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LETTER TO THE EDITOR

Magnetic properties and magnetic entropy change of LaFe$_{11.5}$Si$_{1.5}$H$_y$ interstitial compounds

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Abstract
LaFe$_{11.5}$Si$_{1.5}$H$_y$ interstitial compounds have been prepared by hydrogen absorption and subsequent desorption. The Curie temperatures are easily tunable for a wide temperature range from ∼195 to ∼340 K by hydrogen content. The maximal magnetic entropy changes, under a magnetic field change of 0–5 T, are as large as 16.8–20.5 J kg^{-1} K^{-1}, exceeding that of Gd ($|\Delta S| \sim 9.8$ J kg^{-1} K^{-1} at $T_C = 293$ K) by 70–110% in the vicinity of room temperature. The large magnetic entropy change of all hydrides may be attributed to the first-order itinerant-electron metamagnetic transition confirmed by the Arrott plots. Large $|\Delta S|$, convenient adjustment of T_C and small thermal and magnetic hystereses, make LaFe$_{11.5}$Si$_{1.5}$H$_y$ interstitial hydrides promising candidates for magnetic refrigerants in the corresponding temperature range.

Recently, room-temperature magnetic refrigeration, based on the magnetocaloric effect (MCE), has been demonstrated as a very promising alterative to conventional vapour-cycle refrigeration [1–3]. In order to obtain a larger MCE, much attention has been paid to materials involving a first-order phase transformation [2–10], of which Gd$_5$Si$_2$Ge$_2$ [2, 4]. MnFeP$_{1-x}$As$_x$ [3], LaFe$_{13-x}$Si$_x$ [7, 8] and MnAs$_{1-x}$Sb$_x$ [10] have been found to show giant magnetic entropy changes.

The magnetic entropy change in LaFe$_{13-x}$Si$_x$ has been studied in detail [7, 8]. The results show that when $x \leqslant 1.6$ the compounds exhibit a first-order magnetic transition, resulting in a large magnetic entropy change; however, the T_C is lower than ∼200 K. For use as a room-temperature magnetic refrigerant it is necessary to increase T_C to a higher temperature but retain the large magnetic entropy change. It has been confirmed that two methods, namely the substitution of Co for Si or Al and the introduction of interstitial atoms, are useful for increasing

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the T_C of La(Fe$_x$Al$_{1-x}$)$_{13}$ and La(Fe$_x$Si$_{1-x}$)$_{13}$ [11–23]. The influence of the substitution of Co for Si on magnetic properties [11, 12] and magnetic entropy change [13, 14] has been studied. Interstitial atoms can produce two effects, namely lattice expansion and hybridization, which affect the magnetic properties [15]. Nitrides [16–19] and hydrides [20–23] of La(Fe$_x$Al$_{1-x}$)$_{13}$ and La(Fe$_x$Si$_{1-x}$)$_{13}$ have been prepared and studied, showing that the lattice expansion caused by interstitial atoms produces a considerable increase in T_C. Fujita *et al* [22] and our group [23] have done some work on the magnetic entropy change in LaFe$_{13-x}$Si$_x$ hydrides. However, systematic work on the effect of interstitial H atoms on the Curie temperature, magnetic transition and magnetic entropy change has not been reported; this will be studied in detail in the present letter.

The preparation of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ has been described elsewhere [24]. Preparation of LaFe$_{11.5}$Si$_{1.5}$H$_y$ interstitial compounds is as follows. First, the bulk LaFe$_{11.5}$Si$_{1.5}$ alloy is saturated by hydrogenation in high-purity H$_2$ at 5 MPa and 150 °C for about 5 h. Then, extraction of hydrogen to some extent from the saturated hydride was performed under a vacuum better than 5×10^{-4} Pa at 250 °C for different lengths of time. The hydrogen content, y, was calculated from the variation of the sample weight before/after hydrogen absorption (desorption) and the weight was measured by an electronic analytical balance (AND GR-202) with a readability of 0.01 mg and a repeatability of 0.02 mg in the range 0–42 g. Powder x-ray diffraction (XRD) data were collected using Cu Kα radiation at room temperature. Magnetic measurements were performed on a commercial MPMS-7 type superconducting quantum interference device (SQUID) magnetometer.

Figure 1 shows the room-temperature powder XRD patterns of LaFe$_{11.5}$Si$_{1.5}$ and its hydrides LaFe$_{11.5}$Si$_{1.5}$H$_y$ ($y = 0.3, 1.3, 1.8$). It is confirmed that the lattice constant increases with increasing hydrogen content without changing the cubic NaZn$_{13}$-type structure. The lattice constants of hydrides for $y = 0.3$ ($a \sim 11.483$ Å), 1.3 ($a \sim 11.528$ Å) and 1.8 ($a \sim 11.602$ Å) are obviously larger than that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ ($a \sim 11.475$ Å) by $\sim 0.07, 0.46$ and 1.11% respectively.

Figure 2 shows the temperature dependence of magnetization of LaFe$_{11.5}$Si$_{1.5}$ and its hydrides LaFe$_{11.5}$Si$_{1.5}$H$_y$ measured with increasing (full symbols) and decreasing (open symbols) temperature in a low field of 0.01 T. The Curie temperatures, determined from the M–T curves, are ~195, ~224, ~257, ~272, ~288, ~312 and ~341 K for $y = 0, 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 respectively. The effect of the interstitial H atoms on Curie temperatures in La(Fe, Si)$_{13}$ hydrides is similar to other R–Fe based interstitial compounds, in which the lattice expansion caused by interstitial atoms makes the Fe 3d band narrow and brings about the increase in T_C by reducing the overlap of the Fe 3d wavefunctions [16–23, 25, 26]. So the larger the expansion caused by a higher hydrogen content, the stronger the lattice expansion and the higher the T_C becomes. We also note that the change of magnetization with temperature of the hydrides near T_C is relatively rapid but not so sharp as that of the parent alloy. Furthermore, the magnetization process can be considered as being reversible in temperature because of the small size of the thermal hysteresis (<1 K).

The saturation magnetizations M_s of LaFe$_{11.5}$Si$_{1.5}$H$_y$, determined from the magnetization curves at 5 K under a magnetic field of 0–5 T, are 163.1, 158.9, 164.1, 163.5, 157.2 and 170.9 emu g^{-1} for $y = 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 respectively, nearly the same as that of the parent alloy, 167.1 emu g^{-1}.

Magnetization isotherms of the LaFe$_{11.5}$Si$_{1.5}$H$_y$ compounds for $y = 0, 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 were measured in a wide temperature range with different temperature steps. The temperature step was 2 K in the vicinity of T_C and 5 or 10 K for the range far from T_C. The sweep rate of the field was slow enough to ensure that the M–H curves were recorded in an isothermal process. Figures 3(a)–(c) show the magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$, LaFe$_{11.5}$Si$_{1.5}$H$_{0.9}$
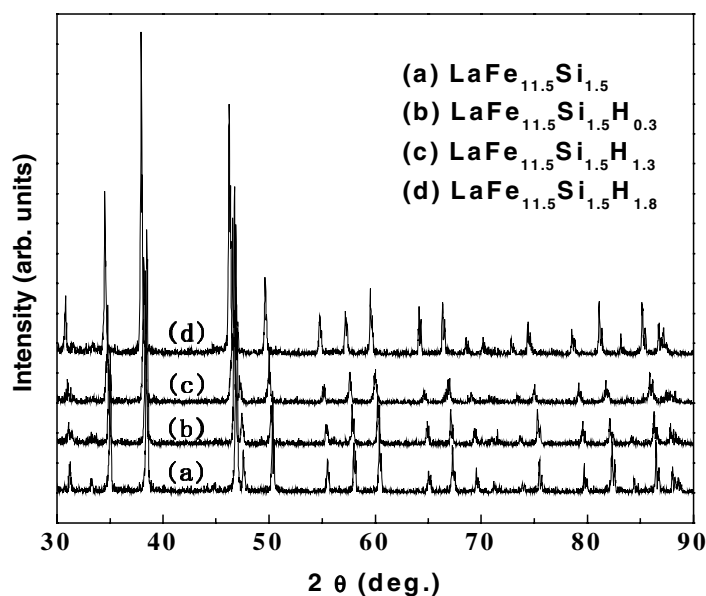
Figure 1. Room-temperature powder XRD patterns for LaFe$_{11.5}$Si$_{1.5}$ and its hydrides LaFe$_{11.5}$Si$_{1.5}$H$_y$ (y = 0.3, 1.3, 1.8).
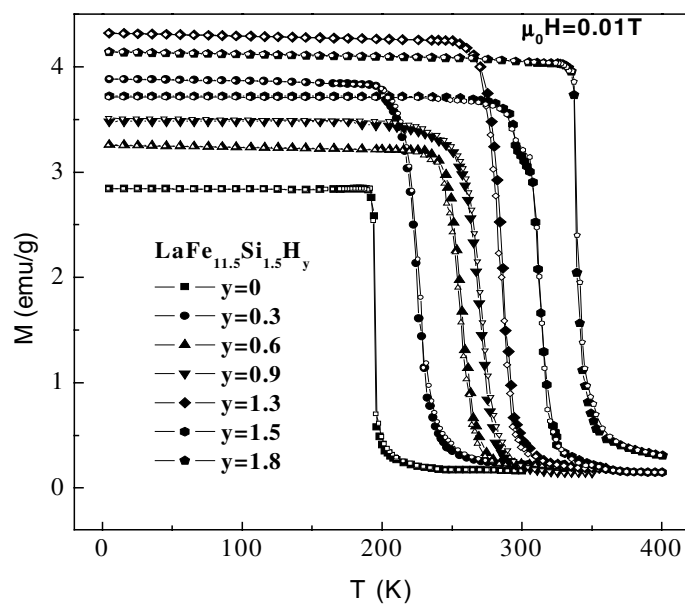

Figure 2. Temperature dependence of magnetization of LaFe$_{11.5}$Si$_{1.5}$H$_y$ for y = 0, 0.3, 0.6, 0.9, 1.3, 1.5 and 1.8. Data are shown for increasing (full symbols) and decreasing (open symbols) temperature in a low field of 0.01 T.

and LaFe$_{11.5}$Si$_{1.5}$H$_{1.8}$ respectively. Isotherms on increasing field (full squares) and decreasing field (open squares) are measured only in the vicinity of T_C. It is noted that the size of the magnetic hysteresis during increasing and decreasing field is much smaller than that of the
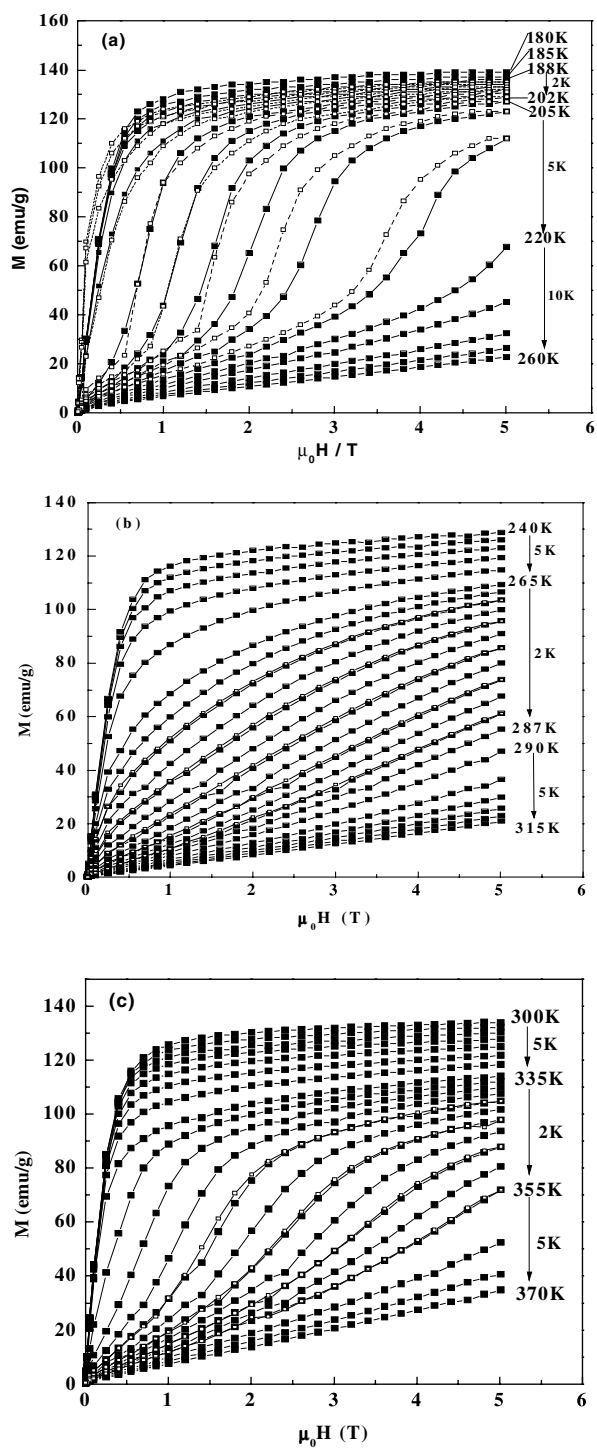
Figure 3. Magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$ (a), LaFe$_{11.5}$Si$_{1.5}$H$_{0.9}$ (b) and LaFe$_{11.5}$Si$_{1.5}$H$_{1.8}$ (c). The temperature step is 2 K in the vicinity of T_C, and 5 or 10 K for the range far from T_C. Isotherms on increasing field (full squares) and decreasing field (open squares) are measured only in the vicinity of T_C.
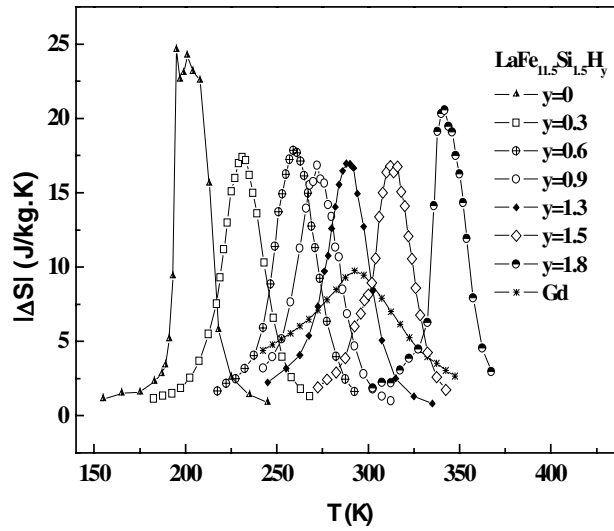
Figure 4. Magnetic entropy changes of the hydrides LaFe$_{11.5}$Si$_{1.5}$H$_y$ for $y = 0.3$, 0.6, 0.9, 1.3, 1.5 and 1.8 in comparison with those of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ and Gd for magnetic field changes of 0–5 T.
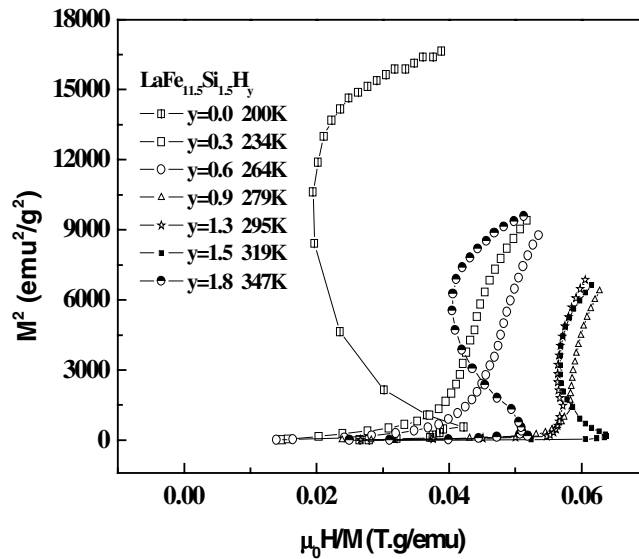

Figure 5. The Arrott plots of LaFe$_{11.5}$Si$_{1.5}$H$_y$ for $y = 0.3$, 0.6, 0.9, 1.3, 1.5 and 1.8 in comparison with that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ just above the respective T_Cs.

parent alloy. So the magnetization process of the hydrides can also be considered as being reversible in magnetic field.

The magnetic entropy change $|\Delta S|$ can be obtained from the Maxwell relation $\Delta S(T, H) = \int_0^H (\partial M / \partial T)_H \, dH$ using the collected magnetization data [2–10, 27, 28]. Figure 4 shows the $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$H$_y$ for $y = 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 in comparison with those of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ and Gd [2] under a change in magnetic field from

0 to 5 T. The maximal $|\Delta S|$ values of $LaFe_{11.5}Si_{1.5}H_y$ for $y = 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 at the respective T_Cs are 17.4, 17.8, 16.9, 17.0, 16.8 and 20.5 J kg^{-1} K^{-1} respectively, while the corresponding values of $LaFe_{11.5}Si_{1.5}$ and Gd are 24.6 and 9.8 J kg^{-1} K^{-1}, respectively. We note that in the wide temperature range of 195–340 K, the maximal magnetic entropy changes of the hydrides at respective T_C are very large ($|\Delta S| \sim 16.8$–20.5 J kg^{-1} K^{-1}), greatly exceeding that of Gd ($|\Delta S| \sim 9.8$ J kg^{-1} K^{-1} at $T_C = 293$) by 70–110%.

Figure 5 shows the Arrott plots of $LaFe_{11.5}Si_{1.5}H_y$ for $y = 0, 0.3, 0.6, 0.9, 1.3, 1.5$ and 1.8 just above the respective T_Cs. It is evident that a negative slope appears for $y = 0, 1.3, 1.5$ and 1.8 and no negative slope but an inflection point appears for $y = 0.3, 0.6$ and 0.9, which confirms that all of the hydrides exhibit a first-order itinerant-electron metamagnetic (IEM) transition [29, 30]. The sudden jump of magnetization near T_C is a striking characteristic of the IEM transition, which has been studied in detail in $La(Fe_{1-x}Si_x)_{13}$ ($x = 0.86$ and 0.88) compounds [31, 32]. It also occurs in $LaFe_{11.5}Si_{1.5}H_y$ hydrides. The higher saturation magnetization, together with the sudden magnetization jump near T_C, leads to large entropy change around T_C. We also note that the IEM transition in the hydrides for $y = 0.3, 0.6$, and 0.9 is not as steep as that in the parent alloy, resulting in a less sharp change in the M–T curve, therefore $|\Delta S|$ is lower than that of the parent alloy.

The Curie temperatures of $LaFe_{11.5}Si_{1.5}H_y$ compounds can be continuously tunable from ~ 195 to 340 K by hydrogen content, while the saturation magnetizations remain nearly the same as that of the parent alloy. The magnetic entropy changes of the hydrides are very large, greatly exceeding that of Gd in the corresponding temperature range. Moreover, the hydrides are of low cost, with small thermal and magnetic hystereses.

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