Magnetic moment distribution in non-stoichiometric Ni-Mn-Ga ferromagnetic shape memory alloys

P Lázpita, J M Barandiarán, J Feuchtwanger, J Gutiérrez, I Rodríguez, V A Chernenko, A Stunault and C Mondelli

1Departamento de Electricidad y Electrónica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Barrio Sarriena s/n 48940, Leioa, Spain
2IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain
3Institut Laue Langevin 6, Rue Jules Horowitz BP 156, 38042 Grenoble Cedex 9, France
4CNR-INFM OGG & CRS-SOFT, c/o ILL, 6 Rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

E-mail: jon@we.lc.ehu.es

Abstract. In this work we present a model for the net magnetic moment per formula unit measured in Ni-Mn-Ga Ferromagnetic Shape Memory Alloys, analyzing the different types of magnetic interactions appearing in such compounds. We have studied four compositions ranging from a 44% to a 52% Ni content. We found that excess Mn atoms occupy empty positions at Ni and Ga sites. We consider that the Mn atoms at Ni sites (Mn/Ni) can determine that Mn/Ga atoms couple either ferromagnetic (FM) or antiferromagnetically (AF) to Mn/Mn atoms. If Mn/Ga are nearest neighbors to properly-sited Mn/Mn atoms they present AF coupling. However, when Mn/Ni atoms are at closer distances than Mn/Ga ones, so that they become nearest neighbors to properly-sited Mn/Mn atoms they present AF coupling. However, when Mn/Ni atoms are at closer distances than Mn/Ga ones, so that they become nearest neighbors to Mn/Mn, the AF coupling between Mn/Ni and Mn/Mn atoms is stronger and overcomes that between Mn/Ga and Mn/Mn ones. Therefore Mn/Ga and Mn/Mn will couple ferromagnetically. Polarized neutron diffraction experiments will help to elucidate the validity of our model.

1. Introduction

Ferromagnetic thermoelastic martensitic transformation takes place in Heusler Ni$_2$MnGa shape memory alloys [1, 2] that, because of the resulting multivariant martensitic phase, represent new multifunctional materials capable of activated twin boundary motion in a controllable way by temperature, stress, magnetic field or their combination [3]. The martensitic structure has been shown to be extremely sensitive to the composition of the alloy. In addition, chemical disorder or preferential order introduces defects of a structural and magnetic nature that may alter the net magnetic moment per formula unit, a key parameter with great influence on the motion of twin boundaries and, in turn, affecting the output strain obtained. This makes a deep study of the magnetic interaction in such alloys desirable.

While the crystal structures of many off-stoichiometry compositions have been studied, there has been few detailed studies of the variation of the magnetic moment distribution with departures from stoichiometry, that seem largely influenced by the exact distribution of the different atomic species on the lattice. As can be seen from different alloys studied so far, the magnetic moment on off...
stoichiometric Ni-Mn-Ga polycrystalline alloys with compositions of 49-52 at. % nickel, excess manganese and deficient in gallium, show a decrease of the magnetic moment per formula unit (FU) with increasing Mn content [4]. This indicates that the Mn displaced to Ni or Ga sites must couple antiferromagnetically to the properly sited Mn moments. The antiferromagnetic coupling is expected due to the close proximity of the Ni (nearest neighbor) and Ga (next-nearest neighbor) sites to the Mn sites. This is based on the general tendency of exchange coupling to change from ferromagnetic to antiferromagnetic at reduced interatomic spacing.

In order to analyze in a deeper way the magnetic moment arising both from the coupling of the Mn atoms at different positions in the unit cell and from itinerant Ni and/or Ga electrons, we have performed an extensive magnetometric study in samples with a large Ni content variation covering the range from 44% to 52% (Ni content percentage). This will allow us to model those interactions and fit the measured low temperature magnetic moment value with the expected (calculated) one.

The validity of our model will be given by a polarized neutron diffraction study performed in off stoichiometric Ni 49% and 52% content single crystals.

2. Experimental procedure

Polycrystalline samples of compositions Ni$_{44}$Mn$_{38}$Ga$_{18}$ (Ni44), Ni$_{49}$Mn$_{31}$Ga$_{20}$ (Ni49), Ni$_{50}$Mn$_{29}$Ga$_{21}$ (Ni50) and Ni$_{52}$Mn$_{26}$Ga$_{22}$ (Ni52), were obtained by crushing single crystals of the same composition. Those were grown at the Ames Laboratory (Iowa, USA) by the Bridgman technique. From performed neutron diffraction measurements and subsequently refinement of the site occupancy, we have demonstrated that excess Mn atoms occupy empty position at Ni and Ga sites. Fully detailed experimental work and structural characterization can be found in [4, 5].

Martensitic transformation and Curie temperatures, and low temperature magnetic moment (measured at 5 K and up to 5 T) were determined by magnetic measurements performed in a SQUID magnetometer.

Polarized neutron diffraction experiments were carried out at the D3 instrument at ILL [6]. In a first step only the cubic austenite phase was studied to avoid structural complications due to the modulated complex structure of the martensite. This fact has no influence when relating low temperature magnetic moment (martensitic phase) and measured spin density at high temperature (austenitic phase), since the magnetic moment does not change appreciably through the martensitic transformation [7].

For these experiments pieces of approximately 3 x 3 x 3 mm$^3$ were cut from large non stoichiometric single crystals of compositions Ni$_{49}$Mn$_{30}$Ga$_{21}$ (Ni49, $M_s = 298$ K and $T_c = 368$ K) and Ni$_{52}$Mn$_{26}$Ga$_{22}$ (Ni52, $M_s = 328$ K and $T_c = 368$ K) respectively. Preliminary experiments were performed to determine the structure of the single crystals on the D10 ($\lambda = 2.36$ Å) and D15 ($\lambda = 0.85$ and 1.17 Å) instruments at ILL (Grenoble, France). Both samples were measured at temperatures in the ferromagnetic martensite and paramagnetic austenite phase.

3. Results and discussion

3.1. Magnetic measurements and modeling of the magnetic interactions

Figure 1 shows one of the measured first magnetization curves, for all the samples. We used the Arrott’s plots fit to obtain the low temperature magnetic moment.

One of the main results obtained in [4, 5] is that we could calculate the occupancies from the neutron diffraction patterns refinement and conclude that the excess Mn atoms are almost equally distributed between Ni and Ga crystallographic positions, and there was no need to introduce vacancies in order to get a good fit with the experimental diffraction pattern. However and for example, for the Ni44 sample (see table 1) magnetic measurements give 3.06 $\mu_B$/FU saturation magnetization at 5 K. If all the off-site Mn atoms do couple antiferromagnetically, as assumed in ref. [4], the expected magnetic moment of the alloy should be 2.30 $\mu_B$/FU, thus departing a 25% from the
measured value. This leads to a revision of the previous assumption about Mn-Mn magnetic coupling in these alloys.

![First magnetization curve measured at 5 K and up to 5 T. The inset shows the Arrott’s plot fit.](attachment:figure1.png)

**Figure 1.** First magnetization curve measured at 5 K and up to 5 T. The inset shows the Arrott’s plot fit.

Works from other authors consider some magnetic moment associated to Ni atoms [8]. As a first approximation, we shall take it as 0.3 \( \mu_B \) irrespective of the atomic Ni concentration, our analysis being focused only on changes on the magnetic moment of the Mn. Let us consider now that the excess Mn atoms at Ni sites (Mn/Ni) are at the shortest distance to properly-sited Mn atoms (Mn/Mn) and can determine whether the Mn atoms at Ga sites (Mn/Ga) couple ferromagnetic (FM) or antiferromagnetically (AF) to Mn/Mn ones. This is because the rapid variation of the exchange interaction with distance will give rise to competing AF interactions (see figure 2).

![Exchange interactions](attachment:figure2.png)

**Figure 2.** Bethe-Slater curve and RKKY interaction one, showing the different types of magnetic interactions as the distance between atoms changes.
It has to be noted that, provided the Mn moment is assumed to present a localized character, the kind of exchange interaction between them turns out to be irrelevant. As can be seen in figure 2, both direct exchange (Bethe-Slater curve) or indirect exchange through conduction electrons (RKKY interaction [9]) have almost the same variation in the range of inter-atomic distances we are dealing with.

Then, if in a given neighborhood no Mn atoms are located in Ni sites, Mn/Ga are nearest neighbors to Mn/Mn atoms (distance = a in a cubic lattice; see figure 3(a)), and they present AF coupling, like in the compositions reported previously [4]. However, when Mn/Ni atoms are present, they are at closer distances than Mn/Ga ones, so that they become nearest neighbors to Mn/Mn (distance = a√3/2 in a cubic lattice, see figure 3(b)). Then, the AF coupling between Mn/Ni and Mn/Mn atoms is stronger than that between Mn/Ga and Mn/Mn ones and overcomes it, so that Mn/Ga and Mn/Mn will couple ferromagnetically. This fact is supported by the semi-empirical Bethe-Slather curve, as shown in figure 2.

In order to estimate the expected magnetic moment for this alloy we have taken into account the calculated occupancies from the neutron diffraction measurements and also that the Ni atom site shows two equivalent positions in the L2₁ structure. That is, the excess Mn sited at those positions is distributed between two equivalent positions. Therefore each Ni site is occupied by (at.%Mn/Ni)/2 and the Mn/Ga atoms which will couple ferromagnetically to the Mn/Mn atoms will be determined by at.%Mn/GaFM = at.%Mn/Ga x (at.%Mn/Ni)/2 , the remaining Mn/Ga atoms being antiferromagnetically coupled.

As a first consequence and following this line of reasoning, we can calculate the expected magnetic moment values by using the expression

\[
\mu(\mu/FU) = \frac{4}{100} \left[ \text{at.} \%, \text{Mn} \cdot m_{\text{Mn}} + \text{at.} \%, \text{Ni} \cdot m_{\text{Ni}} + \right. \\
\left. (\text{at.} \%, \text{Mn/Ga} - \text{at.} \%, \text{Mn/Ga,AF} - \text{at.} \%, \text{Mn/Ni}) \cdot m_{\text{Mn}} \right]
\]

and got a value of 2.96 \(\mu/FU\) for the Ni44 sample, less that a 3.3% difference from the experimentally obtained value. The magnetic moment value calculated for the other alloys do not change by this new refinement of the model, unless they are Ni deficient. In such case, however, the small Ni deficiency does not alter very much the calculated magnetic moment and the overall agreement with the measured values is now excellent for a large Ni content variation covering the range from 44% to 52% (Ni content percentage). A summary of the results obtained by using our improved model and the experimentally determined magnetic moment values in those alloys is shown in table 1.
Table 1. Magnetic moment values, both measured and calculated, for different Ni content alloys.

| Alloy (at.% Ni) | $\mu_{\text{meas}}$ (B/μF) | $\mu_{\text{cal}}$ (B/μF) | Error (%) |
|----------------|---------------------------|---------------------------|-----------|
| Ni52           | 3.59                      | 3.62                      | 0.8       |
| Ni50           | 3.60                      | 3.55                      | 1.4       |
| Ni49           | 3.41                      | 3.46                      | 1.5       |
| Ni44           | 3.06                      | 2.96                      | 3.3       |

The difference between the calculated and measured magnetic moments is always less than a 3.5% which is remarkable, taking into account the rough approximation made. This small discrepancy can arise from the contribution of the conduction band electrons in the total magnetic moment of the alloy thus far neglected, still a subject of discussion [10].

3.2. Polarized neutron diffraction study

To confirm the validity of our assumptions concerning the different type of magnetic interactions appearing in our studied compositions, we performed polarized neutron diffraction experiments in non-stoichiometric single crystals of compositions Ni$_{49}$Mn$_{30}$Ga$_{21}$ (Ni49) and Ni$_{52}$Mn$_{26}$Ga$_{22}$ (Ni52). Direct Fourier transform of the obtained experimental magnetic structure factors determined the spin density distribution map that confirms the role of the different atoms in the total magnetic moment of these alloys.

Figure 4. Spin density map of Ni$_{52}$Mn$_{26}$Ga$_{22}$ single crystal measured with 2 T applied magnetic field at 331 K in the ferromagnetic austenite phase. Main and inset figures show the planes (0 0 1) and (0 0 $\frac{1}{2}$) respectively.

Figure 5. Density of magnetic moment in the (110) plane of Ni$_{52}$Mn$_{26}$Ga$_{22}$ single crystal measured with 2 T applied magnetic field at 300 K in the ferromagnetic martensitic phase. The red line represents the L2$_1$ unit cell used to define the austenitic cubic phase.
From figure 4 and 5 we infer that the Mn and Ni atoms present a localized moment. On the other hand, the negative spin density observed in the interatomic positions can be again assigned to the conduction band electrons polarization [10], as previously mentioned.

Figure 6 shows the variation of the density of magnetic moment along the line joining near neighbor atoms of Mn and Ga and Mn and Mn (in Ga positions) for Ni$_{52}$Mn$_{26}$Ga$_{22}$ and Ni$_{49}$Mn$_{30}$Ga$_{21}$ at a temperature $M_s < T < T_c$. The inset shows the variation along the line joining near neighbor atoms of Ni.

Figure 6 shows the variation of the magnetic moment obtained from the neutron polarization diffraction measurements, for both studied samples. This graph clearly evidences that in both Ni$_{52}$Mn$_{26}$Ga$_{22}$ and Ni$_{49}$Mn$_{30}$Ga$_{21}$ single crystals the magnetic moment of the Mn displaced to the Ga sites couples antiferromagnetically to the properly-sited Mn moments. This result strongly supports the magnetic interaction model described in the previous section where we proposed an antiferromagnetically coupling between Mn atoms at Ga sited and properly-sited Mn atoms to account for all measured low temperature magnetic moment values.

Finally, we also performed measurements of the variation of the density of magnetic moment at different temperatures and we observed a quite complex behaviour that is still under analysis.

4. Conclusions
From our previous works with neutron diffraction measurements and subsequently refinement of the site occupancy, in which we have demonstrated that excess Mn atoms occupy empty position at Ni and Ga sites, we have fitted the measured low temperature magnetic moment value with the expected (calculated) one, just taking into account only the coupling between magnetic moments of the Mn. Ni magnetic moment is assumed to have a constant value of about 0.3 $\mu_B$ and to couple ferromagnetically to the average magnetization.

Polarized neutron diffraction experiments helped us to elucidate about the previously discussed different type of magnetic interactions: we have found that the magnetic moment of this compositions is mostly localized. Also, that the model agrees when Mn atoms are located at the Ni and Ga positions, but a more elaborated work is needed to account for the measured magnetic moment density evolution with temperature.

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