

Magnetocaloric effects in the $\text{La}(\text{Fe}, \text{Si})_{13}$ intermetallics doped by different elements

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The magnetocaloric effects (MCEs) of $\text{LaFe}_{13-x}\text{Si}_x$ compounds doped by magnetic rare earths ($R=\text{Ce}$, Pr , and Nd) and transition metal (Co) are analyzed. It is found that varying the contents of R and Fe produces similar effects on the MCE, both of which cause a rapid decrease in ΔS with the increase in T_C . The $\Delta S-T_C$ relations thus obtained coincide with each other fairly well, which indicates the equivalence of substituting R for La and Fe for Si . In contrast, partially replacing Fe by Co leads to a slow decrease in ΔS with T_C . It is therefore a promising approach to maintain a large ΔS up to high temperatures. As a comparison with these element-doping compounds, the MCEs of hydrides are also discussed. Although interstitial hydrogen can also keep up a large ΔS to high temperatures, the corresponding hydrides are unfortunately unstable above 150°C . Based on these analyses, the potential refrigerants made of $\text{LaFe}_{13-x}\text{Si}_x$ are proposed to have as low as possible Si content (or high R content) and proper Co content simultaneously. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072021]

To meet the demands of practical application, great efforts have been devoted to improving the magnetocaloric effects (MCEs) of the $\text{LaFe}_{13-x}\text{Si}_x$ intermetallics (entropy change $\Delta S \sim 20$ J/kg K, field change $\Delta H = 5$ T),^{1,2} which are potential candidates for magnetic refrigerants because of their large MCEs. It has been found that the MCE of these compounds could be greatly modified by either increasing Fe content, which is equivalent to reducing Si content, or by partially replacing La with magnetic rare earth atoms (R). For instance, ΔS grows from ~ 29 J/kg K to ~ 34 J/kg K after 20% La were substituted by Ce in $\text{LaFe}_{11.7}\text{Si}_{1.3}$,³ and from ~ 13 J/kg K to ~ 29 J/kg K when the Si content in $\text{LaFe}_{13-x}\text{Si}_x$ reduces from 1.8 to 1.3 (field change $\Delta H = 5$ T).^{2,4} In contrast, replacing Fe by Co , though both are transition metals, can lead to a considerable reduction in ΔS . A typical result is the decrease in ΔS from ~ 16.5 J/kg K to ~ 13.5 J/kg K when the Co content in $\text{LaFe}_{11.9-x}\text{Co}_x\text{Si}_{1.1}$ increases from 0.7 to 0.9.⁵ Differing from element substitution, the incorporation of interstitial hydrogen significantly affects T_C rather than ΔS . The Curie temperature can be evenly tuned between 195 and 323 K by simply adjusting the content of hydrogen in the compounds.⁶

We noted that, despite the intensive work and excellent review paper⁷ on substitution effects, a careful analysis of the $\Delta S-T_C$ relations for the $\text{LaFe}_{13-x}\text{Si}_x$ family is still lacking. It has been found that the increase in ΔS always occurs with a decrease in T_C . It is therefore obvious that simply comparing the ΔS produced by various element dopings without paying attention to the temperature where the ΔS appears is inappropriate. It cannot reveal which is the best approach to the optimal MCE. To get a general guidance for the further MCE

study, in this paper we will perform a systematic investigation on the $\Delta S-T_C$ dependence of the $\text{LaFe}_{13-x}\text{Si}_x$ family. Our work shows the equivalence of replacing La by magnetic rare earths and substituting Si by Fe , both of which produce similar $\Delta S-T_C$ relations. The optimal approach to get a large MCE at high temperatures is the proper replacement of Fe with Co in the $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$ compounds that have the lowest Si contents or the highest R contents.

The intermetallics with the nominal compositions $\text{LaFe}_{13-x}\text{Si}_x$ ($x=1.3-2.6$), $\text{La}_{1-y}\text{Pr}_y\text{Fe}_{13-x-z}\text{Co}_z\text{Si}_x$ ($x=1.5$ and 1.8 ; $y=0-0.5$; $z=0-1.0$), $\text{La}_{1-y}\text{Nd}_y\text{Fe}_{11.5}\text{Si}_{1.5}$ ($y=0-0.3$), and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ ($z=0.4-1.2$) were prepared by arc-melting appropriate amounts of starting materials (99.9% or higher in purity) under a purified argon atmosphere. The resultant ingots were first annealed at 1050°C (for $\text{LaFe}_{13-x}\text{Si}_x$) and 1100°C (for other alloys) for 40 days in an evacuated quartz tube then quenched into liquid nitrogen. Powder x-ray diffractions, performed by the Rigaku D/max-2400 diffractometer, show that the samples are of single phase with the cubic NaZn_{13} -type structure.

All the magnetic measurements were performed on a superconducting quantum interference device magnetometer. Details for the calculation of ΔS based on the Maxwell relation can be found elsewhere.^{1,8,9} Figures 1(a)–1(c) show the entropy changes in typical compounds: $\text{LaFe}_{13-x}\text{Si}_x$ ($x=1.3-2.2$), $\text{La}_{1-y}\text{Pr}_y\text{Fe}_{13-x-y}\text{Si}_x$ ($x=1.5, y=0, 0.5; x=1.8, y=0, 0.3$), and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ ($z=0.4-1.2$), for a field change from 0 to 5 T, where the MCE has been modified by the contents of Si , R , and Co , respectively. In Fig. 1(a), the increase in Si causes a growth of T_C and a corresponding decrease in ΔS . A simple calculation gives the reduction in ΔS from ~ 29 J/kg K for $x=1.3$ to ~ 7.3 J/kg K for $x=2.2$ in the compounds $\text{LaFe}_{13-x}\text{Si}_x$ (The spike-shaped

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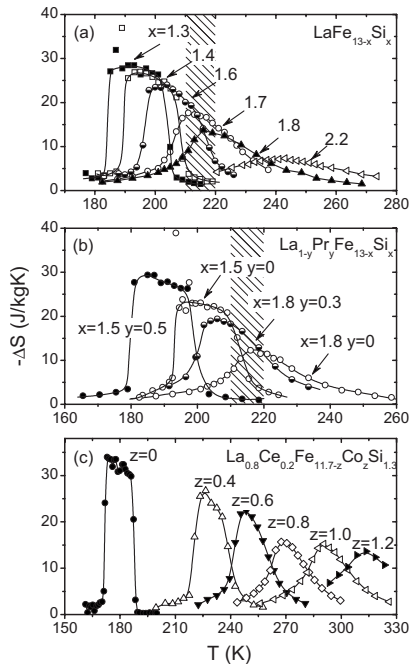


FIG. 1. Temperature-dependent entropy changes (ΔS) of the compounds: (a) $\text{LaFe}_{13-x}\text{Si}_x$ ($x=1.3-2.2$), (b) $\text{La}_{1-y}\text{Pr}_y\text{Fe}_{13-x}\text{Si}_x$ ($x=1.5, y=0, 0.5; x=1.8, y=0, 0.3$), and (c) $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ ($z=0-1.2$). Hatched area marks a crossover of the magnetic transition from first order to second order.

peaks in the samples with low Si contents are artifacts as previously demonstrated,¹⁰ and are not considered here). The ΔS exhibits a tower-shaped peak, when the phase transition is first order, or a lambda-shaped peak, when the phase transition is second order. A visible speedup for the ΔS reduction can be identified as the temperature sweeps through 210–220 K shown by the hatched area in Fig. 1(a), where a crossover of the magnetic transition from first order to second order takes place. However, an opposite effect is produced by the incorporation of Pr, as demonstrated by the decrease in T_C and the increase in ΔS with y , together with the enhancement of the first-order character of the phase transition [Fig. 1(b)]. (Here, we take Pr-substituted compounds as representatives, and similar behaviors are observed in other R -substituted compounds.) Despite of different dopants (R and Si), the similar ΔS - T_C dependence can be observed. It means that the magnetic state of $\text{LaFe}_{13-x}\text{Si}_x$ can be reached by simply tuning the content of R in $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$. Compared with $\text{LaFe}_{13-x}\text{Si}_x$ and $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$, the entropy change in $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x-z}\text{Co}_z\text{Si}_x$ varies in a different manner. Its decay with the increase in T_C is considerably slow. As a result, the MCE remains significant at high temperatures. It can be seen from Fig. 1(c) that ΔS of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ is ~ 29 J/kg K for $T_C \approx 185$ K and ~ 22.4 J/kg K for $T_C = 248$ K. The latter (22.4 J/kg K) is much greater than that of $\text{LaFe}_{13-x}\text{Si}_x$ at the similar temperature (7.3 J/kg K).

To get a quantitative analysis of the substitution effects, in Fig. 2 we give a comparison of the ΔS - T_C relations of different compounds. The data presented are the peak values of ΔS ($\Delta H = 5$ T) at T_C ($H = 0$ T). When considerable data fluctuation takes place around T_C , an averaged ΔS is adopted. Totally four categories of compounds, corresponding to Si, R , Co doping and hydrogenating, respectively, are

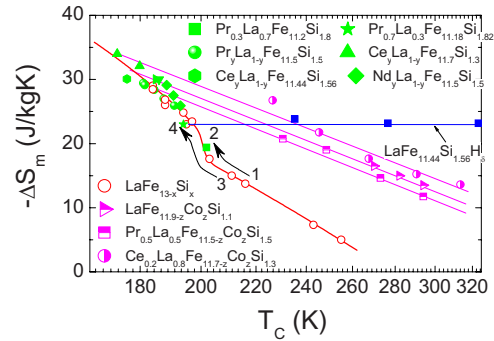


FIG. 2. (Color online) ΔS - T_C relations of magnetic rare earth element-doped and transition metal-doped $\text{LaFe}_{13-x}\text{Si}_x$: $\text{LaFe}_{13-x}\text{Si}_x$ ($x=1.3-2.6$; this work and Ref. 6), $\text{LaFe}_{11.9-z}\text{Co}_z\text{Si}_{1.1}$ ($z=0.7-0.9$; Ref. 5), $\text{Pr}_{0.5}\text{La}_{0.5}\text{Fe}_{11.5-z}\text{Co}_z\text{Si}_{1.5}$ ($z=0.4-1.0$), $\text{Ce}_{0.2}\text{La}_{0.8}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ ($z=0.4-1.2$), $\text{Pr}_{0.3}\text{La}_{0.7}\text{Fe}_{11.2}\text{Si}_{1.8}$, $\text{Pr}_{0.7}\text{La}_{0.3}\text{Fe}_{11.18}\text{Si}_{1.82}$ (Ref. 16), $\text{Pr}_y\text{La}_{1-y}\text{Fe}_{11.5}\text{Si}_{1.5}$ ($y=0.1-0.5$), $\text{Ce}_y\text{La}_{1-y}\text{Fe}_{11.7}\text{Si}_{1.3}$ ($y=0.1, 0.2$; Ref. 3), $\text{Ce}_y\text{La}_{1-y}\text{Fe}_{11.44}\text{Si}_{1.56}$ ($y=0.3$; Ref. 17) $\text{Nd}_y\text{La}_{1-y}\text{Fe}_{11.5}\text{Si}_{1.5}$ ($y=0.1-0.3$). Results of the $\text{LaFe}_{11.44}\text{Si}_{1.56}\text{H}_\delta$ (Ref. 6) are also shown for comparison. Solid lines are guides for the eyes.

analyzed. The data of hydrides is derived from the work of Fujita *et al.*⁶ From Fig. 2, the general tendency is that the ΔS decreases with T_C increasing for all compounds. The maximal ΔS reduction is ~ 29 J/kg K, occurring in $\text{LaFe}_{13-x}\text{Si}_x$ and $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$ as T_C grows from ~ 173 K to ~ 254 K. The ΔS - T_C relations are essentially linear below 195 K and above 205 K, with the remarkably different slopes of -0.40 J/kg K² and -0.23 J/kg K². There is a visible ΔS drop corresponding to the evolution of the magnetic transition from first order to second order at 195–205 K, which is different from the marked temperature range mentioned in Figs. 1(a) and 1(b). The temperature range here is related to the T_C at $H=0$ T, which is different from T_C in Fig. 1 at $H=5$ T. Nearly all ($\Delta S, T_C$) data of $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$ coincide with that of $\text{LaFe}_{13-x}\text{Si}_x$. What of special interest is the reproduction of ΔS - T_C relation for $\text{LaFe}_{13-x}\text{Si}_x$ compounds, even the details, simply by varying y in $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$. For example, the incorporation of 30% Pr in $\text{LaFe}_{11.2}\text{Si}_{1.8}$, which is a typical compound showing a second-order phase transition, causes a scramble of the point from 1 to 2 along the ΔS - T_C curve (shown by an arrow). Similarly, the replacement of 70% La by Pr in $\text{LaFe}_{11.12}\text{Si}_{1.82}$ moves the point from 3 to 4. Scattering of the ΔS below 195 K could be attributed to experimental errors.

A significantly different behavior is observed in the case of Co doping. Although the ΔS shows an approximately linear decrease with the increase in T_C , the ΔS - T_C slope is much small (-0.14 J/kg K²). As a result, the large MCE at low temperatures can be effectively maintained as T_C increases. It can be seen from Fig. 2 that the ΔS value of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ remains to be ~ 15.2 J/kg K even near the ambient temperature ($T \approx 290.6$ K). A remarkable observation is the parallel variation in the ΔS - T_C curves for different compounds $\text{Pr}_{0.5}\text{La}_{0.5}\text{Fe}_{11.5-z}\text{Co}_z\text{Si}_{1.5}$ ($z=0.4-1.0$), $\text{LaFe}_{11.9-z}\text{Co}_z\text{Si}_{1.1}$ ($z=0.7-0.9$), and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.7-z}\text{Co}_z\text{Si}_{1.3}$ ($z=0.4-1.2$). It actually means that the larger ΔS of the parent compound (without Co) is, the greater MCE of the derivative compound will be.

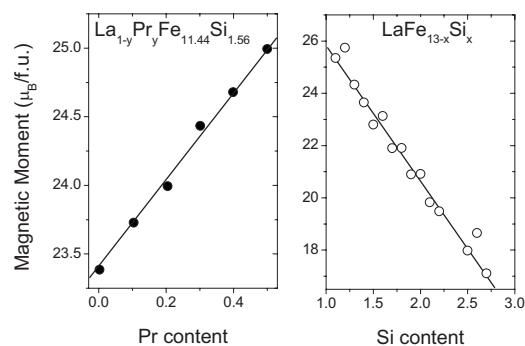


FIG. 3. Saturation magnetizations as functions of the Pr content of $\text{La}_{1-y}\text{Pr}_y\text{Fe}_{11.44}\text{Si}_{1.56}$ (Ref. 16) and the Si content of $\text{LaFe}_{13-x}\text{Si}_x$. Solid lines are guides for the eyes.

Different from the Si, R, and Co substitutions, the incorporation of interstitial hydrogen strongly affects T_C rather than ΔS . It is therefore the most promising approach to get large MCE at high temperatures. In Fig. 2 we show the ΔS - T_C relations for the $\text{LaFe}_{11.44}\text{Si}_{1.56}\text{H}_\delta$ hydrides obtained by Fujita *et al.*⁶ ΔS is ~ 23 J/kg K for $T_C=195$ K and keep the high value up to $T_C=323$ K. Essentially similar phenomena are observed in other hydrides with different compositions.⁶ Although sometimes a visible ΔS reduction appears with the increase in T_C , for example, in $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.44}\text{Si}_{1.56}\text{H}_\delta$, ΔS decreases from 30 J/kg K ($\delta=0$) to 26 J/kg K ($\delta=1.6$),¹¹ the decrease is much smaller compared with the effects of Si and Co doping.

It is believed that R doping is an alternative approach modifying the MCE of $\text{LaFe}_{13-x}\text{Si}_x$ because of its influence on magnetization and Curie temperature. However, the experiment data here shows the equivalence of increasing R to lowering Si. Actually, two contradict effects are expected for the incorporation of R. The first one is the reduction in phase volume, which disfavors the ferromagnetic (FM) exchange between Fe atoms, and the second one is the occurrence of magnetic coupling between R and Fe. The decrease in T_C with R content manifests the dominative role of the Fe-Fe coupling. It is understandable from the great variation in T_C under high pressures.^{12,13} In addition to these, the presence of magnetic rare earth atoms can induce a growth of saturation magnetization (M_S). Figure 3 presents the M_S of $\text{La}_{1-y}\text{Pr}_y\text{Fe}_{11.44}\text{Si}_{1.56}$, obtained by Fujita *et al.*¹¹ as a function of Pr content (left panel). The M_S growth from $\sim 23.4\mu_B/\text{f.u.}$ to $\sim 25\mu_B/\text{f.u.}$ and the T_C diminishment from ~ 195 to ~ 180 K are observed, corresponding to the variation in y from 0 to 0.5. Compared with $\text{LaFe}_{13-x}\text{Si}_x$ (right panel of Fig. 3), the increase in the Pr content by 0.5 is equivalent to the decrease in x by 0.3, the corresponding variations in the T_C and M_S produced by the latter are $\Delta T_C \approx 15$ K and $\Delta M_S \approx 1.6\mu_B/\text{f.u.}$, respectively. These analyses mean that the M_S - T_C relations vary with more or less the same rule, irrespective of the modification approaches. The x lowering and y increasing have the same effect on the MCE of $\text{LaFe}_{13-x}\text{Si}_x$ family.

As proved, either Si or Co can cause an evolution of the phase transition from first order to second order (Fig. 1). This is the main reason of the MCE degeneration as x or z increases in $\text{LaFe}_{13-x-z}\text{Co}_z\text{Si}_x$. The different doping effects of

Si and Co could be due to their different influences on Fe. The incorporation of Si yields a reduction in the magnetic moment of Fe, thus the M_S . As shown in Fig. 3 (right panel), the M_S of the $\text{LaFe}_{13-x}\text{Si}_x$ compounds decreases from $\sim 25.4\mu_B/\text{f.u.}$ to $\sim 17.1\mu_B/\text{f.u.}$ as x increases from 1.1 to 2.7. A first-principles calculation¹⁴ indicated that the hybridization between the Fe 3d and Si 2p electrons and the density of state change below Fermi surface would be the reasons for Fe magnetic moment change and the character of magnetic transitions rapid change with x. In contrast, Co is a transition metal with a comparable magnetic moment to Fe ($\sim 1.7\mu_B$ vs $\sim 2\mu_B$). Its presence yields minor effects on magnetization. This explains the severe decrease in ΔS in Si-doped compounds. Different from Si and Co, interstitial hydrogen has no significant influence on phase transition. As a result, the large MCE of the hydrides persists as T_C increases. However, the hydrides are unstable at high temperature, and considerable hydrogen releases above 150 °C according to our experiments.¹⁵ Based on these, we can conclude that the best approach to get large MCE at high temperature is first enhancing the ΔS of $\text{La}_{1-y}\text{R}_y\text{Fe}_{13-x}\text{Si}_x$ as high as possible, via lowering the content of Si or increasing the content of R, then moving T_C to high temperature by partially replacing Fe with Co.

To summarize, the MCEs of the $\text{LaFe}_{13-x}\text{Si}_x$ compounds doped by magnetic rare earths (R=Ce, Pr, and Nd), transition metal (Co), and interstitial hydrogen are analyzed. It is found that varying the contents of R and Fe produces similar effects on the MCE, both of which cause a rapid decrease in ΔS along with T_C increasing. The ΔS - T_C relations thus obtained coincide with each other fairly well, which indicates the equivalence of substituting R for La and Fe for Si. In contrast, partially replacing Fe by Co leads to a significantly slow decrease in ΔS with T_C increasing. It is therefore a promising approach to maintain a large ΔS up to high temperatures. Although interstitial hydrogen can also keep up a large ΔS to high temperatures, the corresponding hydrides are unstable. It is proposed that the potential refrigerants made of $\text{LaFe}_{13-x}\text{Si}_x$ should have as low as possible Si content (or high R content) and proper Co content simultaneously.

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