EPJ Web of Conferences **40**, 11002 (2013)
DOI: 10.1051/epjconf/20134011002

Pressure dependence of magneto-structural properties of Co-doped off-stoichiometric Ni_2MnGa alloys

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Abstract. A strong effect of pressure on magnetization and paramagnetic moment of the Co-doped Mn-rich $Ni_{50-x}Co_xMn_{25+y}Ga_{25-y}$ (x = 5,7,9 and y = 5,6,7,8) Heusler alloys is presented and compared with very weak pressure sensitivity of magnetization of the stoichiometric Ni_2MnGa alloy. The effects of both, the pressure and the magnetic field, on temperature of the structural martensitic transition in the alloys are discussed with a use of the Clausius-Clapeyron relations. An analysis of pressure and field effects provides a possibility to evaluate structural and magnetic parts of latent heat of the martensitic transitions in the studied alloys. The Curie temperature of martensite phase of the Co-rich alloys is not affected by pressure.

1 Introduction

The huge shape memory effects and the magnetocaloric effects (MCE) in the Heusler Ni_2MnGa alloy are a consequence of the first order magneto-structural transition from the high temperature cubic austenite (A) to the low temperature tetragonal martensite (M) crystal structure [1,2]. In the case of off-stoichiometric or doped Ni-Mn-Ga alloys, the martensitic transition is accompanied by very pronounced changes of their volume and magnetization and so, a large family of these alloys is a subject of long-lasting and extended research not only at ambient but even under high pressure [3-8]. During decades, the effect of high hydrostatic pressure on the Curie temperature T_C^A [3, 5, 8] and on temperatures of the martensitic transformation T_{M-A} and T_{A-M} [4, 6] of the Heusler stoichiometric as well as the off-stoichiometric Ni-Mn-Ga alloys was determined.
We present the results of pressure investigation of a set of the Co-doped Mn-rich Ni-Co-Mn-Ga alloys that exhibit extraordinary magnetic and structural properties that were studied in detail at ambient pressure recently [9].

2 Experimental details

The polycrystalline Co-doped $\mathbf{Ni_{50-x}Co_xMn_{25+y}Ga_{25-y}}$ (x = 0, 5, 7, 9 and y = 0, 5, 6, 7, 8) alloys were prepared by arc melting under protective Ar atmosphere and consequently annealed at 900 K for 72 hours with quenching in water [9]. The final compositions of alloys were verified by EDAX. Temperature and high pressure dependences of magnetization of the alloys were measured with the use of the SQUID magnetometer (MPMS-7T with oven, Quantum Design Inc.) and of the miniature Cu-Be pressure cell [10], (see also Figure 1) in temperature range from 5 K up to 500 K at ambient pressure and up to 400 K in pressure range up to 1.2 GPa at magnetic fields up to 7 T. The magnetic properties of the alloys at ambient conditions are described in detail in our recent papers [9, 11, 12] and hence, we keep the similar labeling of the samples that expresses a content of Co and Mn (**'at.%Co - at.%Mn'**) in the studied alloy. Due to a restricted temperature range that is available for high pressure measurements, four samples were selected from a prepared set of alloys, **'5-30'** ($Ni_{45.5}Co_{4.8}Mn_{30.1}Ga_{19.6}$), **'7-31'** ($Ni_{42.9}Co_{7.1}Mn_{31.3}Ga_{18.7}$), **'9-32'** ($Ni_{41.9}Co_{9.1}Mn_{32.0}Ga_{17.0}$) and **'9-33'** ($Ni_{41.9}Co_{9.3}Mn_{33.1}Ga_{15.7}$).

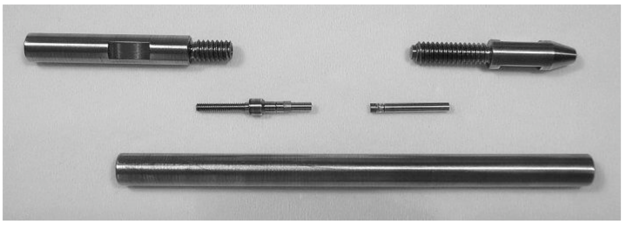

Fig. 1. Pressure cell, inner Ø = 2.5 mm and outer Ø = 8.6 mm.

3 Results and Discussion

The effect of pressure on magnetization of the Co-free Ni-Mn-Ga alloys and their structural transitions was studied recently [5, 7]. We compare here the results of the

Article available at http://www.epj-conferences.org or http://dx.doi.org/10.1051/epjconf/20134011002

pressure study of the Co-doped Mn-rich $Ni_{50-x}Co_x Mn_{25+y}Ga_{25-y}$ alloys with the effect of pressure on magnetization and structural transition of the stoichiometric **'0-25'** ($Ni_{50.5}Mn_{25.5}Ga_{24}$) alloy.

3.1. Magnetization

Both, the substitution of Co for Ni and the introduction Mn for Ga, induce a significant decrease of saturated magnetization of martensite phase, M_M, of all the studied samples. Magnetization of austenite phase, $M_A(H,T_A)$, at temperature T_A just above the martensitic transition temperature $T_{M\text{-}A}$, seems to be slightly affected by the substitutions and consequently, a paramagnetic gap appears in the Co-doped compounds with higher values of x and y. The Figure 2 (increasing temperature is shown only) shows the paramagnetic gap in **'9-32'** and **'9-33'** alloys together with a universal dependence of saturated magnetization of austenite phases $M_A(5\text{T})$ of the Co-doped alloys on the normalized T/T_C^A temperature. In the stoichiometric **'0-25'** alloy, magnetization decreases in course of the martensitic M-A transition and the change of magnetization, $\Delta M_{M\text{-}A}$, is negative in all the Co-free alloys [7]. However due to the rapid decrease of M_M in Co-doped alloys, $\Delta M_{M\text{-}A}$ becomes positive and increases with the increasing content of Co when the content of Mn is kept constant, as it is seen in Figure 2 and presented in [9]. Temperature $T_{M\text{-}A}$ of the martensitic transition increases with increasing Co-content, but due to the positive value of $\Delta M_{M\text{-}A}$, $T_{M\text{-}A}$ strongly decreases with increasing magnetic field in all the Co-doped alloys. In the case of **'9-33'** alloy, $T_{M\text{-}A}$ is higher than its T_C^A and the martensitic transition occurs in paramagnetic state of the austenite phase of the alloy. Due to this, temperature $T_{M\text{-}A}$ of the **'9-33'** alloy is not dependent on magnetic field what was verified by measuring of $dT_{M\text{-}A}/dH$.

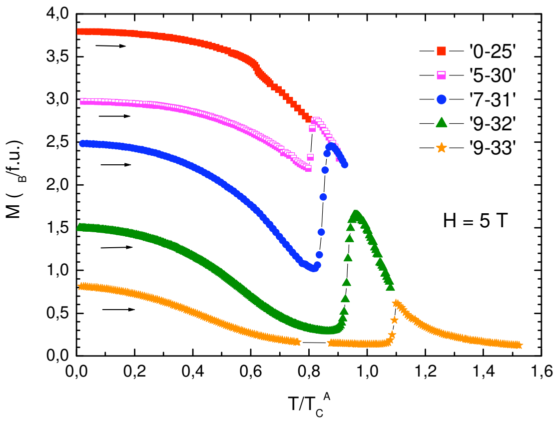

Fig. 2. Magnetization of selected alloys at field 5 T as a function of T/T_C^A.

The very weak negative effect of pressure on magnetization M_M of the stoichiometric **'0-25'** alloy is accompanied by a slight increase of $M_A(H,T_A)$ under pressure in this alloy. The last effect is induced by an increase of the Curie temperature of the austenite phase T_C^A [5]. In contrast to the **'0-25'** alloy, the Co-doped Mn-rich alloys exhibit very pronounced decrease of M_M under pressure, see Table 1. In the case of the **'5-30'** alloy, the decrease of M_M, $d\ln M_M/dP = -29*10^{-3}$ GPa^{-1}, is accompanied by a very slight decrease of $M_A(H,T_A)$

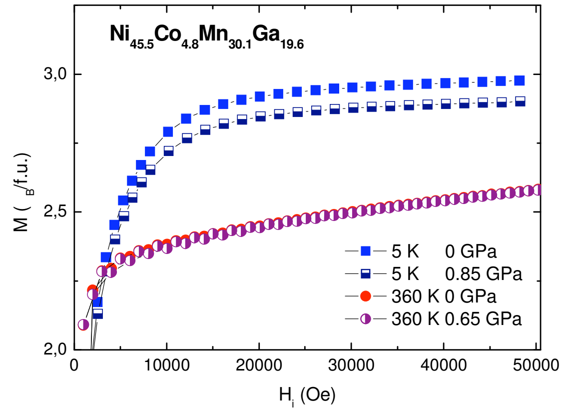

Fig. 3. Magnetization isotherms of martensite (at 5 K) and austenite (at 360 K) phases of **'5-30'** alloy under pressure.

under pressure, $d\ln M_A(5\text{T}, 360\text{K})/dP = -3.7*10^{-3}$ GPa^{-1}, see Figure 3. As a consequence of this big difference between the pressure effects on M_M and $M_A(H,T_A)$, the change of magnetization $\Delta M_{M\text{-}A}$ increases with increasing pressure in the **'5-30'** alloy.

A similar extraordinarily different pressure behavior of magnetization has been observed and described in ordered Ni_3Mn and disordered $Ni_{75}Mn_{25}$ alloys [13]. The theoretical *ab-initio* calculations revealed a relatively slight effect of pressure on magnetic Mn-moments, but, a substantial pressure effect on a number of anti-parallel Mn-moments of atoms that are shifted out of their regular lattice positions in the disordered alloys. As a consequence, low magnetization of the disordered alloys is accompanied by the high sensitivity of magnetization to external pressure.

A presence of paramagnetic state in the Co-rich alloys at a temperature range below the temperature of M-A transition, $T_{M\text{-}A}$, was verified by linear dependence of $\chi_{dc}(T)^{-1}$. Figure 4 shows this dependence in case of the **'9-33'** alloy. The effective paramagnetic moment m_{eff}

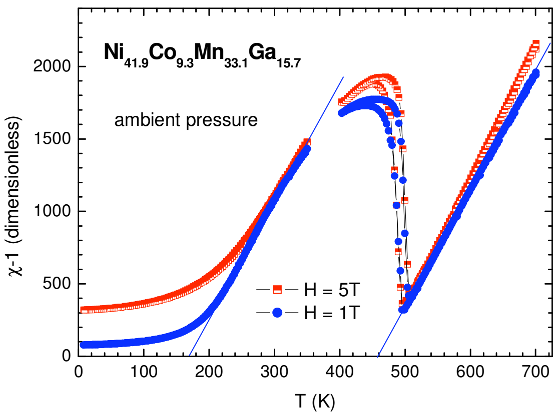

Fig. 4. The inverse susceptibility $\chi_{dc}(T)^{-1}$ of **'9-33'** alloy.

was calculated by using a standard formula:

$$m_{eff} = \sqrt{3kC * mol/\mu_B{}^2 N * \rho} \quad (1)$$

where, k, C and N are Boltzmann, Curie and Avogadro constants, respectively, and ρ is density. Due to a relatively narrow temperature range of linear part of $\chi_{dc}(T)^{-1}$, the values of C and m_{eff} were determined with an accuracy of about 5% of their nominal values. The presented values of m_{eff} of all alloys (including the stoichiometric **'0-25'** alloy) were determined from 1T-curves of $\chi_{dc}(T)^{-1}$. They lie in an interval from 5.08 μ_B to 5.65 μ_B and they agree well with values in reference [3]. The values of m_{eff} also follow the phenomenological relation $m_{eff} = n_V$ -24, where n_V is a number of valence electrons [14]. The values of m_{eff} are identical for both, the martensite and the austenite phases of alloys and they decrease slightly with increasing field, see Figure 4. We have observed a relatively strong effect of pressure on paramagnetic moments of the stoichiometric **'0-25'** and Co-doped **'9-33'** alloys with $\mathrm{dln}m_{eff}/\mathrm{d}P = -17*10^{-3}$ GPa^{-1} and $-24*10^{-3}$ GPa^{-1}, respectively.

3.2 Curie temperature

The Curie temperature of austenite phase of the stoichiometric **'0-25'** alloy increases with pressure by a rate of $\mathrm{d}T_C{}^A/\mathrm{d}P$ = + 5.9 K/GPa. This value of the pressure parameter $\mathrm{d}T_C/\mathrm{d}P$ agrees well with data in literature [3, 8]. A saturation of the pressure shift of $T_C{}^A$ was observed in pressure range above 6 GPa [8]. Unfortunately, $T_C{}^A$ of the Co-doped alloys lies above a today's temperature limit of our pressure measurements.
The Curie temperature $T_C{}^M$ of martensite phase of the Co-doped ($x \geq 7$) alloys that decreases with the increasing content of Co (as can be seen on Figure 2) is practically insensitive to pressure. The pressure parameter $\mathrm{d}T_C{}^M/\mathrm{d}P$ is 0 ± 1 K/GPa.

3.3 Temperature of structural transition

The temperature of structural transition from martensite to austenite, $T_{M\text{-}A}$, increases with increasing of both, the Co- and the Mn-doping in all the studied alloys, see Table1. However as it was stressed recently, a thermal treatment of the Ni-Co-Mn-Ga has a great influence on both, the transition and the Curie temperatures of these alloys [15]. Similarly as in the case of magnetization, very great difference (more than one order) has been observed between the pressure effect on $T_{M\text{-}A}$ of the stoichiometric **'0-25'** alloy and one of the Co-doped Mn-rich alloys. However, the pressure shift of $T_{M\text{-}A}$ is always positive verifying a lower volume of martensite phase with respect to austenite phase in all alloys. The mentioned high sensitivity of magnetization M_M of the alloys to composition induces a change of sign of $\Delta M_{M\text{-}A}$ from negative in **'0-25'** alloy to positive in the Co-doped alloys. As a consequence, the small positive effect of magnetic field on $T_{M\text{-}A}$ in the **'0-25'** alloy changes into very pronounced negative field effect on $T_{M\text{-}A}$ of the Co-doped Mn-rich alloys. Values of a parameter $\mathrm{d}T_{M\text{-}A}/\mathrm{d}H$ that are presented in Table 1 are in good agreement with recent results of high field experiments [16].

Table 1. The values of magnetization M_M, its change $\Delta M_{M\text{-}A}$ and its pressure derivation, effective paramagnetic moment m_{eff}, transition temperature $T_{M\text{-}A}$ of noticed samples with its pressure and field dependence that was used to a determination of ΔS_m.

	0-25	**5-30**	**7-31**	**9-32**
M_M (5K, 5T) (μ_B/f.u.)	3.70	2.98	2.45	1.42
$\Delta M_{M\text{-}A}$ (5T) (μ_B/f.u.)	-0.08	+0.47	+1.51	+1.55
$\mathrm{dln}M_M/\mathrm{d}P$ (10^{-3}GPa^{-1})	-3.0	-29.0	-35.2	-23.3
m_{eff} (μ_B)	5.1	-	5.17	5.58
$T_C{}^M$ (K)	-	-	318	234
$T_C{}^A$ (K)	375	420	440	457
$T_{M\text{-}A}$ (K)	235	347	385	443
$\mathrm{d}T_{M\text{-}A}/\mathrm{d}P$ (K /GPa)	+0.5	+7.5	+35	-
$\mathrm{d}T_{M\text{-}A}/\mathrm{d}H$ (K /T)	+0.6	-1.6	-2.95	-2.8
ΔS_m (J /kgK)	+3.1	+6.9	+12.0	+12.9

A use of the Clausius-Clapeyron (C-C) relations (2) and (3) provides a possibility to analyse an evolution of entropy and/or latent heat of the martensitic transition with increasing doping of the Mn-rich alloys by Co.

$$dT_{M-A}/dH = -\Delta M_{M-A}/\Delta S_m \quad (2)$$

$$dT_{M-A}/dP = \Delta V_{M-A}/\Delta S_s \quad (3)$$

Entropy changes ΔS_m and ΔS_s are relevant to changes of magnetization, $\Delta M_{M\text{-}A}$, and volume, $\Delta V_{M\text{-}A}$, that occur during the transition from martensite to austenite. The positive values of ΔS_m in the Co-doped alloys means that an inverse magnetocaloric effect (MCE) should be observed in these alloys and this was really verified experimentally [11, 12]. However, it is necessary to take into account that due to negative value of $\mathrm{d}T_{M\text{-}A}/\mathrm{d}H$, the structural transition can be induced in these alloys by increasing field at temperature just below $T_{M\text{-}A}$ and hence, both entropy changes, ΔS_m and ΔS_s, participate in such experiments. A possible misleading interpretation of results of experiments with respect to the C-C relations can be clearly demonstrated in the case of the stoichiometric **'0-25'** alloy, where, the positive value of ΔS_m is received by C-C relation too. However, positive value of dT_{M-A}/dH, ensures in this case that the structural transition is not induce by field even at T_{M-A} and a very weak standard MCE connected with arrangement of magnetic domains (with an increase of magnetization) in ferromagnetic phase is observed by a direct MCE measurements [17].

An increase of the entropy change ΔS_m in the Co-doped alloys reflects an increasing magnetic disorder with increasing Co-doping that is also a possible source of the significant decrease of magnetization M_M in these alloys.

We tried to use the measured values of pressure parameter dT_{M-A}/dP together with values of $\Delta V/V$ presented in [11] to the calculation of entropy change ΔS_s by the C-C relation (3). We have obtained ΔS_s = 23.2 J/kgK and latent heat L_s = 9.2 J/g in the case of **'7-31'** alloy. Both values are in a good agreement with data in literature [4, 15, 18, 19]. Values of ΔS_s determined for both, the **'0-25'** and the **'5-30'** alloys were higher than 75 J/kgK. These values seem to be unrealistic in comparison with the calorimetric measurements of the transition latent heat in the Ni-Mn-Ga alloys [19].

4 Conclusions

The saturated magnetization M_M of martensite phase of the studied Co-doped Mn-rich Ni-Co-Mn-Ga alloys decreases significantly with increasing Co- and Mn-content as well as with increasing pressure in contrast to a relevant behavior of magnetization of austenite phase of these alloys. A paramagnetic gap appears in the Co-doped compounds and a change of magnetization ΔM_{M-A} that accompanies the structural M-A transition becomes positive and very pronounced with increasing Co-content. Effects of pressure and magnetic field on transition temperature T_{M-A} were used to evaluate structural and magnetic parts of entropy changes to draw attention to a possible misleading interpretation of experimental results with respect to thermo-dynamical data given by the C-C relations.

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