Magnetic entropy change and magnetic properties of $LaFe_{11.5}Si_{1.5}$ after controlling the Curie temperature by partial substitution of Mn and hydrogenation*

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Magnetic properties and magnetic entropy changes of $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}H_y$ compounds are investigated. Their Curie temperatures are adjusted to room temperature by partial Mn substitution for Fe and hydrogen absorption in 1-atm (1 atm = 1.01325×10^5 Pa) hydrogen gas. Under a field change from 0 T to 2 T, the maximum magnetic entropy change for $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ is -11.5 J/kg. The suitable Curie temperature and large value of ΔS_m make it an attractive potential candidate for the room temperature magnetic refrigeration application.

Keywords: magnetic refrigeration, Curie temperature (T_C), hydrogen absorption, magnetocaloric effect (MCE)

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1. Introduction

The $LaFe_{13}$-based compound with a cubic $NaZn_{13}$-type structure has attracted a great deal of attention in recent years due to its potential applications as a magnetic refrigerant.[1–4] The $La(Fe_xSi_{1-x})_{13}$ compounds (space group $Fm\bar{3}C$) with $0.86 \leq x \leq 0.90$ each show a thermally-induced first-order magnetic transition between the paramagnetic and the ferromagnetic states at the Curie temperature T_C and an itinerant-electron metamagnetic (IEM) transition just above T_C,[5–9] which causes a large magnetocaloric effect (MCE) of the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad}.[6–8,10] However, its lower Curie temperature ($T_C \sim 190$ K)[6] makes it difficult to use in domestic appliances. To realize room temperature magnetic refrigerators, it is necessary to raise its T_C. Now incorporating an interstitial hydrogen atom into $La(Fe_xSi_{1-x})_{13}$ compounds is regarded as an effective way to increase T_C significantly.[11–15] In $La(Fe_xSi_{1-x})_{13}H_y$ interstitial compounds, due to the intrusion of hydrogen into the 24*d* site the Fe^{II}–Fe^{II} (at 96*i* sites) is expanded, resulting in lattice expansion which yields a considerable increase in Curie temperature.[16,17] It has been reported that after hydrogen absorption in H_2 gas under 5-to-50 atmospheric pressures, and T_C increases up to about 280 K–336 K.[11,12,15] However, for the reasons of properties of $La(Fe_xSi_{1-x})_{13}$ compounds and the hydrogenation process, it is difficult to control T_C freely without weakening MCEs. Unsaturated hydrogen absorption can lead to asymmetrical occupation of H atoms in $La(Fe_xSi_{1-x})_{13}$ unit cell, which results in the decrease of magnetic entropy change. Sometimes the Curie temperature is lifted too high to be used at room temperature after saturate hydrogen absorption, such as $T_C = 336$ K for $LaFe_{11.4}Si_{1.56}H_{1.6}$.[11]

Previous research confirmed that the addition of a small amount of Mn brings about the decrease of Curie temperature of $La(Fe_xSi_{1-x})_{13}$, with keeping the IEM transition.[17–20] For $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$, Mn concentration has an influence on T_C which decreases almost linearly from 188 K for $x = 0$ to 127 K for $x = 0.03$.[17] The rapid decrease of T_C may be attributed to the weakening of the magnitude of the exchange coupling between Fe–Fe atoms, caused by Mn substitution. Therefore, it should be an effective way to adjust Curie temperature while remaining a large magnetic entropy change by jointly utilizing Mn substitution for Fe and saturate hydrogen absorption.

In this paper, we prepare $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_y$ compound in hydrogen gas under 1 atmospheric pressure at 473 K and study the effects of substitution of Mn atom and interstitial H atom on the Curie temperature and magnetic entropy change. The structure and magnetic transition properties of the compounds are also investigated.

2. Experimental procedure

$La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ ($x = 0$, 0.01, 0.02, 0.03) compounds were prepared from pure ($\geq 99.9\%$) elements by using the arc-melting method in argon atmosphere. Each arc-melted ingot was flipped over and remelted at least three times to en-

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sure its homogeneity. The ingots were annealed at 1353 K for 10 days, and after that quenched in ice water. The hydrogen absorption took place at 473 K by annealing in a furnace equipped with a vacuum system after the samples had been crushed into powder with about 0.8 mm in size. The pressure of hydrogen was kept under 1 atmospheric pressure. The time of hydrogen absorption is selected to be 2 h to ensure that the saturation was reached.[21] The hydrogen concentration was determined by the weighing method. The structures of all parent alloys and corresponding hydrides were identified by powder x-ray diffraction (XRD) and the magnetic measurements were carried out by vibrating sample magnetometer (VSM). To study the phase transitions of the compounds a differential scanning calorimeter (DSC) was used.

3. Results and discussion

X-ray diffraction analyses of powdered samples are shown in Fig. 1. The $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ ($x = 0.01$, 0.02, 0.03) and $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ compounds each remain a cubic $NaZn_{13}$-type structure. Obviously, neither Mn substitution nor hydrogen absorption has an adverse influence on the formation of 1:13 phase. The diffraction peaks of $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ shift toward low angles compared with those of $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$. It is indicated that hydrogen atoms have entered interstices between crystal lattices as interstitial atoms, leading to an expansion of unit cell volume. In Table 1, the lattice parameters, obtained from the XRD patterns, are 11.65 Å for $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$, 11.58 Å for $La(Fe_{0.98}Mn_{0.02})_{11.5}Si_{1.5}$, 11.48 Å for $La(Fe_{0.97}Mn_{0.03})_{11.5}Si_{1.5}$, and 11.6248 Å for $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$, respectively. Because the ionic radius of Mn is larger than that of Fe, the lattice parameter increases with increasing Mn concentration.

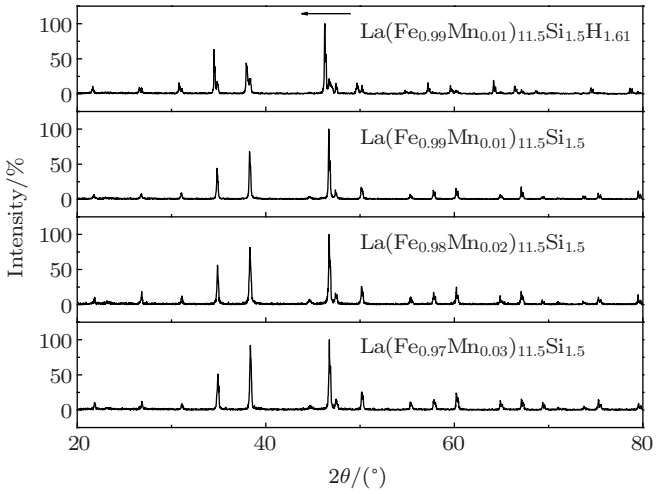


Fig. 1. X-ray diffraction patterns of $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ ($x = 0.01$, 0.02, 0.03) and $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ compounds.

Figure 2 shows DSC curves of $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ ($x = 0.01$, 0.02, 0.03) compounds. As seen from this figure, an endothermic peak is found at each of the Curie temperature T_C values of 194 K, 184 K, 173 K, and 151 K for $x = 0$, 0.01, 0.02, and 0.03, respectively, showing an obvious decease of T_C with increasing Mn concentration. Furthermore, the peak heights of phase transition of $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ compounds decrease with increasing x. The rapid decrease of T_C and changes of phase transition properties may be attributed to the weakening of the magnitude of the exchange coupling between Fe–Fe atoms caused by the antiferromagnetic coupling between Fe and Mn atoms, as previously reported.[17,19]

Table 1. Lattice constants of $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ (x=0.01, 0.02, 0.03) and $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$.

Materials	Lattice constant a/Å
$LaFe_{11.5}Si_{1.5}$[21]	11.4867
$La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$	11.5076
$La(Fe_{0.98}Mn_{0.02})_{11.5}Si_{1.5}$	11.4957
$La(Fe_{0.97}Mn_{0.03})_{11.5}Si_{1.5}$	11.4837
$La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$	11.6248

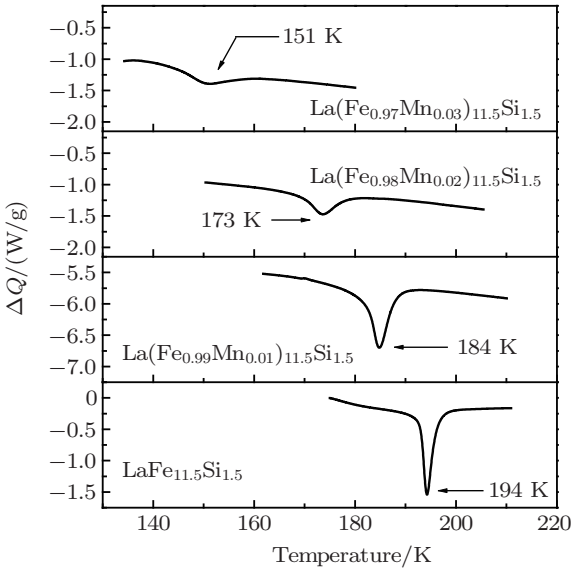


Fig. 2. DSC measurements for $La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}$ ($x = 0$, 0.01, 0.02, 0.03) compounds.

DSC curves of $LaFe_{11.5}Si_{1.5}$, $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$, and $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ compounds are shown in Fig. 3. In this figure, an endothermic peak is found at each 194 K, 184 K, and 313 K temperatures for $LaFe_{11.5}Si_{1.5}$, $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$, and $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$, respectively, indicating that the partial substitution of Mn for Fe leads to the decrease of the T_C, and then, saturate hydrogen absorption significantly lifts T_C to room temperature. In $LaFe_{11.5}Si_{1.5}$, the substitution of smaller Mn atoms for Fe weakens the magnitude of the exchange coupling between Fe–Fe atoms (J_{Fe-Fe}), which gives rise to the decrease of T_C. On the other hand, hydrogen absorption of $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}$ leads to the volume expansion, which enhances the exchange coupling between Fe–Fe atoms

($J_{\mathrm{Fe-Fe}}$) and Fe–Mn atoms ($J_{\mathrm{Fe-Mn}}$), and results in a significant increase of T_{C}. For this reason, $\mathrm{La(Fe_{1-x}Si_x)_{13}}$ compounds with T_{C} around room temperature can be obtained by jointly utilizing the proper proportion of substitution of Mn for Fe and hydrogen absorption. Also, a comparison of endothermic peaks between before and after hydrogen absorption indicates that the temperature range of the phase transition does not become wider.

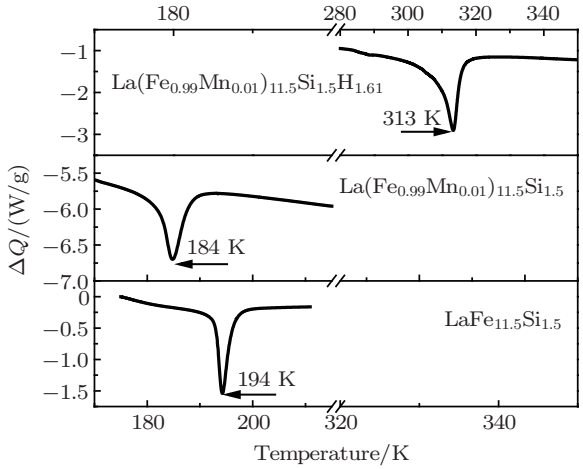


Fig. 3. The differential scanning calorimeter (DSC) measurements for $\mathrm{LaFe_{11.5}Si_{1.5}}$, $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}}$, and $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_y}$ compounds.

Figure 4(a) shows the magnetization isotherms of $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound, measured in a wide temperature range around the Curie temperature. It can be seen that the magnetization of the compound decreases with temperature increasing. When the temperature approaches to T_{C}, the magnetization change becomes large. Figure 4(b) diaplays the Arrott curves of $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound. The negative slopes suggest that a first-order field-induced IEM transition from paramagnetic to ferromagnetic order is preserved[6,9,22,23] after hydrogen absorption, which is of great importance for the large magnetic entropy changes.

The ΔS_{m} is evaluated from the variation of magnetization as a function of M and H in connection with the following Maxwell relation:

$$\Delta S_{\mathrm{m}} = \int_0^{H_{\max}} \mu_0 \left(\frac{\partial M}{\partial T}\right) \mathrm{d}H. \tag{1}$$

The magnetic entropy changes are shown in Fig. 5. For the $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound, the maximum values of ΔS_{m} for magnetic field changes from 0 T to 1 T and from 0 T to 2 T are found to be -8.0 J/kg·K and -11.5 J/kg·K, respectively. Comparing with the scenario of $\mathrm{LaFe_{11.5}Si_{1.5}}$, whose $|\Delta S_{\mathrm{m}}|$ is 18 J/kg·K for a field change of 0 T to 2 T, the maximum magnetic entropy change decreases by substituting Mn for Fe. However, $|\Delta S_{\mathrm{m}}|$ of $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound notably exceeds that of Gd (about 4.5 J/kg·K for a field change of 0 T to 2 T).[24] Therefore, the $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound is an attractive candidate for magnetic refrigerants near room temperature.

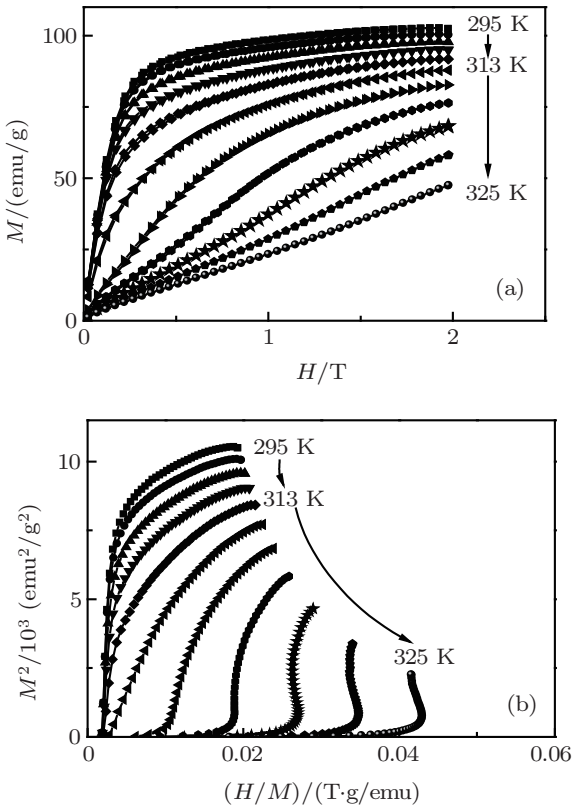


Fig. 4. Magnetization curves (a) and Arrott curves (b) for $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound.

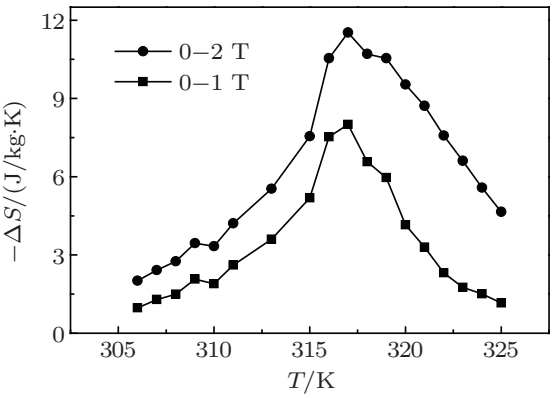


Fig. 5. The temperature-dependent magnetic entropy of $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compound as static magnetic field varies from 0 T to 1 T and 0 T to 2 T.

4. Conclusions

In this study, the room-temperature powder XRD patterns show that the $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}}$ and $\mathrm{La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}}$ compounds each crystallize into a single phase with a cubic $\mathrm{NaZn_{13}}$-type structure. The Curie temperature of $\mathrm{La(Fe_{1-x}Mn_x)_{11.5}Si_{1.5}}$ is adjusted to about 313 K after saturate hydrogen absorption in $\mathrm{H_2}$ gas under 1 atmospheric pressure and partial substitution of Mn for Fe with $x = 0.01$, in the remaining first-order magnetic

transition. For $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ compound, ΔS_m for a magnetic field change from 0 T to 2 T is found to be −11.5 J/kg·K, which is larger than that of Gd. The T_C near room temperature and large magnetic entropy change make the $La(Fe_{0.99}Mn_{0.01})_{11.5}Si_{1.5}H_{1.61}$ compound an attractive candidate for magnetic refrigerants at room temperature.

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