Effect of Si doping on the magnetic properties and magnetic entropy changes in the LaFe_{11.4}Al_{1.6} intermetallic compound

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Abstract

For NaZn₁₃-type LaFe_{11.4}Al_{1.6−x}Si_{x} (x = 0–1.6) compounds, the lattice parameter linearly reduces with the increase of Si concentration. A mixture of antiferromagnetic phase and ferromagnetic clusters has been observed in the compound with x = 0.22. The magnetic phase diagram obtained from the isofield magnetization curves shows that the antiferromagnetic phase changes into the ferromagnetic phase at low temperature with increasing Si concentration. A spike-shaped magnetic entropy change has been found in the sample with x = 0.3, which is a spurious result obtained by using the Maxwell relationship. Meanwhile, a very broad plateau of magnetic entropy change is obtained, which is very favorable for a magnetic refrigerant. For the sample with x = 0.8, a large magnetic entropy change and very small hysteresis losses have been found due to the weak first-order phase transition.

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) of solid-state working substances has attracted tremendous attention in recent years due to their significant advantages over gas refrigerants [1, 2]. The MCE is characterized by the isothermal magnetic entropy change $\Delta S_M$ or the adiabatic temperature change arising from the application or removal of a magnetic field $H$ on a system with magnetic degrees of freedom. The large magnetic entropy change in a La(Fe, Si)$_{13}$ system with a cubic NaZn₁₃-type structure has been intensively investigated [3–6]. The LaFe$_{11.4}$Si$_{1.6}$ compound shows $-\Delta S_M = 19.4$ J kg$^{-1}$ K at its Curie temperature $T_C$ for a field change of 0–5 T, due to a strong first-order ferromagnetic to paramagnetic phase transition near $T_C$ [3].

The LaFe$_{11.4}$Al$_{x}$ compounds with x ranging from 1.04 to 7.02 crystallize in the cubic NaZn₁₃-type structure [7–10]. With the increase of iron concentration, mictomagnetic, ferromagnetic (FM), and antiferromagnetic (AFM) states are observed successively. It is FM and AFM for 1.82 $\leq$ x $\leq$ 4.94 and 1.04 $\leq$ x $<$ 1.82, respectively. Obviously, the ground state is AFM in LaFe$_{11.4}$Al$_{1.6}$, which is different from ferromagnetic LaFe$_{11.4}$Si$_{1.6}$. The substitute of Si for Al could bring about some interesting magnetic properties. In this present paper, we systematically investigate the structure and magnetic properties in LaFe$_{11.4}$Al$_{1.6−x}$Si_{x} (x = 0–1.6) compounds, in addition to the MCE of the selected LaFe$_{11.4}$Al$_{1.6−x}$Si_{x} with x = 0.3 and 0.8.

2. Experiments

Polycrystalline samples with the nominal composition LaFe$_{11.4}$Al$_{1.6−x}$Si_{x} (x = 0–1.6) were prepared by arc melting appropriate amounts of starting materials (higher than 99.9% in purity) under ultrapure argon atmosphere (10 at.% excessive La was used to compensate the weight loss during the arc melting). The ingots were annealed in an evacuated quartz tube at 1223 K for 15 days for x = 0–0.4, 1273 K for 30 days for x = 0.5–0.8, 1273 K for 40 days for x = 0.9–1.5, and 1323 K for 50 days for x = 1.6, respectively. Powder x-ray diffra-
Figure 1. Si concentration dependence of the lattice parameter in LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0–1.6$) compounds. The solid line is the linear fitting result.

Figure 2. Temperature dependence of magnetization on heating in a field of 0.1 T of LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0–1.6$) compounds: (a) for $x = 0–0.22$; (b) for $x = 0.25–0.4$; and (c) for $x = 0.5–1.6$. The inset of (b) clarifies the details in the vicinity of the AFM–PM transition for $x = 0.25–0.4$.

Figure 3 shows the temperature dependence of the real part ($\chi'$) and imaginary part ($\chi''$) of the ac magnetic susceptibility of the LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.22$) compound, measured under a zero external dc magnetic field during heating the sample. There is a peak at $\sim 102$ K. This is in accord with the cusp shown in figure 2(a). A close view of the real part of the ac susceptibility around 102 K is displayed in the inset of figure 3(a). No frequency dependence of the peak position can be observed. Therefore, spin-glass freezing in zero dc $H$ should be ruled out [12–14]. Simultaneously, the nonzero values of $\chi''$ indicate the onset of an energy loss process, usually associated with domain dynamics, which is consistent with a weak ferromagnetism [15]. $\chi''$ also exhibits a broad peak, indicating that some small ferromagnetic
clusters are formed [12]. In Gd3Ge4, this opinion has been confirmed by an in situ x-ray powder diffraction study [11]. Hence, the cusp at \( \sim 102 \) K in the low-field ZFC \( M-T \) curves correlates well with the appearance of ferromagnetic component.

The magnetic phase transitions of LaFe\(_{11}\)Al\(_{1-x}\)Si\(_x\) (\( x = 0–1.6 \)) compounds with the concentration of Si are shown in figure 4, based on the zero-field-cooling isofield magnetization curves under a field of 0.1 T. The AFM-to-PM transition temperature, the FM-to-AFM transition temperature, and the FM-to-PM transition temperature are labeled as \( T_N \), \( T_0 \), and \( T_C \), respectively. As shown in figure 4, \( T_N \) slowly reduces, but \( T_0 \) and \( T_C \) enhance with the increase of Si concentration. The temperature range where FM clusters appear from the AFM background is indicated by an arrow for the compound with \( x = 0.22 \). So it can be concluded that the AFM phase gradually changes into FM phase at low temperature with the increase of Si concentration. In addition, magnetic field has a huge influence on the magnetic transition temperature for \( x \leq 0.4 \) due to the character of the first-order phase transition. For the compounds with \( x = 0.25–0.4 \), the increase of magnetic field reduces \( T_N \) and simultaneously enhances \( T_0 \). \( T_N \) and \( T_0 \) merge to \( T_C \) under a proper field. Namely, only FM-to-PM transition occurs directly when the applied field exceeds a certain value.

The isothermal magnetization curves at 5 K are measured for these compounds. For \( x \leq 0.22 \), there is a sharp metamagnetic AFM–FM transition under a critical field. The saturation magnetizations of the FM state are obtained above the critical field according to the law of approach to saturation. For \( x \geq 0.25 \), the magnetization grows rapidly with increasing the field and then saturates directly, which indicates the characteristic ferromagnetic behavior in these compounds. Figure 5(a) displays the isothermal magnetization curves for the selected compounds. The variation of saturation magnetic moments of these compounds is exhibited in figure 5(b) based on the isothermal magnetization curves. One can find that it decreases slightly with increasing Si concentration. This indicates that the magnetic moment of 3d electrons of Fe is nearly unchanged by the substitution of Si for Al.

In LaFe\(_{13-x}\)Si\(_x\) compounds, the external pressure makes the Curie temperature decrease [5, 6]. On the other hand, the FM ground state of the La(Fe\(_{0.85}\)Al\(_{0.15}\))\(_{13}\) compound can be induced to the AFM state by increasing pressure [16]. Although the crystal lattice is also shrunk by the substitution of Si for Al, the variation of magnetic state with Si concentration is very different from that with the external pressure. Because the configuration of magnetic structure for the AFM La(Fe, Al)\(_{13}\) compounds has not been very clear up to now [17], the mechanism for changes of magnetic properties induced by the substitution of Si for Al is still unknown.

As seen in figure 2(b), LaFe\(_{11.4}\)Al\(_{1-x}\)Si\(_x\) compound with \( x = 0.25–0.4 \) shows similar and plentiful magnetic phase transitions with temperature increasing: an FM-to-AFM transition at low temperature, followed by an AFM-to-PM transition at high temperature. As an example, we focus on the MCE of the compound with \( x = 0.3 \). Its MCE is investigated based on the isothermal magnetization measurement. Figure 6 presents the magnetic entropy change as a function of temperature in typical field changes in the LaFe\(_{11.4}\)Al\(_{1-x}\)Si\(_x\) (\( x = 0.3 \)) compound. The entropy change is evaluated using the Maxwell relationship. In addition to
Figure 5. (a) Isothermal magnetization curves at 5 K for the selected compounds and (b) Fe concentration dependence of the saturated magnetic moments (‘×’ for the compounds with $x \leq 0.22$ and ‘▼’ for the compounds with $x \geq 0.25$). The solid line in (b) is a guide to the eye.

Figure 6. Temperature dependence of the magnetic entropy change $-\Delta S_M$ of LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.3$) compounds for typical field changes.

Figure 7. (a) Temperature dependence of the magnetic entropy change $-\Delta S_M$ of LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.8$) compounds for typical field changes. (b) Arrott-plots of this compound around $T_C$. Inset plot of (a): magnetization versus field curves for this compound at 184 K, arrows indicate the sequence of measurements.

The flat plateau of the height of just several J kg$^{-1}$ K, the magnetic entropy change for this compound is characterized by two peaks: one peak centered at $T_N$ and one extra spike-shaped peak of 25–30 J kg$^{-1}$ K centered round $T_0$. The width of the plateau in a field change of 0–5 T attains $\sim 70$ K due to the superposition of the FM-to-AFM and AFM-to-PM phase transitions. This is very favorable for magnetic refrigeration. The emergence of the peak at $T_N$ is correlated with the AFM–PM transition. However, the spike appears at $T_0$, which is an artifact [18] due to the evaluation of entropy change using the Maxwell relationship. A similar phenomenon has been observed in many other compounds such as MnAs under pressure [19], La$_{0.8}$Ce$_{0.2}$Fe$_{11.4}$Si$_6$ [20], and La$_{0.7}$Pr$_{0.3}$Fe$_{11.5}$Si$_{6.5}$ [18].

As shown in figure 2(c), LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ compounds with $x = 0.5$–1.6 display a simple FM–PM transition. So the MCE of LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ with $x = 0.8$ is investigated as the representative of compounds with $x = 0.5$–1.6. Figure 7(a) presents the temperature dependence of its magnetic entropy change in different field changes. The peak value of $-\Delta S_M$ in a field change of 0–2 T is 9.1 J kg$^{-1}$ K, which is much larger than that of Gd (5.0 J kg$^{-1}$ K) [21]. However, it is lower than that of LaFe$_{11.4}$Si$_6$ in [3]. Arrott-plots [22] around $T_C$ shown in figure 7(b) confirm that the phase transition for LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.8$) is weak first-order, the same as that for LaFe$_{11.4}$Si$_6$ [3]. The hysteretic losses, which are very harmful to magnetic refrigeration, are
determined by computing the area inside the magnetization versus field loop. The inset plot of figure 7(a) gives the loop at 184 K (just 2 K above $T_C$). Obviously, the present compound has scarcely any hysteresis loss. The relatively large $-\Delta S_M$ of LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.8$) compound in a relatively small field change (0–2 T), which can be supplied by a NdFeB permanent magnet, is favorable for practical applications.

Combining the magnetic entropy change of the selected compounds with the results in [3], one can find that the peak value of the $-\Delta S_M$ ascends with the increase of Si concentration under the same field change. This may be associated with the enhancement of the first-order phase transition, not with the saturated magnetic moments.

4. Conclusion
LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0–1.6$) compounds crystallize in the cubic NaZn$_{13}$-type structure. With the increase of Si concentration, the lattice parameter linearly reduces and the magnetic ground state changes gradually from AFM to FM states. A plateau-like $\Delta S_M(T)$ with a height of about 7 J kg$^{-1}$ K has been found in a field change of 0–5 T for the sample with $x = 0.3$. The width of the plateau reaches ~70 K, which is very favorable for magnetic refrigeration. LaFe$_{11.4}$Al$_{1.6-x}$Si$_x$ ($x = 0.8$) compound with a weak first-order phase transition shows a large magnetic entropy change and very small hysteresis losses. Therefore, it is a very attractive candidate for a magnetic refrigerant in the corresponding temperature range.

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References