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

L. Jia\textsuperscript{a)} J. R. Sun, J. Shen, Q. Y. Dong, J. D. Zou, B. Gao, T. Y. Zhao, H. W. Zhang, F. X. Hu, and B. G. Shen

State Key Laboratory for Magnetism, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

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The magnetocaloric effects (MCEs) of LaFe\textsubscript{13−}xSi\textsubscript{x}, compounds doped by magnetic rare earths (R=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 \( T_\text{C} \). The \( \Delta S \sim T_\text{C} \) 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 \( \Delta S \) with \( T_\text{C} \). It is therefore a promising approach to maintain a large \( \Delta S \) 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 \( \Delta S \) up to high temperatures, the corresponding hydrides are unfortunately unstable above 150 °C. Based on these analyses, the potential refrigerants made of LaFe\textsubscript{13−}xSi\textsubscript{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 LaFe\textsubscript{13−}xSi\textsubscript{x} intermetallics (entropy change \( \Delta S \sim 20 \text{ J/kg K} \), field change \( \Delta H = 5 \text{ T} \)).\textsuperscript{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, \( \Delta S \) grows from \( \sim 29 \text{ J/kg K} \) to \( \sim 34 \text{ J/kg K} \) after 20% La were substituted by Ce in LaFe\textsubscript{11.5}Si\textsubscript{1.3},\textsuperscript{3} and from \( \sim 13 \text{ J/kg K} \) to \( \sim 29 \text{ J/kg K} \) when the Si content in LaFe\textsubscript{13−}xSi\textsubscript{x} reduces from 1.8 to 1.3 (field change \( \Delta H = 5 \text{ T} \)).\textsuperscript{4,5} In contrast, replacing Fe by Co, though both are transition metals, can lead to a considerable reduction in \( \Delta S \). A typical result is the decrease in \( \Delta S \) from \( \sim 16.5 \text{ J/kg K} \) to \( \sim 13.5 \text{ J/kg K} \) when the Co content in LaFe\textsubscript{11,9}Co\textsubscript{0.1}Si\textsubscript{1.1} increases from 0.7 to 0.9.\textsuperscript{5} Differing from element substitution, the incorporation of interstitial hydrogen significantly affects \( T_\text{C} \) rather than \( \Delta S \). The Curie temperature can be evenly tuned between 195 and 323 K by simply adjusting the content of hydrogen in the compounds.\textsuperscript{5}

We noted that, despite the intensive work and excellent review paper\textsuperscript{7} on substitution effects, a careful analysis of the \( \Delta S \sim T_\text{C} \) relations for the LaFe\textsubscript{13−}xSi\textsubscript{x} family is still lacking. It has been found that the increase in \( \Delta S \) always occurs with a decrease in \( T_\text{C} \). It is therefore obvious that simply comparing the \( \Delta S \) produced by various element dopings without paying attention to the temperature where the \( \Delta S \) 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 \( \Delta S \sim T_\text{C} \) dependence of the LaFe\textsubscript{13−}xSi\textsubscript{x} family. Our work shows the equivalence of replacing La by magnetic rare earths and substituting Si by Fe, both of which produce similar \( \Delta S \sim T_\text{C} \) relations. The optimal approach to get a large MCE at high temperatures is the proper replacement of Fe with Co in the La\textsubscript{1−}xR\textsubscript{x}Fe\textsubscript{13−}xSi\textsubscript{x} compounds that have the lowest Si contents or the highest R contents.

The intermetallics with the nominal compositions LaFe\textsubscript{13−}xSi\textsubscript{x} (\( x = 1.3–2.6 \)), La\textsubscript{1−}xPr\textsubscript{x}Fe\textsubscript{13−}xCo\textsubscript{x}Si\textsubscript{y} (\( x = 1.5 \) and 1.8; \( y = 0–0.5 \)), La\textsubscript{1−}xNd\textsubscript{x}Fe\textsubscript{11.5}Si\textsubscript{1.5} (\( y = 0–0.3 \)), and La\textsubscript{0.8}Ce\textsubscript{0.2}Fe\textsubscript{11.7}Co\textsubscript{1.3}Si\textsubscript{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 LaFe\textsubscript{13−}xSi\textsubscript{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\textsubscript{13}-type structure.

All the magnetic measurements were performed on a superconducting quantum interference device magnetometer. Details for the calculation of \( \Delta S \) based on the Maxwell relation can be found elsewhere.\textsuperscript{1,8,9} Figures 1(a)–1(c) show the entropy changes in typical compounds: LaFe\textsubscript{13−}xSi\textsubscript{x} (\( x = 1.3–2.2 \)), La\textsubscript{1−}xPr\textsubscript{x}Fe\textsubscript{13−}xCo\textsubscript{x}Si\textsubscript{y} (\( x = 1.5, y = 0.05; z = 1.8, y = 0.3 \)), and La\textsubscript{0.8}Ce\textsubscript{0.2}Fe\textsubscript{11.7}Co\textsubscript{1.3}Si\textsubscript{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 \( T_\text{C} \) and a corresponding decrease in \( \Delta S \). A simple calculation gives the reduction in \( \Delta S \) from \( \sim 29 \text{ J/kg K} \) for \( x = 1.3 \) to \( \sim 7.3 \) J/kg K for \( x = 2.2 \) in the compounds LaFe\textsubscript{13−}xSi\textsubscript{x} (The spike-shaped

\textsuperscript{a)} Electronic mail: linjia.iphy@gmail.com.
The data presented are the peak values taken at the similar temperature that shows by an arrow. Similarly, the replacement of 70% La by Pr in LaFe$_{11+2}$Si$_{1.5}$, which is a typical compound showing a second-order phase transition, causes a scramble of the point from 1 to 2 along the $\Delta S$--$T_C$ curve (shown by an arrow). 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 La$_{1-y}$R$_y$Fe$_{13-x}$Si$_x$ coincide with that of LaFe$_{13-y}$Si$_x$. What of special interest is the reproduction of $\Delta S$--$T_C$ relation for LaFe$_{13-y}$Si$_x$ compounds, the details even, simply by varying $y$ in La$_{1-y}$R$_y$Fe$_{13-x}$Si$_x$. For example, the incorporation of 30% Pr in LaFe$_{11.5}$Si$_{1.5}$, which is a typical compound showing a second-order phase transition, causes a scramble of the point from 1 to 2 along the $\Delta S$--$T_C$ curve (shown by an arrow). Similarly, the replacement of 70% La by Pr in LaFe$_{11+2}$Si$_{1.5}$ moves the point from 3 to 4. Scattering of the $\Delta S$ below 195 K could be attributed to experimental errors.

A significantly different behavior is observed in the case of Co doping. Although the $\Delta S$ shows an approximately linear decrease with the increase in $T_C$, the $\Delta S$--$T_C$ slope is much smaller (~0.14 J/kg K$^2$). As a result, the large MCE at low temperature can be effectively maintained as $T_C$ increases. It can be seen from Fig. 2 that the $\Delta S$ value of La$_{10+2}$Co$_{0.2}$Fe$_{11+2}$Si$_x$ 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 $\Delta S$--$T_C$ curves for different compounds Pr$_{0.5}$La$_{0.5}$Co$_{0.2}$Fe$_{11+2}$Si$_x$ ($z=0.4$--1.0), LaFe$_{11+2}$Co$_{0.2}$Si$_{1.5}$ ($z=0.7$--0.9), and La$_{10+2}$Co$_{0.2}$Fe$_{11+2}$Si$_x$ ($z=0.4$--1.2). It actually means that the larger $\Delta S$ of the parent compound (without Co) is, the greater MCE of the derivative compound will be.

FIG. 1. Temperature-dependent entropy changes ($\Delta S$) of the compounds: (a) LaFe$_{13-y}$Si$_x$ ($x=1.3$--2.2), (b) La$_1-y$Pr$_y$Fe$_{13-x}$Si$_x$ ($x=1.5$, $y=0.5$; $x=1.8$, $y=0.3$), and (c) La$_{1-y}$Ce$_y$Fe$_{11+2}$Si$_x$ ($z=0.1$--1.2). Hatched area marks a crossover of the magnetic transition from first order to second order.
Different from the Si, R, and Co substitutions, the incorporation of interstitial hydrogen strongly affects $T_C$ rather than $\Delta S$. It is therefore the most promising approach to get large MCE at high temperatures. In Fig. 2 we show the $\Delta S$--$T_C$ relations for the LaFe$_{1.44}$Si$_{1.56}$H$_y$ hydrides obtained by Fujita et al.\textsuperscript{6} $\Delta S$ is $\sim 23$ 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.\textsuperscript{6} Although sometimes a visible $\Delta S$ reduction appears with the increase in $T_C$, for example, in La$_{1.0}$Pr$_{0.5}$Fe$_{1.44}$Si$_{1.56}$H$_y$, $\Delta S$ decreases from $30$ J/kg K ($\delta=0$) to $26$ J/kg K ($\delta=1.6$),\textsuperscript{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 LaFe$_{1.23}$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 domintative role of the Fe-Fe coupling. It is understandable from the great variation in $T_C$ under high pressures.\textsuperscript{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 La$_{1.44}$Pr$_{0.5}$Fe$_{1.44}$Si$_{1.56}$, obtained by Fujita et al.\textsuperscript{11} as a function of Pr content (left panel). The $M_s$ growth from $\sim 23$ $\mu_B$/f.u. to $\sim 25$ $\mu_B$/f.u. and the $T_C$ diminishment from $\sim 195$ to $\sim 180$ K are observed, corresponding to the variation in $y$ from 0 to 0.5. Compared with LaFe$_{1.23}$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 $\Delta T_C=15$ K and $\Delta M_s=1.6$ $\mu_B$/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 LaFe$_{1.23}$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 LaFe$_{1.23-x}$Co$_x$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 LaFe$_{1.23}$Si$_x$ compounds decreases from $\sim 25.4$ $\mu_B$/f.u. to $\sim 17.1$ $\mu_B$/f.u. as $x$ increases from 1.1 to 2.7. A first-principles calculation\textsuperscript{14} indicated that the hybridization between the Fe 3$d$ and Si 2$p$ 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 $\Delta S$ 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 temperatures, and considerable hydrogen releases above $150$ °C according to our experiments.\textsuperscript{15} Based on these, we can conclude that the best approach to get large MCE at high temperature is first enhancing the $\Delta S$ of La$_{1.7}$Pr$_{0.5}$Fe$_{1.23}$Si$_2$ 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 LaFe$_{1.23}$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 $\Delta S$ along with $T_C$ increasing. 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 significantly slow decrease in $\Delta S$ with $T_C$ increasing. It is therefore a promising approach to maintain a large $\Delta S$ up to high temperatures. Although interstitial hydrogen can also keep up a large $\Delta S$ to high temperatures, the corresponding hydrides are unstable. It is proposed that the potential refrigerants made of LaFe$_{1.23}$Si$_x$ should have as low as possible Si content (or high $R$ content) and proper Co content simultaneously.

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\begin{footnotesize}
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