Magnetocaloric effect of LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy

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Abstract The aim of the present paper was to study the large magnetocaloric effect observed in LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy. X-ray diffraction (XRD) result reveals a coexistence of two crystalline phases: a dominant La(Fe,Si)$_{13}$-type and a minor $\alpha$-Fe(Co,Si). It is confirmed by the Mössbauer spectroscopy and microstructural observations accompanied by an energy-dispersive spectroscopy (EDS) analysis. The value of the magnetic entropy changes ($|\Delta S_M|$) in the vicinity of the Curie temperature ($T_C = 268$ K) was calculated using thermomagnetic Maxwell relation, and it equals to 21.4 J kg$^{-1}$ K$^{-1}$ under the change in an external magnetic field of $\mu_0 \Delta H = 3$ T. The investigation of magnetic phase transition was carried out using the Landau theory, an analysis of the field dependences of the magnetic entropy change and universal scaling curve, revealing the second order of phase transition in the studied material.

Keywords X-ray diffraction; Mössbauer spectroscopy; Magnetocaloric effect

1 Introduction

The La(Fe,Si)$_{13}$-type alloys belong to a group of magnetic materials known as magnetocaloric materials (MCMs). The magnetocaloric effect (MCE) is temperature change ($\Delta T_{ad}$) of magnetic material under the change in external magnetic field and is strongly related to entropy changes. The intensive investigations of MCE were started in 1997, due to the discovery of the giant magnetocaloric effect (GMCE) by Pecharsky and Gschneidner in Gd$_5$Ge$_2$Si$_2$ alloy [1]. Next to $\Delta T_{ad}$ to describe the quantity of MCE, the isothermal magnetic entropy change ($\Delta S_M$) is used. The maximum magnetic entropy change ($|\Delta S_M|$) calculated for the Gd$_5$Si$_2$Ge$_2$ alloys equals 18.6 J kg$^{-1}$ K$^{-1}$ at $T_C = 276$ K under the change in an external magnetic field ($\mu_0 \Delta H = 5$ T, where $\mu_0$ is magnetic permeability of the vacuum and $H$ is the magnetic field.). The high Gd content and very restrictive processing conditions result in the high price of Gd$_5$Si$_2$Ge$_2$ alloys. Accordingly, Fe-based alloys are more promising. The La(Fe,Si)$_{13}$-type alloys consist of almost 80 at% Fe, so they are relatively cheap (estimated price is about 8 Euro kg$^{-1}$). The La(Fe,Si)$_{13}$ phase does not exist, due to the fact that the enthalpy of mixing between La and Fe is positive. However, a small addition of Si or Al causes a decrease in total free energy and a stabilization of pseudobinary La(Fe,Si)$_{13}$ phase [3]. The La atoms occupy 8a position (in Wyckoff notation) and Fe atoms are placed in two nonequivalent positions 8b (Fe-I) and 96i (Fe-II). As shown in Refs. [3, 4] additions such as Co, Si or Al occupy 96i positions, which is the result of the chemical affinity of the atoms.

The formation of the expected La(Fe,Si)$_{13}$-type phase is achieved by long time annealing from several days up to 2 months [5–8]. The application of rapid cooling processing methods (melt spinning or strip casting) leads to a shortening of the annealing time down to 1 h [9–12]. It is caused by the fineness of the alloy microstructure [12, 13]. Magnetic entropy changes and the Curie temperature of the La(Fe,Si)$_{13}$ alloys are strongly dependent on chemical composition [4–12]. The large value of the magnetic entropy change was measured (under 5T magnetizing field...
induction) for the following alloys: LaFe\textsubscript{11.8}Si\textsubscript{1.2} (\(\sim 31 \text{ Jkg}^{-1}\text{K}^{-1}\)) at \(T_C = 201 \text{ K}\) [9], LaFe\textsubscript{11.2}Co\textsubscript{0.7}Si\textsubscript{1.1} (\(\sim 20.3 \text{ Jkg}^{-1}\text{K}^{-1}\)) at \(T_C = 274 \text{ K}\) [7] and LaFe\textsubscript{11.4}Si\textsubscript{1.6} (\(\sim 19.4 \text{ Jkg}^{-1}\text{K}^{-1}\)) at \(T_C = 208 \text{ K}\) [14]. Recently, investigations of La(Fe,Si)\textsubscript{13}-type alloys in lower magnetizing field induction (\(\sim 2 \text{ T}\)) have also revealed large magnetic entropy change in samples: La(Fe\textsubscript{0.99}Mn\textsubscript{0.01})\textsubscript{11.7}Si\textsubscript{1.4}H\textsubscript{0.6} (\(\sim 16 \text{ Jkg}^{-1}\text{K}^{-1}\)) at \(T_C = 336 \text{ K}\) [15] and LaFe\textsubscript{14.6}Si\textsubscript{1.6} (\(\sim 19.2 \text{ Jkg}^{-1}\text{K}^{-1}\)) at \(T_C = 202 \text{ K}\) [16]. Such high values of magnetic entropy change are caused by the first-order magnetic phase transition observed in these alloys. Owing to the low value of the Curie point (except for LaFe\textsubscript{11.2}Co\textsubscript{0.7}Si\textsubscript{1.1} and La(Fe\textsubscript{0.99}Mn\textsubscript{0.01})\textsubscript{11.7}Si\textsubscript{1.3}H\textsubscript{0.7}) the practical application in domestic magnetic refrigerators is impossible. The tuning of the Curie temperature has been realized by Co [3, 9, 17], Al [12, 18], H [19–21] or C [16, 21] additions, but it has been connected with a decrease in magnetic entropy change. According to these results, it is very difficult to project the optimal chemical composition of the alloy, which has promising magnetocaloric properties near room temperature at a relatively low magnetizing field induction (\(\sim 2 \text{ T}\)) produced by the proper arrangement of modern permanent magnets. Fujita and Fukamichi [22] revealed that the increase in Fe content in an alloy composition causes a raise in magnetic moment and magnetic entropy change. This observation confirms results measured in the mentioned alloy [7, 9, 15, 16]. High magnetic entropy change and Curie temperature close to ambient temperature were the main reason during the preparation of the chemical composition in LaFe\textsubscript{11.35}Co\textsubscript{0.6}Si\textsubscript{1.05} alloy. The aim of the present paper was to study the structure and magnetic properties of LaFe\textsubscript{11.35}Co\textsubscript{0.6}Si\textsubscript{1.05} alloy. Moreover, in order to explain the reason for high magnetic entropy change, the investigation of the nature of the magnetic phase transition was carried out.

### 3 Results and discussion

#### 3.1 Structural analysis

In order to reveal the microstructure of the sample, SEM studies were performed. In Fig. 1, SEM image together with EDS analysis is shown. The microstructure of the LaFe\textsubscript{11.33}Co\textsubscript{0.3}Si\textsubscript{1.05} alloy reveals the coexistence of two phases. The chemical composition of the observed grains is characterized by EDS. As shown in Fig. 1, the homogeneity area is built by La, Fe, Co and Si atoms. This microstructure is typical for La(Fe,Si)\textsubscript{13}-type phase and was observed in Refs. [10, 12, 24, 25]. The chemical composition of inclusions, which are constructed mainly by Fe with addition of Co and Si, is recognized as \(\alpha\)-Fe(Co, Si) phase. Formulas of observed phases are given La\textsubscript{97.8}Fe\textsubscript{80.7}Co\textsubscript{4.2}Si\textsubscript{7.3} (at%) and Fe\textsubscript{99}Co\textsubscript{4}Si\textsubscript{6} (at%) for La(Fe,Si)\textsubscript{13}-type and \(\alpha\)-Fe(Co,Si), respectively. The element contents revealed by EDS analysis correspond quite well with the nominal composition of the prepared alloy. However, the formation of La(Fe,Si)\textsubscript{13}-type phase is realized by the diffusion in solid state during annealing and chemical composition of the some parts of alloy could be slightly different. Owing to this fact, the nominal composition LaFe\textsubscript{11.33}Co\textsubscript{0.6}Si\textsubscript{1.05} was used in further descriptions.

XRD pattern was collected for the sample of the studied alloy, as shown in Fig. 2 together with the fitted pattern.
XRD patterns confirm a biphasic structure constructed by the dominant fcc La(Fe, Si)$_{13}$-type with minor bcc $\alpha$-Fe(Co, Si), and La-rich phase is not found. The Rietveld analysis reveals that the content of La(Fe, Si)$_{13}$-type reaches up to 96 vol%. The lattice constants calculated for the recognized phases are (1.14794 ± 0.00016) and (0.28745 ± 0.00016) nm, for La(Fe, Si)$_{13}$-type phase and $\alpha$-Fe(Co, Si), respectively. A slightly higher value of the lattice parameter of $\alpha$-Fe(Co, Si) suggests an expansion of the unit cell caused by Co and Si additions.

A more detailed study of the phase structure and magnetic state of LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy at room temperature was carried out using Mössbauer spectroscopy. The Mössbauer spectra together with deconvoluted component lines are shown in Fig. 3. Two components are identified during the analysis of Mössbauer spectrum. The sextet line which is typical for ferromagnetic phase corresponds to $\alpha$-Fe(Co, Si) phase. The calculated hyperfine field ($B_{hf}$) equaled to 33.6 T. The increase in this value in reference to pure $\alpha$-Fe ($B_{hf} = 33.1$ T) is caused by Co and Si additions. According to XRD data, a paramagnetic doublet is assigned to La(Fe, Si)$_{13}$-type phase. The doublet is asymmetric and probably it is caused by distribution of the gradient of electrical field [26]. The paramagnetic state of La(Fe, Si)$_{13}$-type phase suggests that its Curie temperature is lower than room temperature. The hyperfine parameters corresponding to component lines that fit the experimental spectrum are given in Table 1. Similar results were obtained in Ref [27].

3.2 Magnetic studies

The Curie point measurements were carried out by the temperature dependence of magnetization ($M$). The $M$ vs. $T$ curve and its first derivative $dM(T)/dT$ are shown in Fig. 4. Both dependences are normalized to maximum and minimum values for $M(T)$ and $dM(T)/dT$, respectively. The minimum of $dM/dT$ vs. $T$ curve is observed at 268 K and shows Curie temperature of La(Fe, Si)$_{13}$-type phase. The $M$
versus $\mu_0 H$ curves collected in a wide temperature range were used to construct Arrott plots in the same temperature range. The Arrott plots are depicted in Fig. 5. The positive slope of the Arrott plots in the vicinity of the Curie temperature suggests a second-order phase transition, according to Banerjee criterion [28].

The magnetocaloric effect was measured indirectly. The $M$ versus $\mu_0 H$ curves allow the calculation of the isothermal magnetic entropy change ($\Delta S_M$) using the following Maxwell thermodynamic relation [29]:

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

where $M(T, H)$ is the magnetization per unit mass.

This equation has been implemented into the Mathematica software in the form of the following algorithm [30]:

$$\Delta S_M(T, H) = \mu_0 \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H$$

where $M_{i+1}(T_{i+1}, H)$ and $M_i(T_i, H)$ are magnetizations measured under the magnetic field ($H$) at temperatures $T_{i+1}$ and $T_i$, respectively.

The temperature dependences of the calculated $|\Delta S_M|$ are shown in Fig. 6. The peaks of $|\Delta S_M|(T)$ are observed in the vicinity of 265 K, which corresponds well with the value of the Curie temperature revealed from the $dM/dT$ curve. The maximum values of $|\Delta S_M|$ are 5.6, 13.1 and 21.4 J·K$^{-1}$·kg$^{-1}$, for the change in the external magnetic fields of 1, 2 and 3 T, respectively. In reference to $|\Delta S_M|$ values measured in Refs. [10, 27], results calculated for LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy are lower, but its Curie temperature is much higher. Similar results of $|\Delta S_M|$ and Curie temperature were investigated in Refs. [7, 31]. However, the value of $|\Delta S_M|$ measured at 3T is comparable or higher than these obtained in Refs. [1, 7, 31, 32], which were investigated at 5T. Such promising magnetic entropy change is caused by a high content of Fe and the high content of La(Fe,Si)$_{13}$-type phase in the alloy composition.

Next to magnetic entropy change ($|\Delta S_M|$), the second important parameter characterizing magnetocaloric materials is refrigeration capacity (RC). It can be calculated using the Wood relation [33]:

$$RC(\delta T, H_{max}) = \int_{T_{m}}^{T_{end}} \Delta S_M(T, H_{max}) dT$$

### Table 1

| Phases          | Hyperfine filed ($B_{hf}$)/T | Isomer shift (IS)/(mm·s$^{-1}$) | Quadrupole splitting (QS)/(mm·s$^{-1}$) | Content/ wt% |
|-----------------|------------------------------|---------------------------------|----------------------------------------|--------------|
| La(Fe$_{0.06}$, Si$_{0.04}$)$_{12.98}$ type | 0.06 ± 0.01                  | 0.45 ± 0.01                     |                                        | 95           |
| Fe$_{0.06}$Co$_{0.04}$Si$_{0.04}$          | 33.6 ± 0.1                   | 0.08 ± 0.01                     | 0.03 ± 0.01                            | 5            |
where RC is cooling capacity, $\Delta T = T_{\text{hot}} - T_{\text{cold}}$ is temperature of thermodynamic cycle ($T_{\text{hot}}$ and $T_{\text{cold}}$ are the corresponding temperatures at full width half maximum of $\Delta S_M$ peak) and $H_{\text{max}}$ is the maximum value of external magnetic field. The RC equals to 65, 177 and 299 J·kg$^{-1}$ for $\mu_0 H_{\text{max}}$ of 1, 2 and 3T, respectively. Calculated values are comparable or lower to those obtained for LaFe$_{13-x}$Si$_x$ ($x = 1.17-2.60$) [34] and GdZn-based composites [35].

High magnetic entropy change in La(Fe,Si)$_{13}$-type alloys is usually caused by the first-order phase transition [5, 6, 9–11, 27]. However, the positive slope of the Arrott plots and the symmetrical shape of the $\Delta S_M$ versus $T$ curves suggest the occurrence of the second-order phase transition in LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy.

Figure 7 shows that the magnetic entropy change strongly depends on the temperature and also on the magnetizing field induction. Franco et al. [36, 37] showed that the maximum magnetizing field induction dependence of magnetic entropy change can be written as the following relation:

$$\Delta S_M = CB_{\text{max}}^n$$  \hspace{1cm} (4)

where $C$ depends on temperature, $n$ is exponent depending on the magnetic state of the sample and $B_{\text{max}}$ is the maximum change in external magnetic field induction corresponding to maximum $\Delta S_M$. The magnetizing field induction dependences of magnetic entropy change below, in the vicinity and above the Curie temperature are shown in Fig. 7. The linear relation was used to fit experimental data collected below and near the Curie point. However, in the case of $\Delta S_M(H_{\text{max}})$ dependence, a parabolic relation was used. The correlation coefficients are higher than 0.999.

As shown in Refs. [36, 37] the value of exponent ($n$) strongly depends on the magnetic state of the sample. If the specimen is in the ferromagnetic state, $n$ amounts to 1. However, when it is at a temperature above Curie point then $n$ equals to 2. The exponent ($n$) at the Curie point is described by $n = 1 + 1/\delta(1 - 1/\beta)$ ($\delta$ and $\beta$ are critical exponents), provided that the material obeys the Curie–Weiss law [36]. These conditions were formulated for materials with the second-order phase transition. The results of fitting $|\Delta S_M(H_{\text{max}})|$ also indicate the second-order phase transition in LaFe$_{11.35}$Co$_{0.6}$Si$_{1.05}$ alloy.

In order to confirm the nature of the phase transition, the Landau theory was used. The Landau theory of phase transitions is based on free energy expanded into a power series near a critical point [38, 39]. The free energy ($F(M, T)$) can be written as:

$$F(M, T) = \frac{c_1(T)}{2} M^2 + \frac{c_2(T)}{4} M^4 + \frac{c_3(T)}{6} M^6 + \cdots - \mu_0 H M$$  \hspace{1cm} (5)

where $c_1(T)$, $c_2(T)$ and $c_3(T)$ are the Landau coefficients. The calculation of Landau coefficients is possible after the reconstruction of Eq. (4) in the following form [40]:

$$\mu_0 H = c_1(T) M + c_2(T) M^3 + c_3(T) M^5$$  \hspace{1cm} (6)

The temperature dependences of the Landau coefficients are shown in Fig. 8. Distinguishing between the first- or second-order phase transition is possible using $c_1(T)$ and $c_2(T)$ curves. The $c_1(T)$ is always positive and reaches minimal value at the Curie temperature, while $c_2(T)$ settles between the first- and second-order phase transitions. In
Fig. 8, two temperatures are marked, Curie point \((T_C)\) and \(T_0\) (\(T_0\) is the point where \(c_s(T)\) curve changes its sign from minus to plus). If \(T_C < T_0\), then the first-order phase transition is observed in the material. However, when \(T_C = T_0\), it indicates the second-order phase transition in the investigated sample. In the case of \(\text{LaFe}_{11.35}\text{Co}_{0.65}\text{Si}_{1.05}\) alloy, \(T_0\) equals to \(T_C\). It confirms the occurrence of the second-order phase transition in the studied alloy.

Another method to investigate the nature of the phase transition was proposed by Franco et al. [36]. It is based on the phenomenological universal curve relating \(\Delta S_M\) to \(H\) and \(T\). The procedure for the construction of the scaling curve is shown in Ref [41]. In the first step, all \(\Delta S_M\) versus \(T\) curves should be normalized to their respective maximum value \(\Delta S_M(T_C)\), or if it is impossible due to the accuracy of measurements, it was needed to use \(\Delta S_M^\delta (T)/\Delta S_M^\delta (T_C)\), where \(\Delta S_M^\delta\) is the maximum value of \(\Delta S_M\) versus \(T\) curve. The second step is based on rescaling the temperature axis \((\theta_i)\) above and below the Curie point by using the following equation [42]:

\[
\theta_i = \frac{T - T_C}{T - T_r},
\]

where \(T_C\) is the Curie temperature and \(T_r\) is the reference point selected for specified fraction of \(\Delta S_M^\delta\). In the present work, the reference temperature has been chosen according to the relation \(\Delta S_M(T_r) = 0.4\Delta S_M^\delta\). The universal scaling curve constructed for the investigated alloy is shown in Fig. 9.

As shown in Fig. 9, all curves measured for \(\text{LaFe}_{11.35}\text{Co}_{0.65}\text{Si}_{1.05}\) alloy collapse onto the same universal curve. However, the collapse is imperfect for temperatures lower than Curie point, but clear disintegration of the scaling curve is not observed. As mentioned in Refs. [36, 41–45], such a shape of the universal scaling curve suggests that \(\text{LaFe}_{11.35}\text{Co}_{0.65}\text{Si}_{1.05}\) alloy displays the second-order phase transition. It corresponds with the previous results derived by the Arrott plots and temperature dependences of the Landau coefficients.

4 Conclusion

The structure and magnetic properties of \(\text{LaFe}_{11.35}\text{Co}_{0.65}\text{Si}_{1}\) alloy were investigated in present work. The microstructural observations together with EDS analysis reveal the coexistence of the expected \(\text{La(Fe, Si)}_{13}\)-type phase and a small amount of \(\alpha\)-\(\text{Fe(Co, Si)}\), which are confirmed by XRD and Mössbauer spectroscopy studies. The Mössbauer spectrum collected for the sample of \(\text{LaFe}_{11.35}\text{Co}_{0.65}\text{Si}_{1.05}\) alloy was fitted by one ferromagnetic sextet and a paramagnetic doublet corresponding to \(\alpha\)-\(\text{Fe(Co, Si)}\) and \(\text{La(Fe, Si)}_{13}\)-type phases, respectively. The positive slope of the Arrott plots reveals the occurrence of the second-order phase transition, which is confirmed by the temperature evolution of the Landau coefficients and construction of a universal scaling curve. However, the maximum value of isothermal magnetic entropy change under the change in the external magnetic field of \(\sim 3\, \text{T}\) equals to \(-21.4\, \text{Jkg}^{-1}\text{K}^{-1}\) at 268 K, which is comparable to that of the same group of alloys. The magnetizing field induction dependences of the isothermal magnetic entropy change are linear below and in the vicinity of the Curie point. However, above \(T_C\), parabolic relation of \(\Delta S_M = C(B_{\text{max}})^n\) has been observed.

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