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XAS and XMCD study of the influence of annealing on the atomic ordering and magnetism in an NiMnGa alloy

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Abstract

The proper annealing of $Ni_{51}Mn_{28}Ga_{21}$ ribbon alloy gives rise to an increase of the saturation magnetization and of the magnetic order T_C (up to 20 K) and martensitic transition T_M (up to 10 K) temperatures. The combined x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) studies indicate that the annealing treatment drives the alloy to a more ordered structure without significantly affecting the local structure in terms of interatomic distances and bonding geometry. By contrast, the annealing strongly affects the near-edge absorption at the Mn K-edge while no effect is observed at either the Ni or Ga K-edge. These results suggest that annealing leads to a modification of the electronic structure of the Mn atoms while that of Ni and Ga atoms remains unvaried. However, strong XMCD signals are detected at both Ni and Ga K-edges whose amplitude increases after annealing. These results point out that despite the change of the magnetic properties of the system being mainly associated with the modification of the electronic properties of the Mn atoms, both Ni and Ga may play a non-negligible role through the polarization of the conduction band.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic shape-memory alloys near the prototype Ni_2MnGa composition are ferromagnetic Heusler alloys [1, 2] in which the coupling of the structural and magnetic degrees of freedom gives rise to an unusual magnetomechanical behavior. This property has made these materials the subject of numerous studies because of their possible technical applications. Such applications appear as a consequence of the martensitic transition, resulting in a low temperature tetragonal or orthorhombic (often modulated) martensite phase that presents large distortions with respect to the high temperature parent phase (cubic $L2_1$ austenitic phase). The martensitic phase accommodates the strain associated to the transition by nucleating twined variants that give an overall shape similar to that of the starting austenite crystal. The subsequent application of a magnetic field of sufficient intensity can rearrange the twinned variants giving rise to huge deformations, reaching 10% of the initial dimensions, in a few milliseconds. Such behavior clearly attracts attention for the actuation of these materials that is, to a large extent, the best reported for any deformable material in terms of stroke and speed of actuation. The magnetic actuation at room temperature is only possible if the alloys are both magnetically ordered and in the martensitic phase at such temperature. As the stoichiometric compound has a martensitic transition temperature of 202 K [1], off-stoichiometric alloys are currently being investigated for magnetic actuation.

Despite this recent interest, there are basic fundamental issues related to the magnetism of such alloys that are still not fully understood. One of these is determining the size of the magnetic moments of the different atomic species included in the alloy and their ordering. The magnetic properties of these ferromagnetic shape-memory alloys are

primarily due to the ordering of the manganese (Mn) moments according to neutron diffraction measurements [1]. Studies of the stoichiometric compound [3] give a moment arising mainly from the manganese atoms, which carry about 3.4 Bohr magneton (μ_B) each. In addition, numerical calculations on neutron diffraction data [3] and the combined analysis of magnetization and nuclear magnetic resonance data [4] suggest the existence of a small moment of about 0.3 μ_B associated to the Ni atoms. However, there is a disagreement between the magnetic moments experimentally determined from polarized neutron scattering and the calculated zero temperature ideal moments [3]. In this respect, the role of the Ni atoms in determining the magnetic properties of this system has been largely studied from a theoretical point of view including the possibility of magnons in these materials involving nickel (Ni) moments [5]. Moreover, several works have discussed the stability of the structure as associated with a dip in the minority-spin density of states (DOS) at the Fermi level that should be related to the formation of hybrid states of Ni-3d and Ga-4p minority-spin orbitals [6, 7].

In off-stoichiometric alloys there are, by far, fewer studies of the fundamental magnetism. A recent paper on Mn deficient alloys [8] reports a linear decrease of the average magnetic moment proportional to the Mn concentration. By comparing both ordered moments and paramagnetic effective moments, Khovailo *et al* [8] assign about 80% of the moment to localized 3d electrons and only about 20% to the itinerant or band electrons. Therefore, it is proposed that in these alloys the Mn magnetic moments are mainly localized, while Ni magnetic moments are essentially delocalized. In excess Mn alloys we have already shown that the net magnetic moment decreases as Mn concentration increases, due to the antiferromagnetic (AF) coupling between near neighbors Mn that appear when excess atoms occupy antisite positions in the $L2_1$ austenite structure (and the corresponding martensite one) [9]. Finally, the study of the local atomic structure of martensitic $Ni_{2+x}Mn_{1-x}Ga$ compounds by extended x-ray absorption fine-structure spectroscopy (EXAFS) suggests the existence of changes in hybridization of Ga-4p and Ni-3d orbitals associated with the local symmetry breaking upon undergoing martensitic transition [10] in agreement with theoretical works showing the importance of Ni doping on the electronic structure of the Ni_2MnGa [11].

All these results point out the importance of the conduction or delocalized electrons, and thus of changes in the composition or topological order, to the magnetic behavior of the alloy. In what follows we will show a study about the magnetic order induced in an annealed polycrystalline ribbon of an off-stoichiometric alloy of composition $Ni_{51}Mn_{28}Ga_{21}$, performed by combining x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) techniques. The proper annealing of this alloy gives rise to an increase of the saturation magnetization accompanied by an increase of the magnetic order T_C (up to 20 K) and martensitic transition T_M (about 10 K) temperatures, although no changes in either composition or topological order are expected. Taking advantage of the element specificity of these core level spectroscopy techniques, we aim to ascertain the influence of the different atomic species (Mn, Ni and Ga) on the modification of the magnetic properties of the alloy.

2. Experimental details

An off-stoichiometric alloy of composition $Ni_{51}Mn_{28}Ga_{21}$ was prepared by the melt spinning method. As a result, an alloy with a morphology of very small crystalline grain has been obtained. Differential scanning calorimetry (DSC) was used to monitor the martensitic transformation. As probed by performing x-ray diffraction experiments at different temperatures, the sample displays a high temperature cubic $L2_1$ structure that undergoes a tetragonal transformation when the material is cooled below a characteristic martensite start temperature $T_M = 337$ K. In its martensite phase, the structure is 7M (tetragonal lattice modulated with periodicity of 7 planes) [12].

Small pieces of the sample were cut from the ribbon and annealed for 18 h at 315 °C (588 K), under argon atmosphere. Analysis of x-ray spectra confirmed the same structural characteristics as for the as-quenched sample. The crystallographic grain size calculated from Scherrer's equation yields a grain size of ∼45 nm for the as-quenched sample. Within the experimental error the same grain size is obtained for the annealed samples, which can be accounted for as being due to the not excessively high temperature of the performed annealing. All magnetic measurements have been performed using VSM magnetometry, running between 5 and 300 K and with applied magnetic fields up to 14 T.

XAS and XMCD experiments were performed at the beamline BL39XU of the SPring8 Facility [13]. Undulator radiation linearly polarized in the orbit plane was monochromatized by a diamond (111) fixed-exit double-crystal monochromator and higher harmonics rejected by an Rh coated mirror. The glancing angle of the mirror was 7 mrad at both the Mn and Ni K-edges, and 5 mrad at the Ga K-edge. In these measurements, an unfocused x-ray beam was used. The beam size at the sample was shaped to 0.5×0.5 mm^2 using slits. Circularly polarized x-rays were generated by using a diamond x-ray phase plate in the 220 Laue configuration [14]. The thickness of the x-ray phase retarder was 0.45 mm at the Mn and Ni K-edge, and 2.7 mm at the Ga K-edge. XAS and XMCD experiments were performed at room temperature in the transmission mode at the K-edge of Mn, Ni and Ga. The XMCD spectra were recorded by using the helicity-modulation technique [15] and under the action of a magnetic field $\mu_0 H = 2$ T tilted 65° away from the x-ray beam direction. Therefore, the sample is magnetized by the externally applied magnetic field and the helicity is changed from positive to negative at each energy point. The XMCD spectrum corresponds to the spin-dependent absorption coefficient obtained as the difference of the absorption coefficient $\mu_c = (\mu^- - \mu^+)$ for antiparallel, μ^-, and parallel, μ^+, orientation of the photon helicity and the magnetic field applied to the sample. For the sake of accuracy, the direction of the applied magnetic field is reversed and XMCD, now $\mu_c = (\mu^+ - \mu^-)$, is recorded again by switching the helicity. The subtraction of the XMCD

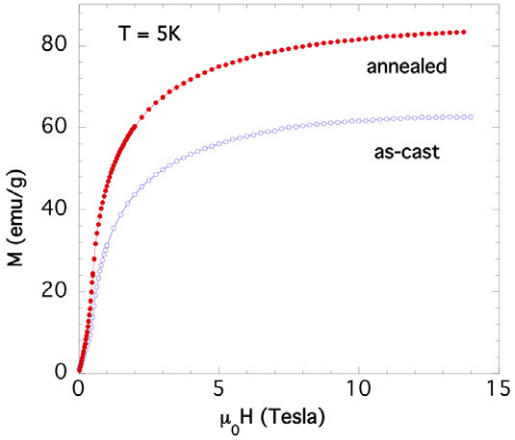

Figure 1. First magnetization curves, recorded at 5 K and measured up to 14 T, for both the as-cast and annealed samples.

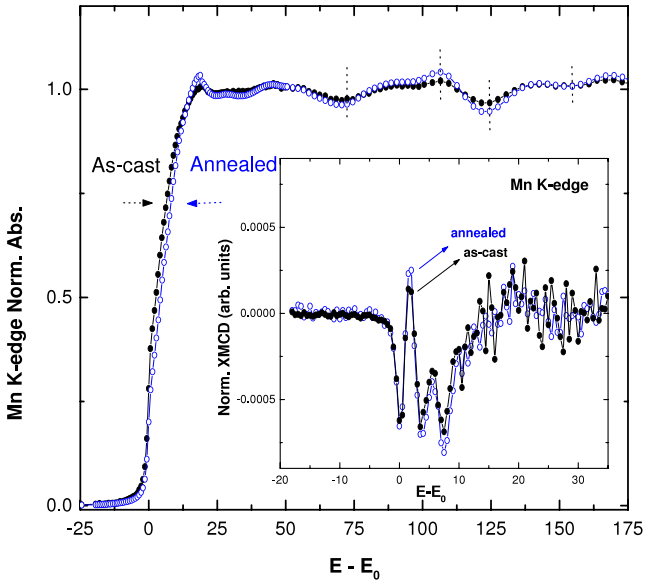

Figure 2. Comparison of the Mn K-edge x-ray absorption spectra for both the as-cast (black, ●) and annealed (blue, ○) samples. In the inset the comparison of the Mn K-edge XMCD spectra for both the as-cast (black, ●) and annealed (blue, ○) samples is shown.

spectra recorded for both field orientations cancels, if present, any spurious signal.

The absorption spectra were analyzed according to standard procedures [16]. The origin of the energy scale, E_0, was chosen at the inflection point of the absorption edge. For both as-cast and annealed samples the same E_0 value (6537.38 eV) has been found. The spectra were normalized to the averaged absorption coefficient at high energy, μ_0, in order to eliminate the dependence of the absorption on the sample thickness. Moreover, because the magnetic field is tilted from the x-ray direction, μ_c has been corrected by a cos(65°) factor in all the cases.

3. Results and discussion

From previous reported measurements [12] we had already observed an increase of ∼20 K in T_C (from 344–364 K) and of ∼10 K in T_M (from 337–347 K) between the as-cast and the annealed sample. An increase also of the room temperature magnetic moment (from 1.2 μ_B for the as-quenched sample to 2.1 μ_B for the annealed one) was also measured. This large change in magnetic moment (75%) is partially due to the increase in T_C.

In order to separate the change in T_C and the intrinsic magnetic moment, first magnetization curves were measured at 5 K (see figure 1) and show clearly this increase of the low temperature magnetic moment (determined by using Arrot plots), from 2.56 μ_B for the as-quenched sample to 3.31 μ_B for the 18 h annealed one, that is a 29.3% relative change. These changes in M_S, T_C and T_M can be addressed to ordering of the Mn/Ga atoms in the $L2_1$ lattice.

The measured magnetic moment changes can be discussed in terms of a simple model previously developed by the authors [9]. Taking as reference values for the magnetic moment those of the stoichiometric Ni_2MnGa alloy [1, 8], that is 3.51 μ_B for the Mn atom (that couples ferromagnetically with Ni atoms) and 0.33 μ_B for the Ni atom, we can estimate the expected magnetic moment value of our alloy under the assumption that excess Ni (1%) go to Mn sites (coupling ferromagnetically) and excess as well as displaced Mn atoms (4%) go to vacant Ga sites where they couple antiferromagnetically to the dominant moment. In this way we obtain an expected value of 3.48 μ_B, very close to the measured 3.31 μ_B magnetic moment value for our 18 h annealed sample. Even so, the measured magnetic moment for the as-cast sample is only compatible with 74% Mn atoms at Mn sites, clearly meaning that Mn and Ga atoms are highly disordered. This rough calculation shows that annealing has already driven the alloy to an almost perfect $L2_1$ ordered structure in the austenite phase, and so to the corresponding low temperature martensite one.

In order to obtain direct information about the modification of the magnetic behavior of the system after annealing, we have combined both XAS and XMCD studies at the K absorption edge of Mn, Ni and Ga in both as-cast and annealed samples.

The near-edge region of the absorption spectrum is extremely sensitive to the modification of the density of states (DOS), while the high-energy region of the spectrum is related to the local structure around the absorbing atom [17]. In order to discern the origin, structural versus electronic, of the differences in the absorption spectra it is instructive to compare the XAS spectra recorded at room temperature at the Mn K-edge on the same compound before and after the annealing treatment. As shown in figure 2 the main difference between both absorption spectra lies in the first 15 eV of the spectrum, i.e. at the rising edge region. This result indicates that the empty DOS of the Mn atoms has been modified upon annealing. By contrast, the shape and the energy position of the x-ray absorption near-edge spectroscopy (XANES) spectral features remain unchanged and only the amplitude is modified. The XANES region of the absorption spectrum is more sensitive to the bonding geometry, including

interatomic distances and bonding angles, than the high-energy EXAFS one. The fact that all the spectral features, maxima and minima, appear at the same energy position (see figure 2) indicates that the local environment of Mn does not change upon annealing. However, the observed increase of the amplitude suggests that the alloy becomes more ordered after the annealing treatment. These results indicate that the change in the magnetic properties of $Ni_{51}Mn_{28}Ga_{21}$ upon annealing can be associated with an electronic-induced effect instead of with structural modifications [18–20].

These results point out the need of getting a deeper insight into the origin of the magnetic modifications from a microscopic point of view. In this respect, XMCD [21, 22] appears to be an outstanding tool as it offers the possibility of probing separately the magnetic moment of each element in a compound.

We have recorded the XMCD spectra at the Mn K-edge on both the as-cast and the annealed sample [20]. The comparison of the Mn K-edge XMCD spectra for the as-cast and annealed $Ni_{51}Mn_{28}Ga_{21}$ sample is reported in the inset of figure 2. As shown in this figure, the spectral shape of the XMCD signal is retained after annealing and only very subtle changes of its amplitude are observed. Despite the level of noise present, these results indicate that the amplitude of the XMCD signal is enhanced after annealing. In principle this behavior can be accounted for in terms of the increase of the Mn magnetic moment in the annealed sample. However, it should be noted that no clear relationship can be established between the XMCD at the K-edges of transition metals and the local magnetic moment of the d-states. While XMCD provides a quantitative measure of the magnetic moments for localized states carrying a magnetic moment (f-states of lanthanides and actinides at the $M_{4,5}$-edges, d-states of transition metals at the $L_{2,3}$-edges), the same does not hold when the delocalized states are being probed. This is the case of the conduction band 4p states of transition metals whose magnetic moments are induced by the hybridization with the localized d-states. XMCD at the K-edge of the transition metals probes the orbital polarization of the conduction p-states [23, 24]. Spin polarization alone is known to be insufficient to produce dichroic effects at the K-edges [25]. Therefore, coupling in the 4p band must be present for XMCD effects as the orbital polarization in the p symmetric states is due to the spin polarization through the spin–orbit interaction [23, 24]. Consequently, the XMCD at the K-edge is, in its integral form, a measure of the orbital magnetism of the 4p shell of the transition metal probed by the x-rays. According to the sum-rule relationship proposed by Igarashi and Hirai [23, 24], the orbital moment of the Mn 4p states can be obtained by integrating the XMCD signals at the Mn K-edge. In the case of $Ni_{51}Mn_{28}Ga_{21}$, a 16% enhancement of the orbital moment of the Mn 4p states after annealing is obtained by applying this sum rule.

As discussed above, no clear relationship between the XMCD at the Mn K-edge and the main 3d magnetic moment can be given. Despite this fact, Islam *et al* [26] conclude from the occurrence of XMCD at the Ni K-edge in the related ferromagnetic shape-memory NiMnGa alloys that Ni carries a significant 3d moment. However, the existence of non-zero XMCD at the Ni K-edge does not constitute itself as evidence of a 3d moment. To elucidate this fact we have investigated the behavior of the XMCD at both Ni and Ga K-edges in the $Ni_{51}Mn_{28}Ga_{21}$ alloy. Gallium atoms do not carry any localized 3d moment and, consequently, the study of the XMCD at the K-edges should shed light into the relationship between XMCD and the polarization of the conduction states of non-magnetic atoms, including Ni. Our main results are shown in figure 3 which reports the comparison of the XAS and XMCD spectra recorded at the Ni and Ga K-edges in both the as-cast and annealed $Ni_{51}Mn_{28}Ga_{21}$ sample. In contrast to the Mn case, no significant difference is found in the near-edge region of the spectra for either Ni or Ga. This result is in agreement with the assignment of the modification of the magnetic properties of the sample upon annealing to the modification of the electronic state of Mn.

However, even though the magnetism in these compounds is thought to be mainly due to Mn atoms, a strong XMCD signal is found at both the Ni and Ga K-edge. Surprisingly, the XMCD signal recorded for the non-magnetic Ga and Ni is significantly more intense than the Mn one. The amplitude of the Ni signal is twice that of Mn, while the Ga XMCD spectrum is five times greater than the Mn K-edge XMCD. As a first consequence, these results pose a serious concern regarding the assignment of localized d magnetic moments to non-magnetic atoms based exclusively on the occurrence of non-zero XMCD signals at the K-edge. Indeed, strong XMCD effects have been observed at the Ga K-edge in the Mn_3MC (M = Zn or Ga) perovskites [27, 28] in which it is well known that Ga does not carry a localized magnetic moment.

The Ga K-edge XMCD spectrum is similar to that found in Mn_3GaC. No XMCD signal is expected at the Ga K-edge as these atoms are thought to be non-magnetic (i.e. they do not carry a localized d magnetic moment). Moreover, the Ni K-edge XMCD spectral profile is completely different to that of fcc Ni. These experimental findings suggest that our results have to be interpreted in terms of the polarization of the conduction band induced by the orbital polarization at neighboring sites through hybridization [23, 24, 28]. The observed modification of the Ga and Ni K-edge XMCD signals points out the possibility of a non-negligible role of both Ni and Ga, through the modification of the polarization of the conduction band, into driving the interplay between annealing and the magnetic properties in these materials. In this respect, the amplitude of the XMCD of both the Ga and Ni K-edge varies with the annealing process. As shown in figure 3, the amplitude of the XMCD recorded at both absorption edges is enhanced by a factor of 1.35 in the case of the annealed sample. This result indicates that as the Mn magnetic moment increases upon annealing, the polarization of the conduction band at the Ni and Ga sites also increases, giving rise to an enhanced induced conduction band magnetic moment. The Mn, Ni and Ga K-edge XMCD intensity integrated up to an energy cutoff of 20 eV [28] is found to be negative. According to the K-edge sum rule [23, 24], the orbital moment in the p symmetric states is found to be positive at the Mn, Ni and Ga sites.

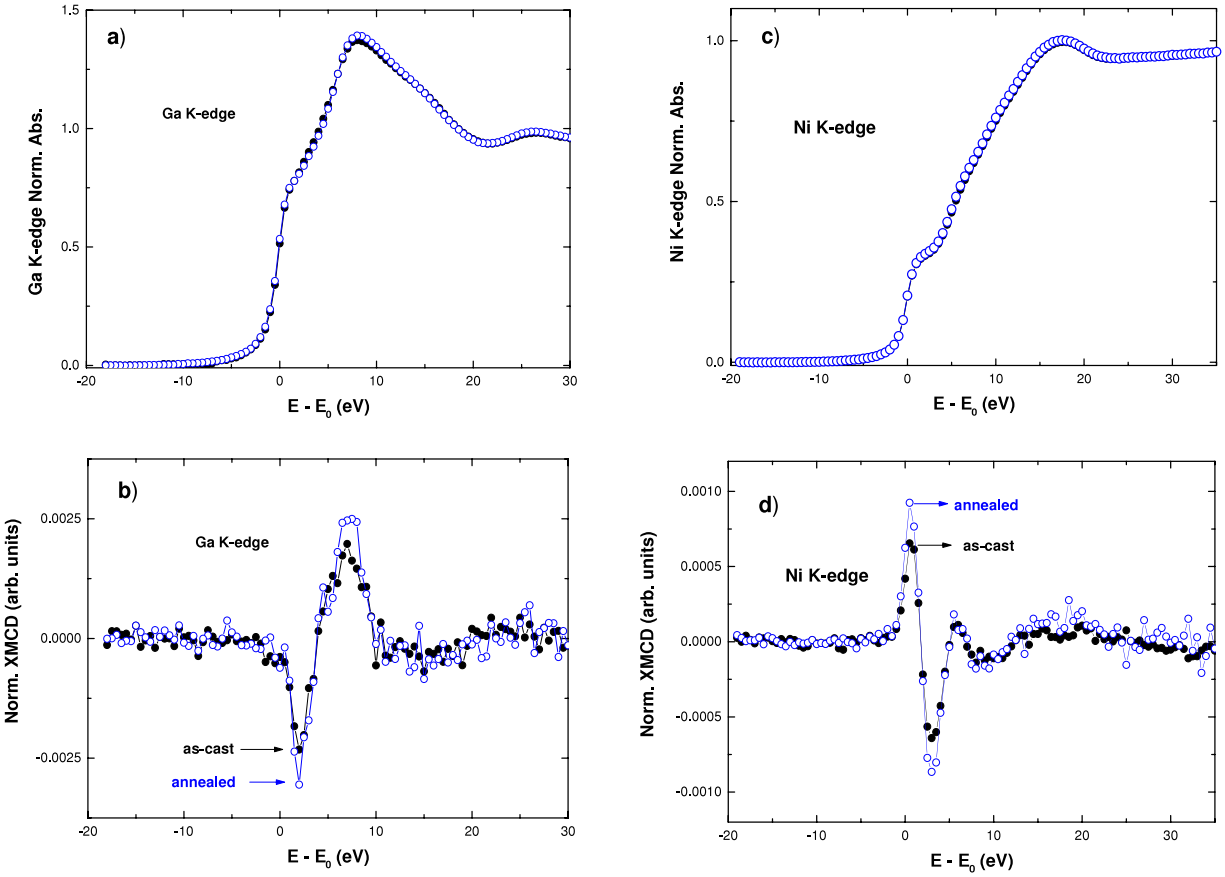

Figure 3. Top: comparison of the x-ray absorption spectra recorded for both the as-cast (black, ●) and annealed (blue, ○) samples at the Ga (panel (a)) and Ni (panel (c)) K-edge. Bottom, same comparison for the XMCD spectra recorded at the Ga (panel (b)) and Ni (panel (d)) K-edge.

Finally, we have verified that the enhancement of the induced magnetic moments at the Ni and Ga sites is not due to the modification of their local structure environment. To this end, we have analyzed the EXAFS recorded for both the as-cast and the annealed samples. EXAFS spectra were obtained from the x-ray absorption (Ni and Ga K-edge) spectra by using the ATHENA program [32]. In this way oscillations were obtained after removing the background by a cubic spline polynomial fitting and EXAFS signal, $\chi(k)$, was obtained by normalizing the magnitude of the oscillations to the edge jump. The corresponding pseudoradial distribution function around the absorbing atom has been obtained by k-weighting of the EXAFS signals, $\chi(k) \cdot k$, multiplying by a Hanning window and Fourier transforming (FT). For comparative study, the Fourier transform of EXAFS signal was performed within the same k-range (2–13.5 Å). In the case of the Mn K-edge, the EXAFS spectra were recorded up to only 7.2 Å^{-1} and they were analyzed in the k-range (1.5–7.2 Å). As shown in figure 4, the EXAFS signals do not vary significantly at the Ni or at the Ga K-edge, after the annealing treatment, while the amplitude of the Mn K-edge EXAFS (see figure 2) is clearly enhanced after the annealing. Indeed, as shown in panels (e) and (f) of figure 4, the Mn signal of the as-cast sample matches that of the annealed sample after applying a 1.5 factor. Moreover, in the case of the Ga K-edge the main peak of the FT, due to the next-neighbors arrangement, slightly increases after annealing, while no modification is observed at the Ni sites. The comparison of these EXAFS spectra indicates that the interatomic distances remain unchanged upon annealing in the three cases and that only the disorder of the next-neighbors environment, entering the EXAFS signals through the Debye–Waller factors, is affected by the annealing. These results are in agreement with the expected diminution of the atomic disorder due to the annealing. The fact that the modification of the Debye–Waller factors is significantly greater for Mn than for Ga, while no effect is detected for Ni suggests that the annealing may induce changes in the chemical order between Mn and Ga.

The theoretical predictions by Ahuja *et al* indicate that the Mn 3d moments are fundamental in the formation of the total spin moment [29]. By contrast, Ayuela *et al* suggest that the Ni contribution to the total changes in the magnetic moments is larger than the Mn ones when going to the tetragonal phase [30]. In this way, recent Ni and Mn $L_{2,3}$-edge XAS and XMCD measurements in epitaxial Ni_2MnGa films have been accounted for in terms of the modification of the electronic structure of Ni in entering the martensitic state [31]. However, contrary to the authors' interpretation, the experimental results show that the Mn XMCD spectra changes significantly going from the high to the low temperature phase

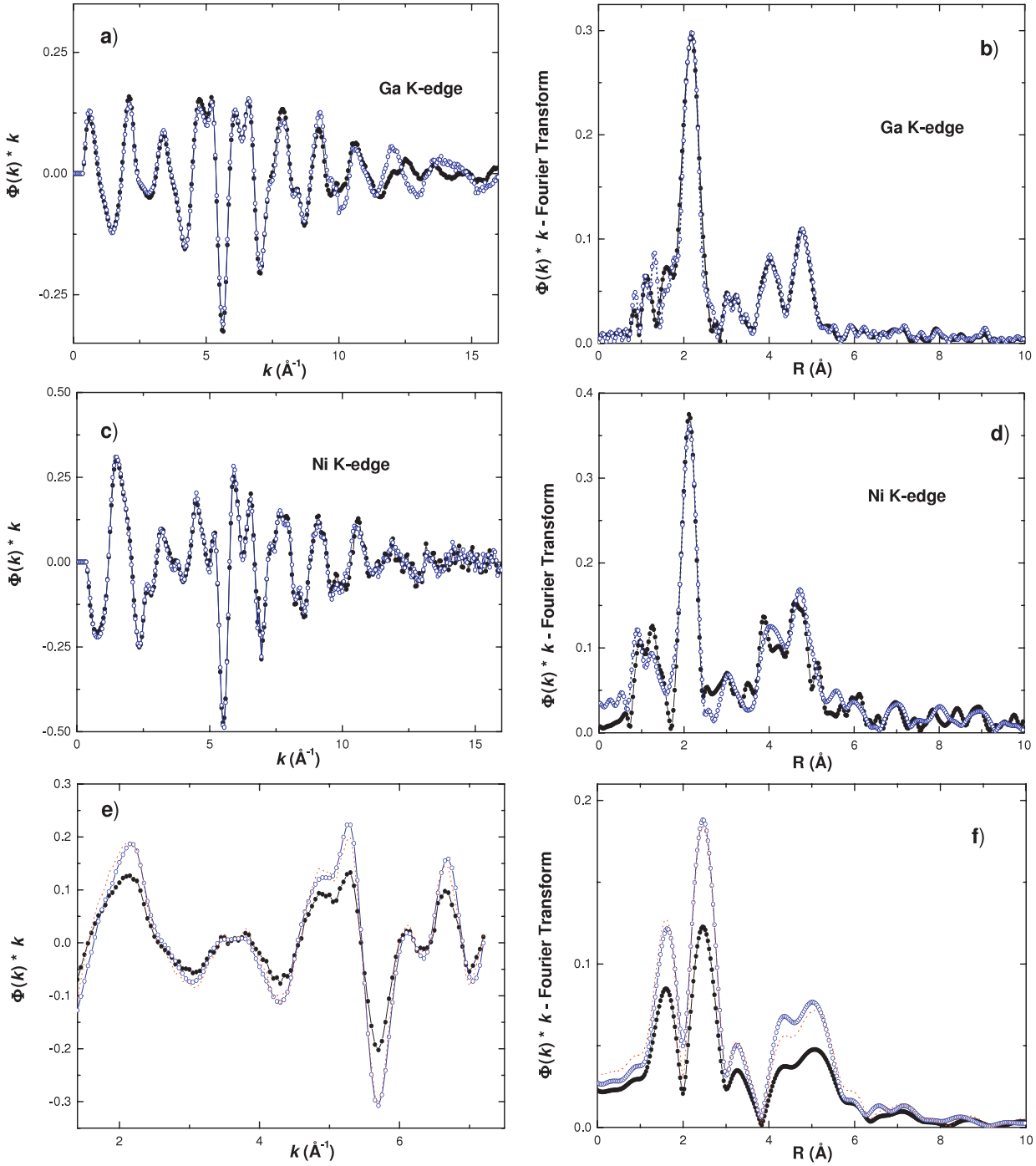

Figure 4. Left: experimental k-weighted EXAFS spectrum of the as-cast (black, ●) and annealed (blue, ○) samples recorded at the K-edge of Ga (a), Ni (c) and Mn (e). The comparison of the modulus of the Fourier transform of the experimental k-EXAFS spectrum is shown in the right-hand panels for Ga (b), Ni (d) and Mn (f). In the case of the Mn K-edge the dotted line corresponds to the signals of the as-cast sample multiplied by a 1.5 factor to match the amplitude of those of the annealed sample (see the text for details).

while those of Ni remain unaltered within the signal to noise ratio. Despite the work by Jakob *et al* demonstrating the presence of magnetic moment at the Ni sites [31], some caution is needed regarding its magnitude because the value of the magnetic moments derived from the XMCD spectra are far from both the theoretical expectations and the experimental ones, and, in addition, the reported saturation moment ($\sim$3 μ_B) is significantly smaller than the bulk ($\sim$4.2 μ_B) one. In contrast to the subtle changes observed at the Ni L-edges, our XAS results indicate that annealing leads to a modification of the electronic structure of the Mn atoms, while that of Ni and Ga remains unaltered. Moreover, the EXAFS analysis excludes a major role of structural effects in terms of the modification of the interatomic distances. Therefore, these results point out that the modification of the magnetic properties of the $Ni_{51}Mn_{28}Ga_{21}$ ribbon alloy upon annealing are mainly due to

the modification of the Mn 3d localized magnetic moment. Indeed, the observed enhancement (∼20%) of the XMCD signals after annealing at the Mn, Ni and Ga K-edges is similar to that of the magnetization. The latter modification should be attributed to the increase of the Mn localized moment and thus the concomitant increase of the conduction band moments is expected to be similar for all the involved elements, in agreement with the XMCD data.

4. Summary and conclusions

We have presented here a combined XAS and XMCD study performed at the K-edge of Mn, Ni and Ga in a $Ni_{51}Mn_{28}Ga_{21}$ ribbon alloy to study the effect of annealing on its magnetic properties.

X-ray absorption spectroscopy data indicate that the annealing strongly affects the near-edge absorption at the Mn K-edge. By contrast, no effect is observed at either the Ni or Ga K-edge. These results suggest that annealing leads to a modification of the electronic structure of the Mn atoms governing the magnetic properties of the system. Such an effect can be due to a change in the DOS at the Fermi level, corresponding to the increase of the FM exchange upon annealing. Moreover, the analysis of the XANES and EXAFS spectra indicates that the annealing treatment drives the alloy to a more ordered structure without significantly affecting the local structure in terms of interatomic distances and bonding geometry.

The analysis of the XMCD spectra recorded at the Mn K-edge reflects the increase of the magnetization after annealing. More interestingly, strong XMCD signals are detected at both the Ni and Ga K-edge. As in the case of the Mn K-edge, the amplitude of the XMCD spectra increases after annealing. The XMCD signals recorded for the non-magnetic Ga and Ni are significantly more intense than the Mn ones. Consequently, the existence of non-zero XMCD at the K-edge of Ni and Ga has been not interpreted in terms of localized d-magnetism in these atoms but in terms of the polarization of the conduction band. These results show that no clear relationship can be established between the XMCD at the K-edges of transition metals and the local magnetic moment of the d-states. On the contrary, the observed Ga and Ni K-edge XMCD signals reflect the polarization of the conduction band and point out the possibility of a non-negligible role of both Ni and Ga, through the polarization of the conduction band, into driving the interplay between annealing and the magnetic properties in these materials, which are associated with the modification of the Mn 3d localized magnetic moment.

Acknowledgments

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