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Large magnetic entropy change near room temperature in the $LaFe_{11.5}Si_{1.5}H_{1.3}$ interstitial compound*

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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 ($|\Delta S| \sim 17.0\,J\cdot kg^{-1}\cdot K^{-1}$ at T_C) is larger than that of Gd ($|\Delta S| \sim 9.8\,J\cdot kg^{-1}\cdot K^{-1}$ at T_C=293 K) by ~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 itinerant-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
PACC: 7530S, 7550B, 6500

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[2,3] 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 ($|\Delta S| \sim 9.8\,J\cdot kg^{-1}\cdot K^{-1}$ 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 $Gd_5Si_2Ge_2$,[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. $LaFe_{11.2}Co_{0.7}Si_{1.1}$ [16]) can increase T_C up to 274 K and keep the large magnetic entropy change ($|\Delta S| \sim 20.3\,J\cdot kg^{-1}\cdot K^{-1}$ 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 $La(Fe_xAl_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}$ 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.[22] Hydrogen absorption into $LaFe_{11.5}Si_{1.5}$ was carried out in a high-pressure kettle in high-purity H_2 of 5 MPa at 180°C and hydrogen desorption was carried out in a vacuum quartz tube with 5×10^{-4} Pa pressure at 250°C.

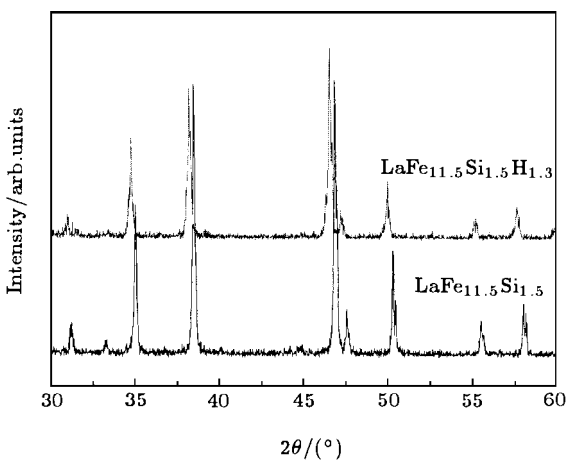


Fig.1. XRD pattern for $LaFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}H_{1.3}$.

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 $LaFe_{11.5}Si_{1.5}H_{1.3}$ (~1.1528 nm) is larger than that of the mother alloy $LaFe_{11.5}Si_{1.5}$ (~1.1475 nm) by ~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 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 0.01 T. The Curie temperature T_C is about 195 K and 288 K, as determined from the 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 ~93 K after hydrogen absorption. It is evident that the slope of the M–T curve of the hydride in the vicinity of T_C is much smaller than that of the mother alloy.

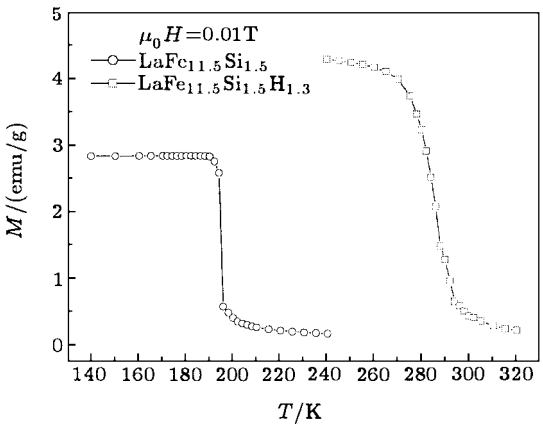


Fig.2. Temperature dependence of magnetization for $LaFe_{11.5}Si_{1.5}$ and $LaFe_{11.5}Si_{1.5}H_{1.3}$ measured under a low magnetic field of 0.01 T.

Figures 3(a) and (b) display the magnetization isotherms of $LaFe_{11.5}Si_{1.5}H_{1.3}$ and $LaFe_{11.5}Si_{1.5}$, respectively, measured on field increase or decrease in a wide temperature range with different temperature steps. The temperature step of 2 K is chosen in the vicinity of the Curie temperature and steps of 5 K or 10 K for the regions far away from T_C. The sweep rate of the field is slow enough to ensure that the 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,[14,23–25] which means that $LaFe_{11.5}Si_{1.5}H_{1.3}$ retains the first-order IEM transition.

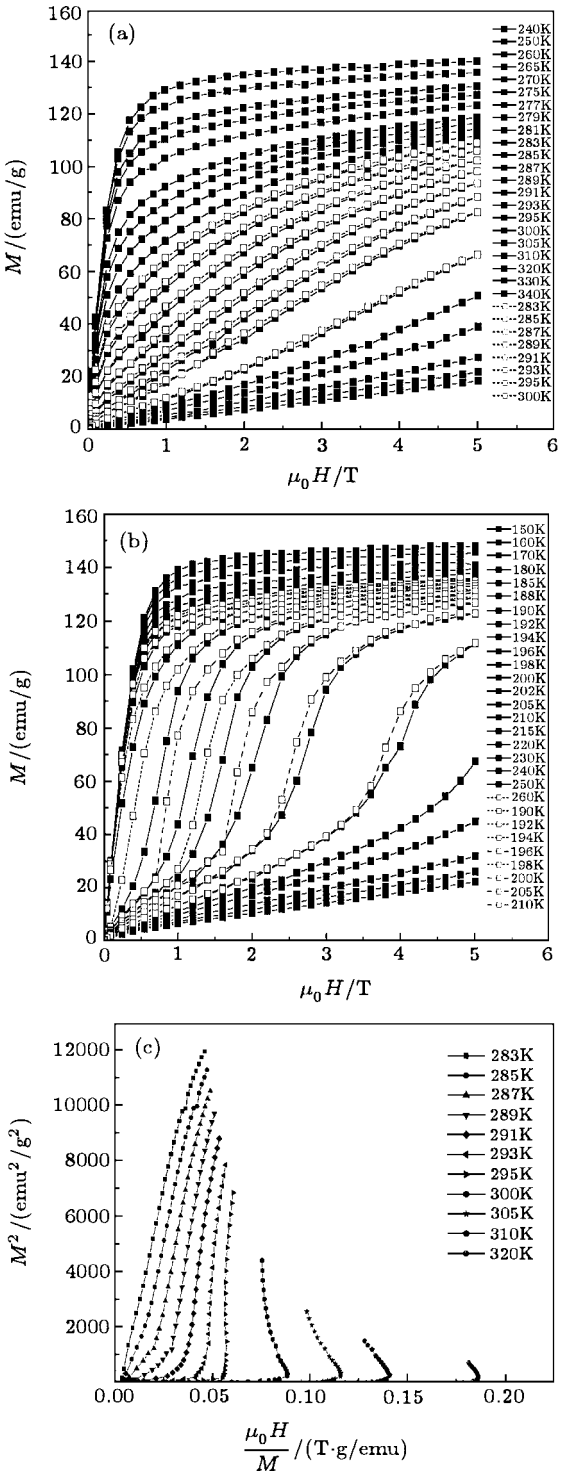


Fig.3. Magnetization isotherms of $LaFe_{11.5}Si_{1.5}H_{1.3}$ (a) and $LaFe_{11.5}Si_{1.5}$ (b) and the Arrott plots of $LaFe_{11.5}Si_{1.5}H_{1.3}$ (c). The temperature step is 2 K in the vicinity of T_C, and 5 K or 10 K for the regions far from T_C. Isotherms on increasing field (full square) and 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 $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$ and the collected magnetization

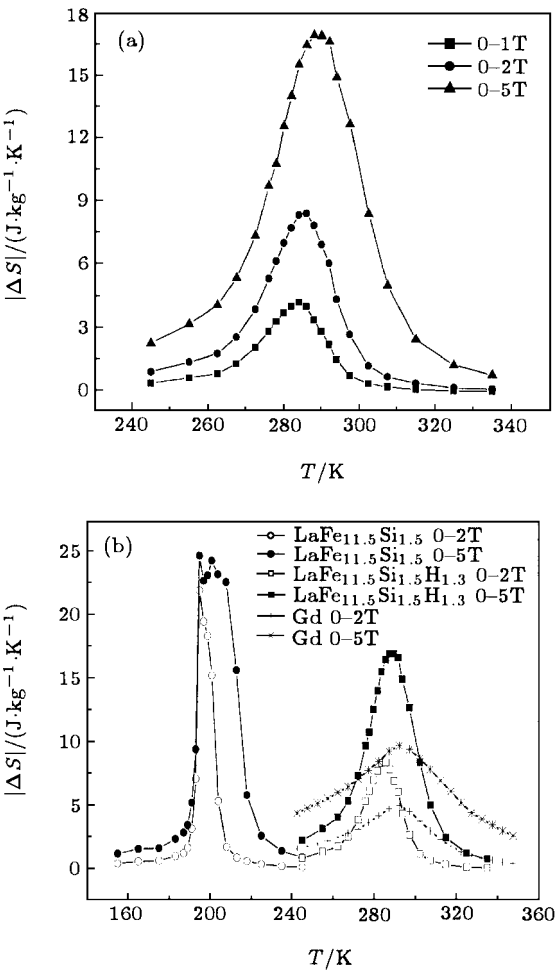


Fig.4. Magnetic entropy change $|\Delta S|$ of $LaFe_{11.5}Si_{1.5}H_{1.3}$ (a) for the magnetic field change of 0–1 T, 0–2 T and 0–5 T (b) compared with that of $LaFe_{11.5}Si_{1.5}$ and Gd for the field changes of 0–2 T and 0–5 T.

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 $J \cdot kg^{-1} \cdot K^{-1}$, 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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