that related stoichiometric alloys such as Ni\(_2\)MnAl, Ni\(_2\)MnIn and Ni\(_2\)MnSn do not exhibit martensitic transition. So, here we report a detailed study of Ga excess Ni-Mn-Ga compositions \[\text{Ni}_{2-x}\text{MnGa}_{1+x} (0.4 \leq x \leq 0.9)\] to study the evolution of physical properties (for example the crystal structure, the magnetic properties and the transition temperatures) from Ni\(_2\)MnGa to Ga\(_2\)MnNi [14].
Experimental methods
The polycrystalline ingots of Ni$_{2-x}$MnGa$_{1+x}$ (0.4 ≤ x ≤ 0.9) have been prepared by melting appropriate quantities of Ni, Mn and Ga with 99.99% purity in an arc furnace under inert argon atmosphere. The ingots were subsequently annealed at 873 K for 12 days and at 723 K for 1 day for homogenization and then slowly cooled down to room temperature [13]. Energy dispersive analysis of x-rays has been used to determine the composition. The powder XRD data at room temperature were obtained with Cu Kα radiation using a Rigaku X-ray diffractometer (RUH3R). The data were recorded at the rate of 2°/min with step size of 0.02°. For XRD, pieces cut from the ingot were manually ground to powder. Differential scanning calorimetry (DSC) measurements were performed using Model 2910 from TA Instruments. Magnetization was performed using vibrating sample magnetometers from Oxford Instruments and Lake Shore Cryotronics.

Fig. 1: Differential scanning calorimetry showing the martensitic transition in Ni$_{2-x}$MnGa$_{1+x}$ for (a) x= 0.9 and (b) x= 0.7 (c) x= 0.43. Arrows indicate the heating and cooling directions.

Results and discussion
Differential scanning calorimetry measurements on Ni$_{2-x}$MnGa$_{1+x}$ (0.4 ≤ x ≤ 0.9) clearly show the first order nature of the transition and the four temperatures [martensitic start (T$_{M}$), martensitic finish (T$_{Mf}$), austenitic start (T$_{As}$), and austenitic finish (T$_{Af}$)]. For Ni$_{1.02}$Mn$_{1.08}$Ga$_{1.9}$ (x= 0.9), the transition temperatures T$_{M}$, T$_{Mf}$, T$_{As}$ and T$_{Af}$ are 780, 732, 789, and 811, respectively. For Ni$_{1.3}$MnGa$_{1.7}$ (x= 0.7) these temperatures are 838, 781, 855, and 900 K, respectively. For Ni$_{1.3}$Mn$_{1.07}$Ga$_{1.43}$, the T$_{As}$ and T$_{Af}$ are 333 and 351 K, respectively. The width of the hysteresis, defined as the difference between (T$_{As}$+T$_{Af}$)/2 and (T$_{M}$+T$_{Mf}$)/2 [5], are 68 and 44 K for x= 0.7 and 0.9, respectively. The relatively small width of hysteresis show that the transition is thermoelastic in nature. The latent heat of transformation turns out to be 0.15, 1.5 and 2.35 kJ/mole, and for x= 0.43, 0.7 and 0.9, respectively. Thus, with increase in Ga content, the latent heat increases.

The room temperature powder XRD patterns of Ni$_{2-x}$MnGa$_{1+x}$ (0.43 ≤ x ≤ 0.9) show that all the samples are martensitic. The XRD data have been analyzed by Lebail fitting procedure [16]. We find that Ni$_{1.02}$Mn$_{1.08}$Ga$_{1.9}$ shows a monoclinic structure with lattice parameters a= 4.31 Å, b= 29.51 Å, c= 5.55Å, β= 90.49°. Ni$_{1.3}$Mn Ga$_{1.7}$ also exhibits a monoclinic structure with lattice parameters a= 4.25 Å, b= 29.56 Å, c= 5.57 Å, β= 90.94°. Thus, for both Ni$_{1.02}$Mn$_{1.08}$Ga$_{1.9}$ and Ni$_{1.3}$Mn Ga$_{1.7}$ b~ 7a, which is indicative of the occurrence of 7M modulation. In contrast, Ni$_{1.5}$Mn$_{1.07}$Ga$_{1.43}$ shows...
a monoclinic structure where $b \approx 5a$ that is indicative of 5M modulation with lattice parameters $a = 4.18$ Å, $b = 21.06$ Å, $c = 5.57$ Å, $\beta = 90.51^\circ$. The 5M and 7M modulation have been also observed in Ni and Mn excess Ni-Mn-Ga [17-20]. The XRD results thus show that all samples $\text{Ni}_{2-x}\text{MnGa}_{1+x}$ ($0.43 \leq x \leq 0.9$) studied here have monoclinic modulated structure in the martensitic phase. Existence of modulation makes the Ga excess Ni-Mn-Ga a good candidate to show magnetic field induced strain [2, 3] since it has been reported that modulated structures have lower twinning stress and hence are expected to exhibit twin boundary motion [21]. It has been reported in literature that the twinning stress is less if $\beta$ is close to $90^\circ$ [22]. Here for all samples, $\beta$ is indeed close to $90^\circ$ and thus the twinning stress is expected to be less.

![X-ray diffraction pattern](image)

**Fig. 2:** X-ray diffraction pattern (solid line) of $\text{Ni}_{2-x}\text{MnGa}_{1+x}$ ($0.43 \leq x \leq 0.9$) for different $x$ at room temperature. (a) $x = 0.9$ and (b) $x = 0.7$ (c) $x = 0.43$. The calculated profiles obtained by Lebail refinement are shown by dashed lines.

Fig. 3 shows the magnetization ($M$) as a function of temperature and the transition temperatures as a function of composition. The magnetization data have been taken in a low applied field of 10 Gauss. Expectedly, all the $M (T)$ curves show sharp decrease in magnetization at $T_C$. For $x = 0.9$ and $x = 0.7$ samples, the magnetic transition takes place in the martensitic state and for $x = 0.43$ the magnetic and structural transition temperatures almost coincide. $T_C$ is found to decrease with increasing $x$ in $\text{Ni}_{2-x}\text{MnGa}_{1+x}$. For $\text{Ni}_2\text{MnGa}$ ($x = 0$), $T_C$ is 378K and it decreases to 330K for
NiMn$_{1.08}$Ga$_{1.9}$. From Fig. 3(d), it is clear that $T_M$ and $T_C$ follow opposite trend, which is in agreement with previous studies done on Ni excess Ni-Mn-Ga where $T_C$ is found to decrease with increasing $T_M$ [5]. $T_M$ and $T_C$ almost merge for $x=0.43$, which might be an interesting composition for further study.

![Graphs showing $M$ vs $T$ and variation of $T_M$ and $T_C$ for Ni$_{2-x}$MnGa$_{1+x}$ (0.4≤ $x$ ≤ 0.9).](image)

**Fig. 3:** $M$ vs $T$ and variation of $T_M$ and $T_C$ for Ni$_{2-x}$MnGa$_{1+x}$ (0.4≤ $x$ ≤ 0.9). (a) $x=0.43$ (b) 0.7 (c) 0.9 (d) $T_M$ and $T_C$ as a function of $x$.

**Summary**

The crystal structure at room temperature, the martensitic and magnetic transition temperatures have been studied for Ni$_{2-x}$MnGa$_{1+x}$ (0.4≤ $x$ ≤ 0.9) as a function of $x$. From the Lebail fitting of x-ray diffraction, we find that Ni$_{1.02}$Mn$_{1.08}$Ga$_{1.9}$ and Ni$_{1.3}$Mn Ga$_{1.7}$ show 7M modulated monoclinic structure, while Ni$_{1.5}$Mn$_{1.07}$Ga$_{1.43}$ shows 5M monoclinic modulation at room temperature. DSC shows that $T_M$ is higher for these samples compared to Ni and Mn excess Ni-Mn-Ga. Magnetization shows that $T_C$ decreases with increasing $x$.

**References**