Neutron Diffraction Study of the Martensitic Transformation of Ni$_{2.07}$Mn$_{0.93}$Ga Heusler Alloy

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Abstract: The martensitic transition featuring the ternary Heusler alloy Ni$_{2.09}$Mn$_{0.91}$Ga was investigated by neutron diffraction. Differential scanning calorimetry indicated that structural transition starts at 230 K on cooling with a significant increase in the martensitic transformation onset compared to the classical Ni$_2$MnGa. The low-temperature martensite presents the 5M type of modulated structure, and the structural analysis was performed by the application of the superspace approach. As already observed in Mn-rich modulated martensites, the periodical distortion corresponds to an incommensurate wave-like shift of the atomic layers. The symmetry of the modulated martensite at 220 K is orthorhombic with unit cell constants $a = 4.2172(3)$ Å, $b = 5.5482(2)$ Å, and $c = 4.1899(2)$ Å; space group Immm(00$\gamma$)s00; and modulation vector $q = \gamma c^* = 0.4226(5)c^*$. Considering the different neutron scattering lengths of the elements involved in this alloy, it was possible to ascertain that the chemical composition was Ni$_{2.07}$Mn$_{0.93}$Ga, close to the nominal formula. In order to characterize the martensitic transformation upon increasing the temperature, a series of neutron diffraction patterns was collected at different temperatures. The structural analysis indicated that the progressive change of the martensitic lattice is characterized by the exponential change of the $c/a$ parameter approaching the limit value $c/a = 1$ of the cubic austenite.

Keywords: Heusler alloys; martensitic transformation; neutron diffraction

1. Introduction

Ni-Mn-X with X = Ga, In, Sn, Sb Heusler alloys are considered the prototypical multifunctional material encompassing a huge magnetocaloric effect (MCE) [1], magnetic field giant induced strains (MFIS), magnetic shape memory effect, and interesting exchange bias phenomena [2–4]. Most of the stunning physical properties of this class of intermetallics are based on the martensitic phase transformation (MT) taking place by temperature change [5,6], application of mechanical loads [7,8], or induced by the application of an external magnetic field [3,4]. In Heusler alloys, the parent phase exhibits the L2$_1$ superstructure, and the martensitic transition is accompanied by a lattice distortion yielding tetragonal, orthorhombic, or monoclinic structures (see Figure 1) depending on the chemical composition [6,7]. In the case of Ni-Mn based alloys, it is frequently observed that the martensitic phases are featured by modulated structural distortions generally associated to five-layered or seven-layered supercells defined 5M or 7M, respectively [7,9]. In Ni$_2$MnGa, the martensitic phase stable below 200 K is characterized by an incommensurate modulated 5M-type crystal structure that was successfully solved within the crystallographic approach called superspace [9,10]. Indeed, the MCE is related to the drastic entropy change that can be induced by a magnetic field change during the martensitic transformation or eventually at the corresponding Curie temperature [11].
Ni$_{2.09}$Mn$_{0.98}$Ga Heusler alloy was undertaken by neutron diffraction experiments. It was found that, below 230 K, the martensitic phase displays an incommensurate 5M modulated crystal structure. The martensitic phase undergoes a magnetostructural first-order transition with a beneficial effect on the MCE outcome. Moreover, in such a Ni-rich alloy both the MT and Curie temperature merge in a magnetostuctural first-order transition with a beneficial effect on the MCE outcome. Besides compositions showing 0.15 $\leq x \leq$ 0.18, the compositional regimes based on $x < 0.1$ include valuable magnetic and MCE properties. Single crystals with Ni$_{2.04}$Mn$_{0.96}$Ga composition were investigated by T. Liang [17] for the giant strains induced by external magnetic field. Strain-temperature curves evidenced that the martensitic phase undergoes below 240 K on cooling. Moreover, it was demonstrated that off-stoichiometric Ni$_{2.08}$Mn$_{1.04}$Ga$_{0.88}$ alloy shows interesting magnetocaloric properties in polycrystalline ribbons [14]. Notably, in a Ni$_{2.09}$Mn$_{1.04}$Ga system, the compositions showing a moderate excess of Ni are still not completely explored, and structural studies of the martensitic transitions have not yet been reported. In this work, the structural investigation of the nominal Ni$_{2.09}$Mn$_{0.98}$Ga Heusler alloy was undertaken by neutron diffraction experiments. It was found that, below 230 K, the martensitic phase displays an incommensurate 5M modulated crystal structure. The structural refinement based on the neutron diffraction data was achieved by employing the model obtained for the Ni$_{2}$MnGa counterpart. Furthermore, the study of the structural transformation versus temperature points out that the progressive change of the martensitic lattice is closely related to geometrical constraints in agreement with the invariant plane strain requirements.

2. Materials and Methods

The sample with nominal composition Ni$_{2.09}$Mn$_{0.91}$Ga was obtained from high purity elements by arc melting and subsequent annealing in a quartz ampoule under Ar atmosphere and quenched in cold water. The annealing treatment was performed at 983 K for 72 h. Afterwards, the small ingots were ground in a mortar and successively annealed at 1073 K for 2 h in order to remove the defects induced by the grinding process. Powder X-ray diffraction measurement, performed with an X’TRA Thermo diffractometer (Thermo Fisher Scientific, Losanna, Switzerland) equipped with a CuK$\alpha$ source and a solid-state detector, indicated the presence of single-phase austenite (see Figure S1 in the Supplementary Information).
Differential scanning calorimetry (DSC) was carried out under nitrogen in the temperature range from room temperature to 200 K and then upon heating from 200 K to 350 K. The cooling and heating scans were performed with a rate of 10 K/min.

Neutron diffraction experiments were performed on the D2B beamline (ILL, Grenoble, France) at ILL (Institute Laue-Longevín, Grenoble, France) with a wavelength of 1.594 Å in the temperature range from 220 K to 350 K, and diffraction patterns were collected at selected temperatures. The low-temperature diffraction pattern (220 K) used to determine the crystal structure of the martensitic phase was recorded at a low scanning rate in order to assure the required statistics and a good peak/background ratio. The structural refinements were based on the Rietveld method [18] with the JANA2006 suite (Institute of Physics Department of Structure Analysis, Praha, Czech Republic).

3. Results and Discussion

The critical temperature of the martensitic transition for the prepared Ni-rich composition was determined by thermal analysis. The DSC measurement, illustrated in Figure 2a, manifested a pronounced transformation at 231 K on cooling, and the reverse martensitic transformation is observed at 244 K. The minute substitution of Mn with Ni in the stoichiometric Ni$_2$MnGa alloy induces an increase of 35 K at the MT onset. Indeed, the critical temperatures recorded by DSC scans are in agreement with those reported for a similar Ni-rich composition [17].

![Figure 2](image_url)

**Figure 2.** (a) DSC scan of the Ni$_{2.07}$Mn$_{0.93}$Ga sample (Ms = start of martensite, Mf = finish of martensite, As = start of austenite, Af = finish of austenite). (b) Neutron diffraction patterns in the 24–37° 2θ range collected at different temperatures.

A neutron diffraction experiment on the polycrystalline alloy with the nominal formula Ni$_{2.09}$Mn$_{0.91}$Ga was undertaken to establish the martensitic structure and the structural evolution of the martensitic transformation. In Figure 2b, a limited region of the neutron diffraction patterns collected at different increasing temperatures is shown. In accordance with the indication provided by DSC, the martensitic transition takes place beyond 240 K.

The phase diagram accounting for the $T_c$ and MT in the Ni$_{2.07}$Mn$_{0.93}$Ga system and reported by V.V. Kovaylo et al. [12] indicates that for a moderate excess of Ni, the paramagnetic state occurs above 350 K. Therefore, a neutron diffraction collection was performed at 350 K above $T_c$ in order to suppress the magnetic contribution to the scattering and determine the chemical composition of the austenitic phase. Neutron diffraction data are particularly suited for the study of the chemical order in the Heusler lattice. The neutron scattering lengths are not Z-dependent as in the case of X-ray diffraction [19], and this allows the faithful determination of occupancy factors for each crystallographic site from powder diffraction experiments. Neutron diffraction studies [20] dealing with the characterization of Heusler alloys have demonstrated that a Rietveld refinement is a suitable tool for the reliable determination of the stoichiometric composition of the pre-
pared alloys. In the case of this Ni-rich alloy, the structural refinement was based on the cubic structure showing the Fm-3m space group typical for the L2₁ superstructure. The crystal data obtained by the structural refinement are listed in the Tables S1 and S2 reported in SI. The structural model was conceived by considering an excess of Ni in the site of Mn; this assumption is in agreement with previous studies [15–17] that accounted for the predominant tendency of the Ni excess to occupy the Mn position. The chemical ratio of Ni and Mn located in the same site was constrained to maintaining the global occupancy of the site equivalent to 1. The best fitting (see Figure S2) was obtained with a cubic structure with the unit cell constant \( a = 5.83194(4) \) Å and occupancy factors of 0.93(5) and 0.07(5) for Mn and Ni, respectively, in the \( 2a \) site, yielding a chemical composition of the austenitic phase corresponding to Ni\(_{2.07}\)Mn\(_{0.93}\)Ga showing a slight deviation from the nominal formula. Since the martensitic transition is a diffusion-less process, the actual atomic distribution in the ordered lattice is preserved in the martensitic phase as well. The neutron diffraction pattern collected at 220 K shows a close analogy with that reported for the stoichiometric Ni\(_2\)MnGa compound [21]. As remarked before, below 200 K, the martensitic phase of Ni\(_2\)MnGa possesses an incommensurate modulated structure that was successfully solved with the application of the superspace approach [22]. The superspace approach has been recurrently employed to analyze the 5M and 7M modulated structures of martensites in Ni-Mn-based Heusler alloys [9,10,23–25]. In agreement with the crystallographic representation of these complex structures [21], the diffraction peaks are divided into two groups: the main reflections are related to the basic body-centered martensitic lattice depicted in Figure 1b, and the weak peaks called satellites are associated with the modulation vector \( \mathbf{q} = \alpha \mathbf{a}^* + \beta \mathbf{b}^* + \gamma \mathbf{c}^* \) connected to the incommensurate distortion of the fundamental crystal structure. To perform the Rietveld refinement of the neutron diffraction pattern collected at 220 K, the orthorhombic model derived for 5M modulated martensite in Ni\(_2\)MnGa Heusler compound [9,10] was adopted. The basic martensitic structure (see Figure 1) originated by the Bain distortion of the austenitic L2₁ lattice is characterized by the body-centered Immm symmetry.

The (3+1)-dimensional structure belongs to the Immm(00γ)s00 superspace group and the modulated atomic positions of Ni Mn and Ga are defined by a wave-like shape expressed by a sinusoidal function:

\[
u^j (x_4) = A_1^j \sin(2\pi n x_4)
\]  

that is based on the \( x_4 \) superspace coordinate for \( j \)-th atomic site and the \( n \) index representing the order of the Fourier series [21]. Further details of the superspace approach are illustrated in the Supplementary Information. Therefore, the refinement of the amplitudes \( A_1^j \) allows to find the incommensurate modulated displacing of the atomic positions. Main reflections and satellites are used in the Rietveld refinement and convergence is achieved for the values summarized in Tables S3 and S4. The refined modulation vector \( \mathbf{q} = \gamma \mathbf{c}^* \) (\( \alpha \) and \( \beta \) variables assume zero value for symmetry) exhibits a deviation from the commensurate value of 0.4 \( c^* = 2/5 \) \( c^* \); indeed, in analogy with what was already found for the stoichiometric Ni\(_2\)MnGa [9], this martensite can be regarded as incommensurate modulated 5M having \( q = 0.4226 \) \( c^* = 2/5(1 + \delta) c^* \) where \( \delta = 0.023 \) defines the aperiodicity of the system. Figure 3a represents the wave-like shift of the atomic layers stacked along the \( c \) axis where the atomic coordinates are extrapolated by assuming an ideal \( q = 2/5 c^* \) commensurate condition. In Figure 3b, the incommensurate deviation from the fundamental positions in the basic lattice is depicted. For all three atomic sites, the amplitudes A1x assume rather similar values, indicating that the systematic shift is damped to the 001 planes. Figure 3c reports the Rietveld plot of the structural refinement with agreement factors \( R_p = 6.45\% \) and \( R_{wp} = 9.23\% \).
constant along the c axis. From 220 K to 240 K, the modulated martensite manifests a slight change of the unit cell parameters as indicated in Figure 4a. The growth of the austenite phase linearly increments its relative amount as the temperature rises. Beyond 240 K, the crystal lattice undergoes a change of the (3+1)-dimensional model. The structural evolution of the martensitic phase across the structural transformation is monitored by collecting neutron diffraction patterns at selected temperatures from 220 K to 250 K. The values associated with each temperature were determined by changing the labelling of the crystallographic axes from abc to acb (with reference to the crystal data reported in Table S3; in this new set the martensitic lattice has the dimensions \( a_m = 4.2167 \, \text{Å}, \quad b_m = 4.1870 \, \text{Å}, \quad c_m = 5.5484 \, \text{Å}, \quad \alpha = \beta = \gamma = 90^{\circ} \)) in order to assign the shorter unit cell constant along the c axis. From 220 K to 240 K, the modulated martensite manifests a slight change of the unit cell parameters as indicated in Figure 4a. The growth of the austenite takes place at around 240 K, and as illustrated in the inset of Figure 4a, this phase linearly increments its relative amount as the temperature rises. Beyond 240 K, the crystal lattice of the martensite displays a progressive change with a marked elongation of the shorter axis. By increasing the temperature, the parameter of the modulation vector shows a decrement of its value toward the 0.4 condition (see Figure 4b) equivalent to the commensurate variant of the 5M martensite [9]. This trend was observed for Mn-rich Ni-Mn-Ga martensitic 5M modulated structures [9,23], and it is a clear indication that the wave-like modulation is dominated by the phonon softening of TA2 modes as remarked by Zheludev et al. [28]. The evolution of the tetragonality parameters is depicted in Figure 4c against the temperature change. The tetragonality is calculated considering a pseudo-tetragonal lattice with \( a = \sqrt{2}t_m \) and \( b = \sqrt{2}b_m \). Indeed, upon heating, the martensite

Figure 3. (a) View of the incommensurate modulated structure of the Ni\(_{2.07}\)Mn\(_{0.93}\)Ga martensitic phase. (b) Sinusoidal displacement of the atomic positions obtained by the Rietveld refinement of the (3+1)-dimensional model. The \( t \) parameter is related to the \( x_4 \) coordinate. (c) Rietveld plot of the structural refinement for the modulated martensite at 220 K. The magnetic characterizations involving Ni\(_{2.07}\)Mn\(_{0.93}\)Ga alloys with a slight excess of Ni revealed ferromagnetism in the low temperature martensitic phase [12]. Therefore, the structural refinement was carried out considering a ferromagnetic alignment of the spins along the b axis of the orthorhombic martensitic lattice as illustrated in Figure S3. The structural refinement returns a magnetic moment located on the Mn site of 2.86(6) \( \mu_B \) for the modulated martensite at 220 K. The decrement of the magnetic moment if compared to that reported for Mn in the classical Ni\(_2\)MnGa [26] is in agreement with magnetic measurements described in previous publications [12,27].

This effect regards the dilution of the Mn atoms distributed in the Heusler sub-lattice with Ni atoms that bring a small, localized moment (0.33 \( \mu_B \) approximately [26]). The magnetic characterizations involving Ni\(^{2+}\)Mn\(_{1-x}\)Ga alloys with a slight excess of Ni revealed ferromagnetism in the low temperature martensitic phase [12]. Therefore, the structural refinement was carried out considering a ferromagnetic alignment of the spins along the b axis of the orthorhombic martensitic lattice as illustrated in Figure S3. The structural refinement returns a magnetic moment located on the Mn site of 2.86(6) \( \mu_B \) for the modulated martensite at 220 K. The decrement of the magnetic moment if compared to that reported for Mn in the classical Ni\(_2\)MnGa [26] is in agreement with magnetic measurements described in previous publications [12,27].
manifests a progressive rearrangement of the lattice dimensions to mitigate the Bain distortion. This behavior is observed below the MT temperature but is particularly evident with the beginning of austenite growth. This evidence confirms that, in agreement with the crystallographic theory of martensitic transformations [29], as long as the structural transition from martensite to austenite is ongoing, the two coexisting crystal structures are metrically correlated to comply with the invariant plane strain requirements. The structural constraint forcing the martensitic unit cell parameters to assume certain values can be also studied by the application of the co-factor approach between 235 and 255 K.

Figure 4. (a) Unit cell parameter change versus temperature. The \( a \) and \( b \) parameters are rescaled to the austenitic lattice. The grey region indicates the temperature range with coexistence of austenite and martensite. Inset: reciprocal amount of parent and product phase during the MT. (b) Temperature dependence of the \( \gamma \) variable of the modulation vector. (c) Tetragonality parameters \( c/a \), \( c/b \), and co-factor \( \lambda_2 \) against temperature.

The co-factor \( \lambda_2 \) was introduced by J.M. Ball and R.D. James [30,31] in order to evaluate the compatibility conditions of martensitic and austenitic lattice. A co-factor parameter \( \lambda_2 = 1 \) indicates zero elastic energy of the austenite/martensite interface, therefore implying a stress-free propagation of the phase boundaries during the MT process [30–34]. One of the implications of the condition \( \lambda_2 = 1 \) is the narrowing of the thermal hysteresis of the first-order martensitic transition. The temperature span of the direct and reverse martensitic transition is a detrimental aspect for the technological application of the MCE, and theoretical tools such as the co-factor method were adopted to predict a favorable compositional chemistry to control the thermal drift. Further, the co-factor was applied to the Ni-Mn-Ga Heusler alloy to evaluate the lattice compatibility between modulated 7M martensites and the corresponding parent phase [35]. In the case of Ni\(_{2.07}\)Mn\(_{0.93}\)Ga the co-factor is calculated to provide additional information on the reciprocal correlation of the martensitic unit cell parameters ruled by the invariant plane strain conditions. The matrix selected for the co-factor extrapolation and the crystallographic assumptions used for this approach are summarized in the Supplementary Information. As indicated in Figure 4c, from 240 to 250 K, the \( \lambda_2 \) parameter moves from 0.8 to 1.01, indicating a linear dependence with the temperature. Interestingly, the co-factor approaches the ideal value when the austenite exceeds 80% in weight.

4. Conclusions

The actual structural study brings new insights into the crystal structure of the martensitic phase characterizing Ni\(_{2+\delta}\)Mn\(_{1-\delta}\)Ga compositions with \( x < 1 \). The crystal structure of the martensitic phase Ni\(_{2.07}\)Mn\(_{0.93}\)Ga was solved by using neutron diffraction data. At 220 K this phase displays an incommensurate modulated 5M structure with a modulation vector closely related to the Ni\(_2\)MnGa stoichiometric compound. The structural analysis of neutron diffraction patterns collected at different temperatures upon heating was used...
to study the progressive mitigation of the classical Bain distortion of the martensite. As expected, the parameters $c/a$ and $c/b$ tend to assume higher values as the temperature increases, indicating the progressive restoring of the cubic symmetry. The co-factor parameter, calculated in the temperature range of the hysteresis of the transformation, highlights that the maximal lattice compatibility between austenite and martensite is reached when the volume of the parent phase is predominant. Likewise, this approach suggests that the mechanism ruling the diffusion-less transformation from orthorhombic martensite to cubic austenite is apparently not influenced by the structural modulation.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/met11111749/s1, Figure S1: X-ray diffraction pattern of the polycrystalline Ni$_{2.07}$Mn$_{0.45}$Ga alloy, Figure S2: Rietveld plot based on neutron diffraction data for the austenitic phase at 350 K. Figure S3: Ferromagnetic orientation of the spins located on the Mn/Ni site of the orthorhombic body centered lattice. Table S1: Crystal data of austenitic phase at 350 K. Table S2: Atomic coordinates, occupancy factors and thermal parameters for the cubic austenite at 350 K. Table S3: Crystal data of the modulated martensitic phase based on the structural refinement of the neutron diffraction data collected at 220K. Table S4: Atomic coordinate, occupancy factors, thermal parameters and modulation parameters A1x for the martensite at 220 K.

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