

Influence of Partial Substitution of Fe by Mn on the Thermomagnetic Properties of Magnetocaloric $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ Alloy

P. GEBARA^{a,*} AND J. MARCIN^b

^aInstitute of Physics, Czestochowa University of Technology, Armii Krajowej 19, 42-200 Czestochowa, Poland

^bInstitute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovakia

The aim of this paper was to study the influence of partial substitution of Fe by Mn in the $\text{LaFe}_{11.2-x}\text{Mn}_x\text{Co}_{0.7}\text{Si}_{1.1}$ (where $x = 0.1, 0.2$ and 0.3) alloys. Measurements revealed that a systematic increase of Mn in the alloy composition resulted in a decrease of the Curie temperature, which correlated with a decrease of the lattice parameter of the $\text{La}(\text{Fe},\text{Si})_{13}$ - type phase. For samples corresponding to Mn content $x = 0.1$ and 0.2 a decrease of magnetic entropy change was observed. However in the case of the sample with $x = 0.3$ an increase of magnetic entropy change was detected.

DOI: [10.12693/APhysPolA.133.648](https://doi.org/10.12693/APhysPolA.133.648)

PACS/topics: 75.30.Sg, 75.50.Bb

1. Introduction

The magnetic cooling based on the magnetocaloric effect (MCE) is an interesting alternative to conventional refrigeration due to its high efficiency ($\sim 60\%$) and environmental-friendliness process [1]. The magnetocaloric materials (MCMs), like $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [2,3], Mn-FeX (where $X = \text{P}, \text{B}, \text{As}$) [4], Ni-Mn-Ga [5] and MnCoGe -based [6] are characterized by structural transformation in the vicinity of T_C , which results in high magnetic entropy change ΔS_M and adiabatic temperature change ΔT_{ad} . These alloys are relatively expensive due to the high content of elements such as Gd, Mn or Co. The $\text{La}(\text{Fe},\text{Si})_{13}$ alloys are an interesting alternative. Relatively high Fe content (almost 80 at.%) induces low price and metamagnetic first order phase transition, which occurs in the vicinity of the T_C of *fcc* pseudobinary $\text{La}(\text{Fe},\text{Si})_{13}$ phase results in high ΔS_M [7]. For the last decade, the $\text{La}(\text{Fe},\text{Si})_{13}$ alloys have been modified by lanthanides (i.e. Pr [8], Ce [9]), transition metals (Co [10], Ni [11] or Mn [12]) and metalloids (i.e. Al [13] or Ga [14]). Wang et al [12] have shown that substitution of Fe by Mn causes a decrease in the T_C and ΔS_M . This type of alloys is very sensitive on changes of chemical composition and i.e. combination of Ni and Co induces alteration of negative lattice expansion [11]. The aim of present paper is to study the substitution of Fe by Mn in the $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$, which characterizes relatively high ΔS_M at ambient temperature [15].

2. Experimental method

Samples of nominal composition $\text{LaFe}_{11.2-x}\text{Mn}_x\text{Co}_{0.7}\text{Si}_{1.1}$ (where $x = 0.1, 0.2$ and

0.3) were prepared by arc-melting of high purity constituent elements under a low pressure of Ar. Ingots were re-melted several times to ensure their homogeneity. Subsequently specimens were sealed-off in quartz tubes under a low pressure of Ar and annealed at 1323K for 15 days. The phase constitution was studied using Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation. The XRD was supported by the Rietveld analysis using the PowderCell 2.4 package [16]. Magnetic properties of the prepared samples were measured in a wide range of temperatures by Quantum Design MPMS-XL 5 equipped with a 5 T superconducting magnet.

3. Results and discussion

The analysis of the XRD patterns indicates that the annealed samples are almost single phase. However, some small amount of α -Fe, less than 10 vol.% was detected in all samples. Results of the Rietveld analysis are collected in Table I. A visible decrease of the lattice constant with the increase of Mn addition is in contradiction with results published by Wang et al in [12]. They observed a rise of cell parameter with an increase in Mn content. Such different behaviour could be related to the chemical composition of the alloy. Moreover, the successive increase of the α -Fe phase was detected with a growth of Mn and such an effect was observed in [12]. As shown in [10-15], the change of the unit cell parameter induces a variation of the Curie temperature. According to that, the temperature dependences of magnetization were collected for all investigated samples during zero-field cooling regime (Fig.1). A successive decrease of T_C with an increase of Mn addition is clearly seen. The values of T_C equal 241, 222 and 198K for $x = 0.1, 0.2$ and 0.3 , respectively. It is well known that the Curie temperature value depends strongly on the Fe-Fe interactions in this type of alloys. The decrease of lattice constant causes a change of distances between Fe atoms and results in the

*corresponding author; e-mail: pgebara@wip.pcz.pl

weakening of Fe-Fe interactions, which is observed as a lowering of T_C .

TABLE I

Results of Rietveld refinement carried out for $\text{LaFe}_{11.2-x}\text{Mn}_x\text{Co}_{0.7}\text{Si}_{1.1}$ (where $x = 0.1, 0.2, 0.3$) ($E_{\text{expected}} = \text{La}(\text{Fe,Si})_{13}$ -type, $P_{\text{parasitic}} = \alpha\text{-Fe}$).

Mn content x	Phase	Fraction [vol.%]	Lattice constant a [Å]
0.1	E	92	11.4745 ± 0.0011
	P	8	2.8605 ± 0.0009
0.2	E	91	11.4708 ± 0.0012
	P	9	2.8607 ± 0.0011
0.3	E	90	11.4676 ± 0.0011
	P	10	2.8608 ± 0.0012

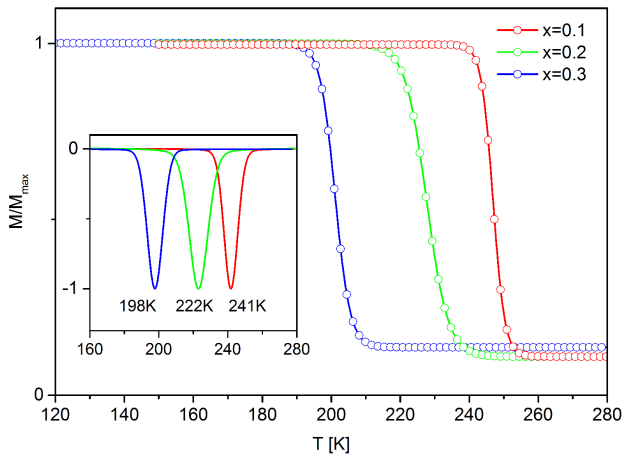


Fig. 1. The M vs. T curves collected for samples with different Mn content and their first derivatives (inset).

From a magnetic cooling point of view, such tailored decreases of T_C gives an opportunity to get multi-step magnetic regenerator working in a wide range of temperatures. However, it is important to reveal the ΔS_M vs. T curves for each alloy. The M vs. H dependences were measured in a wide range of temperatures. The ΔS_M values were calculated using the well-known thermomagnetic Maxwell relation:

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH. \quad (1)$$

where: M is magnetization, μ_0 is magnetic permeability of vacuum and H is magnetic field.

The ΔS_M vs. T curves determined for all studied specimens are depicted in Fig. 2. The highest values of ΔS_M reached 14.93, 12.34 and 14.54 were detected in samples with $x = 0.1, 0.2$ and 0.3 , respectively. Obtained values of ΔS_M are lower than those shown in [15] for base $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ alloy and these presented by Yan et al. in [10]. Such behavior suggests that Mn addition causes weakening of itinerant electron metamagnetic transition and it results in decrease of ΔS_M . Moreover, Wang et

al [12] and Krautz et al [17] observed a systematic decrease of ΔS_M with an increase of Mn addition. Our results partially confirm their studies, due to the fact that for sample $x=0.2$ the decrease of ΔS_M compared to the alloy with $x = 0.1$ is shown. However, the significant increase of ΔS_M for the specimen with $x=0.3$ is found. As shown in [10-15], the decrease of ΔS_M was attributed to the weakening of the itinerant electron metamagnetic (IEM) transition with an increase of alloying additions. However, we observed two effects of weakening and strengthening the IEM transition for samples with $x = 0.2$ and $x = 0.3$ Mn content, respectively. Such behaviour confirms the prediction that properties of the $\text{La}(\text{Fe,Si})_{13}$ phase are strongly related to the chemical composition.

The relative cooling power (RCP) has been calculated using the following relation [18]:

$$RCP = -\Delta S_{M \text{ max}} \delta T_{FWHM}, \quad (2)$$

where: δT_{FWHM} is temperature of thermodynamic cycle (full width at half maximum of ΔS_M vs. T curve).

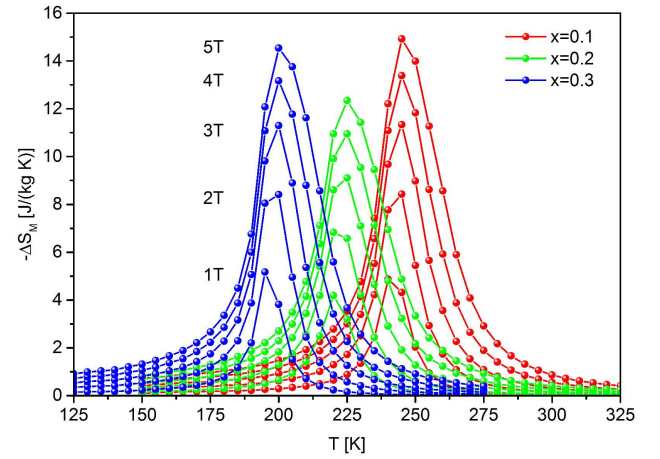


Fig. 2. The temperature dependences of magnetic entropy change determined for all investigated samples.

The RCP and δT_{FWHM} values have been collected in Table II.

TABLE II

The ΔS_M , RCP and δT_{FWHM} values collected for investigated alloys.

Mn content x	0.1		0.2		0.3	
	$\mu_0 H$ [T]		$\mu_0 H$ [T]		$\mu_0 H$ [T]	
$-\Delta S_M$ [J/(kg K)]	2	5	2	5	2	5
δT_{FWHM} [K]	8.43	14.93	6.83	12.34	8.41	14.54
RCP [J/kg]	18	28	20	30	15	26
	151	418	130	358	126	377

As shown in Table II, the δT_{FWHM} increases for the sample with Mn content $x = 0.2$ and it was observed in [12, 17]. However, for the specimen with $x=0.3$, a visible decrease is revealed. Moreover, the δT_{FWHM} values are comparable with results showed by Wang et al [12].

The highest RCP has been noticed in the sample with $x = 0.1$. The RCP values determined in this study are almost two times lower than those delivered by Fujieda et al. [19]. However, Fujieda et al. [19] studied the Ce doped samples and this atom causes an increase in the magnetic entropy change, due to the nonzero magnetic moment. In order to reveal the nature of the magnetic phase transition, the M^2 vs. H/M isotherms (Arrott plots) have been constructed in the vicinity of the Curie temperature (Fig. 3). The positive slope, observed for samples with Mn content $x = 0.1$ and 0.2 , suggests a second order phase transition nature according to the Banerjee criterion [20]. However, the slight “s-shape” of the Arrott plots at temperatures just above the Curie point is visible for the sample with the highest content of Mn. Such a shape of Arrott plots could suggest the occurrence of first order metamagnetic phase transition in this sample [10, 12]. In order to confirm these predictions, more advanced analysis of phase transition nature is required using the Landau theory or scaling method and will be done in further studies of these alloys.

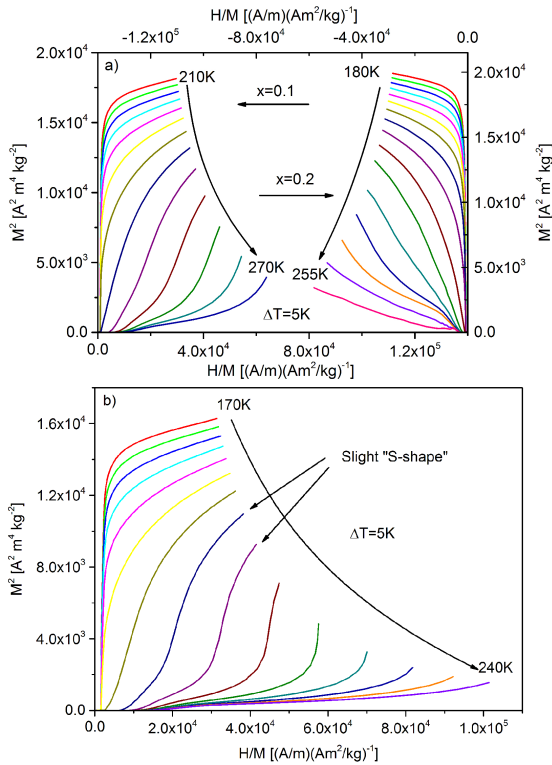


Fig. 3. The M^2 vs. H/M isotherms (Arrott plots) constructed for samples with Mn content $x = 0.1$ and 0.2 (a) and $x = 0.3$ (b).

4. Conclusions

In this paper the influence of partial substitution of Fe by Mn in the $\text{LaFe}_{11.2-x}\text{Mn}_x\text{Co}_{0.7}\text{Si}_{1.1}$ was studied. The successive contraction of the lattice constant with an increase of Mn content was observed, which induces the decrease of the Curie temperature. Moreover, the increase of Mn content ($x = 0.1$ and 0.2) causes the decrease in

magnetic entropy change compared to base alloy, which is attributed to the weakening of the IEM phase transition. However, an increase of ΔS_M is noticed for the sample with $x = 0.3$, which suggests the strengthening of the IEM transition. Such different behaviour was confirmed by constructing Arrott plots. A monotonic positive slope was observed for samples $x = 0.1$ and 0.2 . However, a slight “s-shape” was detected for the specimen with the highest Mn addition, which can suggest the occurrence of weak first order in the IEM transition.

Acknowledgement

This work was supported by the projects APVV-15-0621 and ITMS 26220220061. P.G. would like to thank the Slovak Academic Information Agency SAIA and Head of Institute of Physics Czestochowa University of Technology prof. R. Szczęśniak for financial support.

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