Intermartensitic Transitions in Ni-Mn-Ga

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Abstract

Different phases like five- and seven-layered modulations (referred to as 5M and 7M) and the non-modulated (NM) are observed during the martensite phase formation in the Ni-Mn-Ga system A hysteresis in transport properties during the warming and cooling cycles of measurements is observed and reflect the influence of these modulations on the Fermi surface of such alloys. In this study we have carried out XRD studies on samples with a partial substitution of Ni for Mn in $Ni_{2+x}Mn_{1-x}Ga$ alloys with the composition range x = 0 - 0.19 and the preliminary results are presented here.

INTRODUCTION

Order-disorder transformations have been studied for more than a century and are essentially important from the experimental and theoretical aspect. One such solid-state phase transformation is the diffusionless first order transition from a high temperature austenitic phase to a lower symmetry martensitic phase at low temperatures that plays a key role in the shape memory alloys. The Ni-Mn-Ga system undergoes such thermo-elastic martensite transformations upon cooling from a cubic $L2_1$ Heusler structure to a tetragonal phase. The transformation can be described as a simple contraction along the [100] directions of the cubic phase. Interestingly, Ni-Mn-Ga systems are also ferromagnetic and undergo a second order Curie transition. In Ni_2MnGa the martensitic transformation occurs at $T_M \approx 220K$ while the ferromagnetic Curie transition takes places at $T_C \approx 360K$ [1].

The structural crossover from an austenite to a martensite phase is preceded by pre-martensitic transformation, followed by the intermartensitic five- to seven– layer (5M to 7M) crystallographic modulations. The influence of these transformations is clearly seen on the transport properties like resistivity and thermopower of these alloys where a hysteresis is observed as a function of temperature and implies a clear manifestation of these transformation on the Fermi surface [2]. The aim of the present investigation was to understand these multiphase crystallographic modulations present in Ni-Mn-Ga Heusler alloys by X-ray diffraction measurements.

EXPERIMENTAL

Polycrystalline beads of $Ni_{2+x}Mn_{1-x}Ga$ with x = 0, 0.05, 0.1, 0.13, 0.16 and 0.19 where prepared by arc-melting the constituent elements of 4N purity in argon atmosphere. These were sealed in quartz ampoule with a vacuum of 10^{-6} Torr and annealed at 1000K for 72 hours. The resulting samples were homogeneous and single phase. X-ray diffraction patterns were recorded on the fine powder obtained from the original bead. Rigaku D-MAX IIC diffractometer with Cu K_α radiation in the 2θ range 20° – 100° at a scan speed of 2°/min and a sampling of 0.02° was employed. The region between 35° – 55° was scanned at a slower speed of 0.5°/min.

RESULTS AND DISCUSSION

In $Ni_{2+x}Mn_{1-x}Ga$, with increasing Ni concentration it is seen that T_M increases while the T_C decreases until they merge at x = 0.19. A plot of T_C and T_M versus excess Ni content (x) is presented in Fig. 1. Also, the hysteresis seen in the transport properties extends from above T_M to well below T_M and range of hysteresis differs for different samples. Origin of such hysteresis above T_M is claimed to be due to the pre-martensitic transformation whereas that below T_M is due to the intermartensitic modulations. Earlier structural studies on Ni-Mn-Ga have established a relationship between a ratio of lattice parameters (c/a) and the average number of electrons per atom (e/a), wherein a change from c/a < 1 to c/a >1 takes place as e/a increases. Lanska et al investigated the samples with e/a ranging from 7.6 to 7.82 and have pointed out that the change from c/a <1 to c/a > 1 takes place within a range of e/a from 7.61 to 7.71. They also show that samples with c/a >1 are present in NM phase, while, those with c/a <1 are in 5M/7M phases [3].

In the present study X-ray diffraction technique was employed to investigate the e/a range of 7.5 to 7.64. The room temperature X-ray diffraction patterns of $Ni_{2+x}Mn_{1-x}Ga$ for different x show an evolution of structure from premartensitic region to intermartensitic region. Fig. 2 shows the XRD patterns of x = 2.0 and 2.19 samples. It can be seen that while the diffraction pattern of Ni_2MnGa confirms with $L2_1$ structure of Heusler alloy, that of $Ni_{2.19}Mn_{0.81}Ga$ can be indexed to a orthorhombic structure with a = b = 5.416 Å and c = 6.523Å (c/a = 1.2). This value of c/a lies in the region for which transition from modulated martensitic structure to non-modulated martensitic structure takes place.

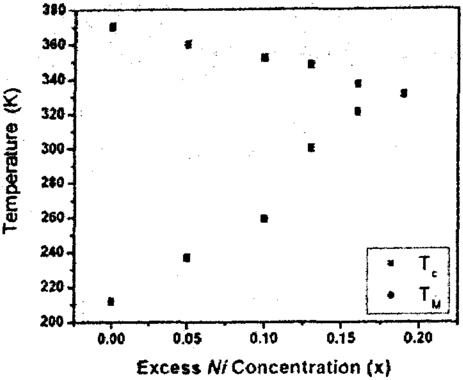

Fig. 1. Plot of T_C and T_M versus excess Ni content

In order to closely observe the transition from premartensitic-modulated martensitic to NM structure, the diffraction pattern in the angular range of 35° to 55° are presented in Fig. 3. It can be clearly seen that with increasing Ni concentration the modulations become more and more pronounced. The appreciating fact is the broadened peak in the pristine Ni_2MnGa for which the T_M lies almost 80K below room temperature, yet the pre-martensitic transformations are quite dominant. These pre-martensitic transformations grow stronger with increasing x. A clear signature of this is the observation of a shoulder on the left side of (220) cubic reflection that grows in intensity with increasing x. Such a pattern can be identified with a modulated structure with $c/a < 1$. At $x = 0.13$ there is a sudden rise in intensity of the shoulder peak leading to a role-reversal between the main peak and shoulder peak as described for $x = 0.1$. Further a new peak also emerges at $2\theta = 47°$ and can be described as a modulated structure with $c/a > 1$. It is noteworthy that such a transition occurs for that x where T_M changes from < 300 K to ≥ 300K. Such modulations are completely absent for $x = 0.19$. The resistivity of this sample also shows an end of thermal hysteresis just above this temperature. Such a trend indicates as if the modulations, which begin in the premartensitic region well above T_M, continue across the martensitic transition.

Inelastic neutron scattering measurements [4] have shown that premartensitic transition in Ni_2MnGa is due to electron phonon coupling which softens the TA_2 phonon mode. This softening extends to well above T_M and infact even above T_C. The thermal hysteresis seen in transport properties therefore could be explained to be due to nesting of Fermi surface wherein the conduction electrons condense and gives rise to different behavior of transport properties during heating and cooling cycles. The hysteresis in intermartensitic transformations could be explained to be of similar origin with differently oriented nesting vector due to varying e/a ratio.

In conclusion, it is seen that the origin of the structural modulations in the Ni-Mn-Ga system observed with increasing Ni concentration is the electron-phonon coupling which extends from well above T_M to well below T_M.

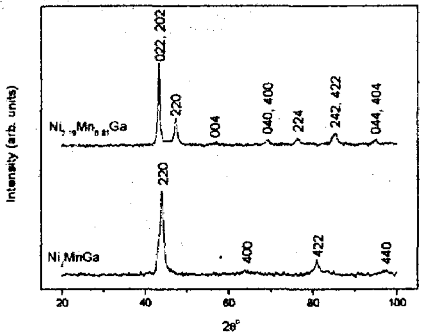

Fig. 2. XRD Plots of Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$

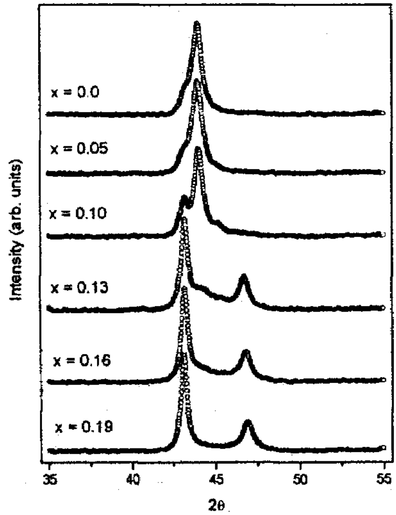

Fig. 3. XRD Plots of $Ni_{2+x}Mn_{1-x}Ga$ in limited 2θ range

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