Reduction of magnetic hysteresis loss in La\(_{0.5}\)Pr\(_{0.5}\)Fe\(_{11.4}\)Si\(_{1.6}\)H\(_x\) hydrides with large magnetocaloric effects

Jin-liang Zhao\(^1,2\), Jun Shen\(^1,2\), Feng-xia Hu\(^1\), Yang-xian Li\(^2\), Ji-rong Sun\(^1\), and Bao-gen Shen\(^1,\text{a}\)

\(^1\)State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
\(^2\)School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, China

Abstract

Magnetic properties and magnetocaloric effects (MCEs) have been investigated in hydrogenated La\(_{0.3}\)Pr\(_{0.7}\)Fe\(_{11.4}\)Si\(_{1.6}\)H\(_x\) \((x=0, 0.9, 1.6)\) compounds. It is found that the Curie temperature \(T_C\) can be tuned from 189 to 317 K by adjusting hydrogen content from 0 to 1.6. It is attractive that both thermal and magnetic hysteresis are remarkably reduced because of the weakness of the itinerant-electron metamagnetic transition after hydrogenation, while the large magnetic entropy change is retained. The maximal hysteresis loss at \(T_C\) decreases from 17.8 to 2.3 J/kg as \(x\) increases from 0 to 1.6. For the samples with \(x=0, 0.9, 1.6\), the maximal values of \(-\Delta S\) are 26.3, 24.1, and 22.1 J/kg at \(T_C\), with efficient refrigeration capacities of 463, 366, and 351 J/kg for a field change of 0–5 T, respectively. Large reversible MCE and small hysteresis with considerable value of refrigeration capacity indicate the potentiality of La\(_{0.5}\)Pr\(_{0.5}\)Fe\(_{11.4}\)Si\(_{1.6}\)H\(_x\) hydrides as a candidate magnetic refrigerant around room temperature.

1. INTRODUCTION

Magnetic materials showing large magnetocaloric effects (MCEs) have attracted much attention due to their potential applications as magnetic refrigerants. MCEs involving a first-order magnetic transition are especially interesting because usually the magnetic entropy change occurs in a narrower temperature range as compared to the second-order magnetic transition. Recently, many compounds with first-order magnetic transition have been discovered exhibiting large MCEs,\(^2,3\) such as Gd\(_x\)Si\(_2\)Ge\(_2\), LaFe\(_{13-x}\)Si\(_x\), MnFe\(_{1-x}\)As\(_x\), and Ni\(_{0.9}\)Mn\(_{0.1}\)S\(_n\), etc. Among these materials, the compounds LaFe\(_{13-x}\)Si\(_x\) with cubic NaZn\(_{13}\)-type structure are one of the most attractive because of their considerably large MCEs, easy preparation and low cost, which were intensively studied in the past decades.\(^7\) The large MCEs in LaFe\(_{13-x}\)Si\(_x\) result from the itinerant-electron metamagnetic (IEM) transition in the vicinity of the first-order phase transition temperature. However, along with the great MCEs, a concomitant hysteresis loss occurs inevitably because of the nature of the first-order phase transition. The large hysteresis losses make magnetic entropy less efficient.\(^4\) Many efforts have been made to increase MCE and to reduce or even eliminate the hysteric loss for the LaFe\(_{13-x}\)Si\(_x\) compounds by the addition of substitutional or interstitial atoms. Partially replacing La with Pr (Ref. 9) or Nd (Ref. 10) in LaFe\(_{13-x}\)Si\(_x\) can increase MCE but lead also to an increase in hysteresis loss in the IEM transition process, which has the same effect as a decrease in Si (Ref. 11) for the strengthened first-order phase transition. The substitution of Cu (Ref. 12) and Co (Refs. 10 and 13) for Fe can lead to an obvious reduction in the hysteresis loss and an increase in Curie temperature, but result in a decrease in magnetic entropy change caused by turning the magnetic transition from first-order to second-order. In addition, the interstitial carbon additions in La(Fe, Si)\(_{13}\) can also increase the \(T_C\) and depress the hysteresis.\(^1\) But the extent of the increase in \(T_C\) is limited to about 50 K with less than 0.5 carbon concentrations and leads to an obvious decrease in MCEs.\(^1\) In contrast to carbon insertion, the interstitial hydrogen addition\(^16-19\) leads to an increase in Curie temperature rapidly, and preserving a large magnetic entropy change as well as maintaining the first-order transition. In the present paper, the influence of hydrogen absorption on the MCE and especially on the magnetic hysteresis in La\(_{0.5}\)Pr\(_{0.5}\)Fe\(_{11.4}\)Si\(_{1.6}\)H\(_x\) \((x=0, 0.9, 1.6)\) compounds are discussed from the viewpoint of magnetic refrigerants, in which a large MCE and a small hysteresis loss are achieved near room temperature.

II. EXPERIMENTAL DETAILS

La\(_{0.5}\)Pr\(_{0.5}\)Fe\(_{11.4}\)Si\(_{1.6}\) sample was prepared by arc-melting in high-purity argon gas atmosphere. The purities of the starting materials were 99% for Pr, 99.9% for Fe, and 99.999% for Si. To obtain NaZn\(_{13}\)-type single phase, the heat treatment was carried out in a vacuum quartz tube at 1423 K for ten days. The hydrogen absorption in the compound was carried out by annealing in a hydrogen atmosphere in a sealed chamber at different pressures and temperatures. The hydrogen contents in the compounds can be determined by ideal gas law \((PV=nRT)\), where \(P\) is the hydrogen pressure, \(V\) is the volume of the sealed chamber, \(n\) is the mole quantity of the hydrogen in the chamber, \(R\) is the ideal gas constant.
equal to 8.3145 J/mol K, and \( T \) is the temperature at which the initial compounds are annealed in the hydrogen. After hydrogenation, we deduced the change of hydrogen from the change in hydrogen pressure in the sealed chamber, which is also corresponding to the concentration of hydrogen in the compounds. X-ray diffraction (XRD) measurement on powder samples was performed by using Cu \( K \alpha \) radiation to identify the phase and crystal structure. The magnetization was measured as a function of temperature and magnetic field around the Curie temperature by using superconducting quantum interference device magnetometer from Quantum Design. By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization data.

III. RESULTS AND DISCUSSION

The XRD patterns show that the prepared \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) compounds with \( x = 0, 0.9, \) and 1.6 are of single phase, crystallizing in a cubic \( \text{NaZn}_{13} \)-type structure. The lattice parameter determined by using the Rietveld refinement method is found to increase with increasing hydrogen content from 1.1446 nm for \( x = 0 \) to 1.1567 nm for \( x = 1.6 \). Our research indicates that the hydrogenation of the \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) compound does not modify the crystal structure of the 1:13 phase but leads to lattice expansion. The Fe–Fe interaction can be attributed to the lattice expansion caused by the introduction of interstitial hydrogen atoms. The Fe–Fe interaction is dominant whereas the \( R–R \) interaction is negligible. The increase in \( T_C \) with increasing \( x \) in \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) compounds can be attributed to the lattice expansion caused by the introduction of interstitial hydrogen atoms. The Fe–Fe interaction is a key factor that influences the Curie temperature.\(^{20,21}\)

The Rietveld analysis for \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) shows that the average Fe–Fe bond length increases from 0.2515 to 0.2541 nm, with increasing hydrogen content from 1.1446 nm for \( x = 0 \) to 1.1567 nm for \( x = 1.6 \). The Curie temperatures of Fe-rich rare-earth compounds are determined by the Fe–Fe, the \( R–Fe \), and the \( R–R \) interactions. Generally, the Fe–Fe interaction is dominant whereas the \( R–R \) interaction is negligible. The increase in \( T_C \) with increasing \( x \) in \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) compounds can be attributed to the lattice expansion caused by the introduction of interstitial hydrogen atoms. The Fe–Fe interaction is a key factor that influences the Curie temperature.\(^{20,21}\)

It is found from Fig. 1 that the sample with \( x = 0 \) has a temperature hysteresis of 2.1 K at \( T_C \) between the transitions on heating and cooling, indicating that in the sample there exists a thermal-induced first-order magnetic transition at \( T_C \). It is very interesting to note that the introduction of interstitial hydrogen atoms can weaken thermal-induced first-order magnetic transition at \( T_C \). For the sample of \( x = 0.9 \), a temperature hysteresis is determined to be 1.4 K at \( T_C \), but almost no temperature hysteresis is observed for the sample with \( x = 1.6 \). However, the thermomagnetic curves still exhibit a rapid decrease in magnetization with increasing temperature around \( T_C \), revealing that the thermal-induced first-order magnetic transition is maintained after hydrogen absorption. We measured the field dependence of magnetization at 5 K and the saturation magnetizations are 25.0, 25.2, and 25.4 \( \mu_B/\text{f.u.} \) for \( x = 0, 0.9, \) and 1.6, respectively. Thus, the high saturation magnetization and the significant change in magnetization around \( T_C \) will reasonably induce a considerable magnetic entropy change.

Figure 2 shows the magnetization isotherms of \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) measured under ascending and descending fields in a wide range of temperature around \( T_C \). A decrease in magnetization with increasing temperature around \( T_C \) by decreasing the overlap of Fe 3d wave functions,\(^{22}\) resulting in the increase in \( T_C \).

![FIG. 1. (Color online) Temperature dependence of the magnetization for \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) (a) \( x = 0 \), (b) 0.9, and (c) 1.6 measured on heating and cooling processes under a magnetic field of 0.01 T, respectively.](image1)

![FIG. 2. Magnetization isotherms of \( \text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x \) measured under ascending and descending fields in a wide range of temperature around \( T_C \).](image2)
remarkable IEM transition from paramagnetic (PM) to ferromagnetic (FM) states above $T_C$ is observed. It can be seen from Fig. 2 that the magnetization curves measured under increasing and decreasing fields for $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ exhibit an obvious magnetic hysteresis loop and a sharp change in magnetization at a critical field $B_C$, indicating a characteristic of the first-order magnetic transition above $T_C$, as observed in $\text{LaFe}_{11.7}\text{Si}_{1.3}$. The Arrott plots of $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$, as shown in Fig. 3, exhibit obvious negative slopes, confirming further the characteristic of first-order magnetic transition. However, with the increase in the hydrogen content, the negative slopes decrease almost monotonically, indicating that the feature of the first-order magnetic transition becomes weak after hydrogenation.

On the other hand, the difference in magnetic transition after hydrogenation leads to the weakness of the first-order transition from the PM to the FM state. It is confirmed that the reduction in energy barrier after hydrogenation leads to the weakness of the first-order magnetic transition and the decrease in hysteresis loss.

The magnetic entropy change $\Delta S$ of $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ is calculated from the magnetization data by using the Maxwell relation

$$\Delta S = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH,$$

which is widely used for evaluating $\Delta S$ even for the systems with the first-order transition. Figure 5(a) shows the temperature dependences of $\Delta S$ for $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ under magnetic field changes of 0–2 T and 0–5 T, respectively. For the samples with $x=0$, 0.9, and 1.6, the maximal values of $\Delta S$ are found to be 22.7, 22.0, and 17.7 J/kg K for a field change of 0–2 T and 26.3, 24.1, and 22.1 J/kg K for a field change of 0–5 T, respectively. It is apparent that the large $\Delta S$ in $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ is due to a field-induced IEM transition from the PM to the FM state above $T_C$ as found in $\text{LaFe}_{11.3}\text{Si}_x$ compounds. The introduction of interstitial hydrogen atoms in $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}$ can weaken the IEM

![Figure 3](image_url)

**FIG. 3.** (Color online) Arrott plots of $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ ($x=0$, 0.9, and 1.6).

![Figure 4](image_url)

**FIG. 4.** Critical field $B_C$ of the IEM transition as a function of temperature for $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}H_x$ [(a) $x=0$, (b) 0.9, and (c) 1.6].
transition and result in a small decrease in $\Delta S$. According to Ref. 9, the $\Delta S$ value estimated by the Maxwell relation could yield an error in the vicinity of $T_C$ due to the magnetic hysteresis caused by the field-induced first-order metamagnetic transition. In order to properly estimate the $\Delta S$ value, we have calculated the $\Delta S$ of La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ based on the isothermal magnetization data under ascending and descending fields around $T_C$ by using the Maxwell relation. In general, the computed $\Delta S$ values should be applicable if the $\Delta S$ values are almost same from the magnetization data in the increasing field and decreasing field. It is observed that the maximal values of $\Delta S$ obtained in the increasing field for $x=0$, 0.9, and 1.6 (26.3, 24.1, and 22.1 J/kg K for a field change of 0–5 T, respectively), are very close to those (26.7, 24.5, and 22.5 J/kg K) obtained in the decreasing field, respectively. Figure 5(b) shows the temperature dependence of hysteresis loss, which is defined as the enclosed area between the ascendent and descendent magnetization curves. The hysteresis loss is found to have a maximum at $T_C$, and it decreases with increasing temperature above $T_C$. The maximum values of hysteresis loss are 17.8, 11.7, and 2.3 J/kg for the samples of $x=0$, 0.9, and 1.6, respectively. For the sample of $x=1.6$, a very small hysterisis loss is observed. This reveals a good reversibility of magnetic entropy change with the applied field, which is very useful for magnetic refrigeration applications. It is seen clearly from Figs. 5(a) and 5(b) that both the $\Delta S_M$ peak and the hysteresis loss peak broaden asymmetrically toward higher temperatures with increasing magnetic field. This is a typical characteristic of the field-induced metamagnetic transition above $T_C$. The magnitude of the broadening above $T_C$ is obviously larger than that below the $T_C$, which is associated with the increase in the critical field $B_C$ for the IEM transition with the increase in temperature as shown in Fig. 4. The large $\Delta S$ only results from the IEM transition with a concomitant hysteresis loss above $T_C$, but the $\Delta S$ value of La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ is very small and no hysteresis loss is observed below $T_C$. Thus, the temperature dependence of both the $\Delta S$ and the hysteresis loss exhibit a sharp rise at $T_C$.

The values of refrigerant capacity (RC) of La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ are calculated by numerically integrating the area under the corresponding $\Delta S$–$T$ curve, with the temperature at half maximum of the peak used as the integration limit. The maximum values of RC are found to be 481, 378, and 353 J/kg for the samples with $x=0$, 0.9, and 1.6 under a magnetic field change from 0 to 5 T, respectively. For the RC value, however, it is necessary to take into account the hysteresis loss. The effective refrigeration capacity ($RC_{eff}$) is the RC value obtained after subtracting the hysteresis loss. The values of $RC_{eff}$ for La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ ($x=0$, 0.9, and 1.6) are determined to be 463, 366, and 351 J/kg under a field change of 0–5 T, respectively. For the sample of $x=1.6$, the value of $RC_{eff}$ at 317 K is comparable to that of Gd$_5$Ge$_2$Ge$_2$ (about 355 J/kg at 305 K). The value is also much larger than those of some magnetocaloric materials in a similar temperature range for a field change of 0–5 T, such as Gd$_5$Si$_2$Ge$_2$ (about 240 J/kg at 275 K), Ni$_3$Mn$_{34}$In$_{16}$ (about 181 J/kg at 304 K), LaFe$_{11.2}$Co$_{0.9}$Si$_{1.1}$ (about 275 J/kg at 294 K), and LaFe$_{11.2}$Co$_{0.75}$Si$_{1.1}$Co$_{0.1}$ (about 320 J/kg at 290 K), where the $RC_{eff}$ values of the latter two compounds are estimated from the temperature dependence of $\Delta S$ reported in the literature. Our study shows that the large values of $RC_{eff}$ and small magnetic hysteresis in La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ are in favor of the practical application of the materials near room temperature.

IV. CONCLUSIONS

Introduction of interstitial hydrogen atoms in La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$ can adjust $T_C$ to around room temperature. The first-order nature of phase transition is weakened after hydrogenation, which leads to a reduction in thermal hysteresis and magnetic hysteresis. It is found that the hysteresis loss of the sample with $x=1.6$ reduces to a negligible value 2.3 J/kg, while the magnetic entropy change remains at the large value of 22 J/kg K for a field change of 0–5 T. A considerable value of efficient refrigerent capacity 351 J/kg is obtained under a field change of 0–5 T. The La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$H$_x$ hydrides are promising candidates as high-performance magnetic refrigerants working in a wide range of temperature covering room temperature.

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