Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound $LaFe_{11.4}Si_{1.6}$

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Magnetization of the compound $LaFe_{11.4}Si_{1.6}$ with the cubic $NaZn_{13}$-type structure was measured as functions of temperature and magnetic field around its Curie temperature T_C of ~208 K. It is found that the magnetic phase transition at T_C is completely reversible. Magnetic entropy change ΔS, allowing one to estimate the magnetocaloric effect, was determined based on the thermodynamic Maxwell relation. The achieved magnitude of $|\Delta S|$ reaches 19.4 J/kg K under a field of 5 T, which exceeds that of most other materials involving a reversible magnetic transition in the corresponding temperature range. The large entropy change is ascribed to the sharp change of magnetization, which is caused by a large negative lattice expansion at the T_C. An asymmetrical broadening of $|\Delta S|$ peak with increasing field was observed, which is resulted from the field-induced itinerant-electron metamagnetic transition from the paramagnetic to ferromagnetic state above the T_C. *© 2001 American Institute of Physics.* [DOI: 10.1063/1.1375836]

Recently, the interest in the research of magnetocaloric effect (MCE) has been considerably enhanced owing to its potential impact on energy savings and environmental concerns.[1–13] A variety of prototype materials and intermetallic compounds were studied in an attempt to achieve a large MCE,[9] of which GdSiGe alloys were discovered exhibiting great MCE in a very wide temperature range.[8] The compounds with cubic $NaZn_{13}$-type structure have been considered to be appropriate materials for investigating the MCE due to their excellent soft ferromagnetism and high magnetization.[11–13] Previous investigations[14–15] indicated that the $NaZn_{13}$-type compounds have abundant physics contents and exhibit interesting magnetic behaviors. Moreover, it was recently found that the compounds $LaFe_{13-x}Si_x$ with a low Si content show an itinerant electron metamagnetic (IEM) transition above T_C and a negative lattice expansion at the T_C,[16,17] which results in a sharp change of magnetization. The simultaneously sharp change of lattice parameter and magnetization at a transition temperature should strongly influence the magnetic entropy change. In this letter, a $LaFe_{11.4}Si_{1.6}$ alloy, with a large negative thermal expansion at T_C(~208 K) and a metamagnetic transition above the T_C, was chosen to investigate the magnetic entropy change ΔS. For comparison, the ΔS of the $LaFe_{10.4}Si_{2.6}$ compound (T_C ~243 K) with a conventionally small lattice expansion was also measured.

The detail of sample preparation was described previously.[11] Powder x-ray diffraction (XRD) patterns obtained at different temperatures in the absence of a field confirmed that both samples of $LaFe_{11.4}Si_{1.6}$ and $LaFe_{10.4}Si_{2.6}$ remain cubic $NaZn_{13}$-type structure upon altering the magnetic state from paramagnetism to ferromagnetism. The temperature dependence of the lattice parameter obtained from XRD patterns is presented in Fig. 1. The lattice parameter of $LaFe_{11.4}Si_{1.6}$ is bigger than that of $LaFe_{10.4}Si_{2.6}$ due to the smaller radius of Si than Fe atoms. It is noteworthy that the lattice parameter of $LaFe_{11.4}Si_{1.6}$ at the ferromagnetic state (~11.52 Å) is larger than that at the paramagnetic state (~11.48 Å) by ~4% in the vicinity of the T_C, and the change of lattice parameter is sharp. In contrast, a small and slow change of the lattice parameter is shown for $LaFe_{10.4}Si_{2.6}$ near the T_C. The impurity of α-Fe phase is observed in the two samples. The amount of the α-Fe phase in $LaFe_{11.4}Si_{1.6}$ is estimated to be ~8 wt % based on the Rietveld refinement of (XRD) data.

All magnetic measurements were performed using a superconducting quantum interference device magnetometer. Figure 2 presents the thermomagnetic curves $M-T$ of $LaFe_{11.4}Si_{1.6}$ measured under a low field of 0.02 T. $M-T$ curves show a completely reversible behavior in heating and cooling processes at the T_C. The values of the T_C about 208 and 243 K are determined from the $M-T$ curves for $LaFe_{11.4}Si_{1.6}$ and $LaFe_{10.4}Si_{2.6}$, respectively. The inset of Fig. 2 shows the $M-T$ of $LaFe_{11.4}Si_{1.6}$ in a field of 1 T in comparison with that of $LaFe_{10.4}Si_{2.6}$. Obviously, the former shows a much sharper change of magnetization than that of the latter, implying that the $LaFe_{11.4}Si_{1.6}$ compound has a larger magnetic entropy change than $LaFe_{10.4}Si_{2.6}$. Magnetic hysteresis loops measurements at various temperatures con-

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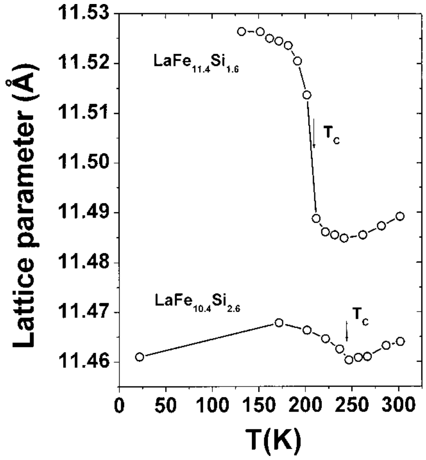

FIG. 1. Temperature dependent lattice parameter of $LaFe_{11.4}Si_{1.6}$ in comparison with that of $LaFe_{10.4}Si_{2.6}$.

firmed the excellent soft magnetic properties of $LaFe_{11.4}Si_{1.6}$. The coercive field is ~18 Oe at 5 K.

Figure 3(a) displays the magnetization isotherms of $LaFe_{11.4}Si_{1.6}$ measured on a field increase and decrease in a wide temperature range with different temperature steps. In the vicinity of the Curie temperature, from 200 to 230 K, the temperature step of 2 K is chosen and a step of 5 K for the far regions of 165–200 K and 230–255 K. The sweep rate of the field is slow enough to ensure that $M-H$ curves are recorded in an isothermal process. It is evident that every isotherm shows a reversible behavior between the field increase and decrease. One knows that a completely reversible MCE requires that there is no hysteresis in the magnetization as a function of both the temperature and the magnetic field. The present sample is just such a case.

As shown in Fig. 3(a), the magnetization M is smoothly saturated and its magnitude gradually decreases with increasing temperature below the T_C. Above the T_C, the plots of $M-H$ are curved significantly but the tendency of saturation is conserved, which is associated with the IEM transition from the paramagnetic to ferromagnetic state. Figure 3(b) shows Arrott plots of $LaFe_{11.4}Si_{1.6}$, in which the appearance of the inflection point confirms the occurrence of a metamag-

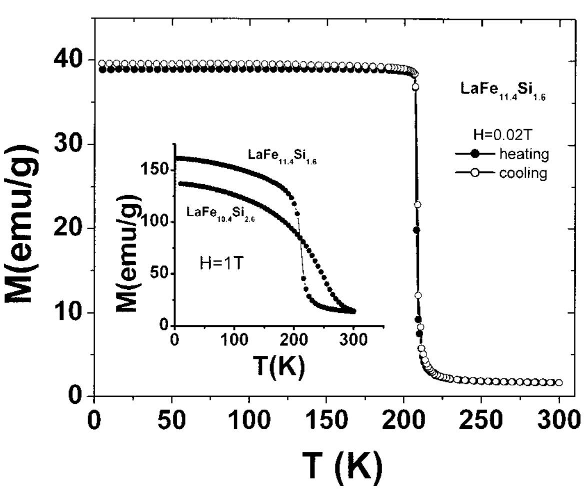

FIG. 2. Temperature dependence of magnetization $M-T$ of $LaFe_{11.4}Si_{1.6}$ measured on heating and cooling under a field of 0.02 T. The inset shows $M-T$ of $LaFe_{11.4}Si_{1.6}$ under 1 T in comparison with that of $LaFe_{10.4}Si_{2.6}$.

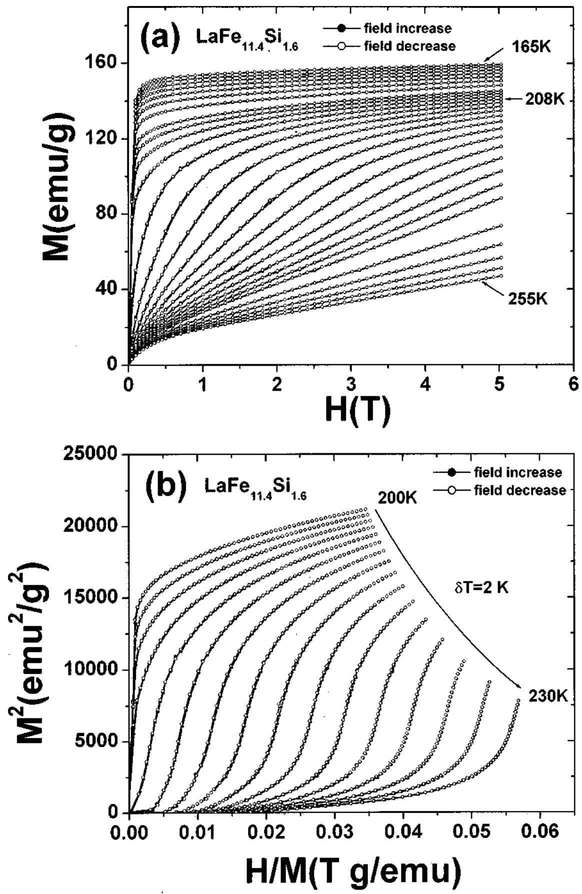

FIG. 3. (a) Magnetization isotherms of $LaFe_{11.4}Si_{1.6}$ on field increase and decrease. Temperature step is 2 K in the region of 200–230 K, and 5 K in 165–200 K and 230–265 K. (b) The Arrott plots of $LaFe_{11.4}Si_{1.6}$.

netic transition from the paramagnetic to ferromagnetic ordering above the T_C.[16,18,19] A slight nonlinearity in the $M-H$ curves [Fig. 3(a)] is found at low fields for temperatures much higher than the T_C, which may be ascribed to the existence of α-Fe impurity.

Magnetic entropy change ΔS can be obtained using the Maxwell relation

$$\Delta S(T,H)=\int_0^H\left(\frac{\partial M}{\partial T}\right)_H dH$$

and the collected magnetization data.[7,9,10,20] Because of the reversibility of magnetization on the field (Fig. 3), the calculated ΔS on the field increase should be equal to that on field decrease. Figure 4 shows the $|\Delta S|$ of $LaF_{11.4}Si_{1.6}$ as a function of temperature for different magnetic fields. One should note that the observed $|\Delta S|$ exceeds that of most materials associated with a reversible phase transition at the corresponding temperature range.[9] The peak values of $|\Delta S|$ under applied fields of 1, 2, and 5 T are 10.5, 14.3, and 19.4 J/kg K, respectively. Such a high magnitude of $|\Delta S|$ was rarely observed in 3d alloys involving a reversible transition at the corresponding temperature range.

Another interesting feature is that the ΔS peak of $LaFe_{11.4}Si_{1.6}$ broadens asymmetrically with the increase of the applied field. The magnitude of the broadening above the T_C is obviously larger than that below the T_C, which can be clearly indicated by differential curves (inset of Fig. 4). The negative peak position in the differential curves shifts to a

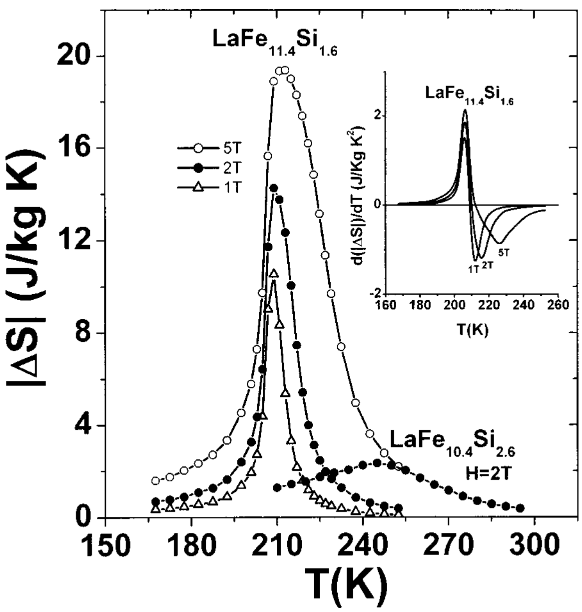

FIG. 4. Magnetic entropy change $|\Delta S|$ of $LaFe_{11.4}Si_{1.6}$ for the magnetic field changes of 0 to 1.0 to 2, and 0 to 5 T respectively. For comparison, the $|\Delta S|$ of $LaFe_{10.4}Si_{2.6}$ under 2 T is also presented. The inset shows the differential curves of $|\Delta S|$ for $LaFe_{11.4}Si_{1.6}$.

higher temperature greatly with a field increase in contrast the positive peak almost fixes at one temperature. The little shift of the ΔS peak position to a higher temperature induced by the applied fields is also clearly shown in the differential curves. It is believed that the field-induced metamagnetic transition above the T_C contributes to the asymmetrical broadening of ΔS. As seen from Figs. 2 and 3, the critical field for the metamagnetic transition increases with the increase of temperature above the T_C. Indeed, a low field only drives the transition at the temperature near the T_C, while a high field can drive the transition at the temperature much higher than the T_C, which results in a considerable entropy change at high temperatures under high fields. Thus, the ΔS peak asymmetrically broadens to a high temperature with an increasing applied field.

The origin of the large $|\Delta S|$ in compound $LaF_{11.4}Si_{1.6}$ should be attributed to the rapid change of magnetization at the T_C, which is caused by a dramatic negative lattice expansion (see Fig. 1). For comparison, Fig. 4 also presents a magnetic entropy change of $LaFe_{10.4}Si_{2.6}$ with a conventionally small lattice expansion under a field of 2 T. Obviously, the magnetic entropy change of $LaFe_{10.4}Si_{2.6}$ is much smaller than that of $LaFe_{11.4}Si_{1.6}$. The saturation magnetization of $LaFe_{11.4}Si_{1.6}$ and $LaFe_{10.4}Si_{2.6}$ was determined as 2.1 and 1.9 M_B/Fe from the $M-H$ curves at 5 K after deducting the contribution of α-Fe. The influence of the small difference of saturation magnetization between the two samples on the magnitude of ΔS should be very weak. Moreover, the temperature range of interest for the two samples is near. Therefore, the large negative lattice expansion should be the key reason for the very large $|\Delta S|$ in $LaF_{11.4}Si_{1.6}$. However, the physics of the large negative thermal expansion in the compound $LaF_{11.4}Si_{1.6}$ is still unclear. In the past, much attention was paid to the coupling between magnetism and lattice, and several theories attempted to describe the magneto-elastic effect in itinerant magnetic systems.[15,21,22] For a better understanding of the origin of the large negative expansion, further investigations on the magnetic-elastic effect in $LaF_{11.4}Si_{1.6}$ are strongly desired.

In summary, a large magnetic entropy change in a 3d alloy of $LaF_{11.4}Si_{1.6}$ with the cubic $NaZn_{13}$-type structure was observed at temperatures near ~208 K. The origin is believed to be due to the unusual magnetic phase transition, at which a large negative lattice expansion and a sharp change of magnetization take place. The field-induced metamagnetic transition from the paramagnetism to ferromagnetism above the T_C makes ΔS peak asymmetrically broaden to a higher temperature with a field increase. The reversible magnetization as a function of both temperature and magnetic field suggests the reversibility of MCE on the temperature and the field. More important is that the compound $LaF_{11.4}Si_{1.6}$ is cheaper than the materials previously reported.[4,8] Therefore, $LaF_{11.4}Si_{1.6}$ alloy is a very attractive candidate for magnetic refrigerant at the corresponding temperature range.

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