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Magnetic properties and magnetic entropy changes of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds with $0 \leq x \leq 0.5$*

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Magnetic properties and magnetic entropy changes in $LaFe_{11.5}Si_{1.5}$ have been investigated by partially substituting Pr by La. It is found that $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds remain cubic $NaZn_{13}$-type structures even when the Pr content is increased to 0.5, i.e. $x = 0.5$. Substitution of Pr for La leads to a reduction in both the crystal constant and the Curie temperature. A stepwise magnetic behaviour in the isothermal magnetization curves is observed, indicating that the characteristic of the itinerant electron metamagnetic (IEM) transition above T_C becomes more prominent with the Pr content increasing. As a result, the magnetic entropy change is remarkably enhanced from 23.0 to 29.4 J/kg·K as the field changes from 0 to 5 T, with the value of x increasing from 0 to 0.5. It is more attractive that the magnetic entropy changes for all samples are shaped into high plateaus in a wide range of temperature, which is highly favourable for Ericsson-type magnetic refrigeration.

Keywords: $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds, magnetic entropy change, magnetic property, itinerant electron metamagnetic transition

PACC: 7530S, 7550C

1. Introduction

Magnetic materials showing large magnetocaloric effects (MCEs) have attracted much attention due to their potential applications as magnetic refrigerants. In recent years, large MCEs have been observed in materials that display the first-order phase transitions, such as $Gd_5Si_2Ge_2$,[1] La(Fe, Si)$_{13}$,[2,3] $MnAs_{1-x}Sb_x$,[4] and $MnFeP_{1-x}As_x$,[5] etc. The families of $NaZn_{13}$-type (La,R)(Fe,M)$_{13}$ such as interstitial compounds LaFeSiH,[6−8] LaFeSiC[9]and the compounds with partial substitutions of La and Fe by R = Ce,[10] and M = Mn[11] or Co,[12,13] etc have been intensively studied as attractive candidates for magnetic refrigerant materials. The cubic $NaZn_{13}$-type $LaFe_{13-x}Si_x$ intermetallic compounds in their ground states are ferromagnetic and have a high magnetization due to the high Fe content. In the paramagnetic state above the Curie temperature T_C, $LaFe_{13-x}Si_x$ exhibits an itinerant electron metamagnetic (IEM) transition behaviour.[14] Although the MCE of $LaFe_{13-x}Si_x$ is enhanced as the content of Si is reduced, the T_C decreases with the increase of x and finally reaches a value much lower than room temperature. In order to increase the T_C of the compound and obtain a large MCE at room temperature, a lot of investigations on magnetic properties and magnetocaloric effects of the $LaFe_{13-x}Si_x$ compounds have been made by substituting Co atoms for Fe atoms[12,13] and/or introducing interstitial hydrogen or carbon atoms.[6−9,11] It has been reported that the $LaFe_{11.2}Co_{0.7}Si_{1.1}$ compound exhibits a magnetic entropy change of 20.3 J/kgK at T_C = 274 K as the field changes from 0 to 5T, due to the IEM transition and the negative thermal lattice expansion above T_C.[12] A large magnetic entropy change can also be obtained in a wide range of temperature by the hydrogenizing of $LaFe_{13-x}Si_x$.[6−8] Recently, it has been found that partial substitution of Ce for La can enhance MCE in the $La(Fe_{0.88}Si_{0.12})_{13}$ compound due to the change in 3d band structure.[10] In the present paper, we report the effect of the substitution of Pr

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for La on magnetic properties and entropy changes in $LaFe_{11.5}Si_{1.5}$. It is found that the compounds remain completely cubic $NaZn_{13}$- type structure even when the substitution of Pr for La is up to 50% in content. According to the magnetic measurements, it is found that the magnetic entropy changes are remarkably enhanced by increasing the Pr content.

2. Experimental details

$La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5) compounds were prepared by arc melting an appropriate quantity of raw materials of Pr (99% in purity), La (99.9%), Fe (99.9%), and Si (99.999%) in a high-purity argon atmosphere. The arc-melted ingots were wrapped by Mo foil, sealed in a quartz tube of high vacuum, annealed at 1373 K for 40 days and then quenched in liquid nitrogen. The ingots were then ground into powders. X-ray diffraction (XRD) measurement on powder samples was performed by using Cu $K\alpha$ radiation to identify the phase and crystal structure. The magnetization was measured as a function of temperature and magnetic field around the Curie temperature by using a physical property measurement system (PPMS) from Quantum Design. By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization.

3. Results and discussion

Figure 1 displays the powder XRD patterns of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ ($0 \leq x \leq 0.5$) measured at room-temperature. The compounds are crystallized in a very clean single phase with a cubic $NaZn_{13}$-type structure. The $Fm3c(O_h^6)$ group-space symmetry remains even when the Pr content, x, is increased to 0.5. The values of crystal lattice parameter a obtained from the XRD patterns for different Pr contents are shown in Fig.2. It can be seen that the substitution of Pr for La leads to a linear reduction of the lattice parameter from 1.1467 to 1.1444 nm, as the value of x increases from 0 to 0.5. This may be related to the difference in atomic volume between La and Pr, i.e. the substitution of smaller Pr atoms for La leads to a contraction of lattice dimensions.

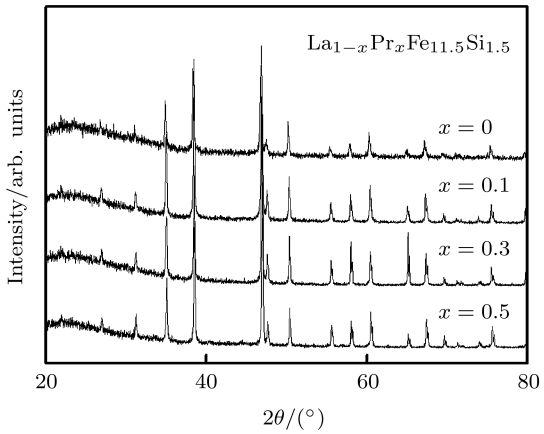

Fig.1. Room-temperature powder XRD patterns of the $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.3 and 0.5.

Figure 2 shows the Curie temperature T_C as a function of Pr content for $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ ($0 \leq x \leq 0.5$) compounds. The T_C is determined from the temperature dependent magnetization measured under an applied magnetic field of 0.05 T. The value of T_C, defined as the temperature corresponding to the maximum slope in the thermal magnetization curves, is found to decrease with the Pr content increasing from 194 K for $x = 0$ to 181 K for $x = 0.5$. Similar behaviours have been observed in $La_{1-x}Ce_x(Fe_{0.88}Si_{0.12})_{13}$,[10] in which T_C decreases with the increase of Ce content. The lattice contraction makes T_C reduce, which is a common feature for the La-Fe-Si systems. It has been verified that the introducing of interstitial hydrogen or carbon atoms can cause T_C to increase due to the lattice expansion in compounds,[6–9,11] while the applying of a static pressure can lead T_C to decrease due to the lattice contraction.[15] A linear relation between T_C and atom spacing has been established by using the Bean–Rodbell model.[16]

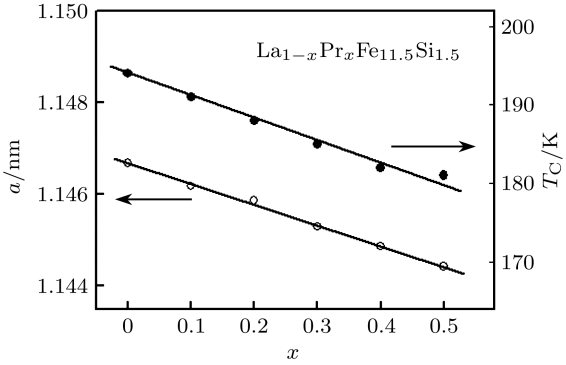

Fig.2. Crystal lattice parameter and Curie temperature for the $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ ($0 \leq x \leq 0.5$) compounds versus Pr content.

Figure 3 shows the typical magnetization isotherms of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ with $x = 0$, 0.2 and 0.4, measured under ascending and descending fields in a wide range of temperature around the Curie temperature. For the compounds with $x = 0$, 0.2 and 0.4, a temperature step of 1 K is chosen in the vicinity of T_C and a step of 3 K for the other regions. The scan rate of the field is low enough to ensure that the $M-H$ curves will be recorded in an isothermal mode. The present compounds $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ show a remarkable IEM transition from paramagnetic (PM) to ferromagnetic (FM) states above T_C. With the Pr content increasing, the characteristic of the IEM transition becomes more prominent and the critical field of the IEM transition increases faster with temperature. A more attractive feature is the appearing of stepwise magnetic behaviours near the Curie temperature T_C in the field-ascending process, but such a two-step change of magnetization disappears in the field-descending process. The detailed analysis indicates that the two-step transition may reflect the coexistence of FM and PM phases near T_C.[17]

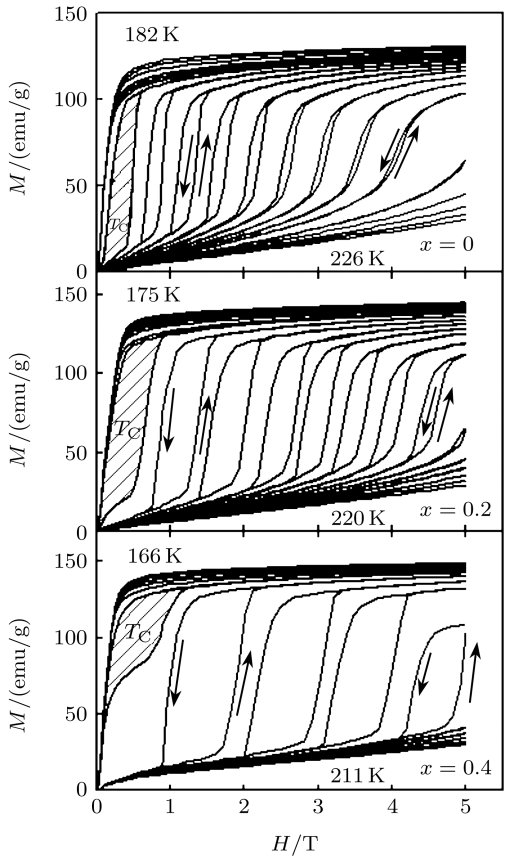

Fig.3. Magnetization isotherms of the $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.2 and 0.4 measured in the field-ascending and field-descending processes.

The magnetic entropy change ΔS is calculated from the magnetization data by using the Maxwell relation $\Delta S(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$, which is widely used for evaluating ΔS even for the systems with the first-order transition.[1−5,18,19] Figure 4(a) shows the magnetic entropy change of $La_{0.6}Pr_{0.4}Fe_{11.5}Si_{1.5}$ compound with temperature measured in the field-ascending process. One can find that the ΔS peak is peculiar in the field-ascending process. The ΔS is peaked at T_C with a very high value and then followed by a plateau. The plateau slightly grows but significantly broadens to higher temperatures with the external field increasing, which results from the field-induced IEM transition at temperatures above T_C. The amplitude of the ΔS plateau for sample $x = 0.4$ reaches ∼29 J/kg K in a temperature range of 182.5–201 K, and for the spike-shape peak at 181.5 K the amplitude attains 92.7 J/kg K for the field changing from 0 to 5 T. A very similar behaviour has been reported in $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ compound, showing a ΔS spike to reach an amplitude of 70 J/kg K at its T_C.[20] It is found that the entropy of $LaFe_{13-x}Si_x$ compounds changes under pressures, showing a ΔS spike to have an amplitude of ∼60 J/kg K which is followed by a plat plateau.[15] The most striking ΔS spike is found to have an entropy change of ∼267 J/kg K in MsAs compounds for the field changing from 0 to 5T under a constant pressure of 0.23 GPa,[21] which is a value much larger than the theoretical result (∼103 J/kg K). In our present study, however, it is found from Fig.4(b) that in the field-descending process, ΔS behaves in quite a different way. The broad plateau of ΔS remains nearly the same shape as that observed in the field-ascending process, but the extremely high peak at T_C disappears. A careful analysis[17] suggested that the extremely high peak did not reflect the intrinsic nature of the entropy change at T_C. It results from the coexistence of FM and PM phases near T_C, which is indicated in Fig.3 by the appearing of the two-step magnetization. Actually, the fraction of FM in the coexistent phases does not contribute to ΔS, and only PM phase makes contributions, with a magnetic field applied. The spike-shape ΔS peak appearing at T_C overrates the ΔS. Nevertheless, in the field-descending process no two-step transition is observed, implying that no observable coexistence of multiphases appears. As a result, ΔS is shaped into a broad plateau only without any spike-like peaks appearing. Specific heat measurements have verified

that the broad plateau reflects the intrinsic nature of ΔS.[17] As is well known, the ideal magnetic refrigerant suitable for use in an Ericsson-type refrigerator should have a constant magnetic entropy change through a thermodynamical cycle.[22] λ-like or tower-like ΔS usually appearing in magnetic materials does harm to the efficiency in an Ericsson-type cycle. The plateau-shape ΔS in the present samples is highly favourable for the Ericsson-cycle refrigerator.

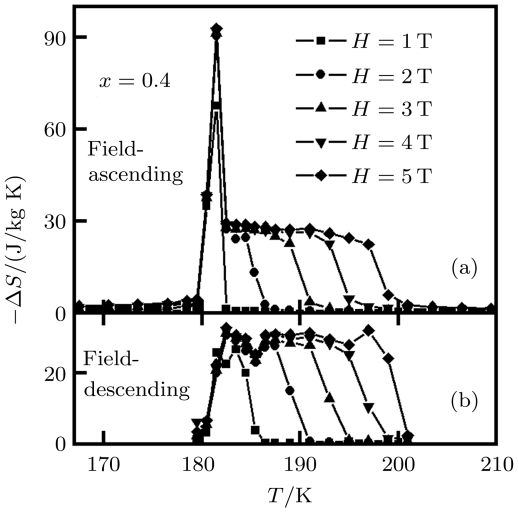

Fig.4. Magnetic entropy changes of $La_{0.6}Pr_{0.4}Fe_{11.5}Si_{1.5}$ compound versus temperature based on magnetization data measured in the field-ascending (a) and field-descending (b) processes.

Figure 5 shows the temperature dependences of the magnetic entropy change for all the compounds studied here, with the field increasing from 0 to 5 T. The changes in maximum magnetic entropy for the $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) compounds are found to be 23.0, 25.9, 27.1, 28.4, 29.1 and 29.4 J/kg K, respectively, as the field changes from 0 to 5T. Here the maximum ΔS is taken as the maximum amplitude of the ΔS plateau (not ΔS spike). We find that the substitution of Pr for La in $LaFe_{11.5}Si_{1.5}$ can lead to a remarkable increase in magnetic entropy change as shown in the inset of Fig.5. The enhancement of ΔS results from the strengthening of IEM transition above T_C, caused by the substitution of Pr for La, which is similar to the case of Ce-doped LaFeSi.[10]

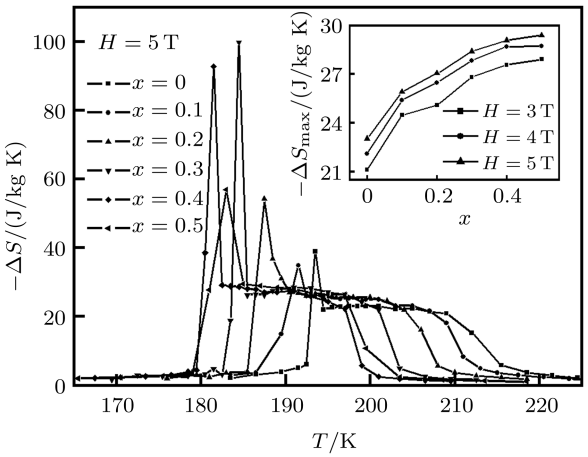

Fig.5. Temperature dependences of the entropy change of $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) compounds in magnetic fields changing from 0 to 5 T. The inset presents the magnetic entropy change as a function of Pr content.

In summary, the influence of the substitution of Pr for La on magnetic properties and magnetic entropy changes was systematically investigated in $La_{1-x}Pr_xFe_{11.5}Si_{1.5}$ compounds. It is found that the substitution of Pr for La does not affect the formation of the cubic $NaZn_{13}$-type structure, but enhance the magnetic entropy change. The structures of the compounds remain the $Fm3c(O_h^6)$ group-space symmetry even when the substitution of Pr for La is increased to 50% in content. The substitution of Pr for La favours the first-order transition at T_C and the IEM transition above T_C, which leads to the enhancement of magnetic entropy change. A great magnetic entropy change and a nearly unchanged plateau of ΔS are discovered in a temperature range from 180 to 220 K, which is highly favourable for the application in Ericsson-type magnetic refrigerator. Therefore, the partial substitution of Pr for La in $LaFe_{11.5}Si_{1.5}$ is highly expected to enhance the MCEs.

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