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# Effects of interstitial H and/or C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$-based compounds

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La(Fe, Si)$_{13}$-based compounds have been considered as promising candidates for magnetic refrigerants particularly near room temperature. Herein we review recent progress particularly in the study of the effects of interstitial H and/or C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$ compounds. By introducing H and/or C atoms, the Curie temperature $T_C$ increases notably with the increase of lattice expansion which makes the Fe 3$d$ band narrow and reduces the overlap of the Fe 3$d$ wave functions. The first-order itinerant-electron metamagnetic transition is conserved and the MCE still remains high after hydrogen absorption. In contrast, the characteristic of magnetic transition varies from first-order to second-order with the increase of C concentration, which leads to remarkable reduction of thermal and magnetic hysteresis. In addition, the introduction of interstitial C atoms promotes the formation of NaZn$_{13}$-type (1:13) phase in La(Fe, Si)$_{13}$ compounds, and thus reducing the annealing time significantly from 40 days for LaFe$_{11.7}$Si$_{1.3}$ to a week for LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$. The pre-occupied interstitial C atoms may depress the rate of hydrogen absorption and release, which is favorable to the accurate control of hydrogen content. It is found that the reduction of particle size would greatly depress the hysteresis loss and improve the hydrogenation process. By the incorporation of both H and C atoms, large MCE without hysteresis loss can be obtained in La(Fe, Si)$_{13}$ compounds around room temperature, for instance, La$_{0.7}$Pr$_{0.3}$Fe$_{11.5}$Si$_{1.5}$C$_{0.2}$H$_{1.2}$ exhibits a large $|\Delta S_M|$ of 22.1 J/(kg·K) at $T_C$ = 321 K without hysteresis loss for a field change of 0−5 T.

**H atom, C atom, La(Fe, Si)$_{13}$**

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## 1 Introduction

The magnetocaloric effect (MCE) is an intrinsic property of magnetic material, which is usually characterized by magnetic entropy change ($\Delta S_M$) and/or adiabatic temperature change ($\Delta T_{ad}$) upon the variation of magnetic field. In recent years, magnetic refrigeration based on the MCE, particularly near room temperature, has attracted considerable research attention because of environmental degradation and energy shortage. In comparison with the conventional vapor compression refrigeration, magnetic refrigeration technique exhibits great advantages in many aspects [1−6] such as being environmentally friendly. Solid magnetic refrigerants and water-based heat transfer medium eliminate the seriously environmental issues as caused by Chloro Flouro Carbon (CFC) refrigerants. Magnetic refrigeration is also energy efficient. The efficiency of Carnot cycle for conventional gas refrigeration is only 5%–10%, while magnetic refrigeration could reach 30%–60% of Carnot efficiency. Lastly, the stable reliability in that the magnetic refrigerator does not need a compressor so that it could have less moving parts, lower noise and longer working life. Therefore,

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magnetic refrigeration has been considered as a new green refrigeration technique which has a promising development potential and wide use for future applications.

As the core part of magnetic refrigeration technique, the MCE of magnetic refrigerant has a great impact on the efficiency of magnetic refrigerator. Thus, the successful development of the magnetic refrigerants with great magnetocaloric properties is critical to the application and commercialization of magnetic refrigeration. Since the MCE of iron was first discovered by Warbury in 1881 [7] researchers have been exploring suitable magnetic refrigerants with great MCE. In the early 1930s, Giauque and MacDougall [8] first attained the temperatures below 1 K by adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$. Later, nuclear demagnetization was successfully used to achieve an ultralow temperature of ~$10^{-6}$ K, and now magnetic refrigeration has become an important technology to obtain ultralow temperature.

Although the magnetic refrigeration has great success in the low temperature range, it has been in slow development around ambient temperature because of the lack of suitable room temperature magnetocaloric materials. The first room temperature magnetic refrigeration was performed by Brown [9] through using rare earth Gd (Curie temperature $T_C$ = 293 K) which was instrumental in the research progress of room temperature magnetic refrigeration. Later, Pecharsky and Gschneidner [10] reported the MCE of $Gd_5Si_2Ge_2$ near room temperature ($T_C$ = 276 K), and it was found that $Gd_5Si_2Ge_2$ exhibited a large $|\Delta S_M|$ of ~18 J/(kg·K) for a field change of 0–5 T, which was much higher than that of Gd (~9.7 J/(kg·K)). This large MCE is attributed to the first-order magnetic transition from a paramagnetic monoclinic to a ferromagnetic orthorhombic symmetry with the variation of temperature. Since then, a great number of magnetic materials with large MCEs around room temperature, such as $La_{1-x}Ca_xMnO_3$ [11,12], La(Fe, Si)$_{13}$ [13–16], MnAs [17], MnFe(P,As) [18], and Heusler alloys [19–21], have been extensively investigated for their potential application of room temperature magnetic refrigeration.

Among these materials, La(Fe, Si)$_{13}$-based compounds with cubic $NaZn_{13}$-type (1:13) structure have been considered as favorable magnetic refrigerants because of the fact that they each have a large MCE, large refrigerant capacity (*RC*), and high thermal conductivity. In addition, their compositions with high Fe content make La(Fe, Si)$_{13}$ compounds the materials with much lower price than other rare earth intermetallic compounds such as $Gd_5$(Si, Ge)$_4$. Moreover, La(Fe, Si)$_{13}$ compounds are preferable because these compounds do not contain toxic elements like MnAs or MnFe (P, As) compounds. However, there are still some serious issues, such as prolonged preparation, low working temperature, large thermal and magnetic hysteresis, and poor mechanical properties, hindering the practical application of La(Fe, Si)$_{13}$ compounds in a magnetic refrigerator.

It is reported that melt spinning technique may be an effective way to reduce the annealing time significantly [22,23]. However, the melt spun La(Fe, Si)$_{13}$ ribbons are usually thinner than the minimum size (~0.2 mm) of practical magnetic refrigerants, and exhibit poor mechanical properties [24]. Our recent study shows that introduction of interstitial C atoms promotes the formation of 1:13 phsae in La(Fe, Si)$_{13}$ compounds, and results in the significant shortening of the annealing time [25]. Concurrently, it is also found that the rate of hydrogen absorption and release can be lowered after carbonization, which is desirable to an accurate control of hydrogen content [26]. In addition, it has been noted that the partial substitution of Fe by Co atoms leads to an increase of the Curie temperature $T_C$ and a notable decrease of hysteresis loss. However, the MCE is also lowered because of the weakening of first-order magnetic transition [27,28]. Conversely, the $T_C$ of La(Fe, Si)$_{13}$ compound can be enhanced considerably by introducing H and/or C atoms, while the MCE still maintains at a high value [29,30].

Herein we give a brief review of our recent progress in the effect of interstitial H and/or C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$-based compounds.

## 2 Effects of interstitial H atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$-based compounds

Although La(Fe, Si)$_{13}$ compounds exhibit large MCE around the ordering temperature $T_C$, it is found that $T_C$ of La (Fe, Si)$_{13}$ is usually lower than 210 K, which is not close to ambient temperature [14]. From the viewpoint of practical application, it is highly desirable to enhance the working temperature of La(Fe, Si)$_{13}$ to around room temperature. Chen et al. [31] found that $T_C$ can be increased from 195 K of $LaFe_{11.5}Si_{1.5}$ to 288 K of $LaFe_{11.5}Si_{1.5}H_{1.3}$ by introducing interstitial H atoms. The increase of $T_C$ is attributed to the lattice expansion caused by interstitial H atoms, which permitted the Fe 3*d* band to narrow and thereby reduced the overlap of the Fe 3*d* wave functions. Unlike the introduction of Co which could depress the itinerant-electron metamagnetic (IEM) transition and change the nature of magnetic transition from first-order to second-order, the IEM transition is still conserved and so the MCE remains high after hydrogen absorption. By carefully regulating the hydrogen concentration, a series of $LaFe_{11.5}Si_{1.5}H_y$ compounds were obtained to exhibit continuous $T_C$ and large MCE values in a wide temperature range of 195–340 K [30]. Figure 1(a) shows the temperature dependences of magnetic entropy change $\Delta S_M$ for $LaFe_{11.5}Si_{1.5}H_y$ compounds with different H contents under a field change of 5 T. It can be noted that the maximum values of $|\Delta S_M|$ are as large as 16.8–20.5 J/(kg·K), greatly exceeding that of Gd by 70%–100% ($|\Delta S_M|$ = 9.8 J/(kg·K) under $\Delta\mu_0 H$ = 0–5 T, $T_C$ = 293 K). Chen et al. [30]

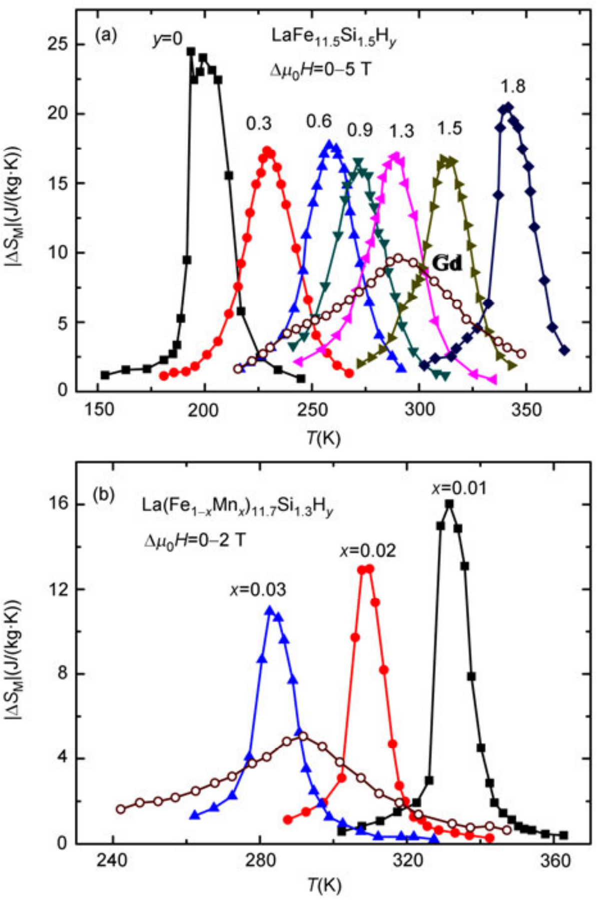

**Figure 1** (Color online) (a) Temperature dependences of $\Delta S_M$ for LaFe$_{11.5}$Si$_{1.5}$H$_y$ compounds in comparison with that of Gd under a field change of 5 T. (b) Temperature dependences of $\Delta S_M$ for La(Fe$_{1-x}$Mn$_x$)$_{11.7}$Si$_{1.3}$H$_y$ compounds in comparison with that of Gd under a field change of 2 T.

also found that the IEM transition in the hydride is less steep than that in parent compound, leading to a slower change in $M$-$T$ curve, so that $|\Delta S_M|$ is lower than that of parent compound.

Wang et al. [32] studied the magnetic properties and magnetic entropy change of La(Fe$_{1-x}$Mn$_x$)$_{11.7}$Si$_{1.3}$H$_y$ compounds. It was found that the $T_C$ values of hydrides are 336 K, 312 K and 287 K for $x$ = 0.01, 0.02 and 0.03, respectively, indicating that the substitution of Fe by Mn lowered the transition temperature. Therefore, the introduction of Mn has been suggested as an effective method to tune the $T_C$ of hydrides to around room temperature. The first-order IEM transition becomes weaker but still remains with the increase of Mn content, implying that the density of states (DOS) curve just below the Fermi level, which is closely associated with the origin of IEM transition, is hardly altered after hydrogenation, thus retaining the first-order IEM transition. This result is consistent with the studies of Fujita et al [33]. The maximum $|\Delta S_M|$ values of La(Fe$_{1-x}$Mn$_x$)$_{11.7}$Si$_{1.3}$H$_y$ compounds as shown in Figure 1(b) are 16.0, 13.0, and 11.0 J/(kg·K) under a magnetic field change of 2 T for $x$ = 0.01, 0.02, and 0.03, respectively, notably higher than that of Gd ($|\Delta S_M|$ = 4.5 J/(kg·K) under $\Delta\mu_0H$ = 0–2 T, $T_C$ = 293 K).

It is known that the $T_C$ of La(Fe, Si)$_{13}$ compound is primarily dominated by Fe-Fe coupling. The systematic studies on the effects of pressure and hydrogenation reveal that the $T_C$ of La(Fe, Si)$_{13}$ hydride increases largely with the increase of H content because of the lattice expansion, whereas the high pressure causes a lattice contraction, thus leading to the remarkable decrease of $T_C$ [34]. Figure 2 shows the dependences of $T_C$ on lattice constant for the cases of the hydrogenised and pressed LaFe$_{11.5}$Si$_{1.5}$ and Ce-doped LaFe$_{11.5}$Si$_{1.5}$. It can be seen clearly that the slope of $T_C$-$a$ relations are effectively the same in the cases of hydrogenating and Ce substitution (~1510 K/Å) but much larger under pressure (~2450 K/Å). This result indicates that the Fe-Fe distance has a dominant role in controlling the magnetic coupling of LaFe$_{11.5}$Si$_{1.5}$, and that the interstitial hydrogen does not affect the electronic structure of these compounds.

It has been reported that partially replacing La with other light rare earth elements such as Ce [35], Pr [36] and Nd [37] in La(Fe, Si)$_{13}$ compounds could enhance the MCE but also result in a decrease of $T_C$ and an increase of hysteresis loss, which is unfavorable to practical applications. Zhao et al. [38] found that the $T_C$ of La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ compounds can be adjusted from 189 to 317 K by increasing the hydrogen content from 0 to 1.6. Moreover, the introduction of interstitial H atoms into La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$ compounds weakens the first-order IEM transition, leading to a remarkable reduction of thermal and magnetic hysteresis loss. Figure 3 shows the temperature dependences of $\Delta S_M$ and hysteresis loss for La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ compounds, where hysteresis loss is defined as the enclosed area between the ascending and descending magnetization curves. The maximum $|\Delta S_M|$ values of La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ compounds for a magnetic field change of 0–5 T are 26.3, 24.1, and 22.1 J/(kg·K), with the maximum hysteresis losses of 17.8, 11.7,

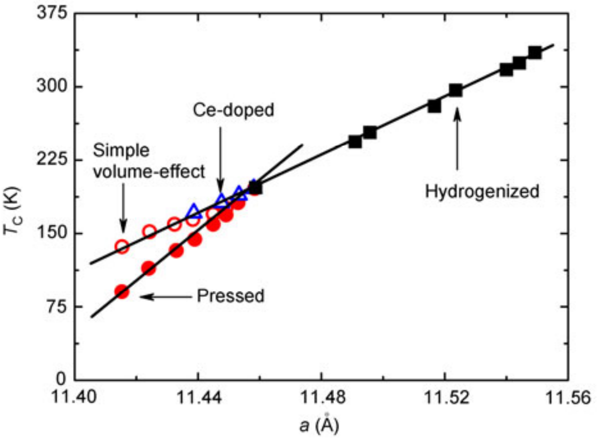

**Figure 2** (Color online) Variations of $T_C$ with lattice constant for the hydrogenised and pressed LaFe$_{11.5}$Si$_{1.5}$ and Ce-doped LaFe$_{11.5}$Si$_{1.5}$. Empty circles denote the pure volume effects while the solid circles indicate the as-detected $T_C$ under pressure.

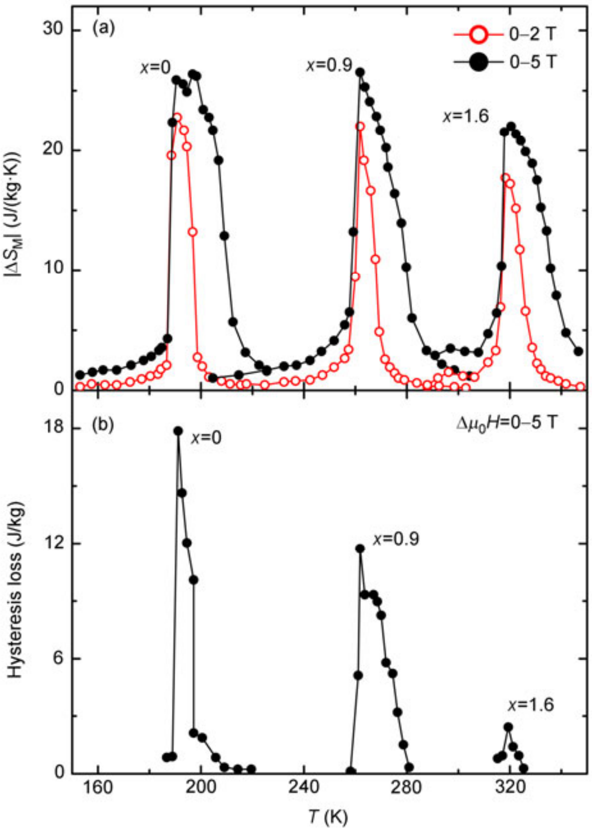

**Figure 3** (Color online) (a) Temperature dependences of $\Delta S_M$ under the magnetic field changes of 0–2 and 0–5 T, respectively, and (b) temperature dependences of the hysteresis loss under a magnetic field change of 0–5 T for $La_{0.5}Pr_{0.5}Fe_{11.4}Si_{1.6}H_x$ compounds.

and 2.3 J/kg for $x$ = 0, 0.9, and 1.6, respectively. It can also be noted that $La_{0.5}Pr_{0.5}Fe_{11.4}Si_{1.6}H_{1.6}$ compound exhibited a large value of effective refrigerant capacity ($RC_{eff}$) of 351 J/kg for a field change of 0–5 T, which is obtained by subtracting hysteresis loss from refrigerant capacity $RC$.

The hydrogenation, crystal structure, and magnetic properties of La(Fe, Si)$_{13}$ hydrides and deuterides have been investigated in order to investigate the isotope effect on the magnetism [39]. The X-ray diffraction (XRD) analyses reveal that both hydride and deuteride retain the $NaZn_{13}$-type structure and the lattice expands with the increase of H(D) content. It is found that the Curie temperature increases significantly with the introduction of H(D) atoms at a rate of ~94 K per H(D) atom. No isotope effect is observed by comparing the results of hydrides and deuterides, suggesting that the strong interplay between magnetism and lattice in La(Fe, Si)$_{13}$ system results only from the magnetovolume effect. It is interesting to note that the middle H(D) absorption samples, whose values of $T_C$ are all around room temperature (286–295 K), are detected to be biphase at room temperature, whereas only single phase is observed in the samples with low and high H(D) content. Figure 4 shows the continuous four runs of differential scanning calorimetry (DSC) measurements for $LaFe_{11.83}Si_{1.17}H_{1.16}$ compound. It can be seen that this biphasic sample shows two endothermic peaks (at 290 K and 310 K) in first heating run, but these peaks merge into a single peak at 295 K at the third and fourth cycles. This fact suggests that the biphasic samples could transform into monophasic samples by heating them up to 353 K on cycling, further implying that these hydrides and deuterides with intermediate absorption concentration are stabilized at higher temperature, but metastable at room temperature since the real thermodynamic equilibrium is two-phase separation. Similar phenomenon is also reported by Krautz et al. [40] and Zimm et al. [41].

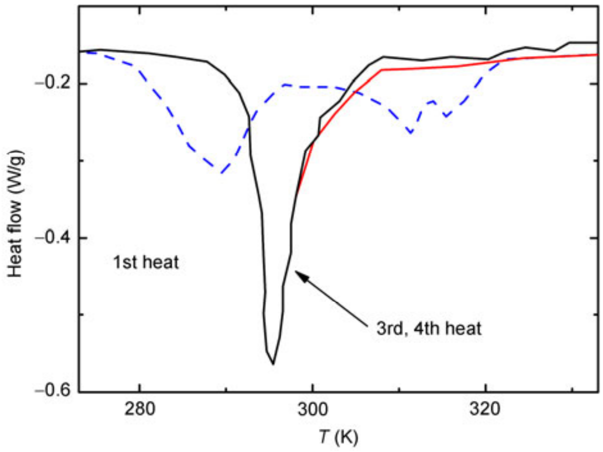

**Figure 4** (Color online) The continuous four runs of differential scanning calorimetry (DSC) measurements for $LaFe_{11.83}Si_{1.17}H_{1.16}$ compound.

Recently, Bao et al. [42] prepared $La_{0.7}(Ce, Pr, Nd)_{0.3}Fe_{11.6}Si_{1.4}$ compounds by using La-Ce-Pr-Nd industrial mischmetal with low purity (99wt.%) and natural ratio of rare earth ($R$) in minerals (La/$R$~28.27wt.%, Ce/$R$~50.46 wt.%, Pr/$R$ ~ 5.55wt.%, Nd/$R$ ~ 15.66wt.%). The XRD patterns confirmed that the impurities in the industrial mischmetal do not impair the formation of $NaZn_{13}$-type structure. However, the ratio of 1:1:1 impurity phase in $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ compound is nearly twice that in $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}$, suggesting that an incomplete peritectic reaction probably occurs during heat treatment. It is also noteworthy that the $T_C$ (~169 K) of $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ is slightly higher than that (~163 K) of $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}$. Higher $T_C$ is caused by the stronger Pr-Fe and Nd-Fe ferromagnetic couplings in the $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ compound based on mischmetal. Incorporation of interstitial H atoms further enhances the $T_C$ to around room temperature (~314 K) for $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}H_{1.6}$. Figures 5(a) and 5(b) show the magnetization isotherms of $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ and the associated hydride exhibiting increasing and decreasing magnetic field. The magnetic hysteresis decreases remarkably after hydrogen absorption, which is attributed to the change of distribution of grain boundaries, the reduction of internal strain, and the possible change of band structure. The maximum values of effective $|\Delta S_M|$ (not the fictitious spike but the high plateau value, see Figures

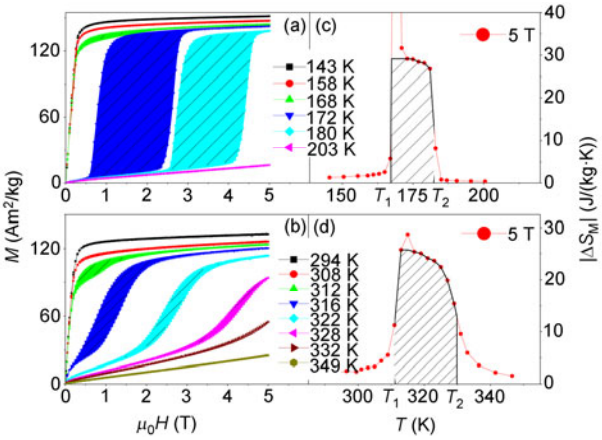

**Figure 5** (Color online) (a) and (b) Magnetization isotherms of $La_{0.7}$(Ce, Pr, Nd)$_{0.3}$$Fe_{11.6}Si_{1.4}$ and its hydride with increasing and decreasing magnetic field, where the shadow area indicates the hysteresis loss in a field cycle. c) and (d) Temperature dependence of $\Delta S_M$ for the corresponding samples under a field change of 0–5 T.

5(c) and 5(d)) are 29.1 and 25.4 J/(kg·K) under a field change of 5 T for $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ and its hydride. Moreover, the $RC_{eff}$ increases largely by ~128% from 166 J/kg for $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}$ to 379 J/kg for $La_{0.7}(Ce,Pr,Nd)_{0.3}Fe_{11.6}Si_{1.4}H_{1.6}$ because of the remarkable reduction of hysteresis loss.

## 3 Effects of interstitial C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$-based compounds

A critical drawback of hydrogenation technique is that the hydrides usually are unstable and would thus desorb hydrogen when the temperature is above 150°C [29,43]. Chemically stable $LaFe_{11.6}Si_{1.4}C_x$ interstitial compounds were prepared by solid-solid phase reaction, that is, arc melting a Fe—C intermediate alloy with La, Fe, and Si elements [29]. It is found that the 1:13 structure keeps unchanged after the introduction of C atoms, except for the presence of minor amounts of $\alpha$-Fe phase when $x \geqslant 0.6$. Moreover, the introduction of interstitial C atoms also had led to lattice expansions of 0.29%, 0.75%, and 0.93% for $x = 0.2$, 0.4, and 0.6, respectively. This lattice expansion further results in the remarkable enhancement of $T_C$ from 195 K for $x = 0$ to 250 K for $x = 0.6$ because of the increase of exchange interaction between Fe atoms by reducing the overlap of Fe 3d wave functions. Unlike hydrogenation which hardly affects the first-order IEM transition, the characteristic of magnetic transition varies from first-order to second-order with the increase of C concentration, and thus leading to the notable decrease of $\Delta S_M$. Figure 6 shows the temperature dependences of $\Delta S_M$ for $LaFe_{11.6}Si_{1.4}C_x$ compounds under a magnetic field change of 0–5 T. The maximum values of $|\Delta S_M|$ are 24.8, 24.2, 18.8, and 12.1 J/(kg·K) for $x = 0$, 0.2, 0.4, and 0.6, respectively. The decrease of $\Delta S_M$ for $x > 0.4$ could be attributed to the weakening of first-order IEM transition and the presence of impurity phase. Similar results have also been observed in $LaFe_{11.5}Si_{1.5}C_x$ interstitial compounds [44].

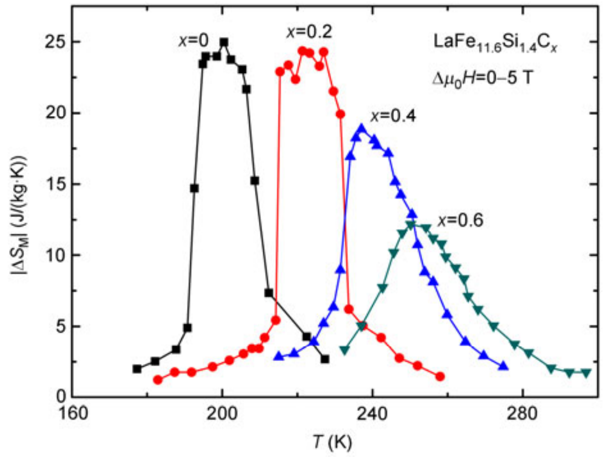

**Figure 6** (Color online) Temperature dependences of $\Delta S_M$ for $LaFe_{11.6}Si_{1.4}C_x$ compounds under a magnetic field change of 0–5 T.

Shen et al. [45] studied the effects of interstitial C atoms on the magnetic properties and magnetic entropy change of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds. The crystal lattice parameter was found to increase from 11.444 to 11.482 Å with $x$ increasing form 0 to 0.3, thus leading to the increase of $T_C$ from 183 K for $x = 0$ to 211 K for $x = 0.3$. Furthermore, the first-order magnetic transition was weakened because of the introduction of C atoms, which resulted in the reduction of thermal and magnetic hysteresis. The maximum hysteresis loss decrease largely from 94.8 J/kg for $x = 0$ to 23.1 J/kg for $x = 0.3$ (see inset of Figure 7). The maximum values of $|\Delta S_M|$ as shown in Figure 7 are obtained to be 30.2 and 25.2 J/(kg·K) under a field change of 0–2 T, 32.4 and 27.6 J/(kg·K) under a field change of 0–5 T for samples with $x = 0$ and 0.3, respectively. It can be seen that the $\Delta S_M$ exhibits a slight reduction because of the weakening of first-order magnetic transition, but still remains significantly larger than those of the Pr- and C-free compounds. Zhang et al. [46] reported similar results by investigating the effects of Ce and C atoms on $T_C$, the magnetic entropy change, and the hysteresis loss in $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds. It is revealed that the partial substitution of Ce for La caused the value of $T_C$ to decrease from 195 K for $x = 0$, $y = 0$ to 179 K for $x = 0.2$, $y = 0$, while the introduction of interstitial C atoms enhanced $T_C$ largely from 179 K for $x = 0.2$, $y = 0$ to 246 K for $x = 0.2$, $y = 0.4$. It can be noted that the $T_C$ increased linearly with lattice parameter $a$ at a rate of ~1132 K/Å for the studied samples, no matter how the phase volume was modified. The maximum values of magnetic hysteresis loss of $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_y$ are 158, 30, and 0 J/kg for $y = 0$, 0.2, and 0.4, respectively. This significant reduction of magnetic hysteresis is attributed to the fact that the

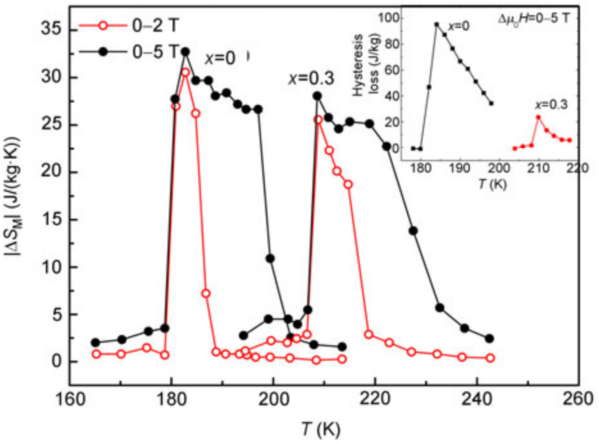

**Figure 7** (Color online) Temperature dependences of $\Delta S_M$ for $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds under the magnetic field changes of 0–2 and 0–5 T, respectively, where the inset shows the temperature dependences of the hysteresis loss for $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ under a magnetic field change of 0–5 T.

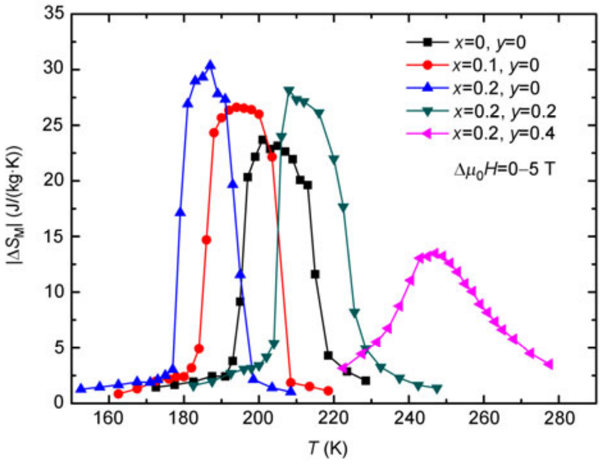

**Figure 8** (Color online) Temperature dependences of $\Delta S_M$ for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds under a magnetic field change of 0–5 T.

first-order IEM transition is weakened after carbonization. Figure 8 shows the temperature dependences of $\Delta S_M$ for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds under a magnetic field change of 0–5 T. It is observed that the $\Delta S_M$ increases with the substitution of Ce for La because of the strengthening of IEM transition, but decreases with the introduction of C atoms due to the weakening of first-order magnetic transition. The maximum $|\Delta S_M|$ of $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$ still attains 28.0 J/(kg·K) at $T_C$ = 207 K, which is larger than that (23.7 J/(kg·K) at $T_C$ = 195 K) of the Ce- and C- free compound. Moreover, the effective refrigerant capacity $RC_{\text{eff}}$ of $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$ is 420 J/kg for a field change of 0–5 T, which is also larger than that (385 J/kg) of the Ce- and C-free parent compound. This study reveals that the enhancements of both $T_C$ and MCE can be achieved simultaneously in $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds by adjusting the concentrations of Ce and C atoms appropriately.

As mentioned above, the partially replacement of Fe with Co has been considered as an effective method to tune the $T_C$ of La(Fe, Si)$_{13}$ compounds to around room temperature [27,43,47]. Therefore, the $T_C$ values of $La_{0.5}Pr_{0.5}Fe_{11.5-x}Co_xSi_{1.5}C_{0.2}$ compounds are enhanced from 206 K to 295 K by increasing the Co concentration from 0 to 0.8 [48]. The addition of Co and C ensures the phase transition in $La_{0.5}Pr_{0.5}Fe_{11.5-x}Co_xSi_{1.5}C_{0.2}$ change from first-order to second-order, and thus the magnetic hysteresis loss reduces remarkably from 23.6 J/kg for $x$ = 0 to near zero for $x$ = 0.2. Although the values of $\Delta S_M$ decrease with the increase of Co concentration because the IEM transition is suppressed by the substitution of Co atoms, the maximum $|\Delta S_M|$ values of $La_{0.5}Pr_{0.5}Fe_{10.7}Co_{0.8}Si_{1.5}C_{0.2}$ still reach 5.8 and 11.6 J/(kg·K) at 295 K for the magnetic field changes of 0–2 T and 0–5 T, respectively, which are higher than those of Gd (5.0 and 9.7 J/(kg·K) for field changes of 0–2 T and 0–5 T). The maximum $RC_{\text{eff}}$ value of $La_{0.5}Pr_{0.5}Fe_{10.7}Co_{0.8}Si_{1.5}C_{0.2}$ is 386 J/kg for a field change of 0–5 T, which is comparable to or much larger than those of some magnetocaloric materials in a similar temperature range, such as $LaFe_{11.0}Co_{0.9}Si_{1.1}$ (~350 J/kg at 294 K) [28], $LaFe_{11.0}Co_{0.8}Si_{1.2}$ (~345 J/kg at 290 K) [49], and $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ (355 J/kg at 305 K) [50].

Large thermal and magnetic hysteresis often accompany the MCE because of the first-order nature of magnetic transition, which is harmful to the refrigeration efficiency in magnetizing-demagnetizing cycles. Lyubina et al. [51] found that the La(Fe, Si)$_{13}$ system with porous architecture exhibited low magnetic hysteresis in comparison with bulk samples, and this was attributed to partial removal of grain boundaries that restrain volume expansion. Recently, Hu et al. [52] reported on the particle size dependent hysteresis loss in $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ first-order systems. Figure 9 shows the magnetization isotherms upon field increase and decrease and the temperature dependence of hysteresis loss for bulk (2.7 mg, size <1 mm×1 mm×1 mm) and small particle (20–50 μm). It can be seen that the maximum hysteresis loss decreases remarkably from 98.4 J/kg for bulk to 38.8 J/kg for small particles with sizes in a range of 20–50 μm. The reduced ratio is as high as ~61%, and such a reduction is ascribed to the notably increased surface area of sample and the partially removed internal strain and grain boundaries. Although the $\Delta S_M$ value decreases slightly with reduction of particle size, the $RC_{\text{eff}}$ increases from 410 J/kg for bulk to 460 J/kg for small particle because of the notable reduction of hysteresis loss. However, the particle size of materials can not be reduced endlessly. It is found that the sample may lose stability and $\Delta S_M$ decreases largely when the size is below a limitation of 10 μm.

## 4 Effects of both H and C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$-based compounds

In order to find out the key factors that govern the magnetic

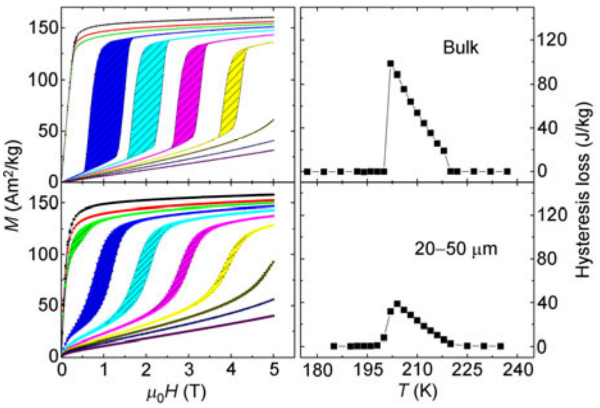

**Figure 9** (Color online) Magnetization isotherms of $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ with increasing and decreasing magnetic field, and the temperature dependences of hysteresis loss for bulk sample (2.7 mg, size <1 mm×1 mm×1 mm) and small particle (20–50 μm), respectively.

coupling in La(Fe, Si)$_{13}$ compounds, Jia et al. [53] performed a comprehensive study on the atomic structure of La(Fe, Si)$_{13}$ compounds with or without interstitial H and/or C atoms. The incorporation of interstitial atoms caused a lattice expansion of the compounds while the 1:13 structure symmetry still remained unchanged. Accompanied with the lattice expansion, Fe—Fe bond exhibited a concomitant variation. Four of the five Fe—Fe bonds showed a tendency to expand, and the shortest inter-cluster bond presented the largest elongation of ~2.53% as H concentration increases from 0 to 2 for $LaFe_{11.5}Si_{1.5}H_x$. In contrast, the longest Fe—Fe bond reduced considerably (–0.53%). It is noteworthy that increase in Ce content produced effectively the same result on Fe—Fe bonds as the decrease of interstitial content, though interstitial atoms occupied different crystallographic sites from rare-earths. The Fe—Fe bond length varies with lattice constant, and then a linear increase of $T_C$ with $a$ were observed at a rate of ~1779 K/Å in $LaFe_{11.5}Si_{1.5}H_x$/$La_{1-x}Ce_xFe_{11.5}Si_{1.5}$ and 1089 K/Å in $LaFe_{11.5}Si_{1.5}C_x$ (see Figure 10). Thus the influence of interstitial H and/or C atoms on magnetic properties of La(Fe, Si)$_{13}$ compound is considered to be dominated by the change of the shortest Fe—Fe bond.

It has been found that the $T_C$ of La(Fe, Si)$_{13}$ compound can not be tuned to room temperature by only introducing C atoms. In this context, Zhang et al. [25] studied the effects of both C and H atoms on the phase formation, the hysteresis loss, and MCE of La(Fe, Si)$_{13}$ compounds. It is interesting to note that the annealing time is significantly reduced from 40 days for $LaFe_{11.7}Si_{1.3}$ to a week for $LaFe_{11.7}Si_{1.3}C_{0.2}$, suggesting that the introduction of interstitial C atoms promotes the formation of 1:13 phase in La(Fe, Si)$_{13}$ compound. The $T_C$ can be further tuned from 212 K for $LaFe_{11.7}Si_{1.3}C_{0.2}$ to around room temperature of 320 K for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ by hydrogen absorption. The first-order magnetic transition was strongly suppressed after carbonization and hydrogenation, thus leading to a large reduction of magnetic hysteresis loss from 41 J/kg for $LaFe_{11.7}Si_{1.3}$ to 5.3 J/kg for $LaFe_{11.7}Si_{1.3}C_{0.2}$ and 1.5 J/kg for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$. Figure 11 shows the temperature dependences of $\Delta S_M$ for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ under magnetic field changes of 0–2 and 0–5 T, respectively. It is found that $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ still retains relatively large $|\Delta S_M|$ values of 13.8 and 19.0 J/(kg·K) around room temperature for the field changes of 0–2 and 0–5 T, respectively. This large reversible MCE under a low field change of 0–2 T is advantageous to practical applications since a magnetic field of 2 T can be provided by a permanent magnet.

Another benefit of introducing C atoms is that the rates of hydrogen absorption and release can be lowered after carbonization, which is favorable to an accurate control of hydrogen content [26]. Figure 12(a) shows the kinetic curves of hydrogen absorption for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ compounds under 0.12 MPa hydrogen pressure at 623 K. It is found that the absorbing process is completed in about 20 min for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ while it proceeds up to 3 h for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$. The variations

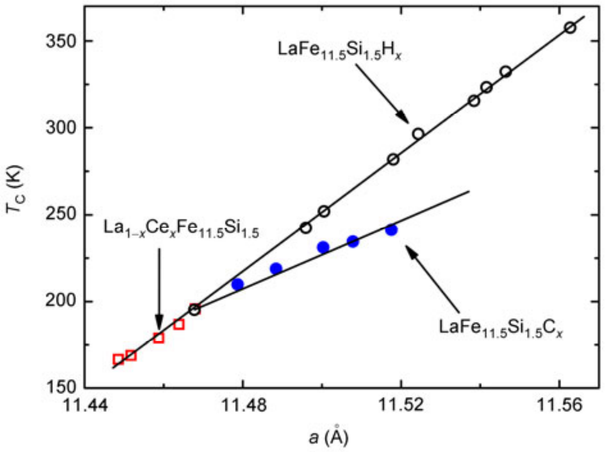

**Figure 10** (Color online) Variations of $T_C$ with lattice constant for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$ ($x$ = 0–0.4), $LaFe_{11.5}Si_{1.5}H_x$ ($x$ = 0–2), and $LaFe_{11.5}Si_{1.5}C_x$ ($x$ = 0–0.5) compounds.

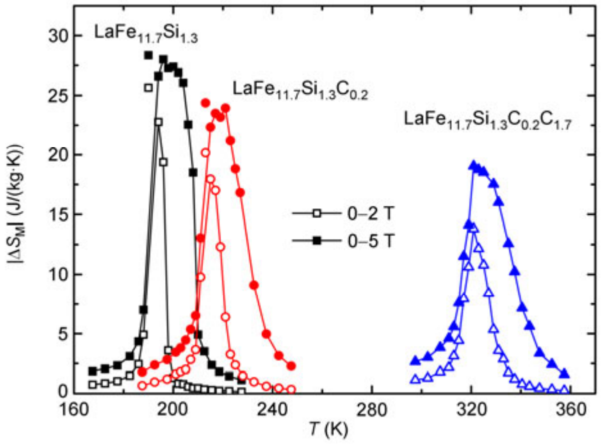

**Figure 11** (Color online) Temperature dependences of $\Delta S_M$ for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ under the magnetic field changes of 0–2 and 0–5 T, respectively.

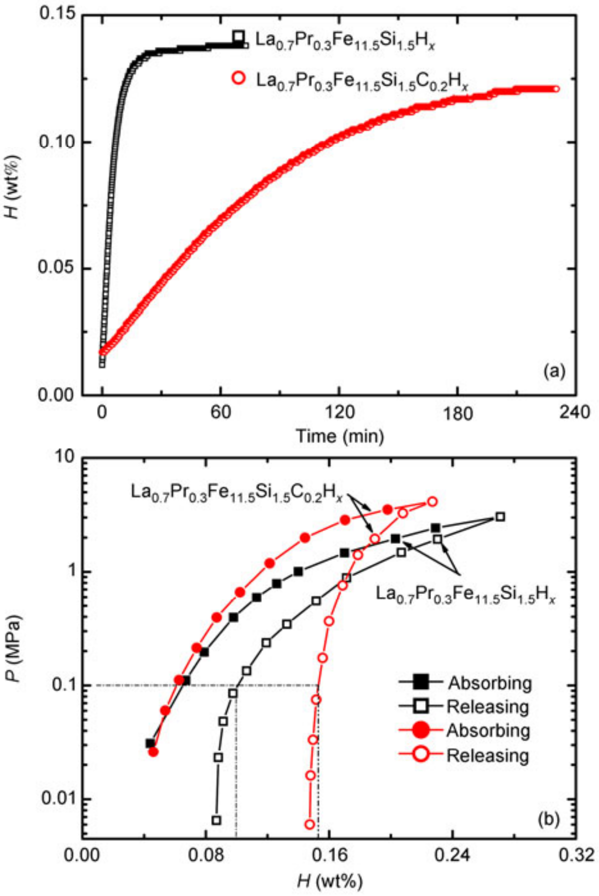

**Figure 12** (Color online) (a) Kinetic curves of hydrogen absorption for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$ compounds under a 0.12 MPa hydrogen pressure at 623 K. (b) Variations of hydrogen content with pressure for these samples measured at 623 K in absorbing and releasing processes.

of hydrogen content with pressure for these samples are shown in Figure 12(b). For the carbon-free compound, the absorbing and releasing curves are relatively close to each other, and about 0.097 wt.% hydrogen (~0.8 H per formula unit) is residual after hydrogen releasing. In contrast, the releasing process lags behind the absorbing process for $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}$, and about 0.153 wt.% hydrogen (~1.2 H per formula unit) is remnant. This result indicates that the addition of interstitial C atoms not only slows down hydrogen absorbing but also prevents hydrogen from being released. The possible reason is that the pre-occupied interstitial C atoms distort the local lattice and may lead to the blocking of the diffusion paths, thus depressing the rates of the hydrogen absorption and release. $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{1.2}$ exhibits a large $|\Delta S_M|$ value of 22.1 J/(kg·K) at $T_C$ = 321 K without hysteresis loss for a field change of 0–5 T, thereby making it a promising candidate for magnetic refrigeration near room temperature.

Furthermore, the influence of particle size on the hydrogenation of La(Fe, Si)$_{13}$ compounds has been investigated systematically [54]. The bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ was crushed into small particles (size < 1.5 mm) and then annealed in a hydrogen atmosphere of 0.2 MPa at 623 K for 6 h. After hydrogenation, these particles were further divided into three different size ranges: big size (0.6–1.5 mm), middle size (0.3–0.6 mm), and small size (0–0.3 mm). Three particles of each size were randomly selected and measured to investigate the homogeneity of the hydrogen absorption. From Figure 13 it can be seen that the average $T_C$ increases largely from 240 K for big size to 308.5 K for small size with the reduction of particle size. The enhancement of $T_C$ is attributed in that the surface area of sample becomes larger with the decrease of particle size, so that more hydrogen atoms could enter into the crystal structure easily. In addition, it is also noted that the temperature span of $T_C$ decreased from 30 K to 9 K with the reduction of particle size and size range, suggesting that small particle size and narrow size range may improve the homogeneity of hydrogen distribution. The maximum $|\Delta S_M|$ values of small $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ reach 14.4 and 18.6 J/(kg·K) around room temperature for the magnetic field changes of 0–2 T and 0–5 T, respectively, and they are still higher than those of some magnetocaloric materials in a similar temperature range. In addition, the hydrogen-saturated $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ behaves great stability under high pressure (1.36 GPa) and this result is conducible to further processing and applications of La(Fe, Si)$_{13}$ hydrides.

## 5 Conclusions

Recent progress in study of the effects of interstitial H and/or C atoms on the magnetic and magnetocaloric properties of La(Fe, Si)$_{13}$ compound is reviewed and the main results are summarized as follows.

Firstly, the introduction of interstitial H and/or C atoms causes a lattice expansion of the La(Fe, Si)$_{13}$ compound while the 1:13 structure symmetry remains unchanged. Accordingly, the lattice expansion permits the Fe 3*d* band to narrow and brings about the increase of $T_C$ by reducing the overlap of the Fe 3*d* wave functions. Furthermore, it is considered that the influence of interstitial H and/or C atoms on magnetic coupling is dominated by the change of the shortest Fe—Fe bond.

Secondly, the DOS curve just below the Fermi level, which is closely associated with the origin of IEM transition, is hardly altered by introducing H atoms. Therefore, the first-order IEM transition is still conserved and the MCE remains high after hydrogen absorption. Conversely, the characteristic of magnetic transition varies from first-order to second-order with the increase of C concentration, which results in large reduction of thermal and magnetic hysteresis.

Thirdly, the introduction of interstitial C atoms promotes the formation of 1:13 phase in La(Fe, Si)$_{13}$ compound, thus reducing the annealing time significantly from 40 days for

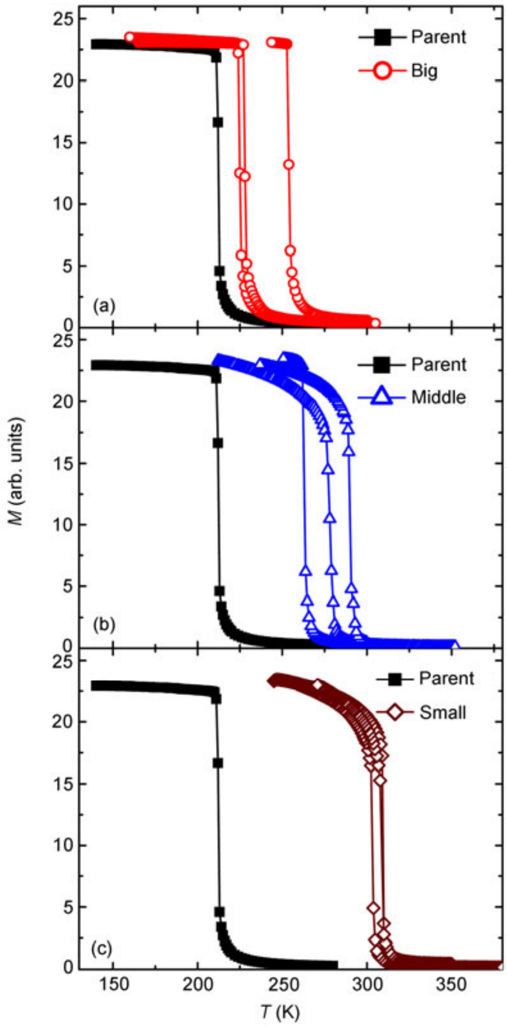

**Figure 13** (Color online) Temperature dependence of magnetizations under 0.05 T for parent $LaFe_{11.7}Si_{1.3}C_{0.2}$ compared with $LaFe_{11.7}Si_{1.3}C_{0.2}H_x$ with different particle sizes, respectively.

$LaFe_{11.7}Si_{1.3}$ to a week for $LaFe_{11.7}Si_{1.3}C_{0.2}$. Moreover, the pre-occupied interstitial C atoms distort the local lattice and may lead to the blocking of the diffusion paths, so that the rates of hydrogen absorption and release will decrease. This is favorable to an accurate control of hydrogen content. By the incorporation of both H and C atoms, a large $|\Delta S_M|$ of 22.1 J/(kg·K) at $T_C$ = 321 K without hysteresis loss for a field change of 0–5 T is observed in $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}C_{0.2}H_{1.2}$, suggesting it as promising candidate for magnetic refrigeration near room temperature.

Lastly, it is found that the reduction of particle size could increase surface area of sample and partially remove the internal strain and grain boundaries, and then the maximum hysteresis loss reduces remarkably by ~61% from 98.4 J/kg for bulk to 38.8 J/kg for small particle with size of 20–50 μm. In addition, the average $T_C$ increases largely with the reduction of particle size, which is also attributed to the fact that the larger surface area of sample allowing more hydrogen atoms to enter into the crystal structure easily. Small particle size and narrow size range would improve the homogeneity of hydrogen distribution.

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