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Neutron diffraction study of the martensitic transformation and chemical order in Heusler alloy $Ni_{1.91}Mn_{1.29}Ga_{0.8}$

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Abstract

Heusler alloys of Ni-Mn-Ga compositions demonstrate ferromagnetic shape memory effect in the martensitic state. The transformation temperature and the chemical order depend strongly on the composition. In the current work, the structure and chemical order of the martensitic phase of $Ni_{1.91}Mn_{1.29}Ga_{0.8}$ were studied using neutron diffraction; the diffraction pattern was refined using the FullProf software. It was determined that the structural transition occurs around 330 K. At room temperature, 300 K, which is below the martensite transformation temperature, all the Bragg reflections can be described by a monoclinic lattice with a symmetry of space group P 1 2/m 1 and lattice constants of a = 4.23047(7) [Å], b = 5.58333(6) [Å], c = 21.0179(2) [Å], beta = 90.328(1). The chemical order is of critical importance in these alloys, and it was previously studied at 363 K. Analysis of the neutron diffraction in the monoclinic phase shows that the chemical order is maintained during the martensitic transformation.

Selection and Peer-review under responsibility of the chairs of the International Conference on Martensitic Transformations 2014.

Keywords: Chemical Order, Ni-Mn-Ga alloy; Magnetic Shape Memory; Neutron Diffraction; Rietveld Method; Structure Refinement

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1. Introduction

Since the discovery of reversible giant magnetic-field-induced strains in Ni2MnGa single crystals 1996 [1], there has been a continually strong interest in this remarkable phenomenon and new applications for these important materials, in medical, aerospace, and automotive are constantly proposed and developed [2]. Their properties and performance depend on their crystalline structure, chemical and magnetic order, modulation and phase transformation.

Stoichiometric Heusler alloys are ferromagnetic (FM) in the high-temperature austenitic phase caused by the Rudermann-Kittel-Kasuya-Yoshida (RKKY) exchange interactions between the manganese atoms mediated by the conduction electrons. When deviating from stoichiometry, some structural disorder results that may result in magnetic exchange interactions between manganese and other atoms. These magnetic interactions greatly depend on the composition and the resulting local disorder [3]. When there is an excess of Mn, there is an additional effect of Ni 3d – Mn 3d hybridization in the low-temperature martensitic phase [3]. In a recent work [4] Ni-Mn-Ga alloys with excess Mn were studied, and the effect of the interaction between Mn atoms occupying the different sites (Mn-, Ni- and Ga-sites) was analyzed and a new model for the exchange interaction proposed. Hence, understanding the chemical order in manganese-rich Ni-Mn-Ga is imperative.

The goal of the present work was the study of the martensitic transformation and chemical order in a Mn-rich Heusler alloy $Ni_{1.91}Mn_{1.29}Ga_{0.8}$ using neutron diffraction.

2. Experimental Description

The samples were prepared by a modified Bridgman method, and homogenized at 1273 K, followed by annealing at 1073 K. One crystal was then crushed into powder with particle size in the range of 56-105 μm. The powder was heat treated in evacuated quartz ampoule for 2 h at 1098 K followed by air cooling. The structure was determined to have a martensite-start temperature (Ms) of 325.3 K. The other crystal was tested as a single crystal.

High-resolution neutron powder diffraction data were collected using the HB2A diffractometer at the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory. An incident neutron beam with wavelength of λ = 1.538 Å, was selected from the (115) plane of a Ge monochromator at a take-off angle of 90°. Data were collected at a broad temperature range up to 363K, followed by cooling.

Single crystal neutron diffraction data were collected at the HB-3A four-circle diffractometer at HFIR at Oak Ridge National Laboratory. Neutron wavelength of λ = 1.542 Å was used with a bent perfect Si-220 monochromator [5]. The data were collected at three selected temperatures of 300 K, 340 K, and 400 K. The purpose of the single crystal measurements was to complement and verify the powder diffraction results.

3. Results and Discussion

The diffraction data were analysed using the Rietveld refinement method with the Fullprof program [6]. Previous results we reported on the chemical order in the Heusler L21 phase indicated the following stoichiometry: $Ni_{1.91}Mn_{1.29}Ga_{0.8}$ (in atomic percent: Ni48-Mn32-Ga20). The results of site-occupancy refinement showed very little mixing on the 4a and 8c sites; however, site 4b ("Ga" site) exhibited a substantial amount of Mn [7].

At room temperature, this alloy is fully martensitic. The structure at this temperature can be described as monoclinic with space group P 1 2/m 1. This is a substantially larger unit cell, in which each atomic species occupies six non-equivalent sites. Fig. 1 depicts the fit of the 300 K data. The site occupancies in the martensite were refined and similar composition was obtained as previously reported for the austenitic phase [7]. Table 1 summarizes the structural results.

From previous magnetic measurements on these samples, it is known that the martensitic phase in this alloy is ferromagnetic [7]. So a ferromagnetic model, with the moments sitting on the Mn sites, was considered. The refined magnitude of the magnetic moment was $2.96(7)\mu_B$ (Rmag =6.3).

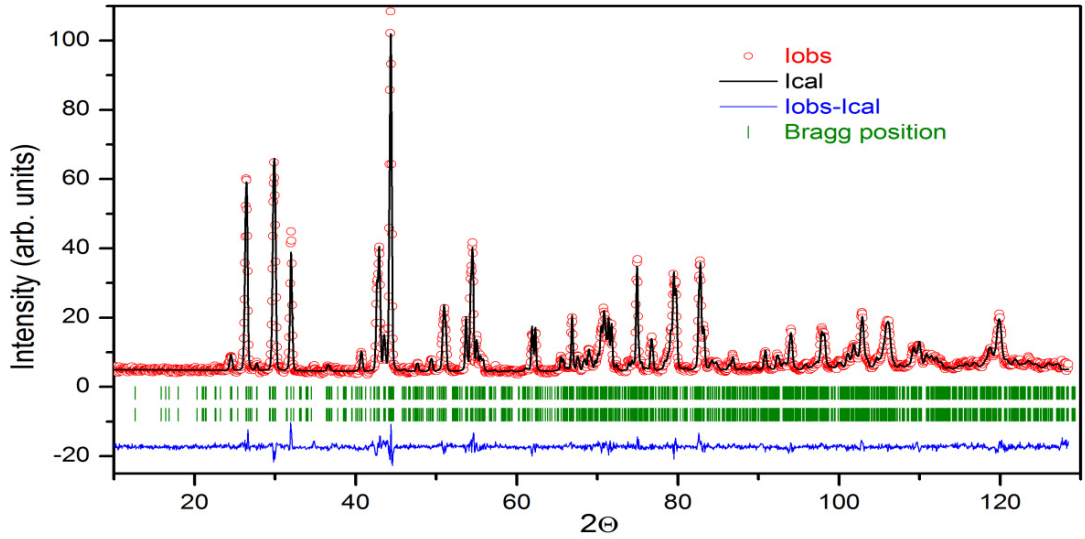

Fig. 1. Rietveld Refinement of the 300 K data, using the P12/m1 structural model.

From diffraction data collected over a broad temperature range, it can be concluded that the structural transition occurs at ~330 K. A contour plot of the change in Bragg intensities for various temperatures is displayed in Fig. 2.

Fig. 3 portrays the temperature dependence of two Bragg peaks representing the two phases, monoclinic $(-1\ 0\ 5)_M$ and cubic $(2\ 0\ 0)_C$, for the warming portions of the experiment. It is essentially a more quantitative version of what is shown in Fig 2. It can be seen that the martensitic transition temperature occurs over a temperature range of about 20K around 330K, where the two phases coexist. This plot does not include the PM to FM transition, as this occurs above 365 K, i.e., above the highest temperature used in the powder neutron experiment.

Table 1. Structural details for monoclinic phase at 300 K.

Phase: Monoclinic (P 1 2/m 1); a=4.22819 (8) Å, b=5.58013(7) Å, c= 21.0056(3) Å, beta = 90.328(1) [°]

Atom	Wyckoff	x	y	z	site occ.
Ni1/Mn	2j	0.5	0.248(5)	0	0.88/0.12(2)
Ni2/Mn	4o	0.078(2)	0.249(3)	0.1012(5)	0.98/0.02(2)
Ni3/Mn	4o	0.538(2)	0.251(3)	0.1990(6)	0.95/0.05(2)
Ni4/Mn	4o	0.965(3)	0.252(3)	0.2996(6)	0.98/0.02(3)
Ni5/Mn	4o	0.447(2)	0.249(3)	0.4003(6)	0.98/0.02(3)
Ni6/Mn	2k	0	0.250(4)	0.5	0.98/0.02(2)
Ga1/Mn	1b	0	0.5	0	1.00/0.00
Ga2/Mn	2m	0.567(6)	0	0.101(1)	0.87/0.13(4)
Ga3/Mn	2n	0.012(6)	0.5	0.200(1)	0.85/0.15(4)
Ga4/Mn	2m	0.449(7)	0	0.304(1)	0.77/0.23(4)
Ga5/Mn	2n	0.938(7)	0.5	0.398(2)	0.84/0.16(4)
Ga6/Mn	1g	0.5	0	0.5	0.65/0.35(4)
Mn1	1a	0	0	0	1
Mn2	2m	0.930(8)	0	0.403(1)	1
Mn3	2m	-0.005(8)	0	0.197(2)	1
Mn4	2n	0.573(8)	0.5	0.104(2)	1
Mn5	2n	0.459(8)	0.5	0.295(2)	1
Mn6	**1h**	**0.5**	**0.5**	**0.5**	**1**

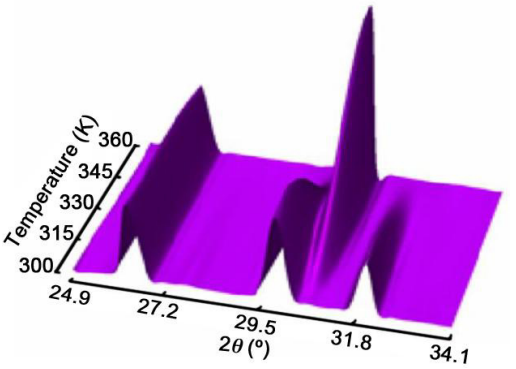

Fig. 2. Change of the scattering intensities with temperature, around the structural transformation (at about 330K).

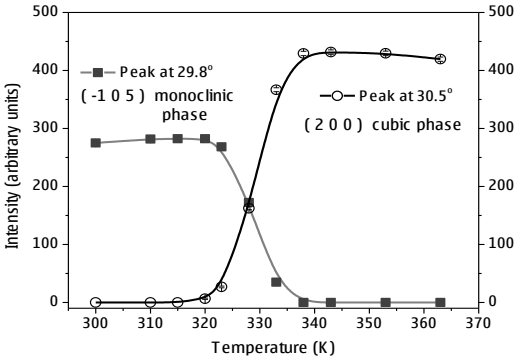

Fig. 3. Variation with the temperature of the Bragg intensities of two representative peaks of the cubic and monoclinic phases.

The change in the phase ratio, for the warming and cooling cycles, is shown in Fig. 4 As expected, a hysteresis is observed; when cooling, the transition temperature is ~315K, compared to ~330K in the warming portion of the experiment.

Single crystal diffraction data, were consistent with those found by powder diffraction. The structural transition was tracked by two reflections $(105)_m$ / $(020)_c$ and $(110)_m/(111)_c$ (Fig. 5). The structural transition from martensite (monoclinic P 12/m1) to austenite (cubic F m-3m) at higher temperatures occurs around 330 K (Fig. 5); the ferromagnetic transition, T_c, occurs ~ 380 K (Fig. 5b, loss of magnetic contribution).

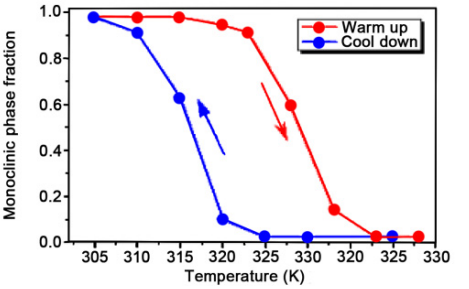

Fig. 4. Monoclinic (P12/m 1) phase fraction vs. temperature for the warming and cooling cycles.

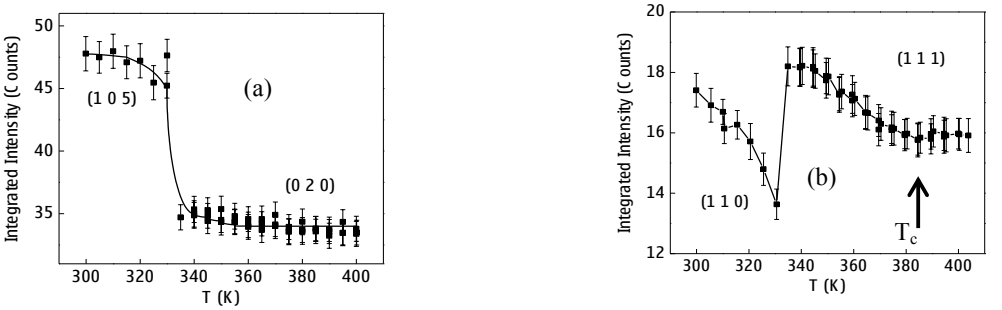

Fig. 5. Single crystal results; shown is the temperature dependence of the (105) and (110) peaks of the monoclinic (martensitic) phase, space group P 12/m1 and (020) and (111) peaks of the cubic phase, space group F m-3m above ~330 K. The increase in the integrated intensity of (111) shows the ferromagnetic transition at ~380 K (Fig. 5b).

4. Conclusions

The sample stoichiometry was found to be Ni 1.91Mn 1.29Ga 0.8. The order was mostly maintained. The Ni sites were 95% Ni and 5% Mn, the Ga sites were 78% Ga and 22% Mn, and the Mn sites were almost exclusively Mn (97%). These results concur with those obtained in [4] for Ni-Mn-Ga alloys with excess Mn, and lower-nickel compositions. The RT structure is monoclinic with P 1 2/m 1 space group; each atomic species occupies six non-equivalent positions. Lattice constants a=4.22819(8) Å, b=5.58013(7) Å, c=21.0056(3) Å, β= 90.328(1). The phase change to martensite occurs around 330 K with a hysteresis of ~ 15 K. Single crystal results agree with the powder data. As a conclusion, the cold work associated with crushing the crystal into powder did not alter the results.

Acknowledgements

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