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 $\sim$208 K. It is found that the magnetic phase transition at $T_C$ is completely reversible. Magnetic entropy change $\Delta S$, 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. A variety of prototype materials and intermetallic compounds were studied in an attempt to achieve a large MCE, of which GdSiGe alloys were discovered exhibiting great MCE in a very wide temperature range. 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. Previous investigations 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 $T_C$, 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 $T_C$ ($\sim$208 K) and a metamagnetic transition above the $T_C$, was chosen to investigate the magnetic entropy change $\Delta S$. For comparison, the $\Delta S$ of the LaFe$_{10.4}$Si$_{2.6}$ compound ($T_C$ $\sim$243 K) with a conventionally small lattice expansion was also measured.

The detail of sample preparation was described previously. 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 ($\sim$11.52 Å) is larger than that at the paramagnetic state ($\sim$11.48 Å) by $\sim$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 $\alpha$-Fe phase is observed in the two samples. The amount of the $\alpha$-Fe phase in LaFe$_{11.4}$Si$_{1.6}$ is estimated to be $\sim$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 $T_C$s 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-
confirmed the excellent soft magnetic properties of LaFe\textsubscript{11.4}Si\textsubscript{1.6}. The coercive field is \(\sim 18\) Oe at 5 K.

Figure 3(a) displays the magnetization isotherms of LaFe\textsubscript{11.4}Si\textsubscript{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 ordering region. Figure 3(b) shows Arrott plots of LaFe\textsubscript{11.4}Si\textsubscript{1.6}, in which the appearance of the inflection point confirms the occurrence of a metamagnetic transition from the paramagnetic to ferromagnetic ordering above the \(T_C\). 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 \(\alpha\)-Fe impurity.

Magnetic entropy change \(\Delta S\) can be obtained using the Maxwell relation

\[
\Delta S(T, H) = \int_0^H \frac{\partial M}{\partial T} \, dH
\]

and the collected magnetization data. Because of the reversibility of magnetization on the field (Fig. 3), the calculated \(\Delta S\) on the field increase should be equal to that on field decrease. Figure 4 shows the \(|\Delta S|\) of LaFe\textsubscript{11.4}Si\textsubscript{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. 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 \(\Delta S\) peak of LaFe\textsubscript{11.4}Si\textsubscript{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
higher temperature greatly with a field increase in contrast the positive peak almost fixes at one temperature. The little shift of the $\Delta S$ 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 $\Delta S$. 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 $\Delta S$ peak asymmetically broadens to a high temperature with an increasing applied field.

The origin of the large $|\Delta S|$ in compound LaFe$_{11.4}$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$_s$/Fe from the $M$–$H$ curves at 5 K after deducting the contribution of $\alpha$-Fe. The influence of the small difference of saturation magnetization between the two samples on the magnitude of $\Delta S$ 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 LaFe$_{11.4}$Si$_{1.6}$. However, the physics of the large negative thermal expansion in the compound LaFe$_{11.4}$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.\textsuperscript{15,21,22} For a better understanding of the origin of the large negative expansion, further investigations on the magnetic-elastic effect in LaFe$_{11.4}$Si$_{1.6}$ are strongly desired.

In summary, a large magnetic entropy change in a 3d alloy of LaFe$_{11.4}$Si$_{1.6}$ with the cubic NaZn$_{13}$-type structure was observed at temperatures near $\sim$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 $\Delta S$ 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 LaFe$_{11.4}$Si$_{1.6}$ is cheaper than the materials previously reported.\textsuperscript{4,8} Therefore, LaFe$_{11.4}$Si$_{1.6}$ alloy is a very attractive candidate for magnetic refrigerant at the corresponding temperature range.

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