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Fe and Co selective substitution in Ni₂MnGa: Effect of magnetism on relative phase stability

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RESEARCH ARTICLE

Fe and Co selective substitution in Ni₂MnGa: Effect of magnetism on relative phase stability

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We studied the effect of Fe and Co 3d elements selective substitution on the structural and magnetic phase transitions in the prototypical magnetic shape memory alloy Ni-Mn-Ga. We determined the phase diagram for each elemental doping substitution by means of calorimetry and ac susceptibility measurements. An effort was made to substitute each constituent element by same amounts of doping and to study the role of parameters other than electronic concentration in controlling phase stability. Specifically, selective doping with atoms of similar atomic radii but different magnetic properties allowed to investigate the role of magnetic interactions on the relative phase stability of the ternary compound. We determined the entropy change associated with the martensitic transition for each quaternary alloy to obtain further information on the effect of magnetism on the relative stability of the involved phases exhibited by these compounds.

Keywords: Magnetic shape memory alloys; Ni₂MnGa; phase transitions; phase diagrams

1. Introduction

Ni-Mn based Heusler alloys are currently under active research due to the magnetic and structural phase transitions they exhibit [1–4]. In these compounds, the existence of structural phase transitions in magnetically ordered states is of great importance both from the fundamental and the application points of view and leads to very interesting phenomena such as magnetic shape memory effects [5–7], large magnetoresistance [8–10] and large magnetocaloric effects [11–17]. The co-occurrence of various of these effects in single alloys belonging to this family makes these compounds multifunctional materials. The interplay between structural and magnetic degrees of freedom is at the origin of such multifunctionality. Thus, a detailed understanding of the phase diagrams of these particular Heusler alloys

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1 is needed in order to improve their functional properties and to search for new
2 applications.

3 The most studied system so far belonging to this alloy family is the prototypical
4 magnetic shape memory alloy Ni-Mn-Ga, for which magnetic field induced strains
5 as large as 10% in a field of 1 T have been reported [18]. From a fundamental point
6 of view, this alloy undergoes a complex multi-stage transformation process from
7 a high temperature paramagnetic cubic phase to a low temperature ferromagnetic
8 martensitic phase. At intermediate temperatures it shows precursor tweed textures
9 which may lock into a modulated premartensitic structure via a first-order
10 phase transition at T_I ($M_s < T_I < T_C$; M_s martensite start temperature, T_C
11 Curie point) [19]. This behavior is related to low resistance against distortions of
12 $\{110\}$ planes along $\langle 1\bar{1}0 \rangle$ directions, as evidenced by the features of the low energy
13 TA_2 acoustic phonon branch [20–22] and the low value of the shear elastic
14 constant $C' = (C_{11} - C_{12})/2$ [23–25]. Furthermore, recent experiments have shown
15 the opening of a pseudogap close to the Fermi energy at T_I , which suggests that
16 the premartensitic transition corresponds to a nesting feature of a single band [26].
17 In addition to the martensitic and premartensitic transformations, intermartensitic
18 transformations also exist in alloys with M_s near or higher than room temperature.
19 Previous investigations have shown that such intermartensitic transformations are
20 first-order phase transitions between different martensitic structures, with char-
21 acteristic temperature T_{IM} ($< M_s$) [27–29]. Several intermartensitic phases have
22 been found, which have modulated lattices with different periodicity of stacking
23 sequences of $\{110\}$ planes along $\langle 1\bar{1}0 \rangle$ directions [27–33]. The particular struc-
24 tures and transformation temperatures depend on stress and chemical composition
25 [29, 33].

26
27 Despite previous attempts of characterizing the structural transitions exhib-
28 ited by these compounds, further experiments are crucial for comprehending their
29 rich functional properties. Premartensitic and specially intermartensitic transitions
30 have only been observed for a restricted number of magnetic shape memory alloys
31 and are not yet fully understood. Also, a better understanding of the parameters
32 which govern phase stability is necessary to optimize materials design and per-
33 formance. Recently, we showed that selective partial substitution of $3d$ elements
34 in Ni-Mn-Ga alloys is a useful tool to study the role of electron concentration
35 on the structural and magnetic phase transitions exhibited by these materials.
36 Specifically, we studied the effect of Fe addition on the Curie, premartensitic and
37 martensitic transitions and we determined a detailed phase diagram of quaternary
38 Ni-Mn-Ga-Fe alloys for low Fe concentrations [34]. Previously, the study of doping
39 in Ni-Mn-Ga alloys had been focused only on its effect on the martensitic and
40 the ferromagnetic phase transitions [35–46]. Here, we extend previous studies by
41 means of investigating the dependence of all transition temperatures (M_s , T_I , T_{IM}
42 and T_C) on Fe and Co $3d$ transition elements doping, with concentrations up to
43 $\sim 5\%$ in both cases. The introduction of such elements of similar atomic radii (and
44 therefore similar volume effects) but different magnetic properties allows study of
45 the effect of magnetic interactions on the structural transitions. We also studied
46 the effect of doping on the entropy change associated with the martensitic transi-
47 tion. Comparison of the composition dependence of ΔS for the studied quaternary
48 compounds and the parent ternary Ni-Mn-Ga system provides further information
49 on the role of magnetism on the relative phase stability of these alloys.
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2. Experimental Details

Polycrystalline Ni-Mn-Ga- Z ($Z = \text{Fe}, \text{Co}$) ingots were prepared by arc melting pure metals under argon atmosphere in a water cooled Cu crucible. The ingots were melted several times for homogeneity and encapsulated under vacuum in quartz glass. They were then annealed at 1073 K for 72 hours to achieve a high degree of atomic order. Finally, the samples were quenched in ice-water. The compositions of the alloys were determined by energy dispersive x-ray photoluminescence analysis (EDX) with an estimated error less than $\pm 0.3\%$. Results are collected in Table 1. The reference system was nearly stoichiometric Ni_2MnGa , which shows a high temperature $L2_1$ structure ($Fm\bar{3}m$).

The alloys were grouped according to their compositions into three different families for each of the doping elements:

(1) Fe substitution:

- $\text{Ni}_{52.5-x}\text{Mn}_{23}\text{Ga}_{24.5}\text{Fe}_x$ ($0 \leq x \leq 5.2$), for which Ni is replaced by Fe.
- $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ ($0 \leq x \leq 5.2$), for which Mn is replaced by Fe.
- $\text{Ni}_{52.7}\text{Mn}_{22.1}\text{Ga}_{25.2-x}\text{Fe}_x$ ($0 \leq x \leq 5.3$), for which Fe replaces Ga.

(2) Co substitution:

- $\text{Ni}_{50.9-x}\text{Mn}_{24.6}\text{Ga}_{24.5}\text{Co}_x$ ($0 \leq x \leq 5.2$), for which Ni is replaced by Co.
- $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ ($0 \leq x \leq 5.1$), for which Mn is replaced by Co.
- $\text{Ni}_{50.6}\text{Mn}_{24.4}\text{Ga}_{25-x}\text{Co}_x$ ($0 \leq x \leq 6.4$), for which Co replaces Ga.

Structural transition temperatures were obtained from ac susceptibility and calorimetric measurements. Specimens cut from the ingots using a low speed diamond saw (typical size $5 \times 1 \times 1 \text{ mm}^3$) were used as samples for susceptibility and calorimetric studies. Magnetic susceptibility measurements were carried out in an ac susceptometer (LakeShore 7120A) in the temperature range $80 \text{ K} \leq T \leq 320 \text{ K}$. The working parameters were 500 A m^{-1} (6.28 Oe) applied field and 375 Hz frequency. For differential scanning calorimetry (DSC) measurements, one side of the samples was ground with SiC abrasive to ensure optimal thermal contact. Calorimetric measurements were carried out by means of a high sensitivity calorimeter in the temperature range $100 \text{ K} \leq T \leq 350 \text{ K}$. Typical heating and cooling rates were 2 K min^{-1} . Magnetic transition temperatures were determined by means of a DSC calorimeter TA 2920 suitable for higher temperatures. All transition temperatures are affected by an error of $\pm 1 \text{ K}$. We also determined the entropy change associated with the martensitic transition from calorimetric measurements. The errors in entropy change are based on reproducibility and shown as errors bars in the figures.

Temperature dependent structural analysis were carried out with a Siemens D-500 x-ray diffractometer ($\text{Cu } K_\alpha$ radiation) equipped with a low temperature stage.

3. Results

In this section, we present representative results of susceptibility and calorimetric measurements for each family and doping element. These selected results illustrate the evolution of the magnetic and structural properties with each of the 3d substituted elements. From the complete set of data we determine a phase diagram for each family and doping element and the transition entropy change at the martensitic transformation.

3.1. Ni substitution

Figure 1(a) shows the ac susceptibility curves for selected samples of the family which results when replacing Ni by Co. For the undoped sample ($x = 0$), susceptibility measurements reveal the presence of a martensitic transformation. The corresponding transition temperatures are: martensite start temperature $M_s = 216$ K, martensite finish temperature $M_f = 203$ K, austenite start temperature $A_s = 215$ K and austenite finish temperature $A_f = 226$ K. The Curie point was determined from complementary DSC measurements as $T_C = 374$ K. In addition to the martensitic transformation, an extra feature is observed in the susceptibility curve at temperatures above the martensitic transition which is associated with the formation of the intermediate or premartensitic phase [19, 24]. The transition temperature is $T_I = 256$ K. As can be seen from the figure, when increasing the amount of Co concentration both premartensitic and martensitic transition temperatures are displaced to lower temperatures and eventually both transitions merge. This behaviour is illustrated by sample $x = 2.6$; for this sample, the features associated with both structural transformations are close to each other and are difficult to distinguish. Here, calorimetric measurements reveal crucial to discern both transitions. Figure 1(b) shows the calorimetric curves for this sample recorded on cooling and heating. At low temperatures, the martensitic transition is revealed by multiple peaks which are consequence of the well-known jerky character of martensitic transformations. The presence of the premartensitic transition is revealed by an additional feature observed in the calorimetric curves at temperatures above the martensitic transition, magnified in the inset of Figure 1(b) for the sake of clarity.

Analogously, Figure 2 shows the ac susceptibility and calorimetric curves for selected samples of the corresponding family when substituting Fe. Note that the $x = 0$ samples for the Fe-doped and Co-doped alloys have different compositions. In this case, for the undoped sample ($T_C = 351$ K), susceptibility measurements reveal the presence of a martensitic transformation on cooling at $M_s = 291$ K and $M_f = 272$ K. On heating, the reverse transformation takes place at $A_s = 274$ K and $A_f = 295$ K. At lower temperatures, there is another distinct structural transformation, namely, the intermartensitic transformation, occurring at $T_{IM} = 211$ K during cooling and at 239 K during heating with a temperature hysteresis of ~ 40 K (estimated as the temperature difference at half intermartensitic transformation). The presence of such intermartensitic transformation was confirmed by the calorimetric measurements shown in Figure 2(b). The intermartensitic transformation was first observed in Ni-Mn-Ga in some prestressed [30, 31] and Mn-rich [27] samples. However, these transformations were non-thermoelastic, only occurring while cooling. Clearly, our observed intermartensitic transformation shows a complete thermoelastic behaviour. Thermoelastic intermartensitic transitions have been reported previously for Ni-Mn-Ga samples within a narrow composition range with e/a values close to 7.6 [18, 28, 29, 32, 33]. More details of the intermartensitic transition will be given in next section.

Figure 3 summarizes the results obtained when substituting Ni by Co and Fe 3d elements. Figure 3(a) shows the dependence of the transition temperatures as a function of Co concentration. It should be noted that all of the transition temperatures associated with the martensitic transformation (M_s , M_f , A_s and A_f) follow similar x dependence. Thus, for the sake of clarity only M_s temperatures are plotted. As can be seen from that figure, the martensitic transformation temperatures decrease as the amount of Co increases. In ternary Ni-Mn-Z systems (where Z is Ga, Al, Sn, In, and Sb), it is well established that martensitic transformation temperatures decrease as the valence electron concentration e/a decreases [3, 4, 47–50]. When replacing Ni ($3d^8 4s^2$) by Co ($3d^7 4s^2$), e/a decreases and a drop

1 in M_s is expected. This behaviour is seen in Figure 3(a). Premartensitic transfor-
2 mation temperatures also decrease as the Co concentration increases but at higher
3 rate than M_s . Thus, when increasing Co concentration both structural transition
4 temperatures M_s and T_I get closer and eventually meet. Note that transition tem-
5 peratures for the $x = 5.2$ sample are in the limit of the temperature range which
6 was accessible in our experiments. For this sample we did not observe the marten-
7 sitic transition and we were only able to determine unequivocally the premartensitic
8 transition temperature. It should be mentioned that Cong *et al.* observed an abrupt
9 decrease of martensitic transition temperatures in $\text{Ni}_{53-x}\text{Mn}_{25}\text{Ga}_{22}\text{Co}_x$ for com-
10 positions $x > 6$, which was attributed to atomic disorder caused by the addition
11 of large amounts of Co [51]. Atomic disorder leads to a substantial suppression
12 of the martensitic transition temperatures also in Ni_2MnGa [52]. All these facts
13 are illustrated by the dashed line in Figure 3(a). We note that for Co doping, T_C
14 increases proportionally with x .

15 On the other hand, Figure 3(b) shows the transition temperatures as a function
16 of Fe content for the (Ni,Fe) alloy family. Again, all transition temperatures as-
17 sociated with the martensitic transformation follow the same x dependence and
18 thus only M_s are included. The same criterion was applied to the intermartensitic
19 transformation and only T_{IM} are shown. Again, the martensitic transformation
20 temperatures decrease as the amount of Fe increases [e/a decreases; Ni ($3d^84s^2$)
21 and Fe ($3d^64s^2$)], consistently with the behaviour of ternary Ni-Mn-Z alloys and
22 the samples with Co substitution. Premartensitic transformation temperatures de-
23 crease as the Fe concentration increases as well but, in this case, at a lower rate
24 than M_s . Thus, when increasing Fe concentration both structural transition tem-
25 peratures M_s and T_I move apart each other. Such behaviour is opposite to the one
26 observed when substituting Co. Furthermore, the temperature of the ferromagnetic
27 transition T_C increases with increasing x , as in the case of Co substitution.

28 Figure 4 shows the entropy change at the martensitic transformation as a func-
29 tion of the doping concentration for both Fe and Co addition. The concentration
30 dependence of ΔS is similar to the behavior of M_s for both systems, i.e., the
31 entropy change decreases as the amount of doping increases. Such a dependence
32 reflects the stabilization of the cubic phase with increasing doping concentration.

32 3.2. Mn substitution

33 Figures 5(a) and (b) illustrate typical results obtained when replacing Mn by Fe
34 and Co, respectively. Figure 5(a) shows the ac susceptibility curves for selected
35 samples of the (Mn,Fe) family. As can be seen from that figure, when increasing
36 the amount of Fe concentration both martensitic and intermartensitic transitions
37 shift to lower temperatures. The presence of the intermartensitic transformation
38 undergone by these samples was again confirmed by calorimetric measurements, as
39 illustrated in the inset of Figure 5(a). On the other hand, Figure 5(b) shows the
40 ac susceptibility curves for selected samples of the corresponding (Mn,Co) fam-
41 ily. In this case, the samples show a rich behaviour when adding Co. While the
42 undoped sample shows a premartensitic transition at $T_I = 256$ K followed by a
43 martensitic transformation at lower temperatures, $M_s = 216$ K, the doped $x = 2.1$
44 sample undergoes a martensitic transformation at $M_s = 246$ K followed by an in-
45 termartensitic transition at lower temperatures, $T_{IM} = 159$ K. In the latter sample
46 no signatures of the premartensitic transformation were observed. As follows from
47 the present results, these alloys transform from the parent phase to a final marten-
48 sitic structure through a thermally induced intermartensitic transformation. These
49 transformations occur both while cooling and heating, thus showing thermoelastic
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behaviour. The small value of the intermartensitic transformation latent heat compared to the one associated with the martensitic transformation (note the large size change of the calorimetric peaks associated with martensitic and intermartensitic transformations in Figures 2 and 5) illustrates the closeness of the free energies of the different martensites.

In order to confirm the presence of the intermartensitic transition in the studied samples, we carried out x-ray diffraction measurements at several temperatures across the martensitic and the intermartensitic phase transitions for one specimen. These results enabled determination of the structure of the different martensitic phases. Figure 6 shows the x-ray diffraction patterns taken at 145 K and 270 K while heating for the $\text{Ni}_{52.5}\text{Mn}_{20.1}\text{Ga}_{25.1}\text{Fe}_{2.3}$ sample. Prior to the measurements, the sample was cooled down to ~ 130 K, i.e., below the intermartensitic phase transition (T_{IM}). Such a sequence ensures that the sample fully transforms to the intermartensitic phase before the measurements take place. All the intense peaks have been indexed and labelled in Figure 6. At low temperatures, the martensite shows a monoclinic modulated $14M$ structure with lattice parameters $a = 0.424$ nm, $b = 0.547$ nm and $c = 2.937$ nm, with $\beta = 94.3^\circ$ [Figure 6(a)]. When the temperature is increased, the diffraction pattern changes clearly indicating the existence of the reverse intermartensitic transition. The corresponding structure is (slightly) monoclinic modulated $10M$ with lattice parameters $a = 0.418$ nm, $b = 0.554$ nm and $c = 2.106$ nm, with $\beta = 90.3^\circ$ [Figure 6(b)]. The present sequence of intermartensitic transitions is $14M \rightarrow 10M \rightarrow P$ while heating. Such sequence is in agreement with previously stress [30, 31] and thermal induced [27, 33] intermartensitic transitions. In the present experiments, however, a second intermartensitic transition to a low temperature non-modulated phase was not observed [33]. Such behaviour can be ascribed to the fact that intermartensitic transitions are very sensitive to internal stresses present in the samples [28, 33] and this can lead to differences in the particular intermartensitic transition sequence observed [18, 28, 29, 32, 33].

The variation of transition temperatures with both Co and Fe concentration for these families are collected in Figures 7(a) and (b), respectively. Several interesting features come up from these phase diagrams. As can be seen from Figure 7(a), M_s increases when increasing the amount of Co concentration, as expected due to the increase of e/a when replacing Mn ($3d^54s^2$) by Co ($3d^74s^2$). On the other hand, both premartensitic T_I and intermartensitic T_{IM} transition temperatures decrease with increasing the doping concentration and T_C slightly increases with x . From our data, it appears that only when the premartensitic transition disappears, i.e., meets the martensitic transformation, the intermartensitic transformation develops. In fact, this was also pointed out in the phase diagram plotted in Figure 3(b) for the quaternary Ni-Mn-Ga-Fe. This behaviour seems to be intimately related to the mechanisms of the structural transitions. Indeed, the appearance of the different structural phases is related to the anomalous instability of the crystal lattice with respect to atomic displacements of $\{110\}$ planes along $\langle 1\bar{1}0 \rangle$ directions and manifests in different modulations of stacking planes in such directions.

Figure 7(b) shows the dependence of the transition temperatures on the amount of Fe substitution. Here, the martensitic transition temperature decreases when increasing Fe concentration, i.e., increasing e/a . This behaviour is unexpected from the scaling of the martensitic transition temperatures with the electronic concentration. However, our present results agree with those reported in most of the literature [35, 39, 44]. Interestingly, a similar behaviour has been recently reported in Ni-Mn-Sn alloys: while a decrease of martensitic transition temperatures when increasing e/a has been observed when replacing Mn by Fe [53], an increase of the

1 transition temperatures with increasing the electron per atom concentration has
2 been reported when substituting Ni by Fe [54]. These results indicate that other
3 parameters than e/a affect phase stability. In particular, our results suggest that
4 magnetic interactions play an important role. The intermartensitic transformation
5 temperatures behave in a similar way and also decrease with increasing Fe con-
6 tent. No intermartensitic transformations were detected for Fe substitution higher
7 than $\sim 4\%$, as illustrated by the dashed line. It should be noted that a decrease
8 of thermoelastic intermartensitic transformation temperatures with the electron
9 concentration has also been previously reported in Ni-Mn-Fe-Cu-Ga system [55].
10 Moreover, the Curie point increases with x .

11 Figure 8 shows the dependence of the entropy change at the martensitic trans-
12 formation on the amount of Fe and Co addition. As can be seen from that figure,
13 $3d$ element substitution does not substantially modify the values of the entropy
14 change at the martensitic transition when replacing Mn by Fe and/or Co. It should
15 be mentioned that it was not possible to evaluate properly ΔS for the (Mn,Co)
16 $x = 5.1$ sample due to the broadening of the martensitic transition and therefore
17 this value is not included in the plot.

19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

3.3. Ga substitution

Finally, we discuss the results obtained for the (Ga,Fe) and (Ga,Co) families. Fig-
ure 9 shows calorimetric curves for selected samples from each family. In this case,
due to the high values of the transformation temperatures only calorimetric data
are discussed. As can be seen from that figure, martensitic transformation temper-
atures strongly increase when substituting both $3d$ doping elements. This is clearly
seen in Figure 10, where we plotted the phase diagrams of these two families. Such
strong x dependence is consistent with the rapid increase of e/a when Fe and/or
Co are substituted for Ga [Ga ($4s^24p^1$), Fe ($3d^64s^2$) and Co ($3d^74s^2$)]. By contrast,
the Curie point shows a different behaviour as a function of x for each family.
On the one hand, in the Co doped samples the Curie point is almost independ-
ent of the doping concentration when the ferromagnetic transition takes place in
the austenitic state, while T_C decreases with increasing x when the ferromagnetic
transition occurs within the martensitic state. On the other hand, for the (Ga,Fe)
samples T_C increases with increasing doping concentration over the entire studied
range, the slope of the increase being larger when the martensitic and the ferro-
magnetic transition meet each other. This behaviour is ascribed to the coupling
between the magnetic and the structural transitions and the significant increase of
 M_s with x [56] and has been previously observed in Ga substituted for Ni and Mn
ternary alloys [57–59]. Finally, notice that no signatures of either premartensitic
or intermartensitic transitions were observed in these families.

The entropy change at the martensitic transition as a function of Fe and Co
concentration is collected in Figure 11. As can be seen from this figure, ΔS par-
allels the behaviour of the martensitic transformation temperatures and increases
as the amount of doping increases, pointing out the stabilization of the the low
temperature phase due to Fe and Co substitution.

4. Discussion

In this paper we have studied the effect of Fe and Co $3d$ elements substitution
on the relative phase stability of the prototypical magnetic shape memory alloy
Ni-Mn-Ga for compositions close to the 2-1-1 stoichiometry. An effort was made

1 to selectively substitute each constituent element by same amounts of doping. In
2 this way, we were able to systematically study the effect of substitution at a par-
3 ticular site for each doping element. The complete set of results for magnetic and
4 structural transition temperatures obtained from calorimetric and ac-susceptibility
5 measurements are shown as a function of the electron concentration e/a in Fig. 12.
6 This representation shows that e/a is a convenient parameter for reducing both
7 magnetic and structural transition temperatures and confirms that phase stability
8 in shape-memory Heusler materials is controlled by electronic degrees of freedom
9 to a large extent [47, 48]. However, the scatter of the data points which is higher
10 than that observed in the phase diagrams corresponding to the three studied com-
11 position related families (see Figs. 3, 7 and 10) already suggests that additional
12 parameters other than electron concentration affect phase stability. In this sense,
13 it is known that the ground state of Ni-Mn- Z alloys (Z as Ga, In, Al, ...) shows the
14 same sequence of phases when e/a is increased [50]. However, for a given value of
15 e/a the corresponding M_s transition temperature displays a strong dependence on
16 the Z element [4, 61]. Khan *et al.* [62] specifically studied the effect of isoelectronic
17 substitution of Ga by In in Ni₂MnGa and concluded that the effect of Z on M_s
18 mainly arise from the change of unit cell volume which modifies the relative posi-
19 tion of the Brillouin zone boundary and Fermi surfaces. The role of volume effects
20 on the martensitic transition has been further studied via doping of Ni-Mn-Ga
21 with several other elements and use of electron density to parametrize structural
22 transition temperatures has been suggested [63, 64]. The effect of magnetism on
23 the martensitic transition, however, has been studied in less detail. Recently, Roy
24 *et al.* [65] have shown that substitution of Mn by non-magnetic Cu has considerable
25 influence on phase stability. Cu gives rise to delocalization of the Mn magnetism
26 which is accompanied by an increase of Ni-covalency and a reinforcement of the
27 Ni-Ga bonds [65]. The result in this case is a decrease of the Curie temperature
28 and an increase of stability of the martensitic phase with respect to the parent
29 compound.
30

31 In order to compare our present results for Fe- and Co-doped alloys to the be-
32 haviour of the ternary system, the phase diagram of Ni-Mn-Ga is indicated in Fig.
33 12 by dashed lines. Such comparison is useful to obtain information about the effect
34 of magnetism on the structural transitions due to our selection of doping atoms
35 with similar atomic radii but different magnetic properties. The general trends of
36 all three systems are similar: M_s and T_I increase as e/a increases, whereas T_{IM}
37 and T_C decrease. Notice that for intermartensitic transitions, only data belonging
38 to thermoelastic transformations have been taken into account. In the case of the
39 Fe substituted system, at constant e/a , we find that the addition of Fe to Ni-Mn-
40 Ga shifts the structural transition temperatures M_s , T_I and T_{IM} to lower values,
41 whereas T_C shifts to higher temperatures. On the other hand, when Co is added
42 to the ternary system the effect of doping on the phase transition temperatures
43 is more complex. While for low values of e/a M_s are displaced to lower values,
44 for higher e/a the martensitic transition temperatures are shifted to higher values.
45 Additionally, M_s and T_I are suppressed for values of $e/a \lesssim 7.50$. Such behaviour
46 differs from the linearity observed in both ternary and Ni-Mn-Ga-Fe systems. As
47 mentioned before, Cong *et al.* observed an abrupt decrease of the martensitic tran-
48 sition temperature in Co-doped systems, which was attributed to atomic disorder
49 caused by the addition of large amounts of Co [51]. However, from the comparison
50 of both quaternary compounds, it can be seen that the Fe-doped system does not
51 show such a dramatic suppression of M_s and T_I for similar amounts of doping (and
52 thus similar e/a values). Due to the similar atomic radii and concentration of dop-
53 ing atoms considered, the differences between both quaternary systems observed
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1 here should be ascribed to the different magnetic properties of Fe and Co. Notice
2 that the Curie temperatures values for these Co-doped samples are significantly
3 higher than the corresponding T_C values for the Fe-doped samples, which suggests
4 that the strengthening of the magnetic interactions stabilizes the austenitic phase.
5 This behaviour is in agreement with the rapid decrease of M_s accompanied by
6 considerable increase of T_C observed in the results from Cong *et al.* [51] and also in
7 recent results from Kanomata and co-workers [68]. On the other hand, the scarce
8 T_{IM} data does not allow a detailed determination of the effect of Co addition on
9 the intermartensitic transformation, although from comparison with both ternary
10 and Fe-doped systems one expects T_{IM} to decrease when increasing e/a . Regarding
11 the Curie point, T_C shifts to higher values when the magnetic transition occurs
12 within the austenitic state (low e/a), while it is slightly displaced to lower values
13 when takes place within the martensitic state (high e/a values).
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15 Preceding results indicate that in both Fe- and Co-doped Ni-Mn-Ga alloys, mag-
16 netic effects play a certain role in controlling relative phase stability. In the re-
17 gion where the martensitic transition occurs in the ferromagnetic phase below the
18 Curie point, the increase of T_C with respect to Ni-Mn-Ga suggests that both Fe-
19 and Co-addition give rise to a strengthening of magnetic exchange coupling and
20 this seems to be responsible for lowering structural transition temperatures. Ad-
21 ditional information on the effect of magnetism on the martensitic transition can
22 be obtained from the e/a dependence of the entropy difference ΔS between the
23 high temperature cubic phase and the low temperature martensitic phase. Due to
24 the diffusionless nature of the martensitic transition, the distribution of atoms in
25 the parent phase is inherited by the martensitic phase and ΔS should only con-
26 tain vibrational, electronic and magnetic contributions. Fig. 13 shows the entropy
27 change at the martensitic transformation as a function of electron concentration
28 per atom e/a for (a) Ni-Mn-Ga-Fe and (b) Ni-Mn-Ga-Co systems. Like in the
29 ternary Ni-Mn-Ga, in both quaternary systems ΔS increases as the electron per
30 atom concentration increases. In the case of Ni-Mn-Ga, the large concentration
31 dependence of the entropy change was attributed by Khovailo *et al.* to changes of
32 the magnetic contributions [67]. Actually, when the martensitic transition occurs
33 above the Curie point, the magnetic contribution to the entropy change should
34 be very small and the entropy change is expected to be largely provided by the
35 lattice vibrational contribution. In contrast, when the transition occurs below the
36 Curie temperature a magnetic contribution to the entropy of opposite sign to the
37 vibrational contribution is expected. This magnetic contribution is responsible for
38 the increase of ΔS with increasing e/a . In the case of Fe and Co substituted alloys
39 the entropy changes for a given value of e/a are lower than those in the correspond-
40 ing ternary Ni-Mn-Ga system. This drop confirms the suggested strengthening of
41 magnetic exchange coupling when adding Fe and Co which results in a decrease of
42 the free energy difference between the parent and martensite phases when the alloy
43 orders magnetically [34], and therefore stabilization of the high temperature phase.
44 The reduction of entropy change at a given electron concentration is considerably
45 larger in Co-doped alloys which means that Co has a stronger effect on magnetic ex-
46 change coupling than Fe. Such stronger effect is consistent with the abrupt decrease
47 of martensitic (and premartensitic) transition temperatures shown in Figure 12(b),
48 and further indicates that the strengthening of magnetic interactions stabilizes the
49 high temperature cubic phase.
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5. Conclusions

We studied the effect of Fe and Co selective substitution on the magnetic and structural phase transitions exhibited by Ni-Mn-Ga alloys. We determined the phase diagrams and the entropy changes at the martensitic transition of the resulting quaternary systems. Similarities between ternary Ni-Mn-Ga and quaternary Ni-Mn-Ga-Fe and Ni-Mn-Ga-Co systems reaffirm that electronic concentration qualitatively controls phase stability in these compounds. However, differences between these systems show that additional parameters affect phase stability and therefore e/a can only be used for examining systematic changes of structural and magnetic properties within a single-alloy system. In particular, differences between both quaternary systems indicate that relative phase stability is strongly modified by the strengthening of magnetic exchange coupling induced by Fe- and Co-doping and evidence that magnetic interactions affect the structural and magnetic phase transitions exhibited by Heusler magnetic shape memory alloys.

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Table 1. Compositions of the Ni-Mn-Ga-Co and Ni-Mn-Ga-Fe samples determined by EDX. For each element doping, different specimens are grouped into three distinct families, depending on the element that is substituted (elements within parenthesis, first and seventh column, respectively). Samples displayed in the first row are the undoped reference Ni-Mn-Ga samples. The estimated error in the compositions is less than $\pm 0.3\%$. Values of valence electron concentration per atom, e/a , are also given.

Family	Ni (at. %)	Mn (at. %)	Ga (at. %)	Co (at. %)	e/a	Family	Ni (at. %)	Mn (at. %)	Ga (at. %)	Fe (at. %)	e/a
	50.8	24.8	24.4	0	7.548		52.7	21.9	25.4	0	7.565
(Ni,Co)	50.0	24.4	24.8	0.8	7.524	(Ni,Fe)	51.3	22.8	24.5	1.4	7.573
	48.1	24.7	24.6	2.6	7.511		50.1	23.1	24.6	2.2	7.541
	47.6	24.8	24.5	3.1	7.510		49.3	23.1	24.5	3.1	7.530
	47.0	24.5	24.4	4.1	7.516		48.1	23.0	24.5	4.4	7.507
	45.8	24.6	24.4	5.2	7.502		47.0	23.1	24.6	5.3	7.479
(Mn,Co)	50.6	24.3	24.2	0.9	7.568	(Mn,Fe)	52.4	21.1	25.3	1.2	7.572
	50.7	22.7	24.5	2.1	7.583		52.5	20.1	25.1	2.3	7.594
	50.5	21.7	24.7	3.1	7.589		52.5	19.4	24.9	3.2	7.611
	50.8	19.8	24.5	4.9	7.642		52.5	18.3	25.0	4.2	7.617
	50.5	20.0	24.4	5.1	7.641		52.4	17.2	25.2	5.2	7.616
(Ga,Co)	50.7	24.4	23.8	1.1	7.591	(Ga,Fe)	52.6	21.9	24.2	1.3	7.623
	50.9	24.1	22.9	2.1	7.653		52.5	22.2	23.0	2.3	7.678
	50.8	24.4	21.7	3.1	7.718		52.6	22.2	22.0	3.2	7.73
	50.5	24.8	20.7	4.0	7.767		52.9	22.0	21.0	4.1	7.788
	49.8	23.9	19.9	6.4	7.826		52.6	22.4	19.7	5.3	7.843

1 Figure 1. $\text{Ni}_{50.9-x}\text{Mn}_{24.6}\text{Ga}_{24.5}\text{Co}_x$ family. (a) Magnetic susceptibility
2 versus temperature for samples of selected compositions. (b) Calorimetric curves for the sample with $x = 2.6$ showing the martensitic
3 and intermediate (magnified in the inset) transformations. Vertical
4 arrows show the position of the premartensitic transition temperature,
5 T_I . Horizontal arrows in panel (b) indicate direction of temperature change.
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8 Figure 2. $\text{Ni}_{52.5-x}\text{Mn}_{23}\text{Ga}_{24.5}\text{Fe}_x$ family. (a) Magnetic susceptibility versus
9 temperature for samples of selected compositions. (b) Calorimetric curves
10 for the sample with $x = 0$ showing the martensitic and intermartensitic
11 (magnified in the inset) transformations. Vertical arrows in panel (a) show
12 the position of the intermartensitic transition temperature, T_{IM} (sample
13 with $x = 0$), and the premartensitic transition temperature, T_I (samples
14 with $x = 1.4$ and 2.2). Horizontal arrows in panel (b) indicate direction of
15 temperature change.
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17 Figure 3. (a) Evolution of the transition temperatures of
18 $\text{Ni}_{50.9-x}\text{Mn}_{24.6}\text{Ga}_{24.5}\text{Co}_x$ as a function of Co concentration. (b) Evo-
19 lution of the transition temperatures of $\text{Ni}_{52.5-x}\text{Mn}_{23}\text{Ga}_{24.5}\text{Fe}_x$ as a
20 function of Fe concentration. Lines are guides to the eye.
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23 Figure 4. Entropy change at the martensitic transformation as a function
24 of doping concentration (Fe or Co) for Ni substitution. Solid lines are
25 linear fits to the experimental data.
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27 Figure 5. (a) $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ family. Magnetic susceptibility ver-
28 sus temperature for samples of selected compositions. Inset illustrates the
29 martensitic and the intermartensitic transformations for the sample $x = 2.3$
30 detected by calorimetry. (b) $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ family. Magnetic sus-
31 ceptibility versus temperature for selected samples. Vertical arrows show
32 the position of the intermartensitic transition temperature, T_{IM} . Horizontal
33 arrows in the inset of panel (a) indicate direction of temperature change.
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35 Figure 6. X-ray diffraction patterns illustrating the change of the
36 martensitic structure through the intermartensitic transition for the
37 $\text{Ni}_{52.5}\text{Mn}_{20.1}\text{Ga}_{25.1}\text{Fe}_{2.3}$ sample. (a) Monoclinic $14M$ structure ($T < T_{IM}$)
38 and (b) $10M$ (slightly) monoclinic structure ($T < M_s$).
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40 Figure 7. (a) Evolution of the transition temperatures of
41 $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ as a function of Co concentration. (b) Evo-
42 lution of the transition temperatures of $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ as a
43 function of Fe concentration. Lines are guides to the eye.
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45 Figure 8. Entropy change at the martensitic transformation as a function
46 of doping concentration (Fe or Co) for Mn substitution. Solid lines are
47 guides to the eye.
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50 Figure 9. Calorimetric curves for samples of selected compositions of
51 (a)–(b) $\text{Ni}_{52.7}\text{Mn}_{22.1}\text{Ga}_{25.2-x}\text{Fe}_x$ and (c)–(d) $\text{Ni}_{50.6}\text{Mn}_{24.4}\text{Ga}_{25-x}\text{Co}_x$
52 families. Vertical arrows show the Curie point, T_C . Horizontal arrows
53 indicate direction of temperature change.
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1 Figure 10. (a) Evolution of the transition temperatures of
2 $\text{Ni}_{50.6}\text{Mn}_{24.4}\text{Ga}_{25-x}\text{Co}_x$ as a function of Co concentration. (b) Evo-
3 lution of the transition temperatures of $\text{Ni}_{52.7}\text{Mn}_{22.1}\text{Ga}_{25.2-x}\text{Fe}_x$ as a
4 function of Fe concentration. Solid lines are guides to the eye.
5

6 Figure 11. Entropy change at the martensitic transformation as a function
7 of doping concentration (Fe or Co) for Ga substitution. Solid lines are
8 guides to the eye.
9

10 Figure 12. (Color online) (a) Phase diagram of Ni-Mn-Ga-Fe sys-
11 tem as a function of electron concentration per atom e/a . Filled
12 symbols stand for $\text{Ni}_{52.5-x}\text{Mn}_{23}\text{Ga}_{24.5}\text{Fe}_x$ family; half-filled symbols
13 stand for $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ family; open symbols stand for
14 $\text{Ni}_{52.7}\text{Mn}_{22.1}\text{Ga}_{25.2-x}\text{Fe}_x$ family. (b) Phase diagram of Ni-Mn-Ga-
15 Co system as a function of electron concentration per atom e/a .
16 Filled symbols stand for $\text{Ni}_{50.9-x}\text{Mn}_{24.6}\text{Ga}_{24.5}\text{Co}_x$; half-filled sym-
17 bols stand for $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ family; open symbols stand for
18 $\text{Ni}_{50.6}\text{Mn}_{24.4}\text{Ga}_{25-x}\text{Co}_x$ family. Lines are fits to the experimental data.
19 Squares stand for M_s , circles stand for T_I , up and down triangles stand for
20 T_C and T_{IM} , respectively. Red dashed lines depict the (fitted) transition
21 lines of the related Ni-Mn-Ga ternary system (data compiled from reference
22 [60]). The open red circles stand for the thermoelastic intermartensitic
23 transformation temperature in Ni-Mn-Ga [18, 29, 32, 33].
24
25

26 Figure 13. (Color online) (a) Entropy change at the martensitic transfor-
27 mation of Ni-Mn-Ga-Fe system as a function of electron concentration per
28 atom e/a . Filled symbols stand for $\text{Ni}_{52.5-x}\text{Mn}_{23}\text{Ga}_{24.5}\text{Fe}_x$ family; half-filled
29 symbols stand for $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ family; open symbols stand
30 for $\text{Ni}_{52.7}\text{Mn}_{22.1}\text{Ga}_{25.2-x}\text{Fe}_x$ family. (b) Entropy change at the martensitic
31 transformation of Ni-Mn-Ga-Co system as a function of electron concen-
32 tration per atom e/a . Filled symbols stand for $\text{Ni}_{50.9-x}\text{Mn}_{24.6}\text{Ga}_{24.5}\text{Co}_x$;
33 half-filled symbols stand for $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ family; open symbols
34 stand for $\text{Ni}_{50.6}\text{Mn}_{24.4}\text{Ga}_{25-x}\text{Co}_x$ family. Solid lines are linear fits to the
35 experimental data. Red dashed lines depict the (fitted) entropy change
36 of the related Ni-Mn-Ga ternary system (data compiled from references
37 [66, 67]).
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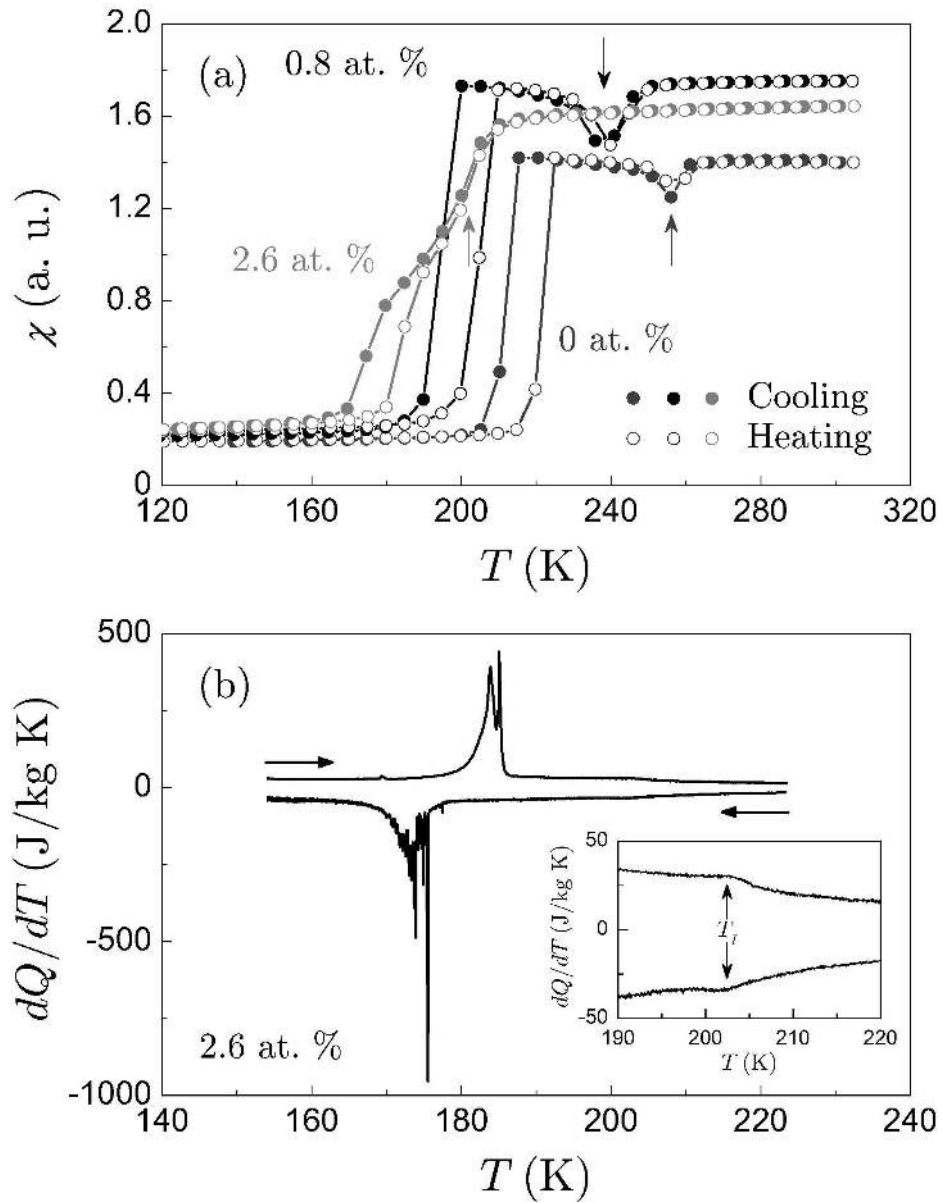


Figure 1
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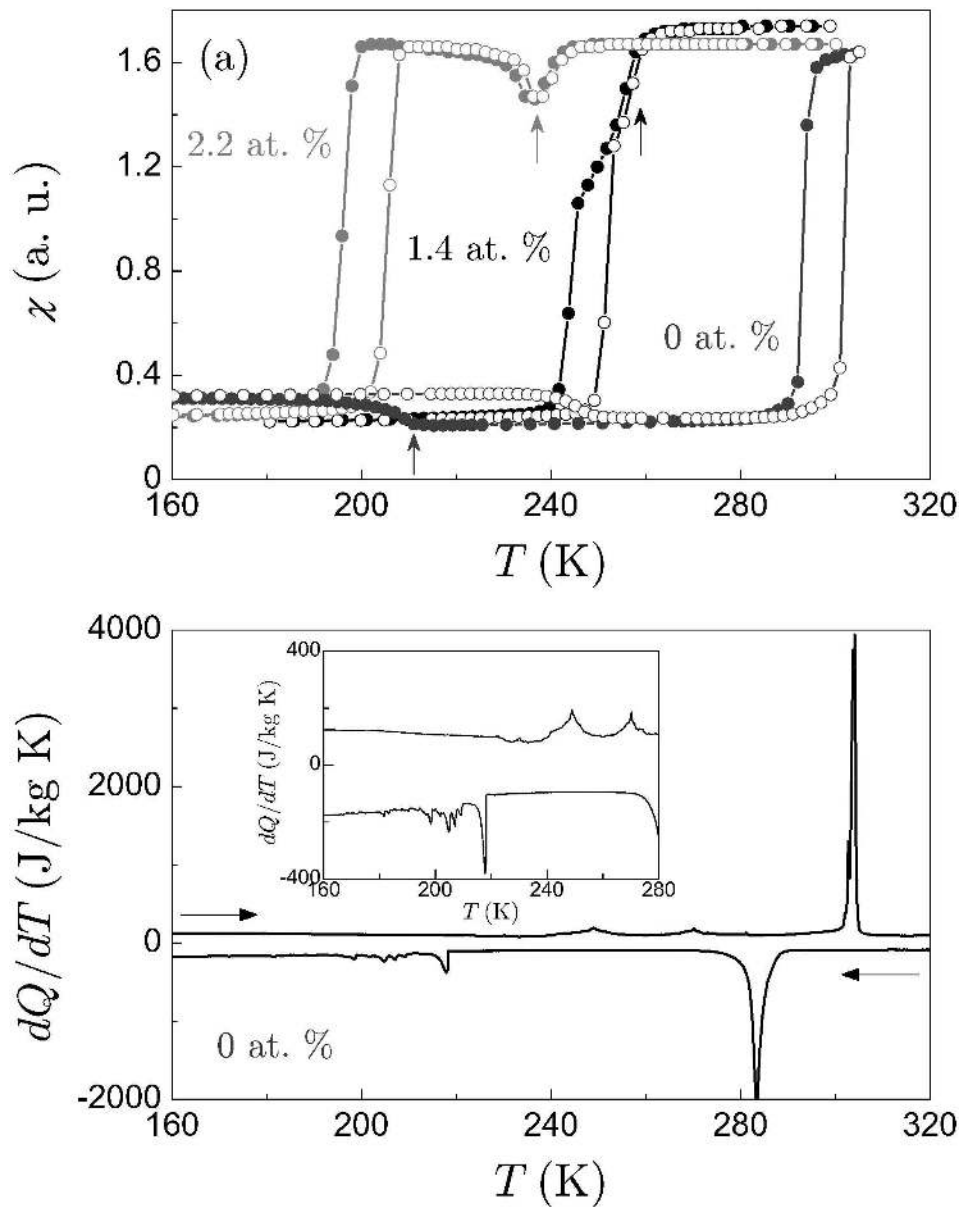


Figure 2
148x188mm (600 x 600 DPI)

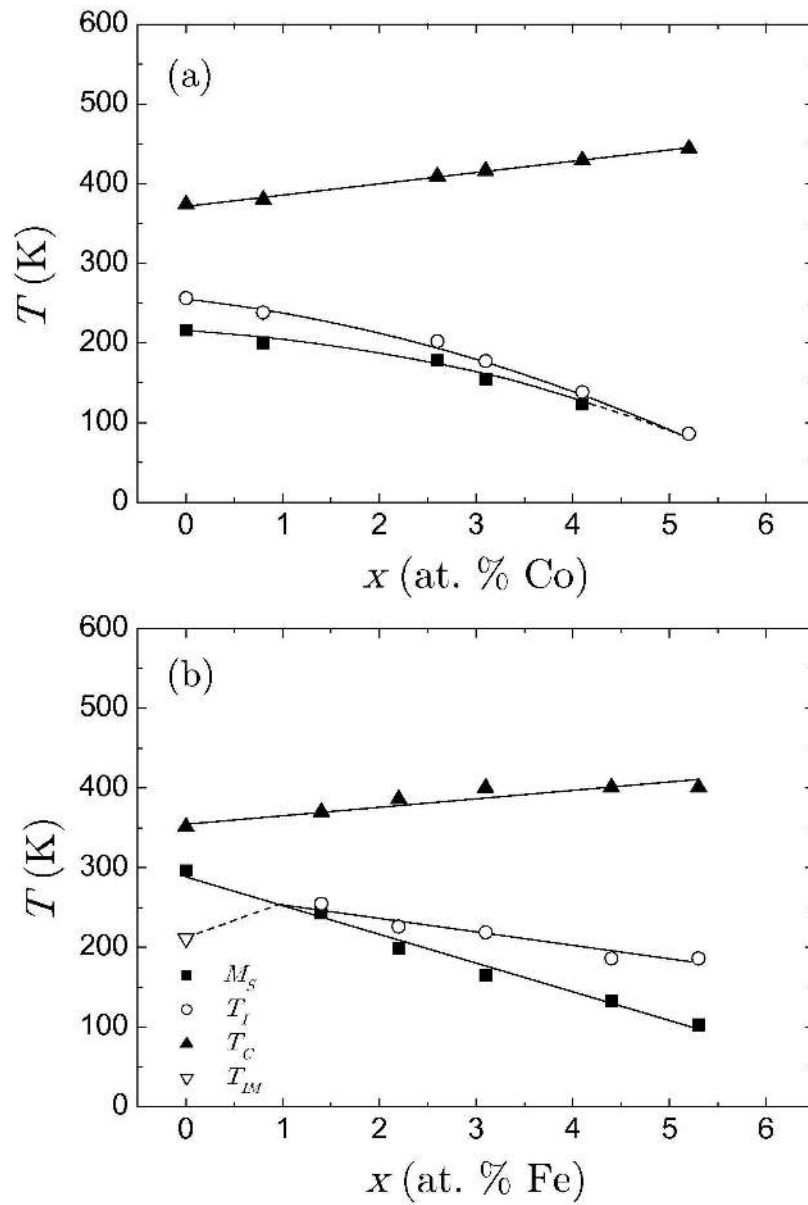


Figure 3
71x105mm (600 x 600 DPI)

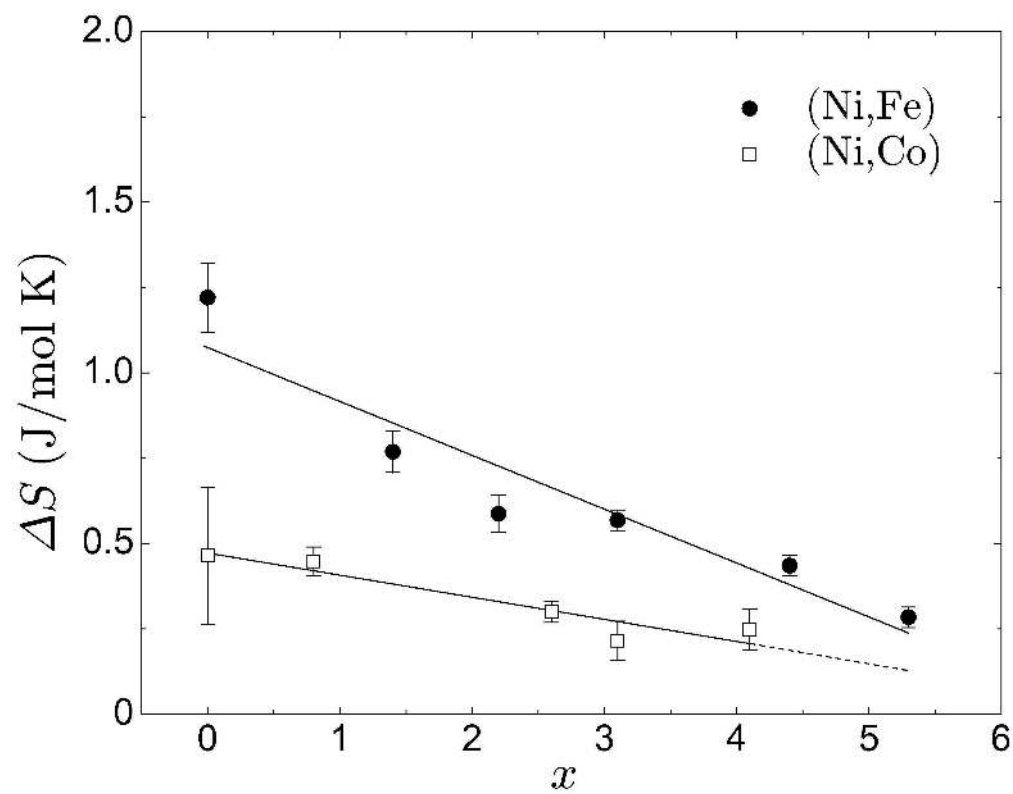


Figure 4
105x82mm (600 x 600 DPI)

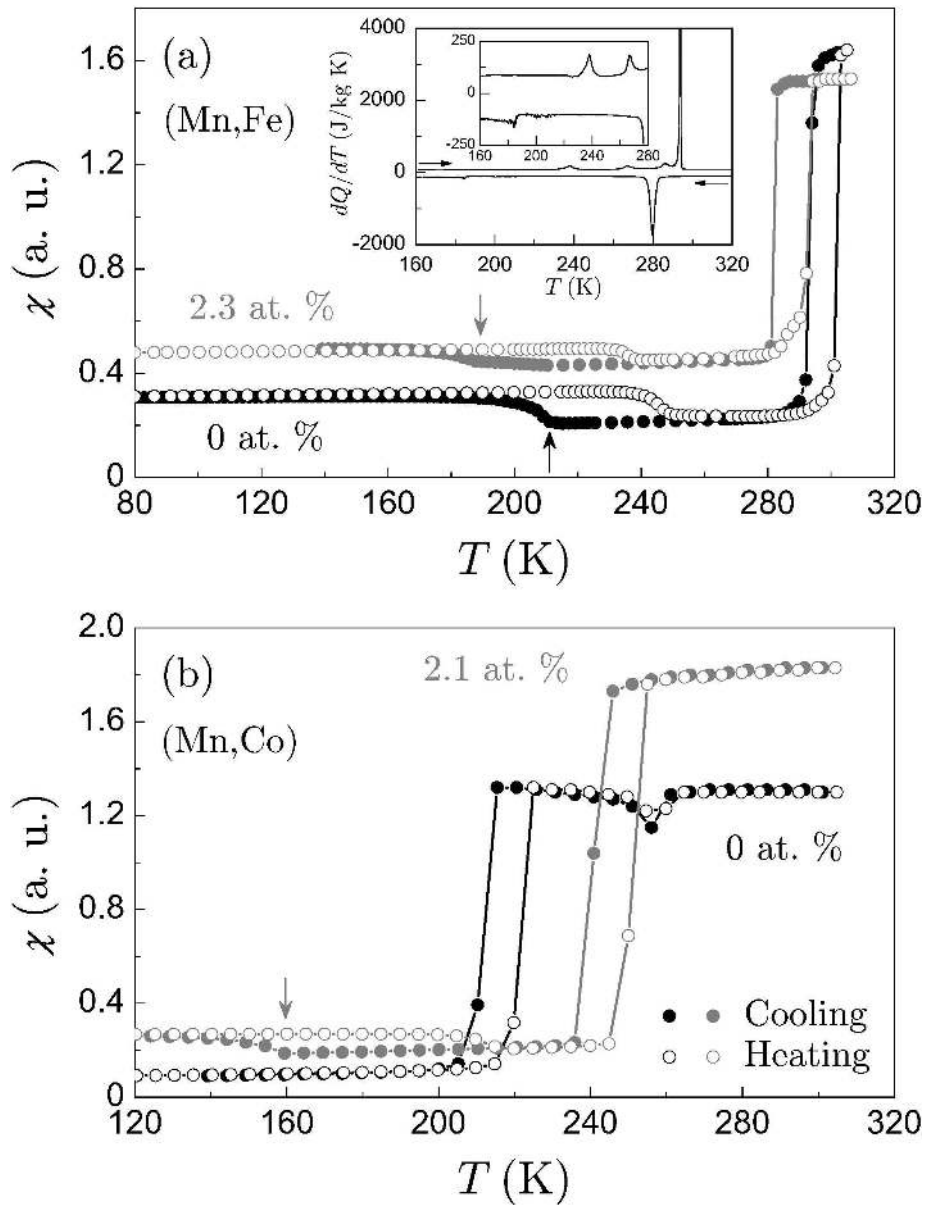


Figure 5
142x188mm (600 x 600 DPI)

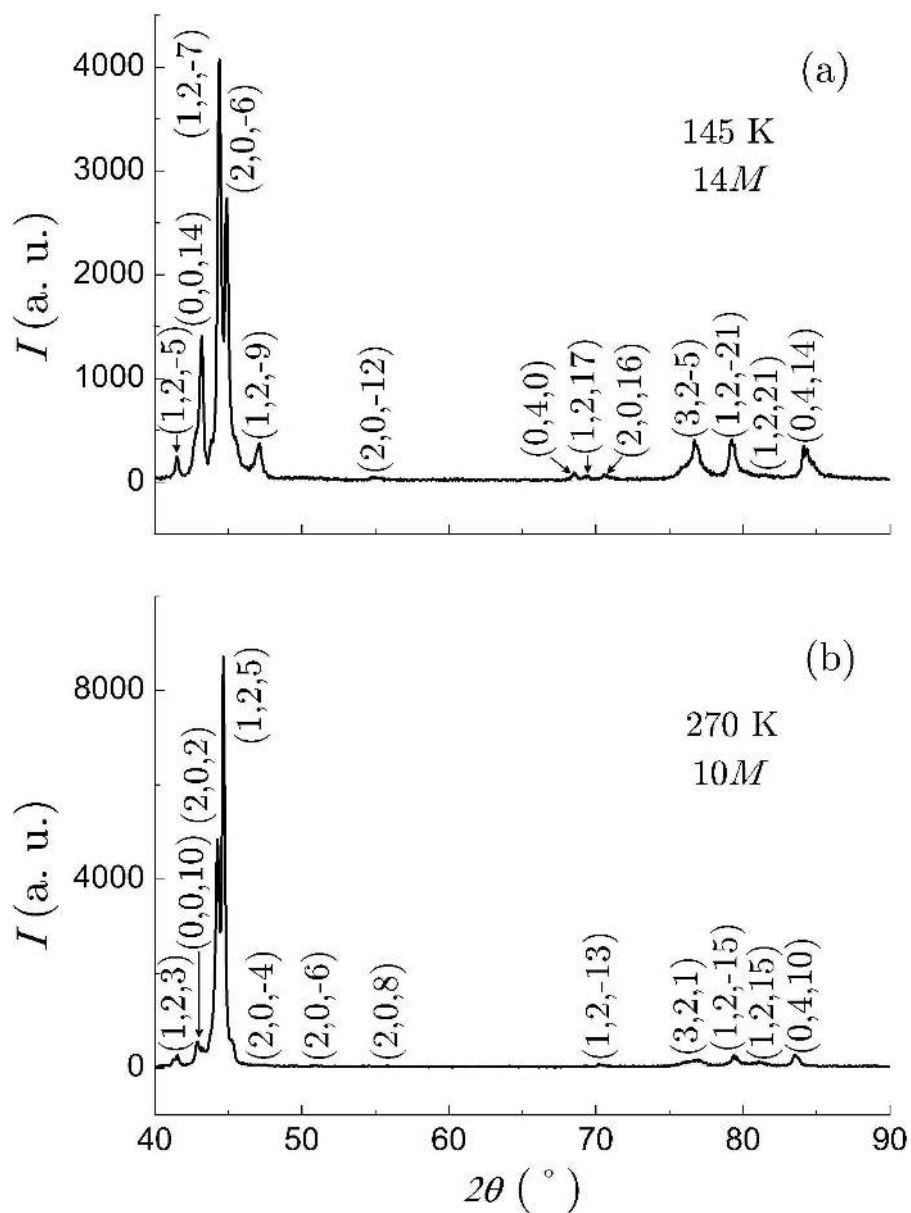


Figure 6
144x194mm (600 x 600 DPI)

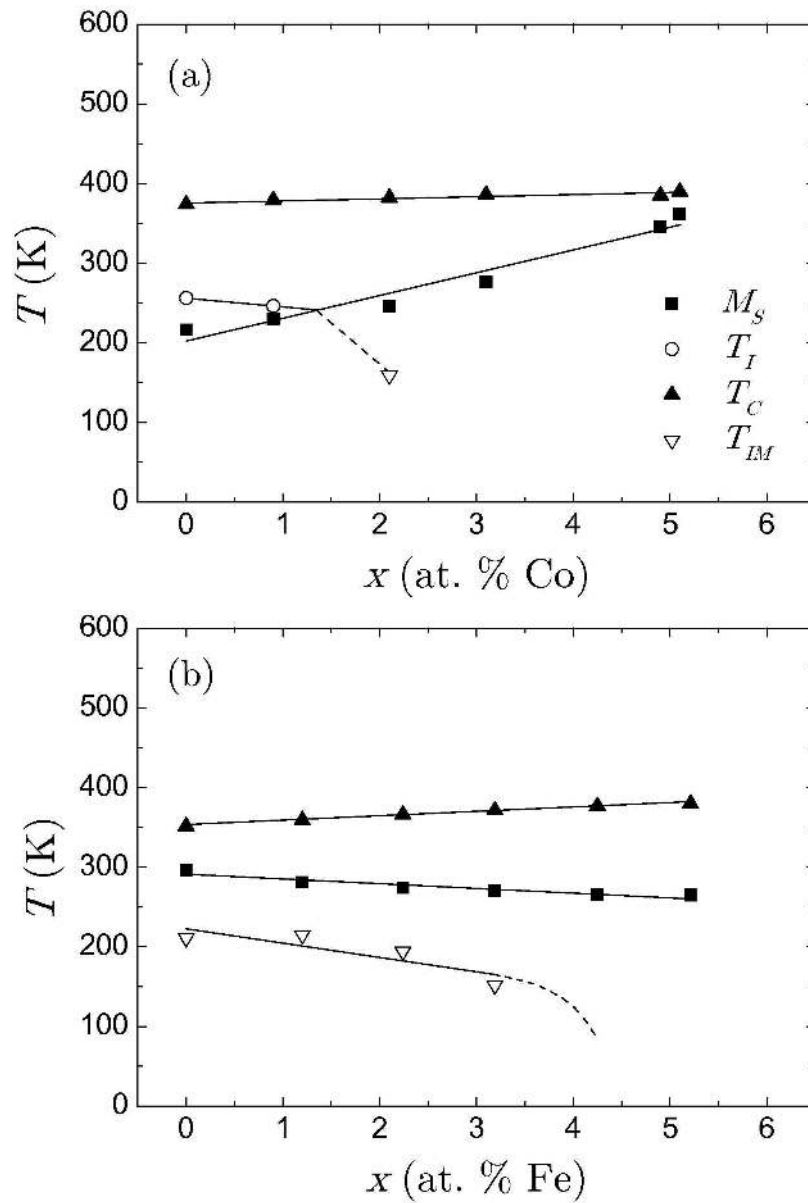


Figure 7
71x105mm (600 x 600 DPI)

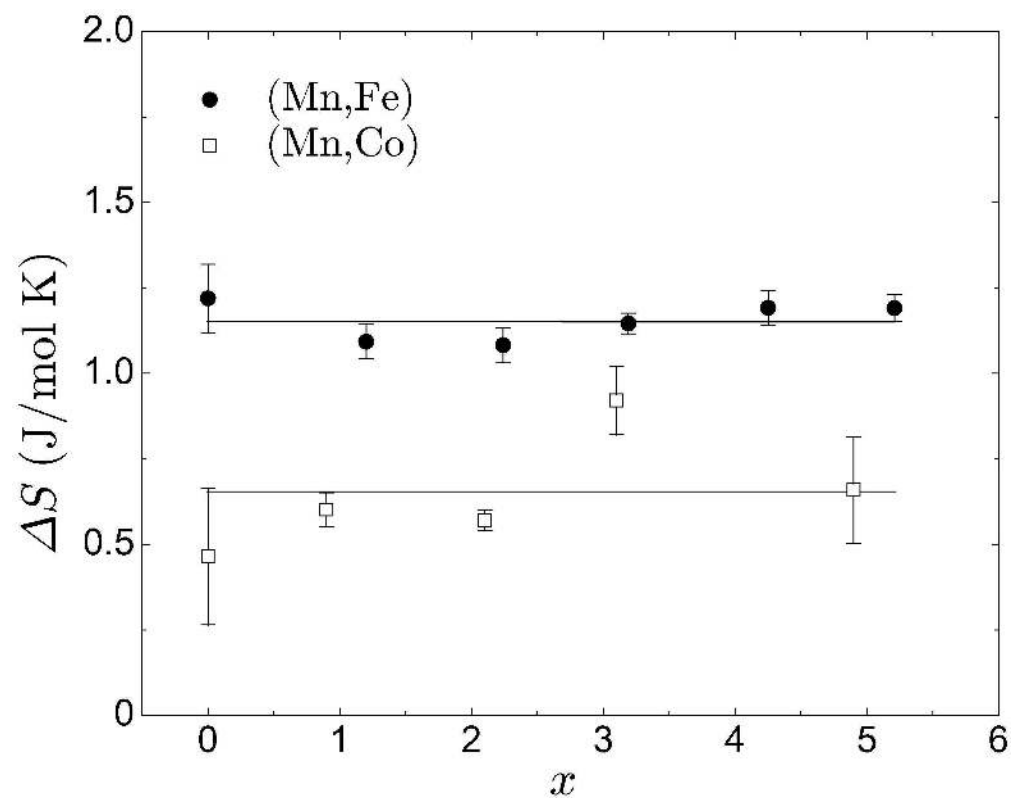


Figure 8
105x83mm (600 x 600 DPI)

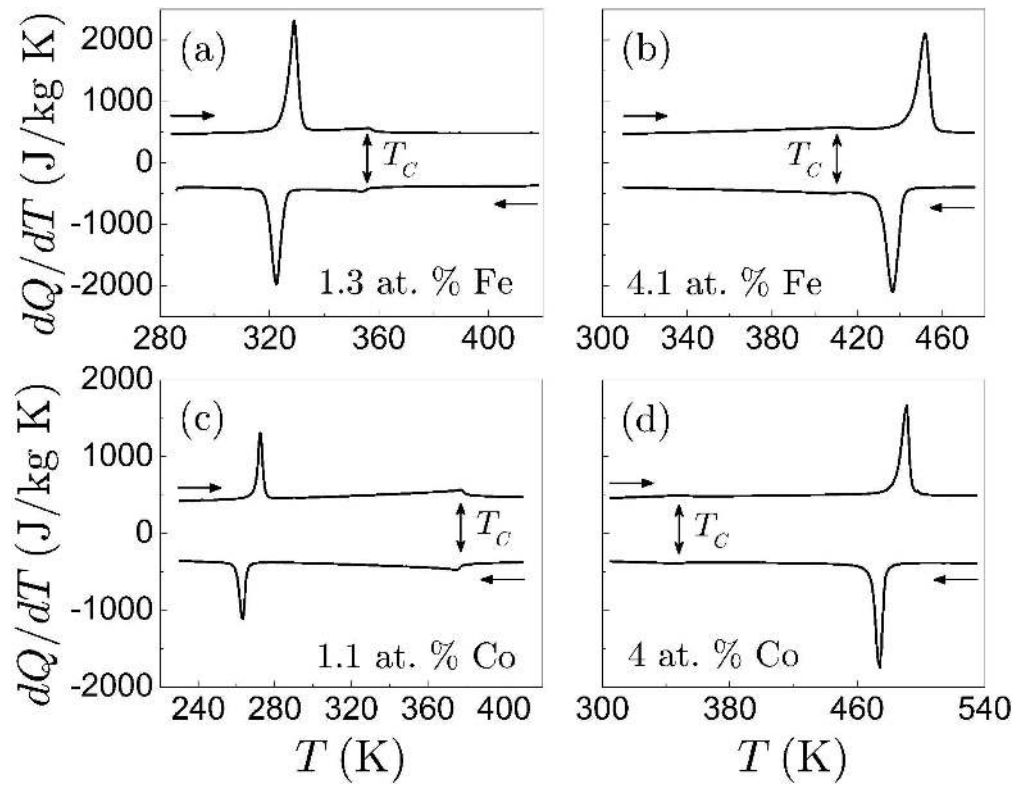


Figure 9
239x185mm (600 x 600 DPI)

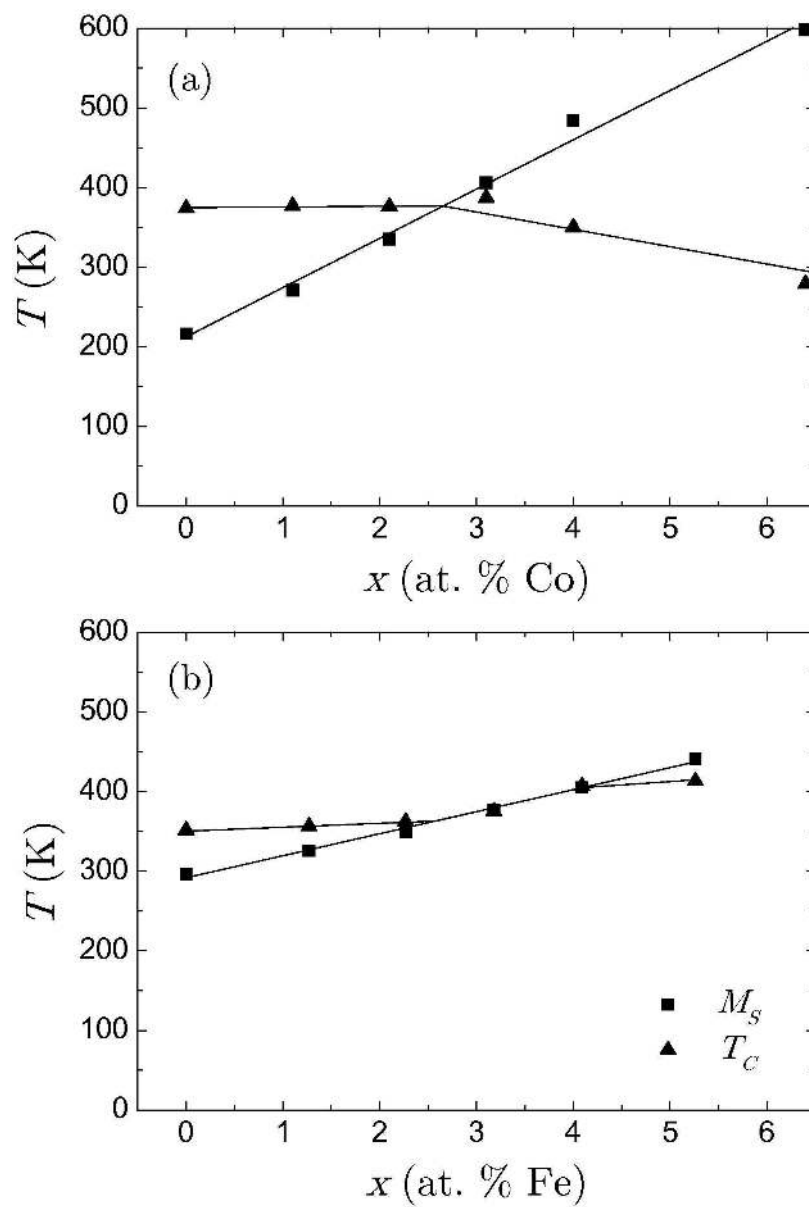


Figure 10
71x105mm (600 x 600 DPI)

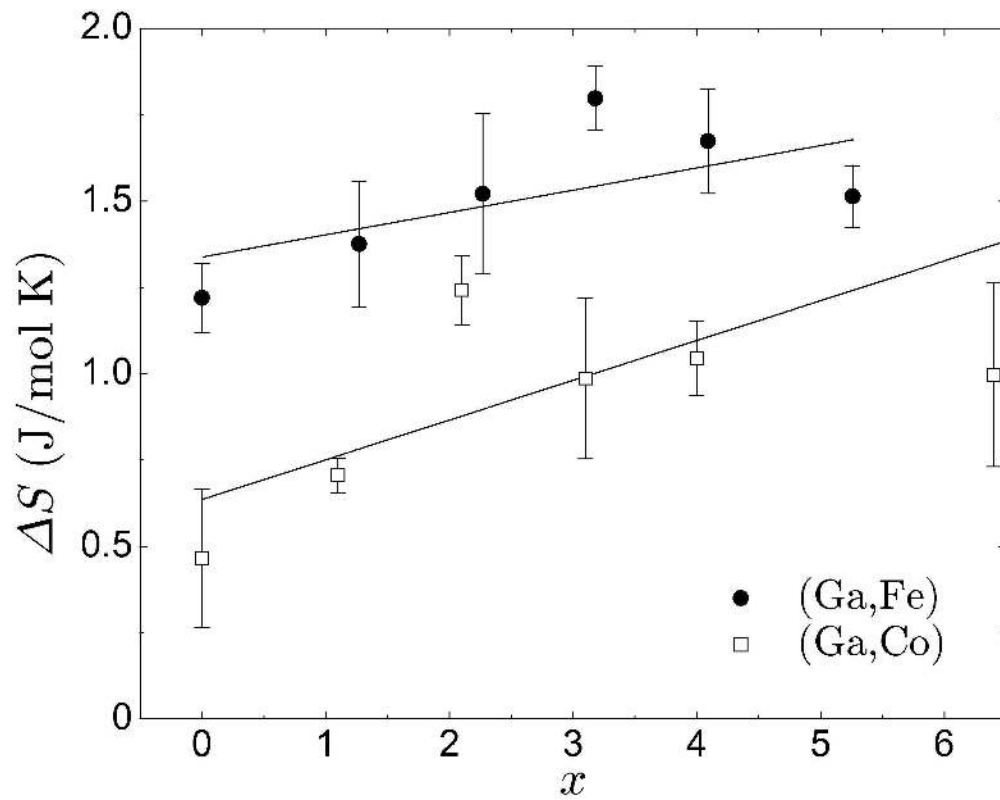


Figure 11
104x82mm (600 x 600 DPI)

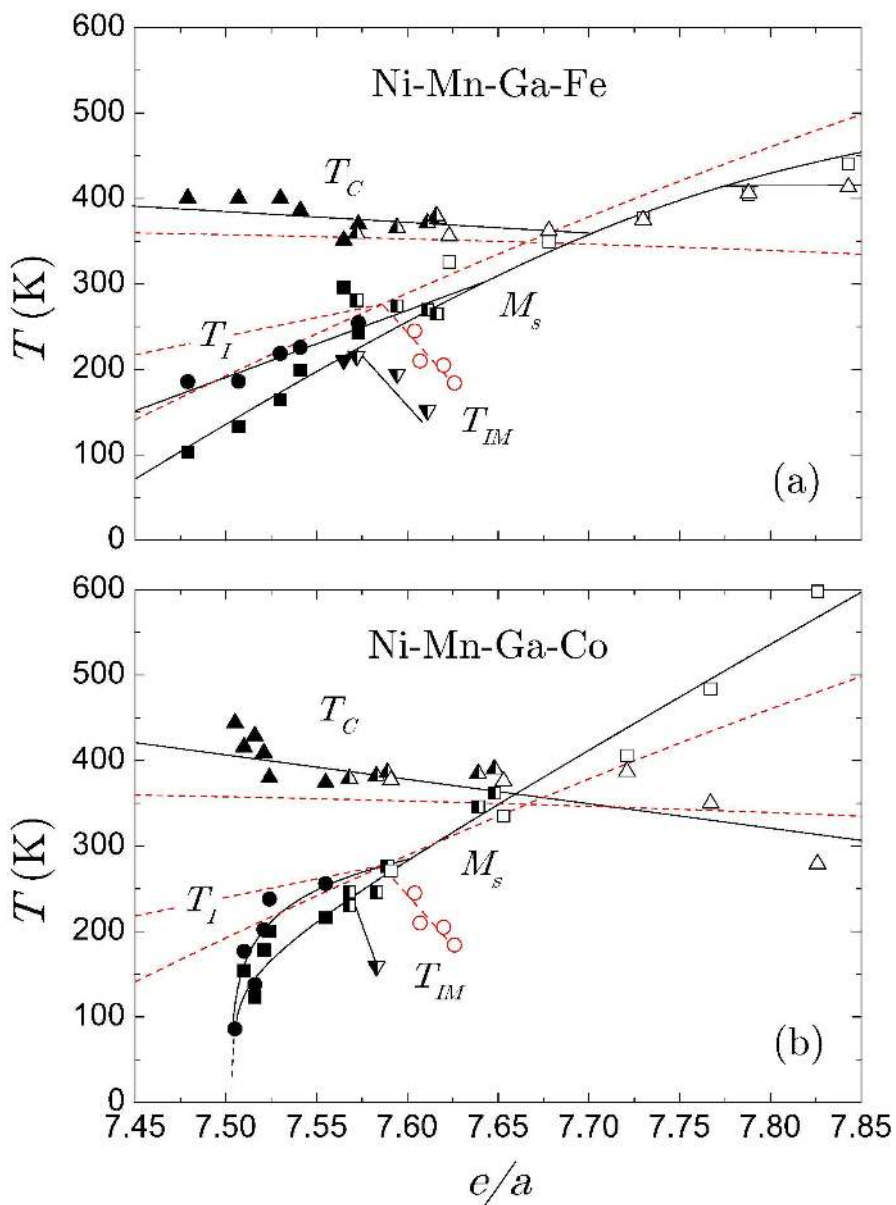


Figure 12
144x196mm (600 x 600 DPI)

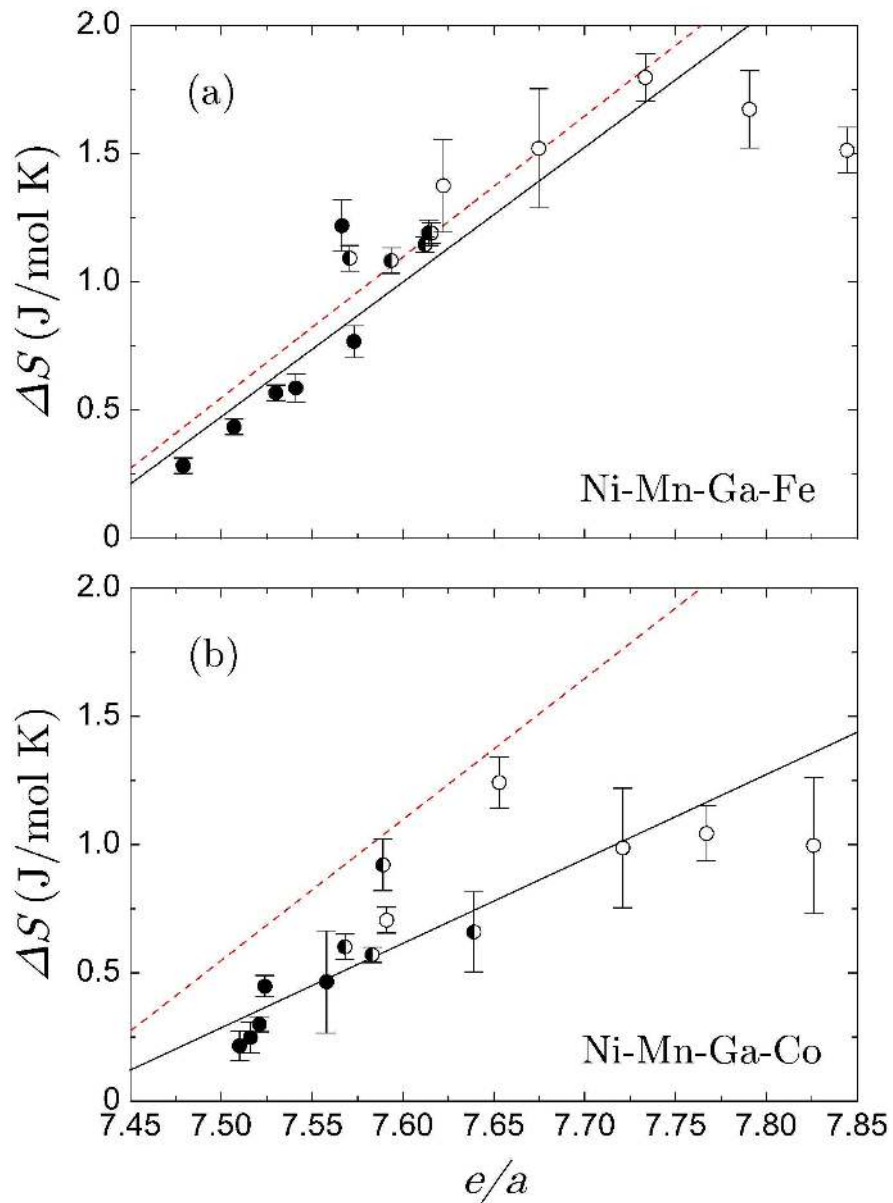


Figure 13
143x196mm (600 x 600 DPI)