Direct measurements of magnetocaloric effect in the first-order system $LaFe_{11.7}Si_{1.3}$

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The magnetocaloric effect was investigated in $LaFe_{11.7}Si_{1.3}$, which undergoes a first-order transition at ~188 K from the ferromagnetic to paramagnetic state. The magnetic entropy change upon a field increase from 0 to 5 T is as large as 29 J/kg K (212 mJ/cm^3 K). The adiabatic temperature change obtained via direct measurements reaches 4 K under a field change from 0 to 1.4 T. The large values of entropy change and adiabatic temperature change confirmed the large potential of present compound $LaFe_{11.7}Si_{1.3}$ as a magnetic refrigerant in the corresponding temperature range. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1563036]

I. INTRODUCTION

Recently, with the test of room-temperature magnetic refrigerators using permanent magnets[1,2] and the finding of materials with the giant magnetocaloric effect (MCE),[3–6] magnetic refrigeration and the search for materials with high MCE are attracting much more attention. The magnetocaloric effect is an intrinsic property of a magnetic solid. It is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change of the applied magnetic field. The MCE can be scaled by the isothermal entropy change ΔS or the adiabatic temperature change ΔT_{ad}.

The compounds with cubic $NaZn_{13}$ -type structure have been suggested to be appropriate materials for exploring efficient magnetic refrigerants,[7–10] and a great magnetic entropy change has been observed in $La(Fe,Si)_{13}$ and its Co-doped compounds.[5,6] In previous literatures[11,12] $LaFe_{13-y}Si_y$ compounds were found stabilizing at the region of $1.4 \leqslant y \leqslant 2.4$. Our researches indicate that a proper post-annealing can further lower the Si content in $LaFe_{13-y}Si_y$ maintaining their cubic $NaZn_{13}$ -type structure. The compounds with relatively low Si content show a first-order magnetic phase transition characterized by a sharp negative thermal expansion near Curie temperature T_C. Moreover, we found that reducing the content of Si strengthens the first-order nature of the magnetic transition. In this paper, we report the great magnetocaloric effect characterized by a large magnetic entropy change and a big adiabatic temperature change observed in the vicinity of the first-order phase transition in system $LaFe_{11.7}Si_{1.3}$.

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II. EXPERIMENT

The samples employed in the present investigation were prepared by repeatedly arc-melting appropriate amounts of the starting materials with purity of 99.9 wt %. The ingots were wrapped with Ta foil and subsequently homogenized in a vacuum-sealed quartz tube for 50 days at 1323 K, then quenched in liquid nitrogen. Quenching is important to obtain a stable compound with low Si content for this type of alloys. A single phase of the $NaZn_{13}$-type structure was identified by x-ray diffraction analysis. The composition of the present sample was checked as $LaFe_{11.7}Si_{1.3}$ by inductively coupled plasma atomic emission spectrometry (ICP-AES). All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The direct measurement of magnetocaloric effect was carried out under adiabatic conditions with a continuous registration of a temperature change upon a fast increase of applied magnetic field. The rate of the field change is about 0.7 T/sec. The accuracy of the measurements is about 5%.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 is the temperature-dependent magnetization measured in a low field of 100 Oe upon heating and cooling with the same rate, 2 K/min in the vicinity of Curie temperature T_C. Here T_C, defined as the maximum in dM/dT, was found to be 188 K in heating process. A temperature hysteresis of ~3 K exists in the temperature cycle, which is a character of a first-order system. The measurements of x-ray powder diffraction (XRD) patterns under different temperatures were performed in order to check the change of crystal structure upon phase transition. Figure 2(a) shows the collected XRD patterns at different temperatures

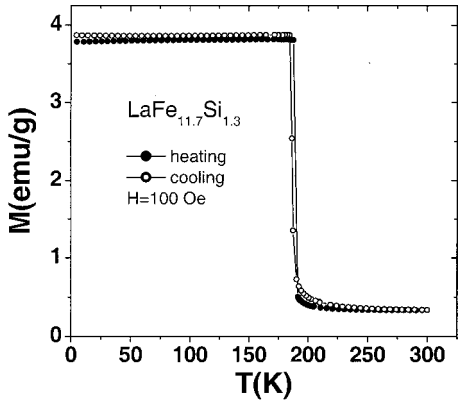

FIG. 1. Temperature-dependent magnetization of $LaFe_{11.7}Si_{1.3}$ measured under a field of 100 Oe upon heating and cooling.

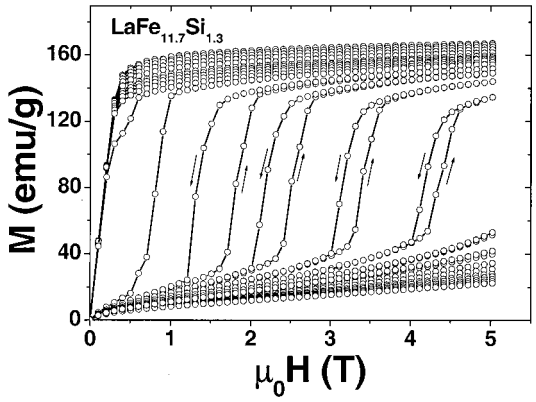

FIG. 3. Magnetization isotherms of $LaFe_{11.7}Si_{1.3}$ on field increase and decrease.

of 125, 185, 205, and 255 K. Marked by an asterisk in the patterns is the impurity of α-Fe. One can find that the crystal structure of $LaFe_{11.7}Si_{1.3}$ remains cubic $NaZn_{13}$ type on changing the magnetic state with temperature. The XRD pattern at 205 K obviously shifts to larger 2θ compared with that at 125 K, indicating the occurrence of a large thermal lattice contraction upon the first-order transition. It is noteworthy that the behavior of the XRD pattern at 185 K just below T_C manifests the coexistence of a large volume phase with a small one [see the details in Fig. 2(b)], which confirms the first-order nature of the phase transition. The inset of Fig. 2(a) displays the temperature dependence of the lattice parameter. A sharp shrinkage of $\sim 0.6\%$ at T_C could be observed, implying the sudden disappearance of the spontaneous magnetization and consequently a large magnetocaloric effect.

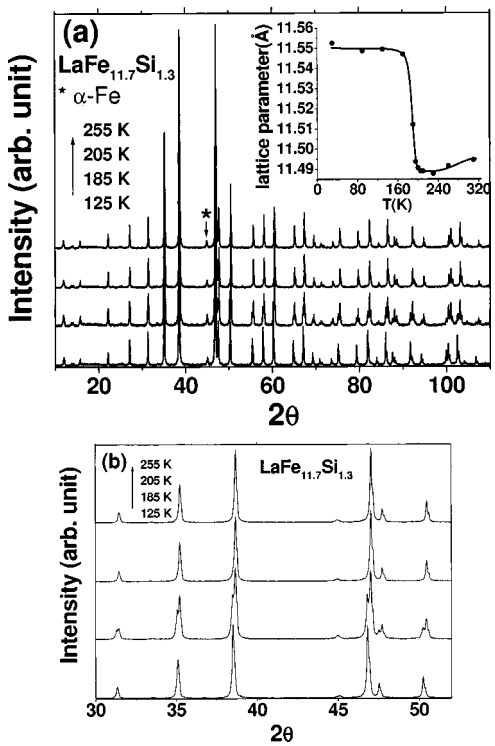

FIG. 2. (a) XRD patterns at different temperatures of 125, 185, 205, and 255 K for $LaFe_{11.7}Si_{1.3}$. The inset shows the temperature dependence of lattice parameter. (b) The detailed XRD patterns.

The measurements of magnetization isotherms of $LaFe_{11.7}Si_{1.3}$ upon field increase and decrease were performed up to 5 T in a wide temperature range with different temperature steps. In the vicinity of T_C a step of 2 K was chosen and a step of 5 K for the regions far away from T_C. Figure 3 shows selected curves for the sake of clarity. The sweep rate of the field is slow enough to ensure that the isotherms are recorded in an isothermal process. At temperatures below T_C, these curves exibit a characteristic ferromagnetic behavior. It should be noted that a sharp change of the magnetization with a hysteresis appears above a critical field H_C, which means that a field-induced first-order phase transition from paramagnetic to ferromagnetic state takes place above T_C. With increasing temperature the hysteresis width becomes narrower and the critical field H_C increases. However, the first-order nature of the transition retains up to at least 5 T. It is inspiring that the magnetic hysteresis does not extend to zero field, which is considered to be a very important characteristic to magnetic refrigerant applications.[13]

The magnetic entropy change ΔS can be obtained using the Maxwell relation $\Delta S(T,H)=\int_0^H(\partial M/\partial T)_H dH$ and the collected magnetization data.[3,4,13–15] This indirect method of using the Maxwell relation to measure the MCE has been verified as a reliable way to evaluate candidate materials for magnetic refrigeration, even for first-order systems.[13,14] Figure 4 shows the calculated $|\Delta S|$ upon field increase as a function of temperature for different magnetic fields. The inset of Fig. 4 shows the comparison of $|\Delta S|$ on field increase and decrease. One can find the shape and height of the $|\Delta S|$ peak on field decrease and increase is very similar. The $|\Delta S|$ peak values on field increase are ~ 23, ~ 25, and ~ 29 J/kg K under fields of 1, 2, and 5 T, respectively. Since the cooling power per unit volume is a critical parameter for a magnetic refrigerator, we give the $|\Delta S|$ by volumetric units, which are ~ 168, ~ 183, and ~ 212 mJ/cm^3 K for 1, 2 and 5 T, respectively. The density used in the unit transformation is estimated according to its structural symmetry and lattice parameter. Such a large magnitude of ΔS was rarely

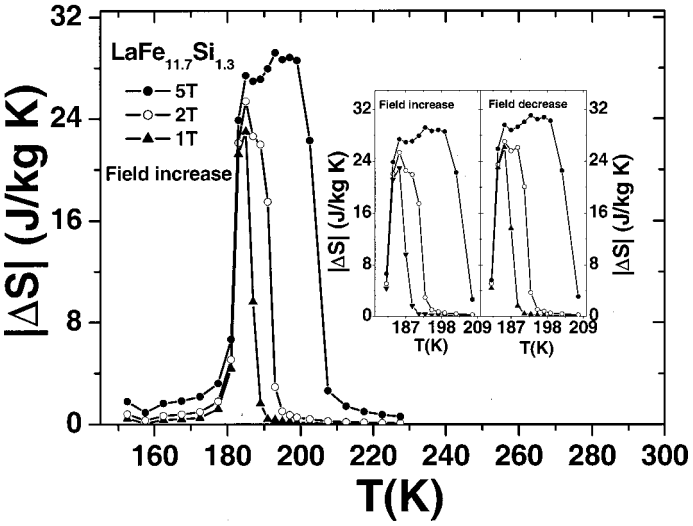

FIG. 4. Magnetic entropy change $|\Delta S|$ of $LaFe_{11.7}Si_{1.3}$ for the magnetic field changes of 0–1, 0–2, and 0–5 T. The inset shows the comparison of $|\Delta S|$ on field increase and decrease.

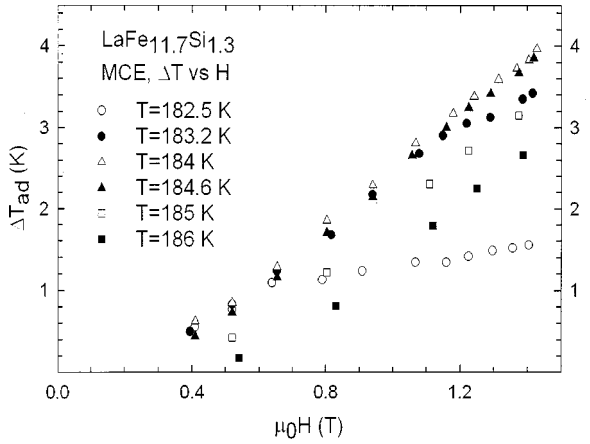

FIG. 6. Adiabatic temperature change ΔT_{ad} as a function of applied magnetic field obtained by direct measurements in the vicinity of T_C.

observed in the corresponding temperature range in the past.[16,17] We may compare these values with that of the well known $Gd_5Ge_2Si_2$ [$|\Delta S| \sim 14$ J/kg K at ~ 276 K under a field change of 0–2 T Ref. 13] and recently published $MnFeP_{0.45}As_{0.55}$ [$|\Delta S| \sim 14$ J/kg K at ~ 300 K under a field change of 0–2 T Ref. 3]. Moreover, the field-induced itinerant-electron metamagnetic transition from the paramagnetic to ferromagnetic state above T_C results in a significant broadening of the ΔS peak to higher temperature with increasing field,[5] which is considered to be favorable to a real refrigerator based on the Ericsson cycle.

In order to further make sure the great potential of present compound $LaFe_{11.7}Si_{1.3}$ as a candidate for magnetic refrigerant, we directly measured the adiabatic temperature change ΔT_{ad} with applying magnetic field up to 1.4 T. Figure 5 displays the temperature-dependent ΔT_{ad} obtained in both heating and cooling processes. One can find that the peak value of ΔT_{ad} reaches 4 K upon a field change from 0 to 1.4 T. This value is larger than that of typical magnetic refrigerant materials, $\Delta T_{ad} \sim 2$ K/T. The observed temperature hysteresis (~ 3 K) of ΔT_{ad} in heating and cooling processes is in agreement with the result obtained from the thermal magnetization curve (Fig. 1).

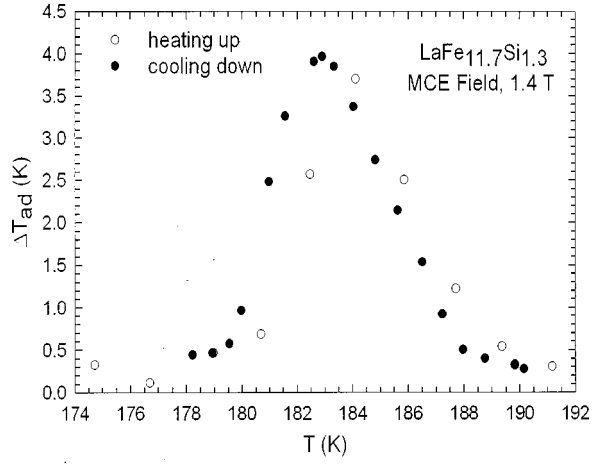

FIG. 5. Adiabatic temperature change ΔT_{ad} as a function of temperature obtained by direct measurements under a field change of 0–1.4 T.

The ΔT_{ad} peak positions were found around 3 K less than T_C defined by thermal magnetization curves. This difference in picking ΔT_{ad} temperature and T_C may be explained in a simple thermodynamic model[18] and could be accounted as quite reasonable.

The field-dependent ΔT_{ad} collected at different temperatures in the vicinity of Curie temperature T_C is shown in Fig. 6. One can find that ΔT_{ad} collected at temperatures from 182.5 to 184.6 K starts to increase at the same magnetic field of $H \sim 0.4$ T, and ΔT_{ad} collected above 183.2 K has a nearly linear dependence on applied field in the region of 0.4 T $< H <$ 1.4 T. Most curves (except for 182.5 and 183.2 K) do not display a saturation behavior. It means that adiabatic temperature change would increase noticeably with increasing field.

IV. CONCLUSION

In summary, we observed a significant large magnetocaloric effect in the first-order system $LaFe_{11.7}Si_{1.3}$ near T_C of 188 K. The results of the adiabatic temperature change obtained by direct measurements in this type of alloys are reported in detail. Large values of the isothermal entropy change and adiabatic temperature change together with nonsaturated behavior of the field dependence of the MCE confirmed the large potential of present compound $LaFe_{11.7}Si_{1.3}$ as a magnetic refrigerant in the corresponding temperature range. Our analysis permits us to conclude that the application of a magnetic field does not impact on the nature of the magnetic phase transition and the transition remains its character of first-order nature up to at least 5 T. This factor permits us to talk about possible applications of this type of compounds in a magnetic refrigeration machine using magnetic field up to 5 T.

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