Magnetic moment and chemical order in off-stoichiometric Ni–Mn–Ga ferromagnetic shape memory alloys

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Abstract. Recent studies have shown that the total magnetic moment in off-stoichiometric Ni–Mn–Ga alloys depends not only on electronic concentration but also on the degree of chemical order in the alloy. We have performed neutron diffraction experiments and magnetization measurements for determining the preferential atomic order and saturation moment in off-stoichiometric compounds (44–52 at.% Ni), having excess Mn and deficient in Ga. These alloys include iso electronic alloys with different magnetic moments and were chosen in an effort to study the impact of chemical order on the magnetic moment distribution. In this work, we present an improved model of magnetic interaction between Mn atoms, which carry most of the localized magnetic moment of the alloys. The Mn atoms at Ga sites, which are nearest neighbors to properly sited Mn, couple antiferromagnetically to the dominant moment. In contrast, Mn atoms at Ga sites, which are nearest neighbors to Mn at Ni sites, couple ferromagnetically. Mn at Ni sites is always antiferromagnetic (AF). The new model is supported by the exchange variation with the Mn–Mn distance and demonstrates excellent agreement between experimental and calculated

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magnetic moments. The proposed model is shown to better explain the observed experimental results as compared to the rigid band model and previous localized moment models that assumed AF coupling for all off-site Mn atoms.

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1. Introduction

Ferromagnetic shape memory alloys (FSMAs), such as those based on Ni–Mn–Ga, are of great technical interest due to their unusual magnetomechanical behavior that provides new possibilities for applications as sensors and actuators [1]. These alloys exhibit an austenite–martensite transition at the martensitic temperature, \( T_M \), and also a ferromagnetic (FM)–paramagnetic transition at the Curie temperature, \( T_C \). The twined structure generated to accommodate the strain in the martensitic phase and the magnetic character of these compounds make it possible to develop the so-called magnetic field-induced strain (MFIS) effect. This phenomenon results from the rearrangement of the variants in the martensitic phase under an applied magnetic field, inducing strains up to 10%, as observed in some Ni–Mn–Ga single crystals [2]–[5].

The martensitic structure, maximum induced strain, Curie and martensitic transition temperatures, magnetocrystalline anisotropy and other materials properties are extremely sensitive to the composition [6]. A successful approach for classifying the behavior of such alloys is to relate all parameters to the electronic concentration (\( e/a \)). Definite trends in Curie and martensitic transition temperatures, as well as martensitic structure, have been found as a function of \( e/a \), irrespective of the exact composition of the alloys [7].

Extensive studies, including polarized neutron diffraction (PND), have been performed to determine the magnetic structure of the stoichiometric Ni\(_2\)MnGa Heusler alloy [8, 9]. This composition presents a total saturation magnetic moment per formula unit of 4.17 \( \mu_B \) FU\(^{-1} \), where the magnetic moment is mainly localized in the Mn atoms and couples ferromagnetically to the moment of the Ni atoms [10]. However, in Mn-rich compositions, a decreased net magnetic moment is observed. This observation agrees with the general tendency of exchange coupling to change from FM to antiferromagnetic (AF) at reduced interatomic spacing, which has been observed in these compounds [11, 12].

This change in exchange coupling can also be explained within the Slater–Pauling rigid band model for 3d alloys [13, 14], where either excess or defect electrons lead to a decrease of the magnetic moment. Recently, published work has used this approach [11, 12, 15] to relate
the magnetic moment directly to the electronic concentration \( e/a \). However, recent studies [16]
of the annealing of rapidly quenched ribbons have shown that for a given composition, and therefore a unique electronic concentration, the total magnetic moment, and to a lesser extent the martensitic and Curie temperatures, depend on the chemical order in off-stoichiometric Ni–Mn–Ga alloys. This effect has been attributed to changes in the electronic structure and ordering of the alloys upon annealing. In a series of three alloys studied in previous work [17], the electron concentration was constant yet the magnetic moment changed, suggesting that the rigid model band is an oversimplified assumption and further considerations are needed.

While the crystal structure of many off-stoichiometric compositions has been actively researched, there have been few detailed studies on the variation of the magnetic moment distribution with departures from stoichiometry. The exact distribution of the different atomic species within the unit cell is expected to impact the various magnetic properties of these alloys. This fact motivates a comprehensive study of the magnetic interaction in such off-stoichiometric alloys. Further understanding the relationship between the atomic structure and the properties of Ni–Mn–Ga is also motivated by the intrinsic interest in the magnetism of these alloys, as well as by the connection between the magnetic moment and the threshold field required for observing MFIS.

In our preliminary study, neutron diffraction experiments were used to determine the preferential atomic order in some off-stoichiometric single-crystal and polycrystalline compounds with excess Mn and various Ni content [17]–[19]. The model proposed in [17] demonstrated that some Mn atoms were located in nearest-neighbor sites and couple antiferromagnetically to give the total magnetic moment. However, this change in site occupancies was only analyzed in alloys with small departures from the stoichiometry. In this work, we present new results including alloys with a large Ni deficiency. These alloys were chosen in an effort to study the impact of chemical order on the magnetic moment distribution. Only excess Mn alloys have been studied, as they are the only ones where AF coupling or band filling effects can give rise to a magnetic moment decrease in response to an increase in magnetic atom concentration. Mn-rich compositions are also the most technologically interesting FSMAs because they have shown large MFIS [14]. A simple model of magnetic interactions that overcomes some of the difficulties of our previous work [17] and that can explain the magnetic structure in Ni–Mn–Ga off-stoichiometric alloys is developed on the basis of the obtained results.

2. Experimental

Polycrystals and single crystals (table 1) of various compositions were prepared by arc-melting and the Bridgman technique, respectively, at Ames National Laboratory (Iowa, USA) and annealed for 24 h at 1273 K, for homogeneity, and for 3 h at 873 K, for ordering. In some cases, pieces of the single crystals were manually crushed in order to obtain powder samples. After crushing, the powders were heat treated for 4 h at 1023 K and slowly cooled to relieve stresses. Compositions were confirmed by energy and wavelength dispersive x-ray spectroscopy (EDS and WDS), determining that the loss of volatile Mn and Ga was less than 1% and that the samples were homogeneous (table 1). Neutron diffraction studies of the powder samples Ni44–Ni52 were performed using the high-flux D20 instrument (\( \lambda = 1.37 \) Å) at the Institute Laue Langevin (ILL; Grenoble, France). A second group of alloys of composition Ni\(_{53-x}\)Mn\(_{25+x}\)Ga\(_{22}\) (denoted \( S_x \) with \( x = 1, 2, 3, 4 \) and 5) were studied at the high-resolution total
Table 1. Composition, in atomic per cent, electron concentration per atom \((e/a)\), martensitic temperature \((T_M)\), Curie temperature \((T_C)\) and structure in the martensitic state of the studied samples.

| Alloy     | at.% Ni | at.% Mn | at.% Ga | \(e/a\) | \(T_M\) (K) | \(T_C\) (K) | Structure |
|-----------|---------|---------|---------|---------|------------|------------|-----------|
| Powder    |         |         |         |         |            |            |           |
| Ni44      | 43.8    | 37.8    | 18.4    | 7.58    | 352        | 366        | 7M        |
| Ni49      | 49.2    | 30.5    | 20.3    | 7.67    | 324        | 374        | 7M        |
| Ni50      | 50.2    | 29.0    | 20.8    | 7.67    | 314        | 374        | 5M        |
| Ni52      | 52.1    | 26.0    | 21.9    | 7.68    | 328        | 366        | 5M        |
| S1        | 52.9    | 25.6    | 21.5    | 7.73    | 363        | —          | 5M        |
| S2        | 51.4    | 26.6    | 22.0    | 7.66    | 324        | 365        | 5M        |
| S3        | 50.4    | 27.5    | 22.1    | 7.63    | 301        | 374        | 5M        |
| S4        | 49.6    | 28.6    | 21.8    | 7.62    | 288        | 373        | NM        |
| S5        | 48.3    | 29.8    | 21.9    | 7.57    | 269        | 374        | NM        |
| Single crystal |     |         |         |         |            |            |           |
| Ni44      | 43.0    | 37.9    | 19.1    | 7.53    | 320        | 367        | 7M        |
| Ni52      | 51.9    | 26.2    | 21.9    | 7.68    | 328        | 362        | 5M        |

scattering powder diffractometer located at Los Alamos Neutron Science Centre (LANSCE; at Los Alamos National Laboratory, NM, USA).

The compositions \(\text{Ni}_{52}\text{Mn}_{26}\text{Ga}_{22}\) and \(\text{Ni}_{43}\text{Mn}_{38}\text{Ga}_{19}\) were also studied in single crystal form. Cubes of 3 mm \(\times\) 3 mm \(\times\) 3 mm with (100)-type faces were cut from the large single crystal and cooled through the martensitic transition under a load of 5 MPa to ensure that the crystals were in a single variant state. The single crystal diffraction experiments were performed on a D10 instrument at the ILL. The diffractometer was equipped with a four-circle goniometer (\(\lambda = 1.25\ \text{Å}\)) and the measurements were carried out at room temperature and 400 K in order to confirm the results obtained with the powder samples. Neutron diffraction data analysis was performed using GSAS [20] and Fullprof [21] software, both based on the Rietveld refinement method [22].

Calorimetric and magnetic measurements were carried out to determine martensitic and magnetic transition temperatures [18]. The magnetic moment was determined by the Arrott plot method [23] from magnetization curves obtained from superconducting quantum interference device (SQUID) magnetometer measurements at 5 K with applied magnetic fields up to 5 T.

3. Results and discussion

3.1. Neutron diffraction and chemical order

Table 1 shows that Curie temperature is not very sensitive to the electronic concentration in the studied range, while martensitic transition temperatures, \(T_M\), linearly increase with \(e/a\), as expected [7]. Only Ni-deficient compositions (such as Ni44 single and poly-crystals) strongly deviate from this behavior and show much higher \(T_M\) than alloys with the same electronic concentration.

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Figure 1. (a) Fit of the neutron diffraction pattern of the polycrystalline sample of composition $\text{Ni}_{44}\text{Mn}_{38}\text{Ga}_{18}$ in the austenite phase ($T = 400$ K). (b) Integrated intensity for the calculated and observed reflections and their difference for an $\text{Ni}_{43}\text{Mn}_{38}\text{Ga}_{19}$ single-crystal in the austenite phase ($T = 400$ K). Inset: a Q-scan along the $b$-axis on the (200) plane, showing a 14M modulated structure in the martensitic phase.

Neutron diffraction patterns were obtained at room temperature and 400 K to determine the structure of martensite and austenite phases, respectively, both in the polycrystalline and single-crystal samples (see figure 1). All of the samples exhibit $L_2_1$ order in the austenite phase and lower symmetry in the martensitic one (see table 1) [17, 18].

In principle, magnetic diffraction could give information about the magnetic structure of the alloys. However, the magnetic intensity was extremely low as compared with the nuclear intensity, even in single-crystalline samples. Therefore, a fit of the magnetic contribution of the neutron scattering is impossible with any degree of accuracy. As a result, this work focused on the analysis of the neutron diffraction data on determining the preferential site occupancies of each element. Neutron diffraction is required to study chemical order in these alloys due to similar x-ray scattering factors of the elements that result in very faint superstructure peaks. The neutron scattering lengths of Ni, Mn and Ga, however, are very different, and in particular Mn is negative, giving a strong contrast that makes the detection of small changes in the preferential occupancy possible. Following this line of reasoning, the diffraction patterns obtained at 400 K in the austenitic phase and above the Curie temperature have been analyzed for all studied compositions. This was done in order to avoid the complex modulated structure of the martensitic phase and the almost negligible magnetic scattering contribution.

The first step used to analyze the collected neutron diffraction patterns was to accurately determine the profile shape function, background and cell parameters using the profile matching option of Fullprof program. Once these parameters were obtained, Rietveld refinement was used to fit the intensities of the whole pattern. To carry out the fit, we fixed the occupancies of the crystallographic positions that are fully occupied with one atomic species and left free those
Table 2. Summary of the fitted parameters for the sample Ni44 (all distances in Å)

| Profile parameters | Cell parameters | \( a = 5.8638(1) \) | \( a = 90.00 \) | \( \alpha = 90.00 \) | \( \beta = 90.00 \) | \( \gamma = 90.00 \) |
|--------------------|-----------------|---------------------|----------------|-----------------|-----------------|------------------|
| Overall scale factor | 0.00778(9) | Eta(\( p-v \)) | 0.02(4) | Half-width parameters | \( u = 0.136(3) \) | \( v = -0.279(6) \) | \( w = 0.236(3) \) |
| Asymmetry parameters | 0.08(1) | \(-0.011(4)\) | \| X and Y parameters | 0.0018(4) | 0.01(0) |

Global parameters

Zero-point 0.448(2)

Atomic parameters

| Name    | \( X \) | \( y \) | \( z \) | Displacement parameters | Occupation number |
|---------|--------|--------|--------|-------------------------|-------------------|
| NiN     | 0.25   | 0.25   | 0.25   | 1.05(5)                 | 1.79(7)           |
| MnN     | 0.25   | 0.25   | 0.25   | 1.59(6)                 | 0.210(8)          |
| MnM     | 0.00   | 0.00   | 0.00   | 1.59(6)                 | 1.00(0)           |
| GaG     | 0.50   | 0.50   | 0.50   | 0.85(5)                 | 0.75(3)           |
| MnG     | 0.50   | 0.50   | 0.50   | 1.59(6)                 | 0.25(1)           |

Reliability factors

Least-squares refinement \( R_p = 2.74 \) \( R_{xp} = 3.89 \) \( R_{xp} = 1.52 \) \( \chi^2 = 6.53 \)

sites filled by two different kinds of atoms, while assuming that all crystallographic positions were fully occupied, i.e. no vacancies were allowed. This assumption was shown to be valid as the inclusion of vacancies did not improve the fitting and in some case resulted in worse overall fits to the experimental data. Moreover, the absence of a significant number of vacancies that could be detected by diffraction has been confirmed by positron annihilation experiments on similar samples after proper annealing [24]. The refined patterns show very good agreement with the experimental patterns in both polycrystalline and single-crystal samples (see figure 1). One example of the full output parameter set obtained in the fitting procedure is shown in table 2. The chosen sample is one of the newly reported ones that motivated this study because of its peculiar behavior.

In our preliminary study [17], three almost isoelectronic compounds, Ni49, Ni50 and Ni52 (see table 1), with different Mn and Ni content, were studied. All samples had excess Mn but were either Ni rich or poor, to balance the electronic concentration. Using this fitting procedure, we determined that in the Ni defective alloys, the excess Mn occupied empty Ni and Ga atomic sites, leaving no vacancies. For the compound with excess Ni, the best fit was obtained by placing all of the excess Ni on Mn sites and the excess and displaced Mn on vacant Ga sites.

For the new compositions reported here (Ni44 and samples S1–S5), the previously observed trend in site occupancies was confirmed in all aspects. The calculated occupancies and agreement factors from the different refinements are shown in table 3 for all of the studied samples. The occupancies are assumed to be the same in the martensitic phase due to the diffusion-less character of the transition.
Table 3. Site occupancies and agreement factor of the Rietveld refinement ($R_{wp}$) calculated for the polycrystalline studied alloys. Overall composition calculated from occupancies matches the measured composition. Errors are indicated in brackets.

| Alloy | Site (Wyckoff designation) | Ni    | Mn    | Ga    | Total | $R_{wp}$ (%) |
|-------|---------------------------|-------|-------|-------|-------|--------------|
|       | Ni(8c)                    | 1.79(7)| 0.210(8)| 0.0 | 2.0 | 3.9 |
| Ni44  | Mn(4a)                    | 0.0   | 1.0   | 0.0 | 1.0 | 4.7 |
|       | Ga(4b)                    | 0.0   | 0.25(1) | 0.75(3) | 1.0 |
|       | Overall composition (at.%) | 44.75 | 36.50 | 18.75 | 100 |
| Ni49  | Ni(8c)                    | 1.97(9)| 0.03(1) | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.0   | 1.0   | 0.0 | 1.0 | 5.6 |
|       | Ga(4b)                    | 0.0   | 0.188(9) | 0.81(4) | 0.998 |
|       | Overall composition (at.%) | 49.25 | 30.45 | 20.25 | 100 |
| Ni50  | Ni(8c)                    | 2.0   | 0.0   | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.0   | 1.00  | 0.0 | 1.0 | 6.7 |
|       | Ga(4b)                    | 0.0   | 0.88(6) | 0.88(6) | 1.0 |
|       | Overall composition (at.%) | 50.2  | 29.0  | 20.75 | 100 |
| Ni52  | Ni(8c)                    | 2.0   | 0.0   | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.080(5)| 0.92(6) | 0.0000 | 1.0 |
|       | Ga(4b)                    | 0.0   | 0.120(8) | 0.88(6) | 1.0 |
|       | Overall composition (at.%) | 52.0  | 26.0  | 22.0  | 100 |
| S1    | Ni(8c)                    | 2.0   | 0.0   | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.116(3)| 0.88(2) | 0.0 | 0.996 |
|       | Ga(4b)                    | 0.0   | 0.140(4) | 0.86(2) | 1.0 |
|       | Overall composition (at.%) | 52.9  | 25.5  | 21.5  | 99.9 |
| S2    | Ni(8c)                    | 2.0   | 0.0   | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.056(2)| 0.94(4) | 0.0 | 0.996 |
|       | Ga(4b)                    | 0.0   | 0.120(5) | 0.88(3) | 1.0 |
|       | Overall composition (at.%) | 51.4  | 26.5  | 22.0  | 99.9 |
| S3    | Ni(8c)                    | 2.0   | 0.0   | 0.0 | 2.0 |
|       | Mn(4a)                    | 0.016(1)| 0.98(3) | 0.0 | 0.996 |
|       | Ga(4b)                    | 0.0   | 0.116(3) | 0.88(2) | 0.996 |
|       | Overall composition (at.%) | 50.4  | 27.4  | 22.0  | 99.8 |
| S4    | Ni(8c)                    | 1.98(6)| 0.016(1) | 0.0 | 0.996 |
|       | Mn(4a)                    | 0.0   | 1.0   | 0.0 | 1.0 | 2.8 |
|       | Ga(4b)                    | 0.0   | 0.128(4) | 0.87(2) | 0.998 |
|       | Overall composition (at.%) | 49.5  | 28.6  | 21.75 | 99.9 |
| S5    | Ni(8c)                    | 1.93(5)| 0.068(2) | 0.0 | 1.998 |
|       | Mn(4a)                    | 0.0   | 1.0   | 0.0 | 1.0 | 2.4 |
|       | Ga(4b)                    | 0.0   | 0.12(1) | 0.88(2) | 1.0 |
|       | Overall composition (at.%) | 48.25 | 29.7  | 22.0  | 100 |

In short, the neutron diffraction analysis of the different samples, in both polycrystalline and single-crystal phases, allows us to confirm that no vacancies are present and also that two different preferential atomic distributions occur in Mn excess alloys:

(a) Mn excess alloys with Ni deficiency or balance: Mn atoms occupy Ni and Ga vacant places.
(b) Mn and Ni excess alloys: Ni excess occupies Mn sites, displacing Mn atoms to the Ga positions.

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Figure 2. Magnetization curves measured at 5 K for selected alloys. The saturation magnetization was determined using the Arrot plot method (see the inset).

3.2. The magnetic moment distribution model

Figure 2 illustrates the typical results of magnetization measurements at 5 K for several Ni–Mn–Ga alloys, and the saturation magnetization, obtained by the Arrot plot method [23] from these curves. Table 4 shows the results for all alloys. As can be seen, the magnetic moment determined for the alloys with Mn excess is smaller than the moment of the stoichiometric composition. The decrease of the moment with increasing Mn content could be explained with the Slater–Pauling rigid band model for 3d alloys, as discussed above, and the expected values predicted by this model are displayed as a continuous line in figure 3. However, this approach shows large deviations from the experimental values even in a reduced range of electron concentration (figure 3 and table 4) and an alternative model is needed.

In our previous work [17], we proposed a simple model of localized moments to overcome the shortcomings of the Slater–Pauling rigid band model. In our model, we took into account the preferential order determined with neutron diffraction and considered that all Mn atoms in antisite positions, i.e. at Ni or Ga sites, couple antiferromagnetically to the properly sited ones because they become nearest neighbors.

To clarify the main assumptions of our model, we explicitly state the following hypothesis:

(a) The magnetic moment of the alloys is mainly localized at Mn atoms that carry 3.51 $\mu_B$ each.
(b) Ni atoms also carry a small, localized moment of 0.33 $\mu_B$.
(c) Mn atoms couple ferromagnetically when located at proper sites in the L2_1 structure.
Table 4. Magnetic moments of the studied alloys, determined experimentally ($\mu_{\text{exp}}$) and calculated using the rigid band model [12] ($\mu_{\text{calc,R–B}}$), the preliminary model ($\mu_{\text{calc,I}}$) and the improved model ($\mu_{\text{calc,II}}$) proposed in this work. The deviation of the model calculation from the experimental value is shown as a percentage of the latter.

| Alloy     | $\mu_{\text{exp}}$ (5 K) ($\mu_B$ FU$^{-1}$) | $\mu_{\text{calc,R–B}}$ ($\mu_B$ FU$^{-1}$) | $\mu_{\text{calc,I}}$ ($\mu_B$ FU$^{-1}$) | $\mu_{\text{calc,II}}$ ($\mu_B$ FU$^{-1}$) |
|-----------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| Ni$_2$MnGa | 4.17                                        | 4.17                                        | 4.17                                        | 4.17                                        |
| Ni44      | 3.06 (22.4%)                               | 2.37 (24.9%)                               | 2.30 (24.9%)                               | 2.96 (3.3%)                                |
| Ni49      | 3.41 (0.6%)                                | 3.39 (0.6%)                                | 3.39 (0.6%)                                | 3.46 (1.5%)                                |
| Ni50      | 3.60 (0.1%)                                | 3.60 (0.1%)                                | 3.55 (1.2%)                                | 3.55 (1.2%)                                |
| Ni52      | 3.59 (12.0%)                               | 4.02 (12.0%)                               | 3.48 (3.1%)                                | 3.48 (3.1%)                                |
| S1        | 3.37 (20.9%)                               | 4.08 (20.9%)                               | 3.31 (1.8%)                                | 3.31 (1.9%)                                |
| S2        | 3.63 (8.4%)                                | 3.94 (8.4%)                                | 3.57 (1.7%)                                | 3.57 (1.7%)                                |
| S3        | 3.83 (0.6%)                                | 3.81 (0.6%)                                | 3.71 (3.1%)                                | 3.71 (3.1%)                                |
| S4        | 3.99 (8.4%)                                | 3.66 (8.3%)                                | 3.66 (8.3%)                                | 3.69 (7.4%)                                |
| S5        | 3.39 (3.0%)                                | 3.49 (3.0%)                                | 3.47 (2.3%)                                | 3.62 (6.9%)                                |

Figure 3. Magnetic moments as a function of electron concentration predicted by the rigid band model [11] and the values measured in this work.

(d) Mn atoms at shorter distances have AF interactions.
(e) Ni always couple ferromagnetically to proper sited Mn atoms.
(f) The magnetic moment does not change appreciably at the martensitic transformation.
The values of the magnetic moment of Mn and Ni are taken from studies of the stoichiometric Ni$_2$MnGa compound [25]. As is generally accepted, we considered that Ga atoms do not contribute to the total magnetic moment. The AF coupling between nearest-neighbor Mn atoms is expected due to the variation of the exchange interaction that becomes AF for small interatomic distances. Figure 4 shows schematically the change in both direct exchange (the Bethe–Slater curve) and indirect exchange through conduction electrons (RKKY interaction) that present almost the same variation in the range of interatomic distances that we are considering in this work.

In the simplified version of the model used in [17], we assumed that all off-site Mn atoms display AF coupling. The results obtained using this approximation are summarized in table 4 as $\mu_{\text{calc},1}$ and show good agreement with the original samples (Ni49, Ni50 and Ni52) and with the new samples with Ni content in the range from 48.5 at.% to about 53 at.%. However, this preliminary model does not fit the experimental value for the sample with large Ni deficiencies (44 at.% Ni) and shows a large error of 24.8%. This discrepancy motivates improving the model in order to expand its validity for a larger composition range. It should be noted, however, that even the simplified model agrees with the experimental results better than the calculations based on the Slater–Pauling rigid band model, displayed in table 4 as $\mu_{\text{calc},\text{R–B}}$.

In the improved model presented here, we take into account that the Ni-deficient samples present three different Mn–Mn distances that can affect the exchange interaction: Mn atoms on proper sites (Mn/Mn) are at $(\sqrt{2}/2)a$ from other Mn/Mn atoms, Mn atoms on Ni sites (Mn/Ni) are at $(\sqrt{3}/4)a$ from Mn/Mn ones and finally Mn at Ga sites (Mn/Ga) are at $a/2$ in the cubic lattice (see figure 5). Similar distances are obtained in the martensite structure.

In the case of absence of Ni deficiency, the excess Mn atoms occupy only Ga sites and couple antiferromagnetically to the Mn/Mn atoms, because the Mn/Ga atoms are nearest neighbors to Mn/Mn atoms (see figure 5(b)). However, in samples with large Ni deficiencies, there are Mn atoms at Ni sites, which present the shortest distance to the Mn/Mn and Mn/Ga atoms (see figure 5(c)). In such a case, the AF coupling between Mn/Ni and Mn/Mn or Mn/Ga atoms is stronger than that between Mn/Ga and Mn/Mn ones (figure 4) and overcomes it. Consequently, in Ni-deficient alloys, some Mn/Ga and Mn/Mn atoms will couple.
Figure 5. (a) Magnetic moment distribution diagram for Ni$_2$MnGa. (b) AF coupling between Mn/Ga and Mn/Mn when Ni atoms are at their proper sites. (c) FM coupling between Mn/Mn and Mn/Ga when Mn excess occupies Ni sites (adapted from [19]).

ferromagnetically. Therefore, the presence of Mn/Ni atoms is decisive in the coupling between Mn/Ga and Mn/Mn atoms that can change from AF to FM.

To calculate the expected magnetic moment for the alloys, within the improved model, we take into account the site occupancies determined by neutron diffraction and the localized magnetic moment for the Mn and Ni atoms, i.e. $m_{\text{Mn}} = 3.51 \mu_B$ and $m_{\text{Ni}} = 0.33 \mu_B$. In addition, Ni shows two equivalent positions in the L2$_1$ structure and so the excess Mn located at Ni positions is distributed between two equivalent positions. Then each Ni site will be occupied by $(\text{at.} \% \text{Mn/Ni})/2$ and the number of Mn/Ga atoms that couple ferromagnetically to the Mn/Mn atoms will be determined by

$$
(\text{at.} \% \text{Mn/Ga}_{\text{FM}}) = (\text{at.} \% \text{Mn/Ga}) \cdot (\text{at.} \% \text{Mn/Ni})/2.
$$

(1)

The remaining Mn/Ga atoms, which couple antiferromagnetically to the Mn/Mn atoms, are calculated by

$$
(\text{at.} \% \text{Mn/Ga}_{\text{AF}}) = (\text{at.} \% \text{Mn/Ga}) - (\text{at.} \% \text{Mn/Ga}_{\text{FM}}).
$$

(2)

Taking into account all of this, we calculate the total magnetic moment per formula unit for the different alloys through the following expression,

$$
\mu (\mu_B/\text{FU}) = \frac{4}{100} \cdot ((\text{at.} \% \text{Mn/Mn}) \cdot m_{\text{Mn}}) + ((\text{at.} \% \text{Ni/Ni}) \cdot m_{\text{Ni}}) + ((\text{at.} \% \text{Mn/Ga}_{\text{FM}})

- (\text{at.} \% \text{Mn/Ga}_{\text{AF}}) - ((\text{at.} \% \text{Mn/Ni})/2) \cdot m_{\text{Mn}}).
$$

(3)

Table 4 presents a summary of the results obtained by using the preliminary ($\mu_{\text{calc.I}}$) and the improved ($\mu_{\text{calc.II}}$) model and the experimental magnetic moments of the studied alloys. As can be seen, the improved model only impacts the Ni-deficient alloys, and the overall agreement with the measured values is now excellent for a large range of Ni content spanning from 44 to
Figure 6. The lines represent the predictions of the improved model for the expected magnetic moment of Mn-rich Ni–Mn–Ga alloys, as a function of the electronic concentration. The filled circles are experimental values determined at 5 K.

52 at.% Ni. The difference between the calculated and the measured moments is less than 7.4%, which is a remarkable improvement taking into account the simplicity of the model that we propose.

Further predictions can be made by calculating the expected magnetic moment that corresponds to any Mn-rich alloy. This calculation is depicted in figure 6 as a function of the electronic concentration, and compared with all magnetic moments measured for a large number of samples. We can see that there is not a single curve describing all situations but the exact Ni content is important in determining the magnetic moment of the alloy. In spite of the crude assumptions of the model, we see that the experimental values are much better represented in these curves than they were in the band model of figure 3. We acknowledge that further improvements must be made to fully account for the magnetic moment evolution in off-stoichiometric Ni–Mn–Ga alloys, but our present description seems to be a good starting point. To improve the model, new data from x-ray magnetic circular dichroism (XMCD) and PND are still lacking. We are aware of recent XMCD publications on different Heusler alloys [26], including non-stoichiometric Ni2MnGa films [27]. These recently published results should offer insights into the orbital and spin contributions to the magnetic moment in each atomic species, and changes at the martensitic transformation can be followed. However, there is always uncertainty in the final density of states of the electronic transition that prevents an accurate determination of the moment. PND has been performed in the stoichiometric Ni2MnGa compound [7, 8], but little has been done on other compositions. PND data would provide a site-sensitive value of the magnetic moment but must be used together with site occupancy determination to assign moments to each atom at each site. Using both XMCD and PND on
the very same compounds is the only way for getting full insight into the magnetic behavior of these alloys.

4. Conclusions

We have determined the preferential atomic order for off-stoichiometric Ni–Mn–Ga alloys with a large range of Ni concentrations (44–52 at.%) from neutron diffraction experiments. We have demonstrated that for alloys with excess Ni, Ni atoms occupy Mn sites and excess and displaced Mn atoms go to the Ga positions. For Ni-deficient alloys, Mn atoms occupy both Ni and Ga sites. Magnetic measurements and the preferential atomic order determined allow us to propose a basic model distribution of magnetic moments that show a strong dependence between the atomic order and the magnetic coupling of Mn atoms at different sites in these off-stoichiometric alloys. Thus, Mn atoms at Ga sites that are nearest neighbors to properly located ones couple antiferromagnetically, whereas Mn atoms at Ga sites with nearest neighbors Mn at Ni sites couple ferromagnetically to Mn/Mn ones. Mn at Ni sites is always AF, and Ni always FM, but with a reduced moment.

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