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

P Lázpita1,a, J Gutiérrez1, J M Barandiarán1, V A Chernenko1,2, C Mondelli3,4, L. Chapon3
1 BCMaterials and Basque Country University (UPV/EHU), Bilbao, Spain
2 Ikerbasque, Basque Foundation for Science, Bilbao 48011, Spain
3 Institut Laue Langevin 6, Rue Jules Horowitz BP 156, 38042 Grenoble Cedex 9, France
4 CNR-INFM OGG & CRS-SOFT, c/o ILL, 6 Rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

aEmail: patricia.lazpita@ehu.es

Abstract. Neutron polarized diffraction technique has been used to elucidate the magnetic moment distribution density in non stoichiometric Ni—Mn—Ga single crystals. These experiments allow us to determine a localized magnetic moment in the Mn position in the austenitic phase, and to validate qualitatively previous models of magnetic distributions where there are antiferromagnetic and ferromagnetic coupling for Mn atoms that are sited out of their proper positions. This measurements show the deep dependence of the magnetic moment with the composition and the atomic order.

1. Introduction
Ferromagnetic shape memory alloys have been focus of interest during the last years due to their unusual magnetomechanical properties. The ferromagnetic thermoelastic martensitic transformation that takes place in the Heusler Ni—Mn—Ga alloys produces a multivariant martensitic phase [1, 2] that make these new multifunctional materials capable of activated twin boundary motion in a controllable way by magnetic field reach strains up to 10 % [3]. This effect is the so called magnetic field induced strain (MFIS) effect [4]. The martensitic structure and the net magnetic moment, key parameters to develop the MFIS effect, have been shown to be extremely sensitive with the composition of these alloys. Moreover they have a great influence on the motion of twin boundaries affecting the output strain. This makes a deep study of the structure and magnetic interactions in such alloys desirable.

Already crystal structures of many off stoichiometric compositions have been studied [5-7]. In previous works Richard et al. [8-10] have been purposed a preferential atomic order for Ni—Mn—Ga alloys with compositions of 44-52 at.% nickel, excess manganese and gallium defective. They present the next atomic distribution: for the alloys that present Ni and Ga defective and excess of Mn, the Mn excess occupies the Ni and Ga vacancies places. Meanwhile, those that present both excess on Ni and Mn, the Ni atoms go to the Mn positions, displacing the excess and the properly placed Mn to the Ga positions. Based on this atomic preferential distribution, and taking into
account the general tendency of exchange magnetic coupling that change from ferromagnetic to antiferromagnetic order at reduced interatomic spacing a new simple model of distribution of magnetic moment was proposed [10].

In order to study in a deeper way the magnetic moment distribution in non stoichiometric Ni—Mn—Ga single crystals we have performed a study by neutron polarized diffraction. These experiments will allow us to confirm the validity of our model.

2. Experimental procedure

Single crystal sample of compositions Ni₅₂Mn₂₆Ga₂₂, Ni₄₉Mn₃₀Ga₂₁ and Ni₄₃Mn₃₈Ga₁₉ were grown by the Bridgman technique at the Ames Laboratory (Iowa, USA). For these experiment pieces of approximately 3 mm x 3 mm x 3 mm were used. Martensitic transformation and Curie temperatures were determined by magnetic measurements performed in a Vibrating Sample Magnetometer. The magnetic moment at different temperatures (from 330 K to 400 K) was determined from magnetization curves with applied magnetic fields up to 2 T.

Preliminary experiments were performed to determine the single crystals nuclear structure on the D10 ($\lambda=2.36\,\text{Å}$) and D15 ($\lambda=0.85\,\text{Å}$ and $1.17\,\text{Å}$) instruments at ILL (Grenoble, France). All the single crystals were measured at temperatures in the ferromagnetic and paramagnetic austenitic phase, and so the atomic order could be determined.

Polarized neutron diffraction measurements at different temperatures in the austenitic phase were carried out at D3 instrument at ILL. The crystals were mounting with it $[001]$ axis vertical inside a superconducting magnet. The data collected were treated with the Cambridge Crystallography Subroutine Libraries (CCSL) obtaining the magnetic structure factors. Maximum Entropy method [11] using MemSys code available on the ILL was used for direct visualization of the atomic magnetization density maps using the Fourier transformed. Neutron diffraction data analysis was performed using flipping ratios fits with the FullProf software [12].

3. Results and discussion

3.1. Magnetic measurements.

Martensitic transformation ($T_M$) and Curie ($T_C$) temperatures have been determined from the low applied magnetic field magnetization curves (Figure 1) and are summarized in Table 1. For all compositions $T_M$ is lower than $T_C$. This allows us to study both paramagnetic austenitic phase and ferromagnetic austenitic one, and to determine in a better way the magnetic moment distribution in the austenitic ferromagnetic phase. The total macroscopic magnetic moment at different temperatures was determined from hysteresis loops obtained in the austenitic phase (Figure 2). Magnetization curves appear to be saturated for applied magnetic fields of about 0.5 T in the ferromagnetic phase, and they reduce to a clear paramagnetic trend at temperatures higher than the Curie one.

3.2. Neutron diffraction measurements.

Neutron diffraction experiments in the paramagnetic austenite phase were done to confirm the $L2_1$ structure, to determine the cell parameter and the atomic distribution at different position for all studied single crystals. These results were used to analyze the intensities obtained in the polarized neutron diffraction measurements. Figure 3 show the magnetic structure factors at different temperatures in the austenitic phase for applied magnetic field of 2 T. We added the value of the bulk magnetization under 2 T at $q=0$. As well as the bulk magnetization, the intensity of the magnetic form factor reduces when the temperature is closer to the Curie one. There is no regular decrease of the dependence of the magnetic form factor with the scattering vector which is indicative of the contribution to the total magnetic intensity of Mn and Ni associated to different magnetic form factors. Figure 4 shows the magnetization maps obtained by the maximum entropy
**Figure 1.** Magnetization of Ni$_{43}$Mn$_{38}$Ga$_{19}$ at low magnetic field (0.05 T) as function of temperature.

**Figure 2.** Hysteresis loops of Ni$_{43}$Mn$_{38}$Ga$_{19}$ at different temperatures in the austenitic ferromagnetic and paramagnetic phases.

| Composition | $T_M$ (K) | $T_C$ (K) | $a$ (Å) | $m$ ($\mu_B$/Mn) | $m_{\text{MnMn}}$ ($\mu_B$) | $m_{\text{MnGa}}$ ($\mu_B$) | $m_{\text{NiNi}}$ ($\mu_B$) |
|-------------|-----------|-----------|---------|-----------------|-----------------|-----------------|-----------------|
| Ni$_{52}$Mn$_{26}$Ga$_{22}$ | 328 | 368 | 5.835 | 2.01 | 1.283(8) | -2.6(2) | 0.131(5) |
| Ni$_{49}$Mn$_{30}$Ga$_{21}$ | 298 | 368 | 5.813 | 1.76 | 1.587(4) | -3.2(1) | 0.151(3) |
| Ni$_{43}$Mn$_{38}$Ga$_{19}$ | 320 | 367 | 5.923 | 1.53 | 1.814(6) | -1.02(3) | 0.098(2) |

Table 1. Martensitic transformation ($T_M$) and Curie ($T_C$) temperatures, cell parameter ($a$) determined by neutron diffraction, magnetic moment ($m$) at 2 T determined by magnetic measurements and magnetic moment obtained by neutron polarized diffraction for Mn atoms placed in their own positions ($m_{\text{MnMn}}$), Ni atoms in Ni sites ($m_{\text{NiNi}}$) and Mn atoms placed on Ga positions ($m_{\text{MnGa}}$) respectively, at the austenitic ferromagnetic phase for the studied alloys.

To determine the magnetic moment distribution at each position we assume an scenario in which all the magnetization is given by the Mn$^{2+}$ and Ni$^{2+}$ spherical free atom form factors site on Ni, Mn or Ga positions depending on the single crystal composition. The average values of magnetic moment determined at different positions are summarized in Table 1. In the stoichiometric Ni$_2$MnGa alloy with a Curie temperature of 376 K, Brown et al. [13] determined higher values for the magnetic moments of Mn atoms properly sited ($2.27 \mu_B$) at 230 K. This difference can be attributed to the proximity of the Curie temperature in our study and the disorder induced by the
non stoichiometric composition. It is remarkable that the magnetic moment average value of the Ni atoms sited at Ni positions (NiNi) for the Ni defective alloy is lower than in the other ones. This fact could be related to the presence of the Mn excess coupling antiferromagnetically with the total moment at the Ni position. Moreover, the Mn magnetic moment behavior depends on the composition and also on the position in the unit cell. In the case of MnMn atoms they show small average values for the Ni excess composition, these results confirm that the excess of Ni occupy the Mn positions prompt the decrease on the total magnetic moment density due the lower magnetic moment linked to the Ni atoms. However, for MnGa atoms the absolute average value is smaller in the lowest Ni content alloy. This can be explain if we take into account the purpose simple model of magnetic moment distribution for this alloy where there is both antiferromagnetic and ferromagnetic coupling of the MnGa atoms. In this case, the drop of the average value of the magnetic moment is related to the sum of the ferromagnetic and antiferromagnetic coupling of the Mn atoms sited at the Ga positions.

4. Conclusions
Polarized neutron diffraction experiments allow us to elucidate about the localized moment nature of the Ni and Mn atoms for non stoichiometric Ni—Mn—Ga single crystals. The determined spin density maps show a negative contribution related to the antiferromagnetic coupling of the Mn sited out of their properly positions. The magnetic moment average value of the Mn depends strongly on the composition and also on their position on the L2₁ structure. The low absolute value of the MnGa moment for Ni defective alloy determined is related to the average of the ferromagnetic and antiferromagnetic coupling of the Mn at these positions. With these results we can confirm, at least qualitatively, the validity of the simple model of magnetic moment distribution previously purposed by the authors: MnMn, and NiNi atoms present a ferromagnetic coupling, while MnNi antiferromagnetic one. However, the Mn atoms at Ga positions couple antiferromagnetic or ferromagnetically depending on their nearest neighbors.

Acknowledgements
Authors would like to thank financial support from the Basque Government (ACTIMAT project, ETORTEK programme) and from CICYT of Spain under contract MAT2011-28217-C02-02. P. L. thanks UPV/EHU for a grant. Technical and human support provided by SGiker (UPV/EHU, MICINN, GV/EJ, ESF) is gratefully acknowledged.
References

[1] Webster P J, Ziebeck K R A, Town S L and Peak M S 1984 Philos. Mag. B 49 295-310
[2] Chernenko V A, Cesari E, Kokorin V V and Vitenko I N 1995 Scr. Metall. Mater. 33 1239-1244
[3] Ullakko K, Huang J K, Kantner C, O’Handley R C and Kokorin V V 1996 Appl. Phys. Lett. 69 1966-1968
[4] O’Handley R C, Murray S J, Marioni M, Nembach H and Allen S M 2000 J. Appl. Phys. 87 4712-4717
[5] Brown P J, Crangle J, Kanomata T, Matsumoto M, Neumann K-U, Ouladdiaf B and Ziebeck K R A 2002 J. Phys.: Condens. Matter. 14 10159-10171
[6] Chernenko V A, Cesari E, Pons J and Seguí C 2000 J. Mater. Res. 15 1498-1504
[7] Pons J, Chernenko V A, Santamarta R and Cesari E 2000 Acta Mater. 48 3027-3038
[8] Richard M L, Feuchtwanger J, Allen S M, O’Handley R C, Lázpita P, Barandiarán J M, Gutiérrez J, Ouladdiaf B, Mondelli C, Lograsso T and Schlage D 2007 Philos. Mag. 87 3437-3447
[9] Lázpita P, Barandiarán J M, Gutiérrez J, Richard M L, Allen S M and O’Handley R C 2008 Eur. Phys. J. Special Topics 158 149-154
[10] Lázpita P, Barandiarán J M, Gutiérrez J, Feuchtwanger J, Chernenko V A and Richard M L 2011 NJP 13 033039 1-14
[11] Papoular R J and Gillon B 1990 Europhys. Lett. 13 (5) 429-434
[12] Rodriguez-Carvajal 1993 Phys. B. 192 55-69
[13] Brown P J, Bargawi A Y, Crangle J, Neumann K-U and Ziebeck KRA 1999 J. Phys.: Condens. Matter 11 4715-4722