Study of the transformation sequence on a high temperature martensitic transformation Ni-Mn-Ga-Co shape memory alloy

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Abstract. Ni-Mn-Ga alloys show the highest magnetic-field-induced strain among ferromagnetic shape memory alloys. A great effort is being done in this alloy system to increase the application temperature range. In this sense, the addition of small amounts of Cobalt to NiMnGa alloys has been proved to increase the MT temperatures through the increase of the electron per atom relation (e/a). In this work, the analysis of the crystal structure of the present phases and the phase transformations has been performed on a Ni-Mn-Ga-Co alloy by neutron diffraction measurements from 10 K to 673 K. The study has been completed by means of calorimetric and magnetic measurements. On cooling the alloy undergoes a martensitic transformation from a face centered cubic structure to a nonmodulated tetragonal martensite. The appearance of intermartensite transformations can be disregarded in the whole temperature range below the martensitic transformation. However, a jump in the unit-cell volume of the tetragonal martensite has been observed at 325 K. Since this temperature is close to the Curie temperature of the alloy both, the structural and magnetic contributions are taken into account to explain the results.

1. Introduction
Ferromagnetic shape memory alloys (FSMA) have attracted great attention as potential actuator materials in recent years [1]. Among these systems, giant magnetic field induced strains of 9.5 % were successfully obtained by rearrangement of martensite variants in ternary Ni-Mn-Ga [2]. In this ternary system a strong dependence of Martensitic Transformation (MT) temperatures [3], crystal structures [4], and magnetocrystalline anisotropy [5] on composition has been observed. The average number of valence electrons per atom (e/a) plays a special role on the stability of martensitic structures and transformation temperatures [6]. Besides, the influence of atomic order on transformation temperatures has been reported in these alloys [7-9]. Therefore the e/a relation and the atomic order are the main factors controlling the transformation temperatures.

In Ni-Mn-Ga-Co alloys with substitution of Mn or Ga by Co the MT temperatures are higher than those in Ni-Mn-Ga alloys [10-13], and the Curie temperature is increased with the substitution of Ni by Co [11-13], so this quaternary alloy is a good candidate for high temperature applications under selected addition of Co.
In this work, the analysis of the crystal structure of the present phases and the phase transformations has been performed on a Ni\textsubscript{50}Mn\textsubscript{26}Ga\textsubscript{20}Co\textsubscript{4} alloy by neutron diffraction measurements from 10 K to 673 K. The study has been completed by means of calorimetric and magnetic measurements.

2. Experimental
A polycrystalline ingot of Ni\textsubscript{49.95}Mn\textsubscript{25.9}Ga\textsubscript{20.2}Co\textsubscript{3.9} alloy was prepared from high purity elements by arc melting under protective Ar atmosphere. The ingot was homogenized in vacuum quartz ampoules at 1273 K during 24 hours. Small samples for calorimetric measurements were obtained from a disc previously cut from the centre of the ingots by slow speed diamond saw. Powder samples for neutron diffraction experiments were elaborated by crushing the samples on an agate mortar. The composition of the samples was analyzed by EDS in a JSM-5610LV Scanning Electron Microscope (SEM). Annealing treatment of 30 minutes at 1173 K followed by quenching into ice water was performed in a vertical induction furnace. Differential Scanning Calorimetry (DSC) measurements in a TA Q100 DSC and thermogravimetric measurements in a TA TGA-29500 were carried out to detect the presence of the different transformations. Powder neutron diffraction measurements were performed at the D1B and D20 installations at the Institute Laue-Langevin. The neutron wavelengths were 1.28 Å and 1.87 Å respectively. The FullProf2000 program [14] was employed to carry out the Rietveld refinement of the different spectra.

3. Results and discussion
Fig. 1 shows the DSC cooling and heating measurements carried out on the as-quenched sample. On cooling an exothermic peak is observed at \(\approx 540\) K, linked to the forward MT (austenite→martensite) with the characteristic MT temperatures \(M_s=573\) K (Martensite start), and \(M_f=485\) K (Martensite finish). On the other hand, the reverse MT (martensite→austenite) temperatures were determined from the endothermic peak detected on heating, \(A_s=523\) K (Austenite start), and \(A_f=615\) K (Austenite finish). The MT enthalpy \(\Delta H=8.7\pm0.2\) J g\(^{-1}\) was estimated from the average of the cooling and heating values, while the transformation entropy was calculated as \(\Delta S=\Delta H/ T_o =15.8 \pm 0.2\) J kg\(^{-1}\), with \(T_o\) equal to average temperature between forward and reverse MT. The thermogram shows a change in the slope of the baseline both on cooling and heating runs at 325 K. Taking into account the characteristics of this change, lack of latent heat and hysteresis between cooling and heating, it must be related to a second order transition as the para-ferromagnetic one. TGA measurements were carried out, see inset in Fig 1, to confirm the presence of this magnetic transition.

![Figure 1. DSC cooling-heating thermogram. Inset, TGA measurement.](image-url)
The transformation sequence on cooling is the following: a MT from a paramagnetic austenite to a paramagnetic martensite occurs at high temperatures followed by a magnetic ordering of the martensite phase at lower temperatures.

In order to determine the structure of the phases, their thermal evolution and the possibility of intermartensitic transitions neutron diffraction measurements were carried out in the whole temperature range between 10 K and 673 K. Fig. 2-a and 2-b show the neutron diffraction pattern of the austenite at 548 K and the martensite at 448 K respectively with the corresponding Rietveld refinement.

The austenite phase has the same crystallographic structure L\textsubscript{2}1 (space group Fm\textsubscript{3}m) than the ternary stoichiometric Ni\textsubscript{2}MnGa, where (0,0,0) positions are occupied by Mn atoms, (1/2, 1/2, 1/2) positions by Ga atoms and (1/4, 1/4, 1/4) positions by Ni atoms. According to [15], the spectra shown in Fig. 2-a was refined with the Co atoms at the (0,0,0)-Mn positions and with the remaining Mn atoms at the (1/2, 1/2, 1/2)-Ga positions. On the other side, the profile of the martensite structure, as shown in Fig. 2-b, corresponds to a non-modulated (NM) tetragonal martensite (I\textsubscript{4}/mmm point group) [16] with Mn and Co atoms at the (0, 0, 1/2) positions, Mn and Ga atoms at (0,0,0) and Ni atoms at the (0, 1/2, 1/4) positions. The set of measurements on the martensite phase shows the existence of the tetragonal non-modulated structure in the whole temperature range. No indication of modulated structures is observed because there are no satellites around the Bragg peaks in all the diffraction patterns. Since the NM is the most stable phase of the martensite structures, it can exist at very low temperatures as the last product of intermartensitic reactions. Besides, the NM phase is the only martensite that transforms at high temperatures in alloys with MT temperatures above T\textsubscript{c} [6]. The substitution of Mn and Ga by Co has been shown to increase the electron-atom e/a of the alloy, thus increasing the MT temperature and promoting the presence of the NM phase. The calculated electron-atom ratio e/a=7.77 is in agreement with the fact that non-modulated tetragonal martensites (NM) are found for alloys with e/a≥7.7 in the Ni-Mn-Ga ternary system [6]. So the stability of the martensitic structures and the transformation temperatures of the quaternary alloys with low Co content can be explained in terms of the e/a ratio in the frame of the ternary Ni-Mn-Ga system [17,18].

Both martensite cell parameters show an opposite behaviour as a function of temperature. A negative and positive thermal expansion is observed along c and a axis, respectively (Fig. 3) while the combination of both behaviours induces an overall positive volume thermal expansion, Fig. 4. A similar behaviour has been reported in different materials [19]. Two possible explanations have been suggested. One is due to the Poisson contraction in a direction arising from the large coefficient of expansion in a perpendicular direction [20], and the other is due to changes in Jahn-Teller distortion with temperature [21]. In our case the absolute values of both coefficients of expansion are similar, so...
the second explanation seems to be more appropriate, even more taking into account that the martensitic transformation in Ni-Mn-Ga has a band Jahn-Teller origin [22]. On the other hand, the c/a ratio decreases as the temperature approaches to the MT temperature. The evolution of c/a ratio with temperature can be explained taking into account that the c/a ratio converges to the value c/a=1 when the temperature approaches to the MT temperature to minimize the distortion linked to this transition. In addition, both cell parameters show a slope change at 325 K. The combined changes in a and c cell parameters with temperature induces a jump in the unit-cell volume at the same temperature, Fig.4. The martensite orders magnetically at $T_C$=325K as DSC and TGA measurements pointed out in Fig. 1. So the magnetic ordering promotes a magneto-volume anomaly reflected as a jump in the unit-cell volume even though the crystallographic structure of the martensite phase does not change in the whole temperature range. The observed lattice contraction with respect to the paramagnetic structure could be related to the magnetoelastic coupling, although no negative thermal expansion [23] has been observed in the present results.

![Figure 3. Temperature dependence of the cell parameters of the martensite](image1.png)  
![Figure 4. Temperature dependence of the unit-cell volume and c/a ratio of the martensite](image2.png)

**Summary and conclusions**
The crystal structures and the sequence of the phase transformations have been performed on a Ni$_{50}$Mn$_{26}$Ga$_{20}$Co$_{4}$ alloy by neutron diffraction measurements from 10 K to 673 K. On cooling the alloy undergoes the martensitic transformation from a cubic L2$_1$ phase to a non-modulated tetragonal martensite. The appearance of intermartensitic transformations can be disregarded in the whole temperature range below the martensitic transformation. However, a magneto-volume effect has been detected linked to the magnetic ordering of the martensite.

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References
[1] Kakeshita T et al. 2002 MRS Bull. 27 105
[2] Sozinov A et al. 2002 Appl. Phys. Lett. 80 1746
[3] Chernenko VA et al. 1995 Scripta Metall. 33 1239
[4] Lanska N et al. 2004 J. Appl. Phys. 95 8074
[5] Sozinov A et al. 2001 Proceedings SPIE 4333 189
[6] Chernenko VA 1999 Scripta Mater. 40 523
[7] Sánchez-Alarcos V et al. 2007 Acta Mater. 55 3883
[8] Sánchez-Alarcos V et al. 2010 J. Phys.: Condens. Matter 22 166001
[9] Sánchez-Alarcos V et al. 2011 Mater. Sci. Forum 684 85
[10] Nakamura H et al. 2001 Trans. Mater. Res. Soc. Jpn. 26 287
[11] Khovailo V V et al. 2003 Mater. Trans. 44 2509
[12] Khan M et al. 2005 J. Appl. Phys. 97 10M3004
[13] Cong D Y et al. 2008 Mater. Sci. Eng. A 473 213
[14] Rodríguez-Carvajal J 1993 Physica B 192 55
[15] Ayila S K et al. 2012 Phys. Status Solidi B 249 620
[16] Wedel B et al. 1999 J. Alloys and Comps. 290 137
[17] Sánchez-Alarcos V et al. 2008 Mater. Sci. Eng. A 481–2 293
[18] Sánchez-Alarcos V et al. 2008 Acta Mater. 56 5370
[19] Krishna Rao K V and Iyengar L 1969 Acta Crystallogr. A 25 302
[20] Krishna Rao K et al. 1968 J. Phys. Chem. Solids 29 254
[21] Siratori K and Tida S 1962 J. Phys. Soc. Jpn. 17 208
[22] Brown P J 1999 J. Phys.: Condens. Matter 11 4715
[23] Alvarez-Alonso P et al. 2012 Phys. Rev. B 86 184411