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Structural and Magnetic Studies of the $LaFe_{11.2}Co_{0.7-x}Mn_xSi_{1.1}$ (where $x = 0.1$, 0.2) Alloys

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The aim of present work was to study the influence of partial substitution of Co by Mn in the $LaFe_{11.2}Co_{0.7}Si_{1.1}$ alloy on its structure and magnetic properties. The X-ray diffraction studies revealed coexistence of dominant pseudobinary fcc La(Fe,Si)$_{13}$-type phase with minor fraction of α-Fe. Moreover, the increase of Mn content causes decrease of the lattice parameter and the Curie temperature. The values of magnetic entropy change obtained for both investigated alloys are almost identical and close to 12 J/(kg K) under the change of external magnetic field ≈ 5 T. Investigations of magnetic phase transition confirmed its second order nature in the case of both specimens.

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PACS/topics: La(Fe,Si)$_{13}$ alloys, magnetocaloric effect, scaling analysis

1. Introduction

The Fe-based alloys are intensively studied due to their specific magnetic properties, including the magnetocaloric effect (MCE) in the vicinity of room temperature [1–6]. The MCE is currently the most efficient cooling technique with efficiency reaching up even 60% (in the Ericsson cycle) [7]. From practical view point, an active regenerator of magnetic refrigerator should exhibit a high magnetic entropy change ΔS_M, the Curie temperature close to ambient temperature, relatively low price, and non-toxicity. The La(Fe,Si)$_{13}$ group of alloys obeys these conditions, due to high Fe content and excellent magnetic properties of fcc $NaZn_{13}$-type structure [1–3, 8]. As it was shown in [1–3, 8], even a slight devation of chemical composition of the La(Fe,Si)$_{13}$ alloys causes changes in magnetic properties. Therefore, in the present studies, we have investigated the effect of substitution of Co by Mn in the $LaFe_{11.2}Co_{0.7}Si_{1.1}$. This alloy was selected, due to its relatively high ΔS_M and the Curie temperature T_C of 274 K [8].

2. Sample preparation and experimental details

Ingot samples corresponding to the following compositions $LaFe_{11.2}Co_{0.7-x}Mn_xSi_{1.1}$ (where $x = 0.1$ and 0.2) were produced by melting of high purity constituent elements under low pressure of Ar at the arc-furnace. Specimens were re-melted several times in order to ensure in their homogeneity. Subsequently, the samples were sealed-off in quartz tubes under low pressure of Ar and annealed at 1323 K for 15 days. The X-ray diffraction (XRD) was carried out using Bruker D8 Advance X-ray diffractometer with Cu K_α radiation and semiconductor LynxEye detector. Furthermore, the X-ray diffraction (XRD) patterns were subjected to the Rietveld refinement using PowderCell 2.4 package [9]. Magnetic properties were studied in the wide range of temperatures by Quantum Design MPMS-XL 5 equipped with 5 T superconducting magnet.

3. Results and discussion

The XRD patterns exhibit typical reflections for the dominant fcc La(Fe,Si)$_{13}$ phase for both investigated samples. Moreover, a weak reflex at $2\Theta = 44.6°$, corresponding to α-Fe, was detected. The Rietveld analysis revealed just insignificant differences in lattice constant of investigated specimens. The lattice parameter is equal to 11.477±0.001 and 11.476±0.001 Å for samples $x = 0.1$ and 0.2, respectively. Moreover, the volume fraction of the expected La(Fe,Si)$_{13}$ phase amounts to 93 ($x = 0.1$) and 90 vol.% ($x = 0.2$). The decrease of volume fraction with the increase of Mn addition was also observed by Wang et al. [10].

In order to reveal the T_C of the investigated samples the M vs. T curves were measured and are shown in Fig. 1. It is clearly visible that the T_C is shifted toward lower temperatures with the increase of Mn content in the alloy composition. It is well known that the T_C of RE–TM (RE = rare earth element, TM = transition metal) depends on the RE–RE, RE–TM, and TM–TM interactions. In the La(Fe,Si)$_{13}$ compounds, the T_C is determined only by TM–TM interactions, due to the fact that the magnetic moment of the La ($4f$ electron shell) is zero. The XRD studies revealed decrease of lattice parameter of the La(Fe,Si)$_{13}$ structure. Such behaviour causes the decrease of distance between Fe atoms and weakening of their exchange interactions. It results in the decrease of the T_C.

The MCE was investigated indirectly by measurements of field dependences of magnetization in a wide temperature range. The ΔS_M values were calculated using the following thermomagnetic Maxwell relation:

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$$\Delta S_M(T, H_{\max}) = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H, \qquad (1)$$

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

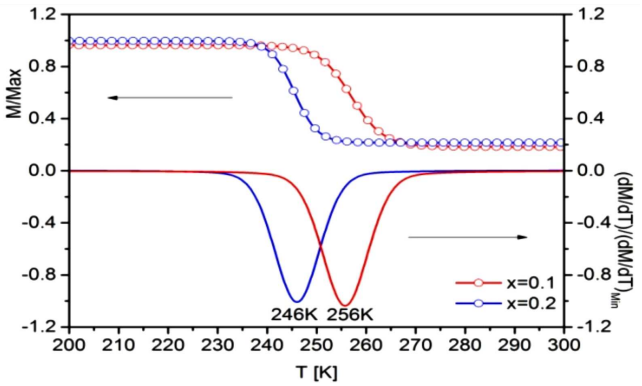

Fig. 1. The temperature dependences of magnetization collected for samples with different Mn content and their first derivatives.

The temperature dependences of magnetic entropy change are shown in Fig. 2. Maximum values of ΔS_M are equal to 11.81 and 11.71 J/(kg K) for $x = 0.1$ and 0.2, respectively. Temperatures of ΔS_M maxima correspond well with the Curie temperatures determined for both specimens. A lack of significant changes in maximum value of ΔS_M caused by substitution of Co by Mn in the $LaFe_{11.2}Co_{0.7}Si_{1.1}$ alloy is observed. The Fe content is 80 at.% of the $3d$ element quantity and is the same in each alloy. Thus the intensity of the respective itinerant electron metamagnetic transition does not change with Mn doping, which would eventually result in magnetic entropy change. Similar effect of tuning the Curie temperature without modification in the magnetic entropy change has been observed by M'nassri [11] and Caballero-Flores et al. [12].

The coefficient of refrigerant performance (CRP) was calculated on the basis of ΔS_M vs. T curves, according to the following relation [13]:

$$CRP = \frac{\Delta S_{M\,\max} \Delta T}{\int_0^{B_{\max}} M(T_C, B)\mathrm{d}B}, \qquad (2)$$

where ΔS_M is the magnetic entropy change, ΔT corresponds to δT_{FWHM} and B is the magnetic induction.

The CPR and maximum values of ΔS_M are collected in Table I.

As shown in Table I, the CRP values for sample with $x = 0.2$ are slightly higher than those for sample with $x = 0.1$ and decrease with increasing magnetic field. Moreover, revealed CRP values exceed those reported in [14].

The shape of ΔS_M vs. T curves is symmetrical, which suggests a second order nature of the magnetic phase transition. A simple method to determine the nature

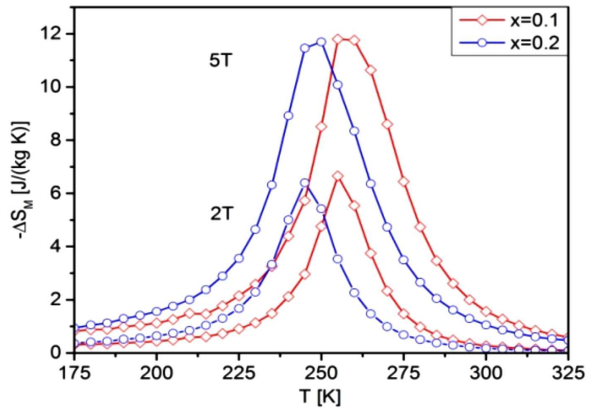

Fig. 2. The temperature dependences of magnetic entropy change determined for all investigated samples.

TABLE I

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

	Mn content x = (0.1 || 0.2)			
$\mu_0 H$ [T]	ΔS_M [J/(kg K)]		CRP	
1	3.37	3.58	0.75	0.78
2	6.65	6.41	0.74	0.78
3	8.81	8.52	0.72	0.74
4	10.48	10.14	0.72	0.74
5	11.81	11.72	0.71	0.73

of phase transition is construction of M^2 vs. H/M isotherms (the Arrott plots depicted in Fig. 3). The positive slope of the Arrott plot suggests the occurrence of a second order phase transition in both investigated samples, according to the Banerjee criterion [15].

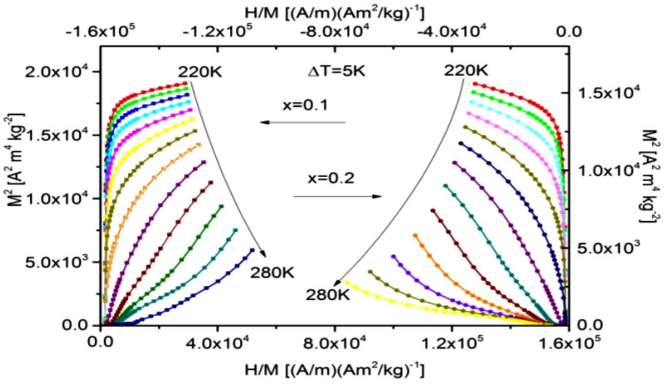

Fig. 3. The Arrott plots constructed for samples with Mn content $x = 0.1$ and 0.2.

Franco et al. [16] have shown more sophisticated method to investigate the nature of phase transition. It is based on the phenomenological universal curve relating ΔS_M to H and T. The procedure of universal curve construction was described in detail in Ref. [17]. In the

beginning, the construction of universal curve requires rescaling of $\Delta S_M(T)$ curve to its maximum value. Further, the temperature axis (θ_1) is rescaled above and below T_C using the following equation [18]:

$$\theta_1 = \frac{T - T_C}{T_r - T_C}, \tag{3}$$

where T_C is the Curie point and T_r is the reference temperature related to specific fraction of maximum value of ΔS_M. In the present work, the reference temperature has been chosen according to the relation $\Delta S_M(T_r) = 0.7\Delta S_{M\,\max}$. The universal scaling curve constructed for the investigated alloys is shown in Fig. 4. As it can be seen in this figure, all the temperature dependences of magnetic entropy change revealed collapse into one universal curve for both investigated alloys. Such a behaviour confirms the second order nature of the magnetic phase transition. Moreover, due to the fact that the universal curves constructed for both alloys collapse into one curve, the critical exponents for these two alloys should be similar [19].

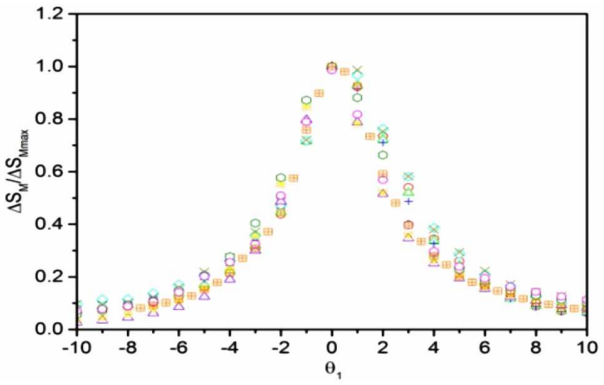

Fig. 4. The universal curve constructed for both samples.

Franco et al. [16] have also shown the field dependence of ΔS_M, which can be described as

$$\Delta S_M = C B_{\max}^n, \tag{4}$$

where C — temperature dependent parameter, n is an exponent depending on the magnetic state of the sample and $B_{\max}$ is the maximum external magnetic field corresponding to $\Delta S_{M\,\max}$.

The magnetic field dependences of $\Delta S_{M\,\max}$ below, near, and above T_C are plotted in Fig. 5.

The n exponent amounts to 1, when the material is in the ferromagnetic state. If material is in a paramagnetic state, n equals 2. The value of n at T_C is described by the formula $n = 1 + 1/\delta(1 - 1/\beta)$ (δ and β are critical exponents), provided that the material obeys the Curie–Weiss law [16]. In our case values of n at T_C amount to 0.69 and 0.70 for $x = 0.1$ and 0.2, respectively. Based on critical exponents typical for mean-field theory ($\beta = 0.5$, $\gamma = 1$, $\delta = 3$), the n amounts to 0.67. It confirms the conclusions drawn on the basis of universal scaling curve.

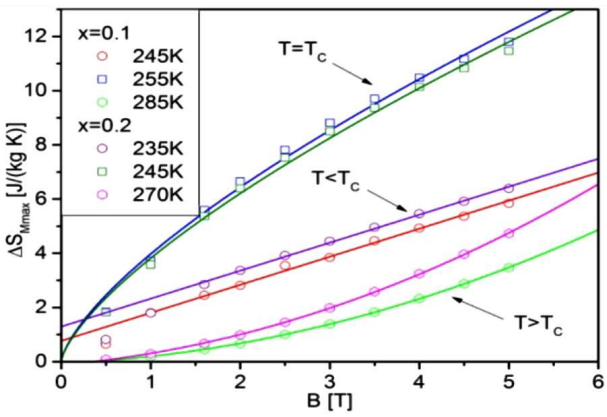

Fig. 5. Magnetizing field induction dependences of magnetic entropy change collected below, near, and above Curie point for both samples.

4. Conclusions

The influence of partial substitution of Co by Mn in the $LaFe_{11.2}Co_{0.7-x}Mn_xSi_{1.1}$ was studied in the paper. The XRD patterns did not reveal significant changes in the lattice constant with doping. Moreover, the obtained values of ΔS_M practically do not differ between both investigated alloys, despite of significant difference in the Curie points. The lack of changes in maximum values of ΔS_M with doping is attributed to a constant Fe content, which preserves the intensity of the IEM phase transition. The Arrott plots and the universal scaling curves confirm a second order nature of the magnetic phase transition in both investigated samples. The analysis of field dependence of ΔS_M reveals values of n exponent, which are very close to the value predicted by the Landau mean field theory.

Acknowledgments

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