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Incommensurate modulated structure of the ferromagnetic shape-memory Ni_2MnGa martensite

Lara Righi[a,*], Franca Albertini[b], Gianluca Calestani[a], Luigi Pareti[b], Antonio Paoluzi[b], Clemens Ritter[c], Pedro A. Algarabel[d], Luis Morellon[d], M. Ricardo Ibarra[d]

[a]*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale delle Scienze, I-43100 Parma, Italy*
[b]*IMEM, Consiglio Nazionale delle Ricerche, Parco Area delle Scienze 37/A, I-43010 Fontanini, Parma, Italy*
[c]*Intitut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France*
[d]*Departamento de Fisica de la Materia Condensada-ICMA, Universidad de Zaragoza CSIC, 50009 Zaragoza, Spain*

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Abstract

The ferromagnetic shape memory (MSM) alloy Ni_2MnGa undergoes a martensitic transformation (MT) at $T = 220$ K on cooling. The structure of this phase is studied by powder X-ray diffraction experiment. The analysis of the experimental data combined with the huge information reported in literature allowed to conclude that the Ni_2MnGa martensite shows an incommensurate modulated structure closely related to a five-fold layered superstructure. The symmetry of the basic structure is found to be orthorhombic. The structure is refined by Rietveld method with superspace group $Immm(00\gamma)s00$ having $a = 4.2187(1)$ Å, $b = 5.5534(1)$ Å and $c = 4.1899(1)$ Å and modulation vector $\mathbf{q} = 0.4248(3)\mathbf{c}^*$. The results show that the modulation is mainly related to the periodic shuffling of the atomic layers perpendicular to the c-axis of the orthorhombic basic structure.

Keywords: Ferromagnetic shape memory alloy; Ni_2MnGa; Incommensurate modulation; Rietveld refinement

1. Introduction

Ni_2MnGa Heusler alloys are attracting a great deal of interest due to the possibility of inducing huge strains, by applying magnetic fields of moderate intensity [1,2]. The fundamental properties at the basis of the magnetic-field-induced strain (MFIS) [3] for this class of materials are the ferromagnetic state stable up to $T_c \sim 370$ K, a martensitic structural transformation at lower temperatures (220 and 235 K, respectively, on cooling and heating for Ni_2MnGa composition), together with the presence of high magnetocrystalline anisotropy (MCA) in the low temperature phase [4]. The huge MFIS in the ferromagnetic martensitic phase is originated by twin-boundaries motion, which is favoured with respect to magnetization rotation [3,5]. The change of the direction of the magnetization in theses crystals requires an energy larger than those necessary to change the orientation of the twins through the motion of the twin boundaries. Therefore the system aligns the spins for each unit cell with the motion of the twin boundaries producing large strains and giving rise to the so-called magnetic shape memory (MSM) effect. In the case of Ni_2MnGa up to 6% of strain is achieved in the process [3].

A first structural description of the phases involved in the martensitic transformation (MT) of Ni_2MnGa was reported firstly by Webster et al. in 1984 [6] on the basis of neutron diffraction studies. The parent cubic phase stable at high temperature was found to belong to the *Fm-3m* space group, with a $L2_1$ structure having a lattice parameter $a_a = 5.833$ Å. On cooling below 220 K (T_M) a reversible transformation takes place giving rise to a martensitic phase. The MT involves a strain mechanism, generally defined as Bain strain, consisting of a contraction of the c-axis accompanied by the elongation of the two remaining vectors. The cell parameters of Ni_2MnGa martensitic structure $a_a = 5.920$ Å and $c_a = 5.566$ Å [6] are referred to the face-centred $L2_1$ lattice; the maximum

*Corresponding author. Fax: +39 0521 905 556.
E-mail address: lara.righi@unipr.it (L. Righi).

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possible strain achieved by magnetic-induced shape memory effect in the martensitic phase is associated to the tetragonality c/a parameter as calculated from the parent phase lattice. Despite the usual description of the martensite as a lattice distortion of $L2_1$ structure [2,7,8], the real symmetry of the structure of the product phase is properly described with a body-centred unit cell obtained from the parent FCC lattice by applying the transformation:

$$\begin{pmatrix} \mathbf{a}_m \\ \mathbf{a}_m \\ \mathbf{c}_m \end{pmatrix} = \begin{pmatrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_a \\ \mathbf{a}_a \\ \mathbf{c}_a \end{pmatrix}. \quad (1.1)$$

As it is displayed in Fig. 1 the tetragonal lattice has the fundamental parameters coinciding with the $[1\bar{1}0]$, [110] and [001] directions of the $L2_1$ superstructure. In the case of Ni_2MnGa the unit cell constants become $a_m = 4.186$ Å and $c_m = 5.566$ Å.

Nevertheless neutron and X-ray diffraction experiments [6,9,10] have demonstrated that the structure of martensite of the stoichiometric compound Ni_2MnGa is actually more complex. Four satellites, observed between main reflections in X-ray diffraction pattern of Ni_2MnGa martensite, have been interpreted in terms of a superstructure constituted by five unit cells (five-fold modulation, 5 M) along $[100]_m/[-110]_a$ by considering the presence of periodical shuffling of the $(010)_m/(110)_a$ atomic layers. Further electron diffraction (ED) investigations [11,12] confirmed the existence of satellites associated to a 5 M modulated structure. An important element about the nature of the modulation was found by Zheludev et al. [13]. From elastic neutron scattering experiments performed on a single crystal of Ni_2MnGa at low temperature, the authors found that the modulation period, even if close to five unit cells, is incommensurate with respect to the basic tetragonal lattice.

Different martensitic structures of shape memory alloys exhibit structural modulation, as reported in several publications [14,15]. Ni–Al and Ni–Ti martensites show, as a function of the composition, a variety of structural modulations which are generally viewed as periodical stacking faults of $\{110\}_a$ atomic planes along determined crystallographic directions [16]. The insurance of such structural modulations is in agreement with Zener [17] who suggested the centred lattice of the austenite to be unstable with respect the shear/shuffle of the $\{110\}_a$ planes. This instability is manifested by the softening of the TA_2 phonon mode, observed when the martensitic transition is approached on cooling [13]. Also off-stoichiometric $Ni_{2\pm x}Mn_{1\pm y}Ga_{1\pm z}$ $(x+y+z=1)$ alloys show martensitic structures characterized by different types of structural modulations. The composition dependence of structures of thermally induced martensites has been described by Chernenko et al. [12] by ED studies. Besides to different kinds of lattice distortions the structural modulation can involve 5, 7 or even 10 unit cells (five-fold 5 M, seven-fold 7 M or ten-fold 10 M modulation) along the $[110]_a/[100]_m$ direction. The number, n, of observed satellites between the main reflections indicates the type NM of the modulation being $N = n+1$.

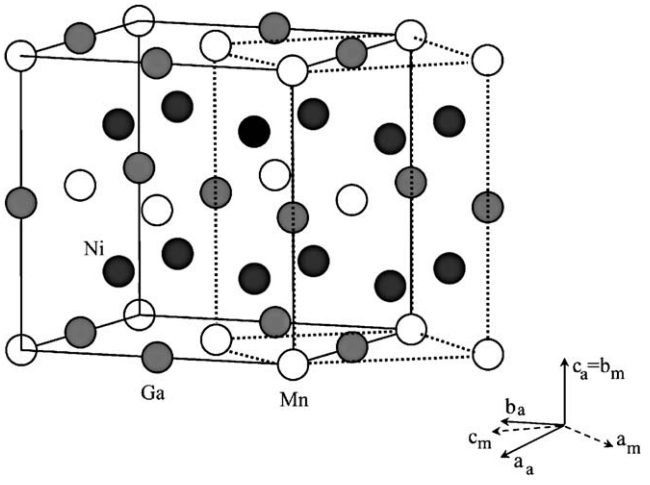

Fig. 1. Perspective view of the $L2_1$ cubic structure of Ni_2MnGa austenite. The dotted lines define the basic structure of the incommensurate modulated martensite.

In spite of the intense research dealing with the study of the magnetic and structural properties of the Ni–Mn–Ga system, the structural characterization of such phases is still a controversial matter. As an example, the first structural refinement of the thermally induced Ni_2MnGa martensitic structure has been reported by Brown et al. [19] in terms of a commensurate seven-fold 7 M modulation. On the basis of powder neutron diffraction (PND) measurements carried out at 20 K, they refined, by Rietveld method, an orthorhombic superstructure having unit cell constants $a = 4.2152$ Å, $b = 29.3016$ Å and $c = 5.5570$ Å. This result seems to be in contrast with the earlier structural studies performed on Ni_2MnGa martensite.

In the present work a novel structural determination of thermally induced Ni_2MnGa martensite is performed on the basis of PXRD data. The investigation of this modulated structure has been carried out by taking into account all the suitable information present in literature. It will be demonstrated that this phase presents an incommensurate modulation whose structure has been solved within superspace approach.

2. Experimental details and methods

Samples of composition Ni_2MnGa were prepared by means of the arc melting technique followed by thermal annealing at $T = 1223$ K. The samples were found to be homogeneous and single phase by X-ray diffraction and thermomagnetic analysis (TMA). From TMA measurements the Curie temperature and the T_M temperatures (on cooling and on heating) were found to be, respectively, 370, 220 and 235 K. The powder, obtained by milling the pellets, were annealed at 1073 K for 48 h.

Powder X-ray diffraction pattern were collected with Cu$K\alpha$ wavelength, by using a Thermo ARL X'tra

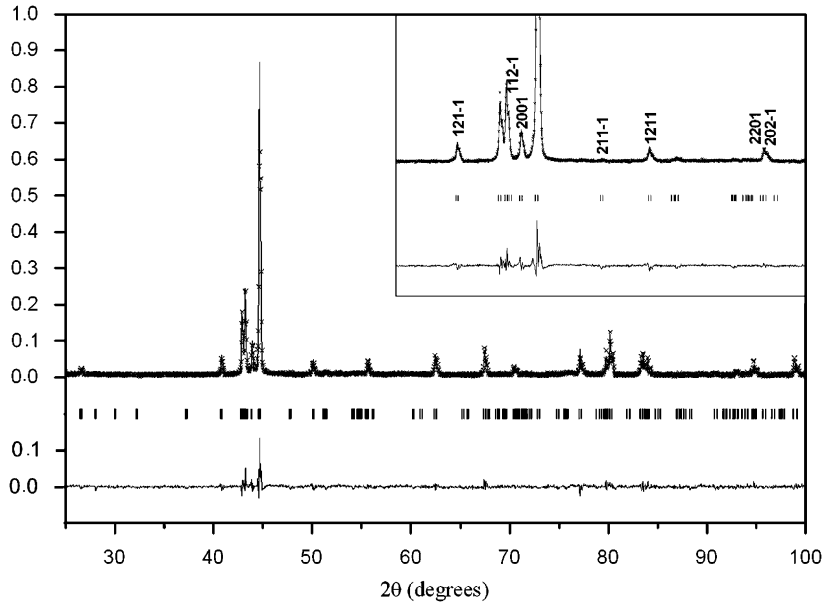

Fig. 2. Rietveld graphical output of the structural refinement of the incommensurate modulated phase Ni_2MnGa martensite. The black and grey ticks specify the main reflections and satellites, respectively. The inset shows the region 38–59 of $2\theta(^\circ)$: satellites are labelled with Miller indexes.

diffractometer equipped with a Thermo Electron solid-state detector. This experimental set-up permits to cut off the fluorescence radiation deriving from Mn atoms with Cu$K\alpha$ radiation. Low temperature diffraction experiment were performed with a TTK450 Anton Paar chamber mounted on the same diffractometer.

The indexing of the PXRD pattern and the structure solution by means of superspace approach were achieved by using JANA2000 software [20]. The same software was adopted to analyse the results.

3. Results

3.1. Structure determination of the martensitic phase

As mentioned before, in previous investigations the Ni_2MnGa martensite was often described by the basic tetragonal lattice and omitting the modulation [21–23]. In the present work, the basic structure is refined by the Rietveld method taking into account only those peaks of PXRD pattern, the main reflections, supported by this simple structure. The high resolution of the diffraction pattern allowed to detect a deviation from the tetragonal symmetry consisting in a slight difference between a_m and b_m lattice parameters. The best fit ($R_w = 0.0826$) is achieved with an orthorhombic lattice having *Immm* space group with unit cell parameters $a_m = 4.2187(1)$ Å, $b_m = 5.5534(2)$ Å and $c_m = 4.1896(2)$ Å. The setting of the crystallographic axes is changed, for convenience, from **abc** to **acb** being actually a_m and c_m parallel to $[1\text{-}10]_a$ and $[110]_a$, respectively. Each atom in the unit cell has a single symmetrical independent position having atomic thermal displacements taken as isotropic (see Table 2). The y coordinate of the Ni 4*h* position is fixed to $\frac{1}{4}$.

By assuming a commensurate modulation, the five-fold 5 M superstructure should be properly described by the super-cell $a = a_m$, $b = b_m$ and $c = 5c_m$ or alternatively $a = 5a_m$, $b = b_m$ and $c = c_m$. However anyone of these two unit cells is adequate to the complete indexing of the PXRD pattern. Indeed, as previously mentioned, for stoichiometric Ni_2MnGa martensite, Zeludev et al. [18] observed an incommensurate periodicity represented in the FC lattice by the wave vector $\pi/a_a[0.43,0.43,0]$. This wavevector, originally oriented along the $\langle 1\,1\,0\rangle_a$ of the distorted FC lattice, would lie in the actual orthorhombic setting either along the $[001]_m$ or the $[100]_m$ direction. Both possibilities were verified and the complete indexing of all the observed reflections of the PXRD pattern was obtained with four integers related to the four-dimensional base $\mathbf{H} = h\ \mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\ \mathbf{q}$ taking into account the basic orthorhombic cell **a***,**b***,**c*** and a modulation vector $\mathbf{q} = 0.43\mathbf{c}^*$. Therefore in agreement with what already observed [18] the Ni_2MnGa martensite has a structure incommensurately (IC) modulated. The solution of the incommensurate modulated structure imply the determination of a (3 + 1)-dimensional model [24]. Systematic extinctions analysis, based on the set of reflections obtained by a full-profile fitting of the PXRD pattern, indicates the presence of translational symmetry ($0klm$ with $k + l + m = 2n$) fulfilled by the superspace group $Immm(00\gamma)s00$. The classical definition of the MT conjugates a lattice distortive process with a shuffling of atomic layers [16]. The choice of a wave-like function seems therefore to be appropriate to model the harmonic displacement of the atomic layers. The general atomic position in the basic structure is written as

$$\bar{x}_i = L + x_i^0, \tag{3.1}$$

where the i index corresponds to ith atom in the unit cell and L is the primitive translation vector. Following the embedding procedure for the structure in the $(3+1)$-dimensional superspace, the generic atomic position is given by

$$x_i = \bar{x}_i + u_i(\bar{x}_{x4}), \tag{3.2}$$

$$u^i(\bar{x}_4) = \sum_{n=1}^{\infty} A_n^i \sin(2\pi n\bar{x}_4) + B_n^i \cos(2\pi n\bar{x}_4), \tag{3.3}$$

where u^i defines the modulation function which depends on the x_4 superspace coordinate, the n index being associated to the order of the Fourier series.

Since the observed satellites are all included in the $hkl\pm1$ family, only the first order of the Fourier expansion have been considered in the Rietveld refinement.

Among A_n^i and B_n^i coefficients of Eq. (3.3), the symmetry rules allow to refine only A_{1x} for all the three atomic species (Ni, Ga and Mn). Main reflections and satellites are used in the Rietveld refinement (see Fig. 2) and the convergence is achieved for the values summarized in Tables 1 and 2. The atomic displacement parameters (ADP) are refined as isotropic. The preferred orientation of the 1 2 1 reflection affecting the PXRD pattern has been corrected with a March–Dollase function. The particular platelets-like shape [16] of the martensite crystals is the main cause of such expected preferred orientation.

3.2. Structural analysis of the refined IC structure

The deviation from the fundamental atomic positions can be estimated by the graphical output of the modulation function (t-plots). As it is displayed in Fig. 3 the x component of the modulation function for all the three atoms has the same phase and nearly the same amplitude. The maximum amplitudes of the modulation can be

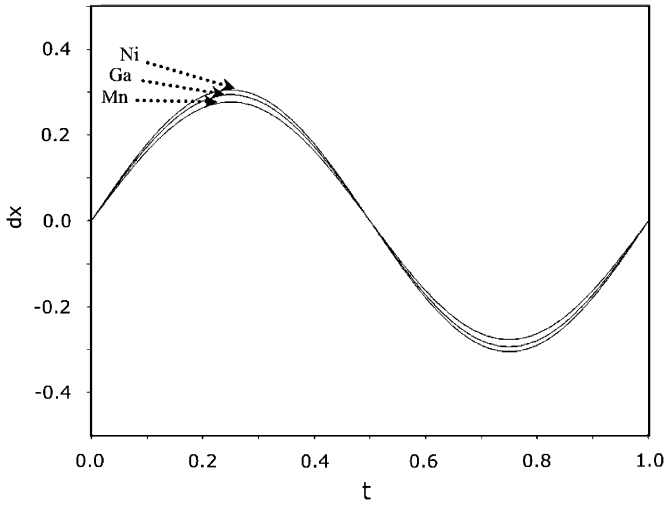

Fig. 3. Graphical representation of the x component of modulation function for Ni, Mn and Ga versus t parameter, defined by $t = x_4 - \mathbf{q} - \mathbf{r}$, where $\mathbf{r}$ is the position vector in the unit cell of the basic structure.

Table 1
Experimental details and crystallographic data of Ni_2MnGa martensite

Wavelength (Å)	Cu$K\alpha$
Radiation type	X-ray
2θ range (°)	10.00–140.00
Step (deg)	0.050
Temperature (K)	100
Criterion for observed reflections	$I > 2\sigma(I)$
Space group	$Immm(00\gamma)s00$
Modulation vector **q**	0.4248(2)**c***
a (Å)	4.2187(1)
b (Å)	5.5534(1)
c (Å)	4.1899(1)
Volume (Å^3)	98.163(3)
Z	2
Calculated density (g cm^3)	16.3720(5)
No. observed reflection (main + satellites)	518
Number of parameters	21
Agreement factors	
R_{wF} (main reflections)	0.0668
R_{wF} (first-order satellites reflections)	0.1370
R_p/R_{wp}	0.0837/0.1317

compared with those obtained by first-principles calculations performed by Zayak et al. [25] on the basis of a theoretical structural model of Ni_2MnGa martensite constituted by a commensurate five-fold super-cell ($a \approx 4.17$ Å, $b \approx 20.73$ Å and $c \approx 5.63$ Å). Using a conjugate-gradient algorithm the energy of the system has been minimized by shuffling the atomic layers staggered along the b direction. They found that the minimum energy required for atomic displacements of 0.29 Å for Mn and Ga, and 0.32 Å for Ni. Although the computational study has been carried out with a different set of cell parameters, these values are similar to those found in the present refinement.

The interatomic distances, summarized in Table 3, are consistent with the typical bond lengths for such type of atoms in intermetallic compounds [26,27]. The analysis of the modulated interatomic distances assumes fundamental importance if the close relation between ferromagnetic state and $L2_1$ lattice is taken into account. It is well known that the MT does not destroy the magnetic ordering [6]. The insurance of the ferromagnetic state among Heusler alloys regards the interaction of the Mn sub-lattice with the rest of the structure [28,29]. As demonstrated by ab initio calculations performed on several Mn-based Heusler alloys, the ferromagnetic state depends from Mn–Mn interaction within $L2_1$-type structure [30]. Fig. 4a represents the schematic ferromagnetic spin orientation in the basic unit cell as it is usually described for Ni_2MnGa in literature [29,31], whereas in Fig. 4b it is reported the Mn–Mn interatomic distances as a function of the t period. In Ni–Mn–Ga martensitic phases the ferromagnetic state is always associated to the alignment of the magnetic moments along the shorter vector of the $L2_1$ distorted lattice [31]. In the case of Ni_2MnGa the ferromagnetic structure should have the spins, confined on Mn atoms,

Table 2
Atomic positions (x, y, z), ADP (U_{iso}) and amplitudes of the modulation function of the incommensurate modulated phase (A_i, B_i)

Atom	Wych.		x	y	z	U_{iso}
Mn	*2a*		0	0	0	0.0011(11)
		A_1	0.066(8)	0	0	
		B_1	0	0	0	
Ga	*2d*		0	0.5	0	0.0016(10)
		A_1	0.070(6)	0	0	
		B_1	0	0	0	
Ni	4*h*		0.5	0.25	0	0.0011(27)
		A_1	0.072(6)	0	0	
		B_1	0	0	0	

The A_{1y}, A_{1z} and B_1 terms are constrained to zero value by symmetry rules.

Table 3
Selected interatomic distances of the incommensurate structure

	Basic structure (Å)	Average (Å)	Min (Å)	Max (Å)
Mn1–Mn1	4.0679	4.075(15)	3.901(8)	4.256(11)
	4.0679	4.072(14)	3.901(8)	4.256(11)
	4.1899	4.207(3)	4.1899	4.224(6)
Mn1–Ga1	2.9729	2.98(2)	2.73(1)	3.23(2)
	2.9729	2.97(2)	2.73(1)	3.23(2)
Mn1–Ni1	2.5252	2.52(2)	2.50(3)	2.55(4)
	2.5132	2.526(2)	2.5132(2)	2.539(2)
Ga1–Ga1	4.0679	4.086(17)	3.899(11)	4.255(10)
	4.0709	4.066(17)	3.906(11)	4.257(10)
	4.1899	4.209(1)	4.1899	4.229(4)
Ga1–Ni1	2.5329	2.538(13)	2.448(17)	2.597(12)
	2.5135	2.527(9)	2.472(14)	2.581(7)
Ni1–Ni1	2.9729	2.981(16)	2.718(9)	3.252(11)
	4.0679	4.076(12)	3.886(6)	4.276(8)
	4.1899	4.211(2)	4.1899	4.232(4)

oriented along b_m direction of the basic structure. The IC modulated structure of Ni_2MnGa martensite is characterized by a complex evolution of the Mn–Mn interaction with respect the t period. Besides to the eight closer interactions related to the I-centred sub-lattice, four interatomic positions with larger distances are encountered as well. The latter interactions are less affected by the incommensurate modulation and the Mn–Mn distances with average length 4.21 Å are completely unvaried by the modulation. On the other hand, as reported in Table 3, the displacive distortion tends to enlarge the Mn–Mn distance of 4.1899 Å coinciding with the a_m unit cell parameter of the orthorhombic basic structure. Indeed the nonequivalence of a_m and c_m constants play an important role in determining the crystallographic orientation of the structural modulation. The modulation strongly affect the first shell of Mn–Mn interaction and it is reasonable to suppose that the spin orientation could assume local canting configurations as the displacive distortion changes the atomic environment. This hypothesis should be obviously verified by investigations devoted to the interpretation of the magnetic properties in view of the new structural results. In a prior study [29], the interaction of magnetic lattices in Ni_2MnGa austenitic $L2_1$ structure has been studied in terms of spin spirals within density functional theory. The authors considered the possible noncollinear ordering by calculating the total energy as a function of a spiral wave vector **q**. Although the lowest energy is found for a collinear ferromagnetic configuration, a minima in correspondence of an incommensurate spiral order is also reported. Furthermore, it has been found that also the Ni sublattice play an important role in defining the magnetic properties of the material. The same kind of calculations could be performed on the basis of the incommensurate modulated structure of Ni_2MnGa martensite in order to indicate possible associated spin configurations.

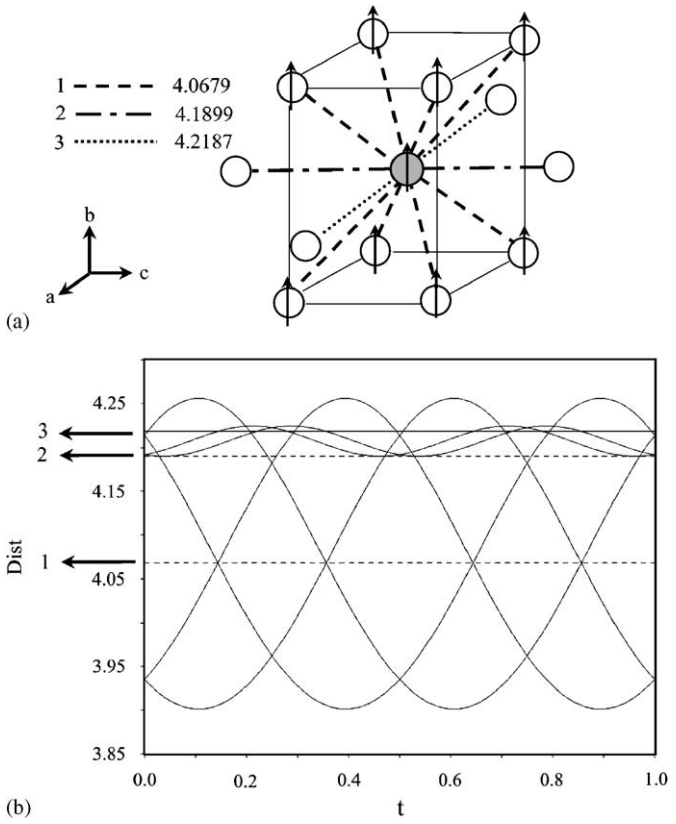

Fig. 4. (a) Schematic representation of the Mn–Mn interaction with the scheme of the ferromagnetic spin arrangement as cited in literature (Ga and Ni atoms are neglected for clarity). (b) Plot of Mn–Mn distances in Å against the t parameter.

4. Discussion

The present results are in contrast with those reported by Brown et al. [19], who reported a structural refinement of Ni_2MnGa martensitic phase from PND data collected at 20 K. Considering a commensurate seven-fold modulation, they refined by Rietveld method the structure of the martensite with an orthorhombic superstructure having unit cell constants $a = 4.2152$ Å, $b \approx 7a = 29.3016$ Å and $c = 5.5570$ Å and space group *Pnnm*. It is important to note that any thermally induced intramartensitic transformation has been observed in Ni_2MnGa, therefore the reported PND and our PXRD data pertains the same martensitic phase. Hence the neutron diffraction pattern has been indexed on the basis of this commensurate superstructure simply because $\mathbf{q}$ is $\sim 3/7\mathbf{c}^*(=0.428\mathbf{c}^*)$. This coincidence leads the authors to interpret the structure of this phase as 7 M modulated. However, if the usual meaning of martensitic 7 M modulation is adopted, this is not strictly correct, since a similar modulation in Ni_2MnGa martensite should be related to the appearing of six satellites between the main reflections of the reciprocal space [2,11]. It should be also underlined that, the proposed orthorhombic superstructure contains some particularly short Ni–Mn and Ni–Ga distances of 2.09 and 2.06 Å, respectively. These interatomic distances are unrealistic if compared to the characteristic bond lengths of these atomic species in intermetallic compounds [26,27].

On the other hand, starting from the $(3+1)$-dimensional model it is possible to derive a 3-D model involving seven unit cells of the basic structure along the c-axis. The superstructure, described by the nonstandard *Pnmn* space group, has four independent atomic positions for Mn, Ga and Ni. The Fig. 5a displays the superstructure that can be viewed as a good approximation of the real incommensurate structure. The wave-like displacement of the $(001)_m$ planes is the characteristic element of such structural modulation. In the Table 4 the crystal data of the 3-D model are summarized.

A final attempt to refine, by Rietveld method, the atomic positions of the commensurate model led the refinement to diverge, even by using strong damping factors. A typical problem in refining modulated structure as superstructure is the increase of strongly correlated parameters not compensated by a suitable number of observations. The advantageous ability of the superspace approach in describing a structural modulation, either commensurate and incommensurate with few parameters is particularly evident when powder diffraction data are used. It is also important to underline that, owing to the incommensurate nature of the structure, the calculated satellites, even after refinement of the unit cell parameters, are slightly misaligned from the observed 2θ positions. As a consequence, the seven-fold superstructure must be viewed as an approximate model very similar to the real incommensurate structure. Furthermore, this commensurate model can be exploited for simulating reciprocal space projections. In calculated XRD pattern along 0 1 0 zone axis (see Fig. 5b) four satellites between main reflections are well visible, in agreement with what recurrently reported in diffraction studies of Ni_2MnGa martensite [6,9–13]. As it is displayed in Fig. 5c, the same simulation based on the so-called 7 M structure [19] is characterized by a completely different pattern of reflections never reported for this type of martensites. With respect the modulation vector $\mathbf{q}$, the calculated satellites of Fig. 5b belong to first and second order, i.e. $hkl \pm 1$ and $hkl \pm 2$. As it is previously mentioned, we have detected only the first-order satellites, otherwise SAED measurements [11,12] revealed the presence of second order. A possible reason can explain such contradiction. The second-order satellites, having low intensity, are probably not distinguishable from the background. The employment of the low temperature chamber mounted on the diffractometer could prevent the recognition of weak diffraction peaks. However, the atomic displacements due to the modulation have a maximum amplitude of ca. 0.3 Å. This amplitude is large enough to generate second-order satellites. Diffraction experiments aimed to detect the second-order satellites of Ni_2MnGa martensites could add new useful information in order to better define the displacive modulation function.

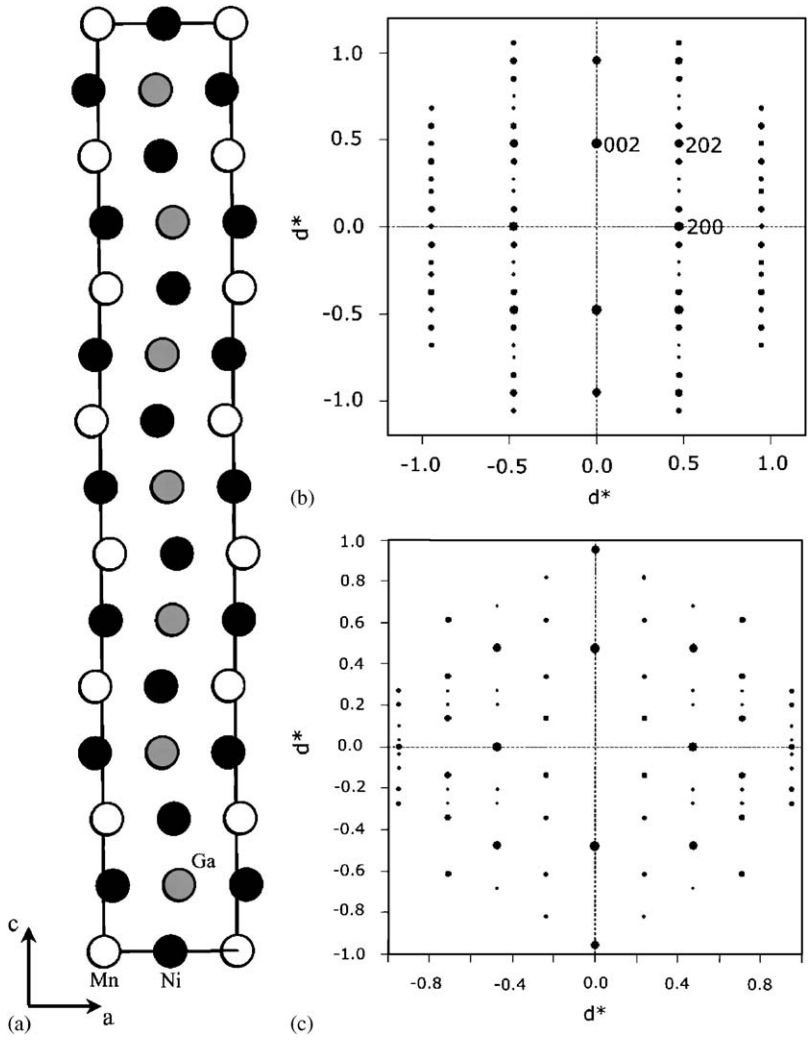

Fig. 5. (a) View parallel to the **b**-axis of the structural model involving seven adjacent unit cells along **c**-axis. (b) [010] projection of the reciprocal space calculated from the commensurate model derived by the (3 + 1)-dimensional structure. The Miller indexes are referred to the orthorhombic basic structure. (c) [010] projection of the reciprocal space calculated from the seven-fold superstructure reported in Ref. [19].

Table 4
Crystal data of seven-fold superstructure with fractional coordinates and isotropic thermal parameters as derived from the (3 + 1)-dimensional structure

Crystal system			Orthorhombic		
Space group			*Pnmn*		
Unit cell formula			$Ni_{28}Ma_{14}Ga_{14}$		
a (Å)			4.2194		
b (Å)			5.5539		
c (Å)			29.332		
Atom type	Wych.	*x*	*y*	*z*	U_{iso}
Mn1	*2a*	0	0	0	0.0011
Mn2	*4g*	0.0289	0	0.1428	0.0011
Mn3	*4g*	−0.052	0	0.2857	0.0011
Mn4	*4g*	0.0649	0	0.4286	0.0011
Ga1	*2b*	0	0.5	0	0.0016
Ga2	*4g*	0.0298	0.5	0.1428	0.0016
Ga3	*4g*	−0.054	0.5	0.2857	0.0016
Ga4	*4g*	0.0669	0.5	0.4286	0.0016
Ni1	*4f*	0.5	0.25	0	0.0011
Ni2	*8h*	0.5314	0.25	0.1428	0.0011
Ni3	*8h*	0.4434	0.25	0.2857	0.0011
Ni4	*8h*	0.5705	0.25	0.4286	0.0011

5. Conclusions

In the present work the martensitic phase of the stoichiometric Ni_2MnGa Heusler alloy has been studied at 100 K by PXRD experiment. The combined analysis of the experimental data and information arising from literature allowed to conclude that this phase shows an incommensurate modulated structure, whose diffraction features are closely related to the typical ones usually interpreted in terms of a five-fold layered structure. The symmetry of the basic structure was found to be orthorhombic and not tetragonal, as it was generally considered [2,7,8,25,32]. The Rietveld refinement of a $(3+1)$-dimensional structural model permitted to describe the modulation function. On the other hand the symmetry of the system, joined with the typical sequence of observed satellites in the reciprocal space, allowed us to conclude that the Ni_2MnGa martensite can be regarded as *almost* five-fold modulated 5 M having the modulation vector $\mathbf{q} = (2/5+\delta)\mathbf{c}^* = (0.4+\delta)\mathbf{c}^*$ where δ represents the incommensurateness degree of the structure. Very recently, from PXRD data collected at room temperature on $Ni_{1.95}Mn_{1.12}Ga_{0.86}$ martensite we have observed commensurate 5 M modulation. The diffraction pattern presents the same characteristics detected for Ni_2MnGa except for the periodicity of satellites which is related to the modulation vector $\mathbf{q} = 0.4\mathbf{c}^*$. Therefore two different types of ''5M'' modulation are possible: commensurate and incommensurate. In view of these results the classification of martensitic modulated structures based on the number of observed satellites is not appropriate to interpret the structural features especially when incommensurate modulation takes place.

The crucial question regarding the possible origin of the incommensurability is far from an exhaustive explanation. The martensitic transition is promoted by the softening of the specific phonon branch TA_2 at the wavevector $\mathbf{q}$ corresponding to the structural modulation. The structural phenomenology of martensitic phases in different metallic compounds has often accounted the presence of incommensurate modulation. In some studies focused on Li [33] and NiAl [34] martensitic phases, the incommensurateness of the modulation is supposed to depend on the existence of coherency stresses derived by the coexistence of the parent phase with the martensitic phase. For Ni_2MnGa no evidences of residual cubic austenitic phase have been observed below T_M. In the special case of Ni_2MnGa the freezing of such particular phonon mode is favoured by the magnetism through magnetoelastic coupling [35]. Therefore, the incommensurate displacive modulation of Ni_2MnGa martensite cannot be completely analysed without a detailed description of the magnetic structure. Moreover, concerning the ferromagnetic state coexisting with the nuclear incommensurate modulated structure a series of considerations emerges from the analysis of the actual results. The displacive modulation of the Mn atoms must be taken into account when a possible model of the spin arrangement is formulated. The large MCA of this system has been always treated considering only the lattice of the basic structure, but, it has been demonstrated that the modulation produces atomic displacements that should be correlated with the magnetic properties. The complete structural study of Ni–Mn–Ga MSM Heusler alloys will be achieved taking into account the complex interplay between incommensurate nuclear structure, magnetic structure and characteristic microstructure of martensitic phase. In this frame, the result here reported can be considered as the first step in this structural research. Single crystal neutron diffraction experiments performed on detwinned samples could supply important elements to the structural study of the ferromagnetic shape-memory Ni_2MnGa alloy.

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