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Hydrogen absorption of $LaFe_{11.5}Si_{1.5}$ compound under low hydrogen gas pressure*

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Hydrogen absorptions of $LaFe_{11.5}Si_{1.5}$ compound in 1-atm hydrogen gas at different temperatures are investigated. The hydrogen content in the hydrogenated sample does not increase with the increase of temperature of hydrogen absorption but changes complicatedly. The characteristic of first-order transition in $LaFe_{11.5}Si_{1.5}$ compound is weakened after hydrogen absorption. It leads the peaks of magnetic entropy to become wider and the hysteresis loss to reduce significantly, but relative cooling power (RCP) is not changed considerably.

Keywords: magnetic refrigerant, Curie temperature, hydrogen absorption temperature, magnetocaloric effect

PACC: 7530S, 7550

1. Introduction

Magnetic refrigerator research indicates that the $La(Fe_xSi_{1-x})_{13}$-based compound is a kind of magnetic refrigeration material with very promising practicability.[1−4] The cubic $NaZn_{13}$-type $La(Fe_xSi_{1-x})_{13}$ compounds (space group $Fm\bar{3}C$) with $0.86 \leq x \leq 0.90$ show a thermally-induced first-order magnetic transition between the paramagnetic and the ferromagnetic states at the Curie temperature T_C and an itinerant-electron metamagnetic (IEM) transition just above T_C,[5−9] which causes large magnetocaloric effects (MCEs) of the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad}.[6−8,10] However, its lower Curie temperature (T_C ∼190 K)[6] makes it difficult to be used in domestic appliances. To realise room temperature magnetic refrigerators, it is necessarily to raise its T_C. Now incorporating interstitial hydrogen atom in $La(Fe_xSi_{1-x})_{13}$ compounds is regarded as a very effective way to increase T_C of $La(Fe_xSi_{1-x})_{13}$ compounds.[11−15] In $La(Fe_xSi_{1-x})_{13}H_y$ interstitial compounds, hydrogen atoms occupy the interstitial hole site at 24*d*, corresponding to the face-centre position in cubic lattice formed by the Fe^I atoms at 8*b* sites.[16] Due to the intrusion of hydrogen into the 24*d* site the Fe^{II}–Fe^{II} (at 96*i* sites) is expanded, resulting in lattice expansion which yields a considerable increase in Curie temperature.[16,17] After controlling hydrogen absorption in a 50-atm H_2 atmosphere, T_C increases up to about 280–330 K, keeping obvious metamagnetic transition properties.[11,14,15,17] Hydrides of $LaFe_{11.57}Si_{1.43}$ intermetallic compound were studied by high-energy ball milling in the presence in a 5-atm hydrogen gas.[12] It is an effective way for incorporating hydrogen into $LaFe_{11.57}Si_{1.43}$ intermetallic compound, but little study on hydrogen absorption has been carried out so far.

In the present work, we study hydrides of $LaFe_{11.5}Si_{1.5}$ compound in 1-atm hydrogen gas at different hydrogen absorption temperatures. The magnetocaloric effect and the magnetic transition of the hydrides are investigated.

2. Experimental procedure

$LaFe_{11.5}Si_{1.5}$ compound was prepared from pure (≥99.9%) elements by using the arc-melting method in argon atmosphere. Each arc-melted ingot was flipped over and remelted at least three times to ensure its

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homogeneity. The ingots were annealed at 1323 K for 10 days, and after that quenched in ice water. The hydrogen absorption took place in a furnace equipped with a vacuum system. The samples were crushed into powder with about 0.8 mm in size. Then the powders were kept in a quartz tube with one end sealed, which was inserted into the centre of the furnace. The powders were heated in vacuum and then hydrogen was poured into the tube. The pressure of hydrogen was kept 1 atm. The temperature of samples was measured by a thermocouple very close to the quartz tube. The duration of hydrogen absorption was determined by curves of time dependence of hydrogen content, which were shown in Fig.1. As shown in this figure, the powders absorbed the hydrogen gas quickly and after about 50 min the saturation is reached. About 100 min later, the amount of hydrogen in the sample trends to decrease slightly at 623 K. It indicates that a process of releasing hydrogen comes into being because of higher temperature. So the time of hydrogen absorption is selected to be 2 h. The structures of all parent alloys and corresponding hydrides were identified by powder x-ray diffraction (XRD) and the magnetic measurements were carried out by physical property measurement system (PPMS). To study the phase transition of the compounds differential scanning calorimeter (DSC) was used.

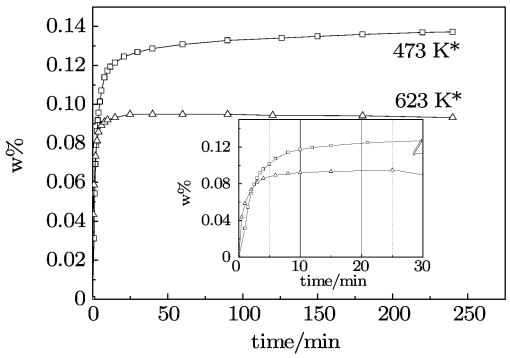


Fig.1. Time dependences of hydrogen content for hydrogen absorption of $LaFe_{11.5}Si_{1.5}$ compounds at 473 K and 623 K, where the symbol * refers to the hydrogen absorption temperature.

3. Results and discussion

The x-ray diffraction analysis on powdered sample is shown in Fig.2. All the compounds after hydrogen absorption at different temperatures remain a cubic $NaZn_{13}$-type structure. The diffraction peaks shift toward low angles compared with those of original compounds. It is indicated that hydrogen atoms have entered interstices between crystal lattices as interstitial atoms, leading to an expansion of unit cell volume, but the diffraction peak shifts of hydrogenates do not increase with hydrogen absorption temperature increasing, but change complicatedly. After hydrogen absorptions at 473, 553 and 623 K, (a=1.4867 Å), the values of lattice constant a increase from 1.4867 to 11.6004, 11.5692 and 11.6505 Å (1 Å=0.1 nm), respectively.

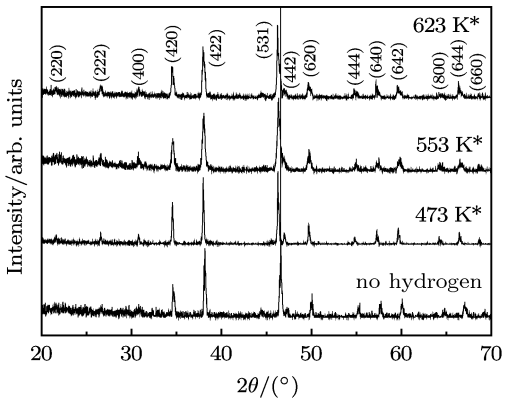


Fig.2. The x-ray diffraction patterns of $LaFe_{11.5}Si_{1.5}$ compounds before and after hydrogen absorption, where symbol * refers to hydrogen absorption temperature.

DSC curves of $LaFe_{11.5}Si_{1.5}$ compound and hydrogenated samples are shown in Fig.3. After the $LaFe_{11.5}Si_{1.5}$ compound is hydrogenated, its endothermic peak shifts from 194 K to room temperature for hydrogenated compounds. In Fig.4, Curie temperature T_C can be determined from differential of DSC (DDSC) curves. T_C decreases when hydrogenation temperature rises from 473 K to 553 K. Then T_C increases with hydrogenation temperature increasing. Because hydrogen absorption is an exothermic reaction, high temperature is not conducive to hydrogen absorption. At high temperatures, the compounds have a tendency to dehydrogenation. Therefore, with temperature of hydrogen absorption increasing, the Curie temperature of hydride changes complicatedly. The results indicate that higher temperature is of no advantage for hydrogen absorption. The influence factors and the change rule of Curie temperatures of hydrides remain to be studied in the future. Also, a comparison between endothermic peaks before and after hydrogen absorption indicates that the temperature range of the phase transition becomes much wider.

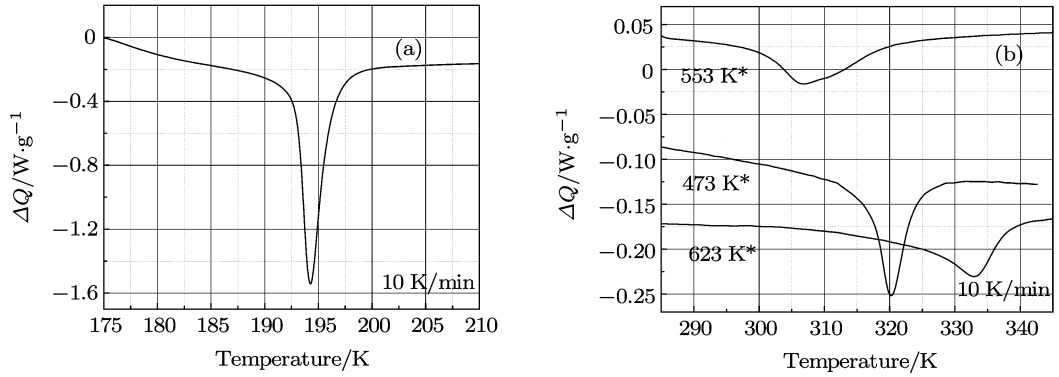


Fig.3. DSC measurements for $LaFe_{11.5}Si_{1.5}$ (a) and compounds after hydrogen absorption (b), where symbol * refers to hydrogen absorption temperature.

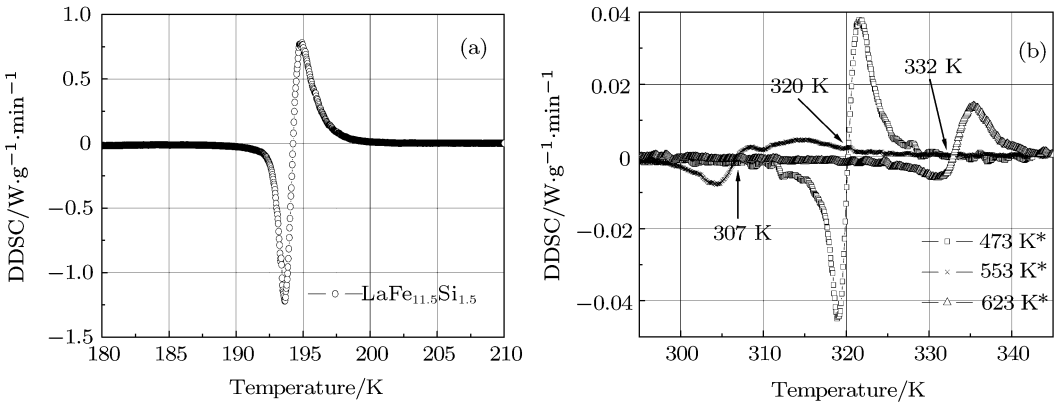


Fig.4. DDSC measurements for $LaFe_{11.5}Si_{1.5}$ (a) and compounds after hydrogen absorption (b), where symbol * refers to hydrogen absorption temperature.

Figures 5(a) and 5(b) show the magnetisation curves for parent compound and hydrogenated samples at 553 K, respectively. The magnetisation curves of parent compound exhibit evidently the features of IEM transition. The paramagnetic state transforms into the ferromagnetic state with the applied magnetic field rising when the temperature is above 194 K of T_C temperature. The feature of IEM transition in the magnetization curves is not so clear for hydrogenated sample as those for parent compound. Also it is noteworthy that magnetisation curves for parent compound show larger hysteresis effect than those for hydrogenated sample, which might result from relatively low hydrogen pressure we used.

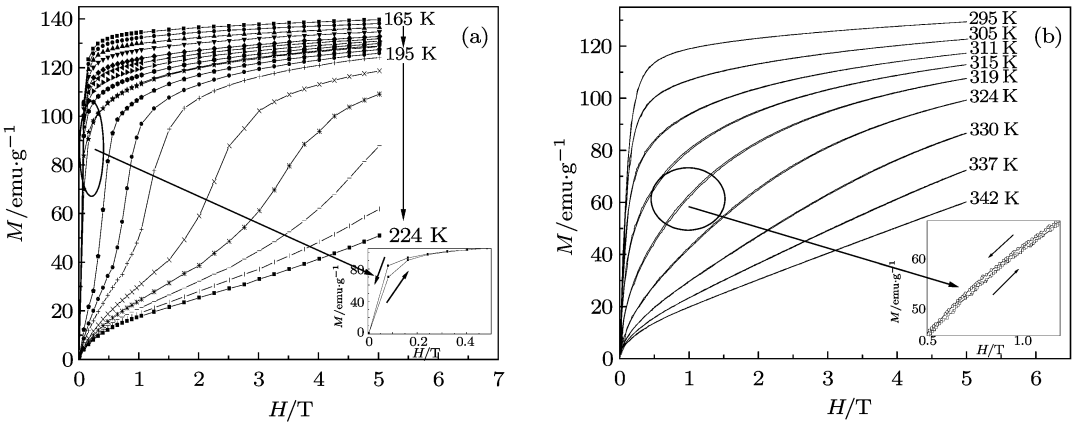


Fig.5. Magnetization curves for $LaFe_{11.5}Si_{1.5}$ (a) and compounds after hydrogen absorption at 623 K (b).

For H_2 atmosphere at a high pressure, 50 atm for example, studies have shown that the lattice expansion due to the interstitial hydrogen atoms is highly symmetric, with keeping the IEM transition.[17] According to that, the IEM transition could be weakened by asymmetrical hydrogen absorption in unit cell of $LaFe_{11.5}Si_{1.5}$ compound in a 1-atm H_2 gas. From Fig.6 we can see that in the cubic lattice formed by the Fe^{I} atoms, interstitial hydrogen atoms occupy 24*d* sites, corresponding to the face center position. In compounds after hydrogen absorption at a low pressure, hydrogen atoms might occupy different 24*d* sites in each cell, resulting in asymmetrical hydrogen absorption. So the quantity of hydrogen atoms and their position in unit cell are sensitive to the pressure of hydrogen atmosphere.

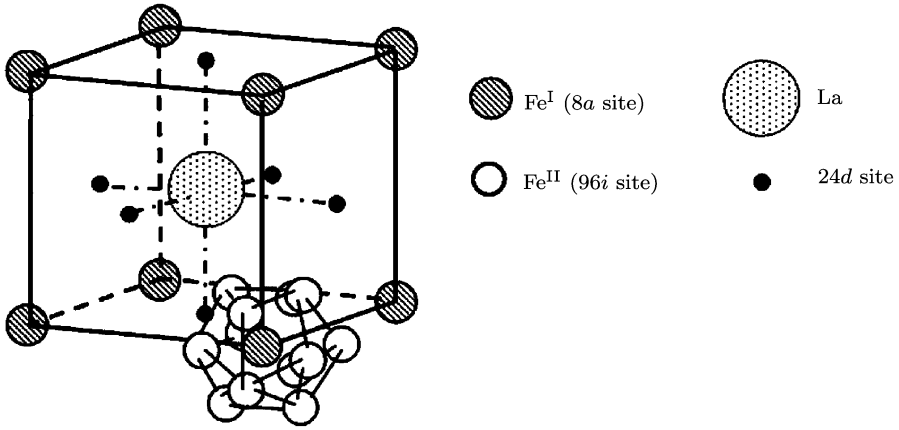


Fig.6. Schematic structure of the 1/8 part of a cubic unit cell for $La(Fe_xSi_{1-x})_{13}$. One typical Fe^{II} icosahedral cluster is depicted but others are omitted for brevity.

The value of ΔS_m is evaluated from the variation of magnetization as a function of M and H as follows:

$$\Delta S_m = \int_0^{H_{max}} \mu_0 \left(\frac{\partial M}{\partial T}\right) dH. \quad (1)$$

In Fig.7, the variations of ΔS_m are plotted as a function of T and ΔB for parent and hydrogenated compounds, with a magnetic field changing from 0 to 2 T. The ΔS_m shows a maximum ~18 J/kg·K around 195 K for $LaFe_{11.5}Si_{1.5}$. For hydride samples, the ΔS_m shows a maximum at room temperature. The maximum value becomes lower than that of $LaFe_{11.5}Si_{1.5}$ because the phase transition temperature range becomes wider. For a practical application to magnetic refrigerator, relative cooling power (RCP) is calculated (see Table 1). The RCP of compounds after hydrogen absorption is quite similar to that of the parent compound, especially for samples hydrogenated at 553 K and 623 K separately. However, a huge reduction of hysteresis loss in hydrides of $LaFe_{11.5}Si_{1.5}$ can be found in Table 1. The hysteresis loss is reduced from 35.37 to about 3 J/kg·K after hydrogen absorption compared with that of original compound. The peak broadening of the magnetic entropy and the lower hysteresis due to weak IEM transition are of advantage for application. Similar phenomenon was also observed in Ref.[12].

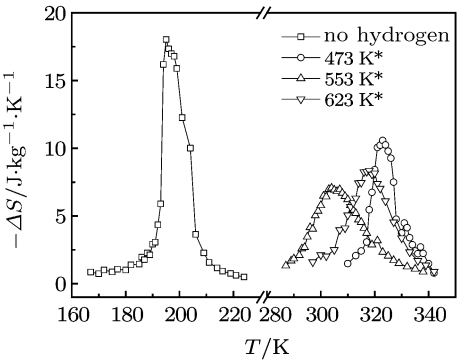


Fig.7. Temperature dependences of change in magnetic entropy, $|\Delta S_m|$ of $LaFe_{11.5}Si_{1.5}$ and compounds after hydrogen absorption as static magnetic field varies from 0 to 2 T, where symbol * refers to hydrogen absorption temperature.

Table 1. Curie temperatures, magnetic entropies, relative cooling powers, hysteresis losses, and lattice constants of $LaFe_{11.5}Si_{1.5}$ and compounds after hydrogen absorption with magnetic field changing from 0 to 2 T ($\Delta H = 2$ T).

compounds	hydrogen absorption temperature/K	T_C/K	$\lvert\Delta S_m\rvert$/(J/kg·K)	RCP/(J/kg)	hysteresis loss(J/kg·K)	a/Å
$LaFe_{11.5}Si_{1.5}$	/	194	18.00	176.4	35.37	11.4867
$LaFe_{11.5}Si_{1.5}H_{1.5}$	473	320	9.70	110.3	2.56	11.6004
$LaFe_{11.5}Si_{1.5}H_{1.26}$	553	307	7.06	158.9	3.02	11.5692
$LaFe_{11.5}Si_{1.5}H_{1.66}$	623	332	8.38	166.1	2.82	11.6505

4. Conclusion

The effects of hydrogen absorption temperature on magnetic property and magnetocaloric effect are investigated for the $LaFe_{11.5}Si_{1.5}$ compound in a 1-atm H_2 gas. The hydrogen content in the hydrogenated sample does not increase with the increase of temperature of hydrogen absorption but changes complicatedly. For the $LaFe_{11.5}Si_{1.5}$ compound, the Curie temperature T_C increases from 194 to 320, 307, and 332 K with the hydrogen absorption temperature at 473, 553, and 623 K, respectively. After hydrogen absorption, the features of first-order transition in $LaFe_{11.5}Si_{1.5}$ compound are not so clear. The hysteresis loss is significantly reduced but the relative cooling power (RCP) is not changed considerably.

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