Large magnetic entropy change near room temperature in the LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ interstitial compound$^*$

Chen Yuan-Fu(陈远富), Wang Fang(王 芳), Shen Bao-Gen(沈保根),
Hu Feng-Xia(胡凤霞), Cheng Zhao-Hua(成昭华),
Wang Guang-Jun(王光军), and Sun Ji-Rong(孙继荣)

State Key Laboratory of Magnetism, Institute of Physics and Center of Condensed Matter Physics,
Chinese Academy of Sciences, Beijing 100080, China

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The LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ interstitial compound has been prepared. Its Curie temperature $T_C$ (288 K) has been adjusted to around room temperature, and the maximal magnetic entropy change ($|\Delta S| \sim 17.0$ J·kg$^{-1}$·K$^{-1}$ at $T_C$) is larger than that of Gd ($|\Delta S| \sim 9.8$ J·kg$^{-1}$·K$^{-1}$ at $T_C = 293$ K) by $\sim 73.5\%$ under a magnetic change from 0 to 5 T. The origin of the large magnetic entropy change is attributed to the first-order field-induced itineminon-electron metamagnetic transition. Moreover, the magnetic hysteresis of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ under the increase and decrease of the field is very small, which is favourable to magnetic refrigeration application. The present study suggests that the LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ compound is a promising candidate as a room-temperature magnetic refrigerant.

Keywords: NaZn$_{13}$-type hydride, magnetic entropy change, room temperature magnetic refrigerant
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1. Introduction

Currently, room-temperature magnetic refrigerants with large magnetocaloric effect (MCE) are of particular interest because of their wide potential applications.$^{[1]}$ Rare earth and its compounds involving second-order magnetic transitions have been investigated in an attempt to achieve a large MCE, of which Gd was considered historically to be the best room-temperature refrigerant for its ideal Curie temperature $T_C$ (293 K) and its large magnetic entropy change ($|\Delta S| \sim 9.8$ J·kg$^{-1}$·K$^{-1}$ under a magnetic field change from 0 to 5 T at $T_C$).$^{[4]}$ In order to gain a larger MCE, much attention has been paid to materials with a first-order phase transformation,$^{[1,5-13]}$ of which Gd$_2$Si$_2$Ge$_2$,$^{[4]}$ MnAs$_{1-x}$Sb$_x$,$^{[8]}$ and MnFeP$_{1-x}$As$_x$,$^{[1]}$ have been found to show large magnetic entropy changes near room temperature.

The magnetic entropy change of LaFe$_{13-x}$Si$_x$ has been studied in detail.$^{[14,15]}$ The results show that, when $x \leq 1.6$, the compounds exhibit a first-order magnetic transition resulting in a large magnetic entropy change. For the practical use of room-temperature refrigerants, it is necessary to adjust $T_C$ to around room temperature and to retain the large magnetic entropy change in the meantime. It has been confirmed that a proper combination of Si and Co (e.g. LaFe$_{11.5}$Co$_{0.5}$Si$_{1.5}$)$^{[16]}$ can increase $T_C$ up to 274 K and keep the large magnetic entropy change ($|\Delta S| \sim 20.3$ J·kg$^{-1}$·K$^{-1}$ under a magnetic field change from 0 to 5 T at $T_C$). Moreover, $T_C$ can be increased up to room temperature by subsequently substituting Co for Si. However, the first-order transition nature is changed to second-order, which decreases the magnetic entropy change greatly.$^{[1]}$ Another useful method to increase $T_C$ up to room temperature is to introduce interstitial atoms such as H and N. Some hydrides$^{[17-19]}$ and nitrides$^{[20,21]}$ of NaZn$_{13}$-type La(Fe$_x$Al$_{1-x}$)$_{13}$ and La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds have been investigated. However, no one has studied the influence of the interstitial atoms on magnetic phase transition and magnetic entropy change. Therefore, in order to adjust $T_C$ to around room temperature and to retain the large magnetic entropy change, the interstitial H atom is introduced into the LaFe$_{13-x}$Si$_x$ compound. The influence of the interstitial H atom on the magnetic properties, magnetic phase transition and magnetic entropy change

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$^1$Hu Feng-Xia, Private communication.
are studied in this paper.

2. Experimental details

The preparation of the mother alloy LaFe_{11.5}Si_{1.5} has been described elsewhere.\textsuperscript{122} Hydrogen absorption into LaFe_{11.5}Si_{1.5} was carried out in a high-pressure kettle in high-purity H\textsubscript{2} of 5MPa at 180°C and hydrogen desorption was carried out in a vacuum quartz tube with 5 x 10\textsuperscript{-4} Pa pressure at 250°C.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{XRD pattern for LaFe_{11.5}Si_{1.5} and LaFe_{11.5}Si_{1.5}H_{1.3}.}
\end{figure}

Powder x-ray diffraction (XRD) patterns of LaFe_{11.5}Si_{1.5} and LaFe_{11.5}Si_{1.5}H_{1.3} obtained at room temperature are shown in Fig.1. It is confirmed that the lattice constants are increased by hydrogen absorption without changing the cubic NaZn_{13}-type structure. It is noteworthy that the lattice constant of LaFe_{11.5}Si_{1.5}H_{1.3} (\sim 1.528 nm) is larger than that of the mother alloy LaFe_{11.5}Si_{1.5} (\sim 1.475 nm) by \sim 0.46%.

All magnetic measurements were performed on a commercial MPMS-7 type superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Figure 2 presents the thermomagnetic curve \textit{M–T} of LaFe_{11.5}Si_{1.5} and LaFe_{11.5}Si_{1.5}H_{1.3} measured under a low magnetic field of 0.01T. The Curie temperature \( T_C \) is about 195K and 288K, as determined from the \textit{M–T} curves for LaFe_{11.5}Si_{1.5} and LaFe_{11.5}Si_{1.5}H_{1.3}, respectively. It is noteworthy that \( T_C \) has been increased up to room temperature by \sim 93K after hydrogen absorption. It is evident that the slope of the \textit{M–T} curve of the hydride in the vicinity of \( T_C \) is much smaller than that of the mother alloy.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{Temperature dependence of magnetization for LaFe_{11.5}Si_{1.5} and LaFe_{11.5}Si_{1.5}H_{1.3} measured under a low magnetic field of 0.01T.}
\end{figure}

Figures 3(a) and (b) display the magnetization isotherms of LaFe_{11.5}Si_{1.5}H_{1.3} and LaFe_{11.5}Si_{1.5}H_{1.3}, respectively, measured on field increase or decrease in a wide temperature range with different temperature steps. The temperature step of 2K is chosen in the vicinity of the Curie temperature and steps of 5K or 10K for the regions far away from \( T_C \). The sweep rate of the field is slow enough to ensure that the \textit{M–H} curves are recorded in an isothermal process. One can find that the magnetic hysteresis of LaFe_{11.5}Si_{1.5}H_{1.3} upon increase and decrease of the field is much less than that of LaFe_{11.5}Si_{1.5}, which is considered to be a very favourable characteristic for magnetic refrigeration applications since a completely reversible MCE requires that there is no hysteresis in the magnetization as a function of both the temperature and the magnetic field. LaFe_{11.5}Si_{1.5}H_{1.3} is just such a case. The obvious hysteresis of LaFe_{11.5}Si_{1.5} upon increase and decrease of the field is the characteristic of the first-order field-induced itinerant-electron metamagnetic (IEM) transition. Figure 3(c) displays the Arrott plots of LaFe_{11.5}Si_{1.5}H_{1.3}, in which the appearance of the negative slope confirms the occurrence of a metamagnetic transition from paramagnetic to ferromagnetic order above \( T_C \),\textsuperscript{14,23–25} which means that LaFe_{11.5}Si_{1.5}H_{1.3} retains the first-order IEM transition.
Fig. 3. Magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ (a) and LaFe$_{11.5}$Si$_{1.5}$ (b) and the Arrrott plots of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ (c). The temperature step is 2 K in the vicinity of $T_C$, and 5 K or 10 K for the regions far from $T_C$. Isotherms on increasing field (full square) and decreasing field (open square) are only performed for the regions in the vicinity of $T_C$.

The magnetic entropy change $|\Delta S|$ can be obtained using the Maxwell relation $\Delta S(T, H) = \int_{H_0}^{H} (\partial M/\partial T)_{H} dH$ and the collected magnetization data.[1,4,5,8,10,26,27] Figure 4(a) shows $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ as a function of temperature for different magnetic field changes. The peak values of $|\Delta S|$ under a magnetic change from 0 to 1 T, 0 to 2 T and 0 to 5 T are 4.2, 8.4, and 17.0 J-kg$^{-1}$-K$^{-1}$, respectively. Such a high magnitude of $|\Delta S|$ was rarely observed in 3d alloys involving a reversible transition at the corresponding temperature range. $|\Delta S|$ of Gd is also measured for comparison. Figure 4(b) shows $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ in comparison with that of the mother alloy LaFe$_{11.5}$Si$_{1.5}$ and Gd under a magnetic field change from 0 to 2 T and 0 to 5 T. It is evident that the $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ notably exceeds that of Gd ($T_C = 293$ K). The origin of the large magnetic entropy change in the present LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ interstitial compound should be attributed to the first-order IEM. Also, $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$H$_{3}$ is lower than that of the mother alloy LaFe$_{11.5}$Si$_{1.5}$, which is mainly
because its first-order IEM nature is much weaker. This can also be observed in the $M$–$T$ curve (Fig. 2), in which the slope of the $M$–$T$ curve of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ in the vicinity of $T_C$ is much smaller than that of the mother alloy.

4. Conclusion

In this paper, by introducing interstitial H atom into LaFe$_{11.5}$Si$_{1.5}$ alloy, we have prepared the LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ interstitial compound, for which $T_C$ (288 K) has been adjusted to around room temperature, and the magnetic entropy change $|\Delta S|$ notably exceeds that of Gd. The origin of the large magnetic entropy change is attributed to the first-order IEM transition. Moreover, the magnetic hysteresis of LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ on increase and decrease of the field is very small, which is favourable to magnetic refrigeration applications. This suggests that the LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$ compound is a promising candidate as a room-temperature magnetic refrigerant.

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