Hydrogenation, structure and magnetic properties of $La(Fe_{0.91}Si_{0.09})_{13}$ hydrides and deuterides*

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Hydrogenation, crystal structure and magnetic properties of $La(Fe_{0.91}Si_{0.09})_{13}H(D)_y$ have been studied by pressure-composition isotherms (PCI), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and magnetization measurements. The maximum absorption capacity is found to be 1.9 H(D) atoms per formula unit as a solid solution. All hydrides and deuterides crystallize in the $NaZn_{13}$-type cubic structure with the lattice parameter increasing linearly with H(D) concentration. The H(D) absorption enhances the Curie temperature significantly. The magnetic entropy change of the highly H-absorbed compound $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$ reaches ∼26 J/kg·K under a magnetic field change of 5 T near the Curie temperature $T_C = 350$ K. No observable isotope effect seems to imply that only the magnetovolume effect is responsible for the strong interplay between magnetism and lattice.

Keywords: magnetocaloric effect, magnetic entropy change, isotope effect

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1. Introduction

Magnetocaloric effect (MCE), which maps out the magnetic phase transition induced by temperature and magnetic field, is one of the fundamental physical phenomena in magnetic materials. Materials with large MCE have potential applications as effective refrigerants.[1−7] Magnetic refrigeration at the room temperature is of particular interest because of energy saving and environmental protection. The Fe-based intermetallic compounds with cubic $NaZn_{13}$-type structure have been suggested to be potential magnetic refrigerants due to their excellent soft ferromagnetism, high magnetization and low cost.[7−12] Large MCE has been indeed reported in $La(Fe_xSi_{1-x})_{13}$ with low Si content, the magnetic entropy change in $La(Fe_{0.90}Si_{0.10})_{13}$ was reported up to $|\Delta S| = 30$ J/kg·K at $T_C = 184$ K under a field change of 5 T.[7,8] Unfortunately, $La(Fe_xSi_{1-x})_{13}$ compounds are not appropriate materials as room temperature magnetic refrigerants because of their low T_C. A small amount of Co substitution can enhance the T_C to room temperature.[7−9] For $LaFe_{11.2}Co_{0.7}Si_{1.1}$, $|\Delta S| = 20.3$ J/kg·K under a magnetic field of 5 T at $T_C = 274$ K[9] is twice larger than $|\Delta S| = 9.8$ J/kg·K of Gd, which is a typical room temperature magnetic refrigerant. Another way to enhance the Curie temperature is through introducing interstitial atoms into $La(Fe_xSi_{1-x})_{13}$.[7,10,11] For example, T_C for $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound is up to 287 K with $|\Delta S| = 28$ J/kg·K and 31 J/kg·K in $\Delta H = 2$ T and 5 T, respectively.[10,11] Further studies have considered the existence of strong interplay between magnetism and lattice in La(Fe, M)$_{13}$ (M=Si, Al) and the ferromagnetism was observed to prefer large crystal lattice.[7−18] Therefore, it might be reasonable to speculate that the isotope effect on magnetism could be detected in comparison of La(Fe, M)$_{13}$ hydrides and deuterides. A large isotope effect has been indeed reported in the $YFe_2(H,D)_{4.2}$ intermetallic system.[17] In this paper, the hydrogenation, crystal structure and magnetic properties of the hydrides and deuterides of

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$La(Fe_{0.91}Si_{0.09})_{13}$ are investigated.

2. Experimental

Intermetallic compound $La(Fe_{0.91}Si_{0.09})_{13}$ was prepared by arc melting with La, Fe and Si in an atmosphere of ultrapure argon gas with nominal chemical composition, then vacuum annealed for one month at 1273 K. Three hydrides and three deuterides $La(Fe_{0.91}Si_{0.09})_{13}H(D)_y$ with $y \sim 0.47$, 1.1 and 1.8, as listed in Table 1, were elaborated by H(D) charging at 470 K and subsequent cooling down to room temperature. The phase composition and crystal structure were checked by X-ray diffraction (XRD) at room temperature with a θ–θ diffractometer (Bruker AXS D8Advance equipped with backscattered rear graphite monochromator) using Cu Kα radiation. The magnetocaloric transition of these compounds was studied by differential scanning calorimetry (DSC) in a Q100-TA device in the temperature range 173 K–373 K with a temperature change rate of 20 K/min. The magnetization as a function of field (M–H) and temperature (M–T) was recorded by a commercial superconducting quantum interference device magnetometer (SQUID, Quantum Design MPMS-7) and the M–T was recorded with a temperature increasing rate of 5 K/min.

3. Results and discussion

Figure 1 shows the pressure-composition isotherms (PCI) of $La(Fe_{0.91}Si_{0.09})_{13}$ obtained at 470 K under hydrogen and deuterium atmosphere in the pressure range 10^{-3} bar to 10 bar. A solid-solution behaviour is marked by absence of plateau pressure without any hysteresis effect between absorption and desorption, regardless of H or D. The maximum H(D) uptake is ∼1.9 atoms per formula unit (f.u.) at 10 bar of $H_2(D_2)$ pressure. From the PCI result, we obtained three hydrides and three deuterides $La(Fe_{0.91}Si_{0.09})_{13}H(D)_y$ with low ($y \sim 0.47$), middle ($y \sim 1.1$) and high ($y \sim 1.8$) H(D) concentration. To check phase composition and crystal structure, the X-ray diffraction was performed on all samples. Indexation shows that the parent compound $La(Fe_{0.91}Si_{0.09})_{13}$ can be indexed with an $NaZn_{13}$-type cubic structure (space group $Fm\bar{3}c$) and a further Rietveld refinement confirmed that the sample crystallizes in this main phase with Fe (∼ 3 wt%) and La_5Si_3 (∼ 1.5 wt%) as impurity phases. The hydrides and deuterides still keep the NaZn13-type cubic structure with the reflection peaks just shifting to low angles due to the lattice expansion of H(D) absorption, as seen in Fig. 2. It is interesting to note that all diffraction peaks of the middle H(D) absorption samples ($y \sim 1.1$) split and can be refined with two hydrogenated or deuterated $NaZn_{13}$-type phases, whereas only one hydride phase is observed in the samples with low and high H(D) absorption ($y \sim 0.47$ and $y \sim 1.8$). This characteristic is also validated in the DSC and M–T measurements below. The lattice parameters are summarized in Table 1.

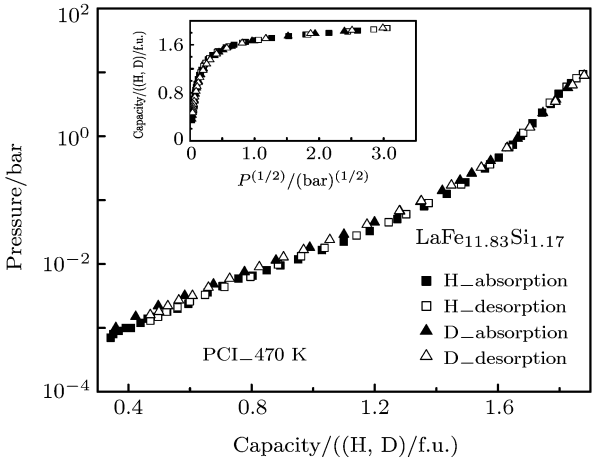


Fig. 1. Hydrogen and deuterium PCI curves at 470 K of $LaFe_{11.83}Si_{1.17}$. The inset shows the Sievert's representation of PCI curves (1 bar=10^5 Pa, f.u. means per formula unit).

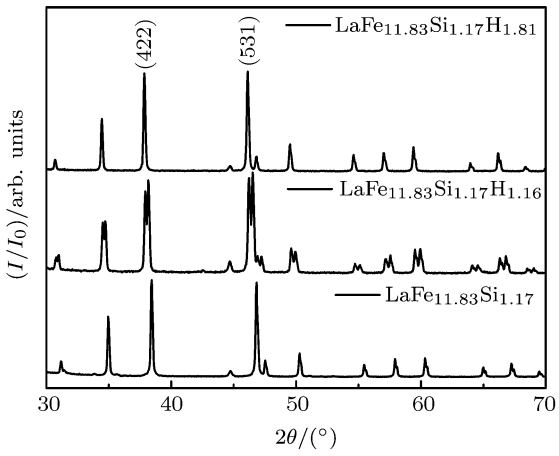


Fig. 2. The X-ray diffraction patterns at room temperature for $LaFe_{11.83}Si_{1.17}H_y$ ($y = 0$, 1.16 and 1.81) samples.

Table 1. The lattice parameter and the Curie temperature of $LaFe_{11.83}Si_{1.17}H(D)_y$.

y	a/Å	T_C/K		Transition heat/J·g^{-1}
		DSC	M–T	
0	11.473	175.85	177.2	2.5
Hydrides: 0.47	11.501	236.90	238.2	7.0
1.16	11.533	295.49	288.0	8.7
	11.606		319.0	
1.81	11.631	352.67	350.7	9.2
Deuterides: 0.47	11.492	222.09	231.4	6.5
1.13	11.523	286.48	286.0	9.0
	11.595		316.0	
1.86	11.626	350.43	350.2	9.6

The DSC measurements with several heating and cooling runs at 20 K/min were performed to check the transition reproducibility. Figure 3 shows the temperature-dependent heat flow of all hydrided/deuterated samples. The interstitial H(D) atoms give rise to a significant increase of phase transition temperature. This phase transition is related to the first-order ferro-para magnetic transition confirmed by the magnetization measurement. For the biphasic samples $La(Fe_{0.91}Si_{0.09})_{13}H_{1.16}$ and $La(Fe_{0.91}Si_{0.09})_{13}D_{1.13}$, two endothermic signals are observed in the first heating run (at 290 K and at 310 K with a peak splitting). However, these signals merge into a single endothermic peak at 295 K at the 3rd and 4th cyclings, which can be clearly seen in the inset of Fig. 3 for $La(Fe_{0.91}Si_{0.09})_{13}H_{1.16}$. This evolution could be attributed to the formation of a single-phase hydride (deuteride) as a result of the thermal treatment on cycling. In other words, the biphasic hydride (deuteride) transforms into a monophasic one during sample heating up to 353 K. Therefore it is speculated that such single-phase samples should be stabilized at higher temperature, but metastable at room temperature since that the true thermodynamic equilibrium is the two-phase separation. The transition heat listed in Table 1 is derived from the integral area of the DSC peak. It also increases with the H(D) concentration (see below), from 2.5 J/g for $La(Fe_{0.91}Si_{0.09})_{13}$ to 9.2 J/g for $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$. The M–T curves of $La(Fe_{0.91}Si_{0.09})_{13}H(D)_y$, plotted in Fig. 4, clearly show the enhancement of the magnetic phase transition temperature, i.e. the Curie temperature, with increasing interstitial H(D) concentration. The coexistence of two magnetic phases in the samples with H(D) content $y \sim 1.1$ is also found, in consistence with the XRD and DSC results. As seen in Fig. 5(a), those Curie temperatures of magnetic measurements are consistent with the phase transition temperatures

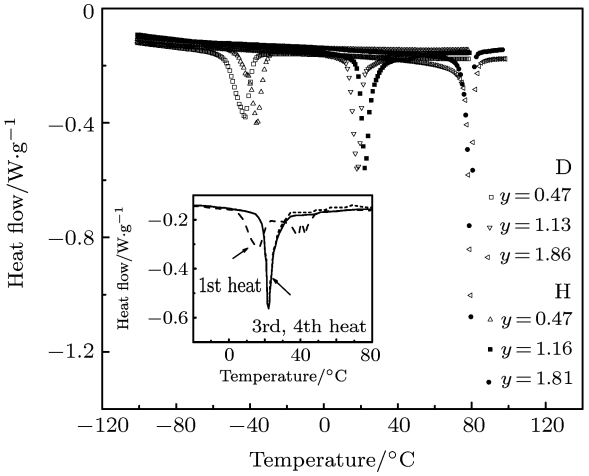


Fig. 3. The heat flow as a function of temperature of $LaFe_{11.83}Si_{1.17}H(D)_y$ by DSC heating runs. The inset, the continuous four DSC runs for $LaFe_{11.83}Si_{1.17}H_{1.16}$, clearly shows that two separated phases at room temperature is merged into a single phase.

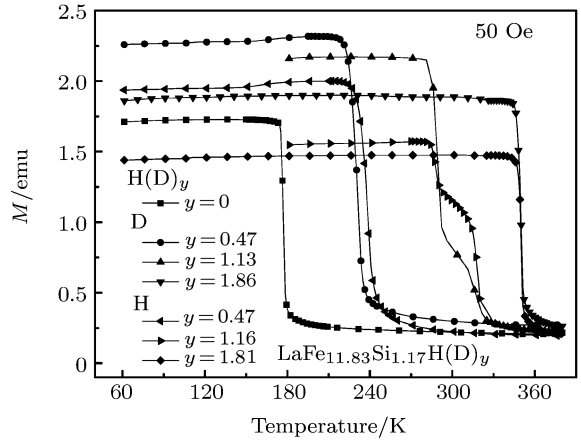


Fig. 4. The magnetization as a function of temperature of $La(Fe_{0.91}Si_{0.09})_{13}H(D)_y$ in a field of 50 Oe (1 Oe=79.5775 A/m).

of the DSC measurements in the range of experimental errors, which increase with a rate of ∼ 94 K per H(D) atom. But no obvious isotopic effect has been found in these materials.

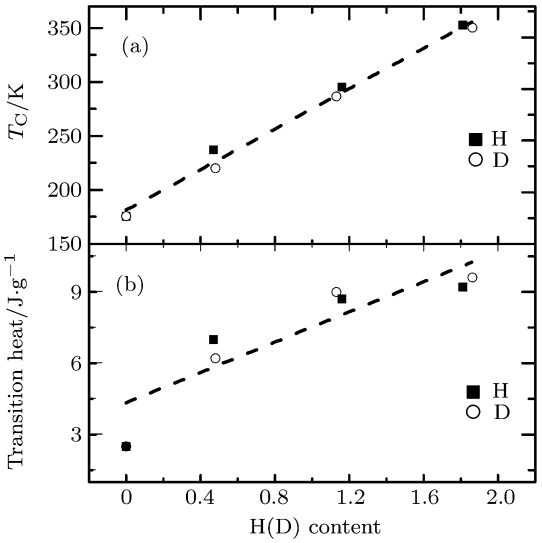


Fig. 5. Curie temperature (a) and transition heat (b) as functions of the absorbed H(D) concentration.

Finally the magnetic entropy change of $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$ was studied as an example since it can be considered as a potential magnetic refrigerant. Figure 6(a) shows its magnetization isotherms measured under the applied field up to 5 T from 340 K to 365 K. A para- to ferro-magnetism transition induced by the external magnetic field can be clearly marked by abnormal rapid increase of magnetization at the temperatures a bit above the Curie temperature. The magnetic entropy change $\Delta S_M(T,H)$ can be obtained using the Maxwell relation[18]

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \approx \sum_i \frac{1}{T_{i+1}-T_i}(M_{i+1}-M_i)\Delta H_i,$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} in a field H, respectively.

Figure 6(b) illustrates the magnetic entropy change $-\Delta S_M$ as a function of temperature of $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$ under different applied fields of 1.0, 2.0, 3.0, 4.0, and 5.0 T. The maximum of $-\Delta S_M$ is ∼26 J/kg·K under a magnetic field change of 5 T. However, a spike of the magnetic entropy change (∼ 40 J/kg·K) was observed in the process of field increase when the magnetization isotherms were recorded with a small interval of 1 K. The magnitude (∼ 38 J/kg·K under 3 T) is quite smaller than 43 J/kg·K in its parent compound $La(Fe_{0.91}Si_{0.09})_{13}$. Compared with $La(Fe_{0.91}Si_{0.09})_{13}$, the $-\Delta S_M$ is augmented by hydrogen and deuterium absorption.[17] The origin of the great magnetic entropy change should be attributed to IEM[10] transition near T_C.

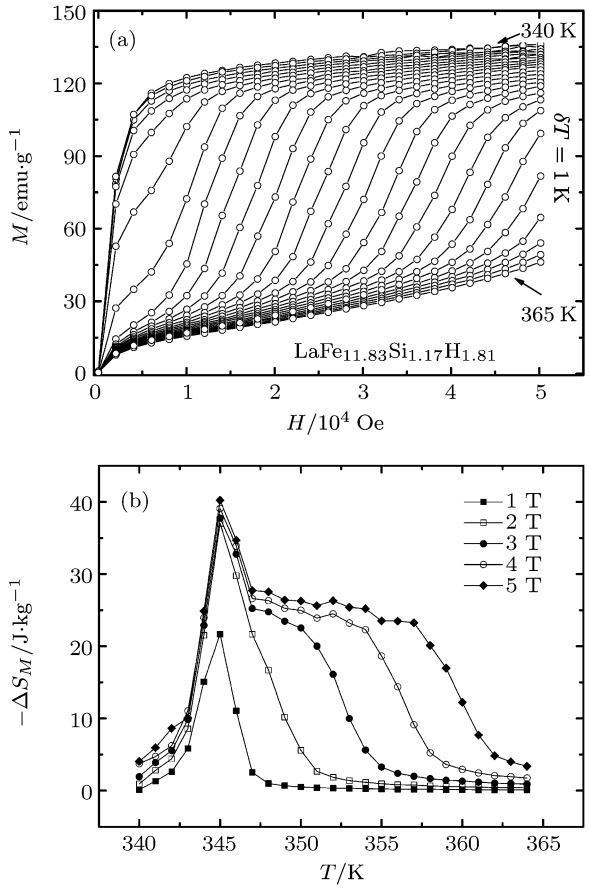


Fig. 6. (a) The magnetization of $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$ as a function of applied magnetic field measured near the Curie temperature and (b) the magnetic entropy change as a function of temperature with a magnetic field change of 1.0, 2.0, 3.0, 4.0, and 5.0 T calculated from data in panel (a).

4. Conclusions

The hydrides (deuterides) of $La(Fe_{0.91}Si_{0.09})_{13}$ have been synthesized by the gas–solid reaction with $NaZn_{13}$-type cubic structure, same with their parent compound. The maximum of the H(D) absorption capacity at 470 K is ∼ 1.9 H(D)/f.u. and the lattice expands with increasing the H(D) content. For the intermediate absorption concentration (∼ 1.1 H(D)/f.u.), two phases with different interstitial H(D) contents are checked out at room temperature, whereas slight heating up to 353 K drives them to a single phase. The Curie temperature increases linearly with the H(D) content. The mag-

netic entropy change of $La(Fe_{0.91}Si_{0.09})_{13}H_{1.81}$ reaches ~ 26 J/kg·K under a magnetic field change of 5 T near the Curie temperature $T_C = 350$ K. No isotope effect in our experimental observations seems to imply that the strong interplay between magnetism and lattice results only from the magnetovolume effect.

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