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Large magnetic entropy change and magnetic properties in $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds*

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Magnetic properties and magnetic entropy change in $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds have been investigated. A significant increase of the Curie temperature T_C and a small increase of the saturation magnetizations μ_S have been observed after the introduction of interstitial H, which caused a slight volume expansion. The first-order field-induced itinerant-electron metamagnetic (IEM) transition remains and brings about a large magnetic entropy change around room temperatures for the compounds. The maximal magnetic entropy change is about 23.4, 17.7 and 15.9J/kg·K under a magnetic field change from 0 to 5T for x=0.01, 0.02 and 0.03, respectively. Therefore, the compounds appear to be potential candidates for magnetic refrigerants around room temperatures.

Keywords: magnetic entropy change, itinerant-electron metamagnetic transition
PACC: 7530S

1. Introduction

Magnetic refrigeration(MR) research near the room temperatures has attracted much attention in recent years due to its potential applications with higher efficiency and environmentally clean in comparison with conventional gas refrigeration. Magnetic refrigeration utilizes the magnetocaloric effect (MCE) which is manifested as the isothermal magnetic entropy change of materials. So, materials displaying large magnetic entropy changes at the temperature of interest are very important in MR technology.[1−10] Recently, large magnetic entropy changes have been observed in 3d-transition-metal-rich systems $La(Fe,M)_{13}$ (M=Al and Si) compounds[11−15] and their interstitial compounds.[16−18] Previous research also confirmed that the addition of a small amount of Mn will bring about obvious changes in the magnetic properties and magnetic entropy change of $LaFe_{13-x}Si_x$ compounds.[19] In this paper, we prepared the $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds and studied the effects of interstitial H atoms on the magnetic properties and magnetic entropy changes.

2. Experimental procedure

The preparation of the parent alloys $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$ compounds with x=0.01, 0.02 and 0.03 has been described elsewhere.[19] The hydrogen absorption was carried out in high-purity H_2 of about 3MPa at 250°C for 5 h. The hydrogen concentration y was estimated at about 2.0 by weighing the mass before and after hydrogen absorption. The sensitivity of the balance used in weighing was 10^{-5}g. X-ray diffraction (XRD) measurements of powder samples using Cu $K\alpha$ radiation were performed to examine the phase purity and determine the crystallographic structure. Magnetic measurements were performed on a commercial MPMS-7 type superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

The cubic $NaZn_{13}$-type structure ($Fm3c$) of the $LaFe_{13-x}Si_x$ compounds remains, while the samples exhibit a remarkable volume expansion (about 3%) after hydrogen absorption. The thermomagnetic curves for the $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$ and

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$La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds under an applied magnetic field 0.01T are presented in Fig. 1. It shows that the Curie temperature T_C, defined as the temperature corresponding to the minimum of dM/dT, is increased significantly by hydrogen absorption and has values 287K, 312K and 336K for x=0.01, 0.02, and 0.03, respectively. The effect of hydrogenation on the magnetic properties is caused mainly by 3d band-narrowing due to the decrease in the overlap of the Fe 3d wavefunctions as the distance between the Fe-icosahedral clusters increases. The magnitude of J_{TT} (namely J_{Fe-Fe} and J_{Fe-Mn}), the exchange coupling between T-T atoms, enhances due to the volume expansion associated with the hydrogen absorption, leading to the significant increase of T_C. The thermomagnetic curves also show a sharp change near the magnetic ordering temperature, that is, the magnitude of $\partial M/\partial T$ around T_C remains very large, which is of great importance to the large magnetic entropy changes.

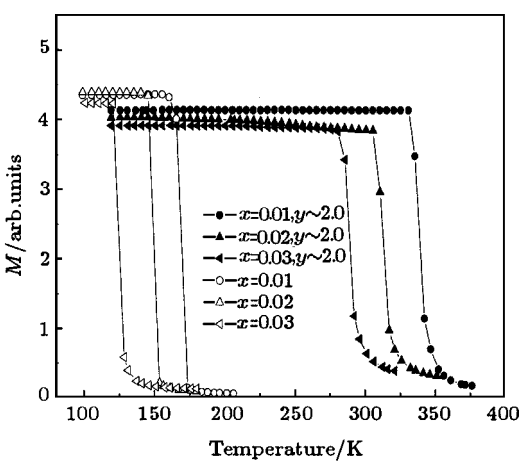


Fig.1. Thermomagnetic curves as a functions of temperature under an applied magnetic field 0.01T for $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$ and $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds.

The saturation magnetization μ_S at 5K was determined from the M-1/H curves for the La $(Fe_{1-x}Mn_x)_{11.7}$ $Si_{1.3}$ and La $(Fe_{1-x}$ $Mn_x)_{11.7}$ $Si_{1.3}$ H_y compounds, which are found to increase slightly after hydrogen absorption, as shown in Fig.2. The decline of the saturation magnetization of $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$ compounds with increasing the Mn concentration has been discussed elsewhere.[19] The increase of μ_S after hydrogen absorption has two reasons. The first is the volume expansion which makes the 3d band narrower and brings about the increase in the Fe magnetic moment by reducing the overlap of the Fe 3d wavefunctions. The other is that the increased Fe–Mn or Mn–Mn distance makes transition metals to couple in parallel.

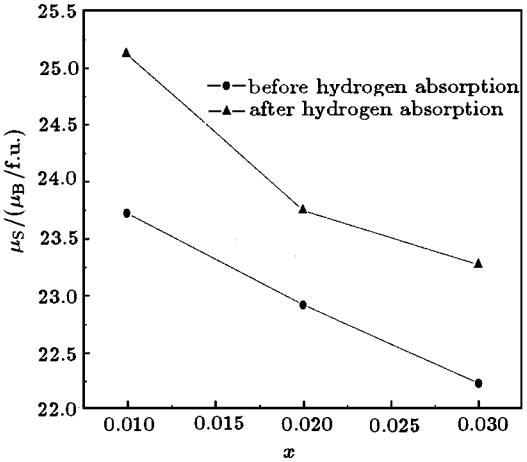


Fig.2. Saturation magnetization μ_S at 5K for $La(Fe_{1-x}$ $Mn_x)_{11.7}Si_{1.3}$ compounds before and after hydrogen absorption.

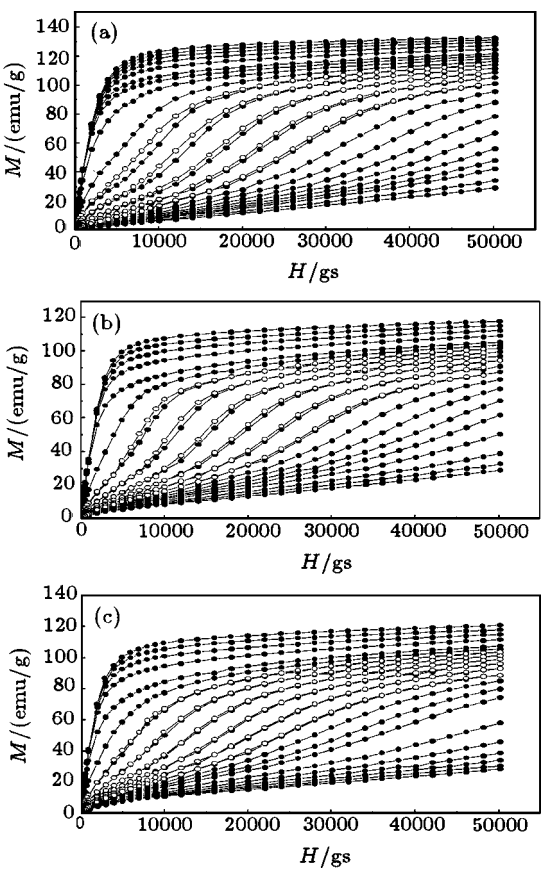


Fig.3. Magnetization isotherms for $La(Fe_{1-x}Mn_x)_{11.7}$ $Si_{1.3}H_y$ compounds (a) x=0.01 (b) x=0.02 (c) x=0.03. Isotherms on increasing field and decreasing field are performed in temperature regions in the vicinity of T_C.

The magnetization isotherms for all samples were measured in the field increase or decrease mode in a

wide temperature range. The sweep rate of the field was slow enough to ensure the M-H curves should be in isothermal equilibrium. The temperature step was 2K in the vicinity of T_C and 5K in ranges far from T_C. Figure 3 shows the magnetic isotherms of $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds. The magnetization processes show that there exits a field-induced first-order itinerant-electron metamagnetic (IEM) transition from paramagnetic to ferromagnetic order. The negative slopes of the Arrott plots (shown in Fig.4) for all samples above the respective T_C confirm this conclusion, which indicates that the hydrogen atoms do not seriously influence the shape of the density of the states around the Fermi level.[20] However, the IEM transition becomes weaker with increasing the Mn content. It is one reason for decreasing the magnetic entropy change with increasing Mn concentration. One can also see that the hysteresis of the $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds upon field increase and decrease becomes smaller with increasing the Mn concentration. It is considered to be a very favourable characteristic for magnetic refrigeration applications.

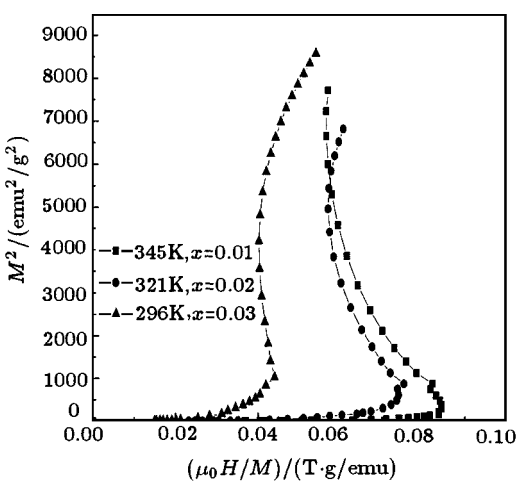


Fig.4. Arrott plots above the Curie temperature for $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds.

The magnetic entropy change $|\Delta S|$ is calculated from Maxwell relation $\Delta S(T,H) = -\int(\partial M/\partial T)_H dH$ using the collected magnetization data.[21] Fig. 5 shows the plots of $|\Delta S|$ versus temperature at the magnetic field change H=0–2T and 0–5T. The peak value of $|\Delta S|$ is 23.4, 17.7 and 15.9J/kg·K under a magnetic field change from 0 to 5T and 16.0, 13.0 and 11.0J/kg·K under a magnetic field change from 0 to 2T for x=0.01, 0.02 and 0.03, respectively, notably exceeding that of Gd($|\Delta S|$ ~9.8J/kg·K under ΔH=5T and $|\Delta S|$ ~4.5J/kg·K under ΔH=2T, T_C=293K).[5] So the large values of $|\Delta S|$ are obtained around the room temperature in the range between 287 and 336K.The realization of large magnetic entropy change is restricted to a certain temperature interval around the Curie temperature. Increasing the field change, the temperature interval will increase and the maximum $|\Delta S|$ extends to higher temperatures. The origin of the large magnetic entropy changes in the $La(Fe,Mn)_{11.7}Si_{1.3}H_y$ compounds can be attributed to the high saturation magnetization and the considerable variation of the magnetization near T_C.

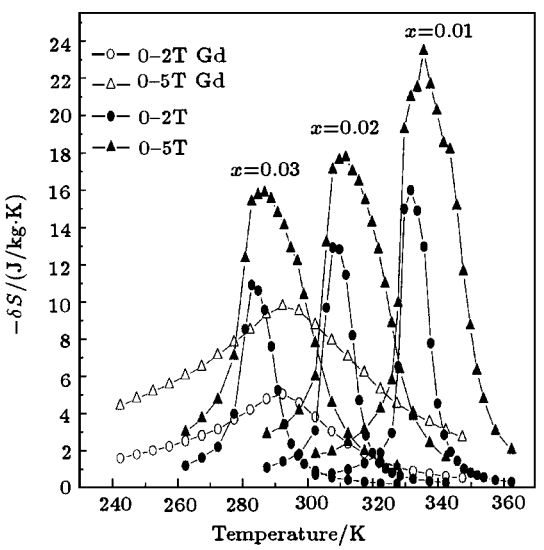


Fig.5. Temperature dependence of the magnetic entropy change $|\Delta S|$ for $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds in comparison with rare earth metal Gd under different magnetic field changes of 0–2T and 0–5T.

4. Summary

Magnetic properties and large magnetic entropy change of the $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds have been investigated. The Curie temperature T_C increases significantly, up to room temperature, and the saturation magnetization rises slightly due to the volume expansion after hydrogen absorption. The hydrogen atoms do not seriously influence the shape of the density of the states around Fermi level, and the first-order field-induced itinerant-electron metamagnetic (IEM) transition remains. This results in a large magnetic entropy change $|\Delta S|$ around the room temperature. Furthermore, the hysteresis of $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds upon

field increase and decrease becomes smaller with increasing the Mn concentration. Therefore, the $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}H_y$ compounds appear to be potential candidates for magnetic refrigerants around room temperatures.

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