Effects of carbon on magnetic properties and magnetic entropy change of the LaFe$_{11.5}$Si$_{1.5}$ compound

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Effects of the interstitial carbon atoms on the magnetic properties, especially on the magnetic entropy change, of the LaFe$_{11.5}$Si$_{1.5}$ compound, have been studied. X-ray diffraction patterns reveal a monotonous increase of the lattice constant with the concentration of carbon, while the cubic NaZn$_{13}$-type structure remains unchanged. The Curie temperatures $T_C$ of LaFe$_{11.5}$Si$_{1.5}$C$_y$ are 195, 225, and 241 K for $y = 0$, 0.2, and 0.5, respectively, increasing with the increase of carbon concentration. The maximal magnetic entropy changes $\Delta S_D$ of LaFe$_{11.5}$Si$_{1.5}$C$_y$ at the respective $T_C$ under a magnetic field change of 0–5 T are 24.6, 22.8, and 12.7 J/kg K for $y = 0$, 0.2, and 0.5, respectively, notably exceeding that of Gd ($\Delta S_D = 9.8$ J/kg K at $T_C = 293$ K). The $\Delta S_D$ of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ is nearly as giant as that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ due to the first-order field-induced itinerant-electron metamagnetic transition that occurs in both compounds clearly observed for the LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ compound. With the increase of carbon concentration, the nature of magnetic transition has been changed from first order to second order, which results in the significant decrease of the magnetic entropy change. The large $\Delta S_D$, convenient adjustment of $T_C$ and relatively low cost make the LaFe$_{11.5}$Si$_{1.5}$C$_y$ interstitial compounds promising candidates for magnetic refrigerants in the corresponding temperature range. © 2003 American Institute of Physics.

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I. INTRODUCTION

Magnetic properties and magnetic entropy change of LaFe$_{13-x}$Si$_x$ have been studied in detail.$^1,2$ The results show that, when $x \leq 1.6$, the compounds exhibit a first-order magnetic transition, resulting in a giant magnetic entropy change. However, the Curie temperature $T_C$ is lower than $\approx 210$ K. For the purpose of practical use, it is necessary to increase $T_C$ to higher temperature and retain the large magnetic entropy change. It has been confirmed that the $T_C$ of La(Fe$_x$Al$_{1-x}$)$_{13}$ and La(Fe$_x$Si$_{1-x}$)$_{13}$ can be increased by the introduction of interstitial N or H atoms.$^3$–$^{13}$ In this article, the effects of interstitial C atoms on the magnetic properties, magnetic transition and magnetic entropy changes, of LaFe$_{11.5}$Si$_{1.5}$, have been studied. LaFe$_{11.5}$Si$_{1.5}$ was selected as the parent alloy because it exhibits obvious first-order itinerant-electron metamagnetic (IEM) transition, which results in a giant magnetic entropy change.

II. EXPERIMENT

The preparation of LaFe$_{11.5}$Si$_{1.5}$ has been described elsewhere.$^{14}$ The LaFe$_{11.5}$Si$_{1.5}$C$_y$ ($y = 0.2,0.5$) compounds are prepared by solid-solid phase reaction, i.e., by arc melting the intermediate alloy Fe–C with La, Fe, and Si. The subsequent heat treatment procedure is the same as that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$. Powder x-ray diffraction data were obtained using Cu $K\alpha$ radiation at room temperature.

All magnetic measurements were performed on a commercial MPMS-7 type superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the powder x-ray diffraction patterns of LaFe$_{11.5}$Si$_{1.5}$ and LaFe$_{11.5}$Si$_{1.5}$C$_y$ ($y = 0.2,0.5$) obtained at room temperature. It reveals a monotonous increase of the lattice constant with the concentration of carbon, while the cubic NaZn$_{13}$-type structure remains unchanged. It is noted that the lattice constants of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ($a = 11.481$ Å) and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ ($a = 11.518$ Å) are $\approx 0.052\%$ and...


0.375% larger than that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ ($a = 11.475$ Å), respectively. About 5% $\alpha$-Fe phase has been found in the LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$.

Figure 2 shows the temperature dependence of magnetization of LaFe$_{11.5}$Si$_{1.5}$ and its carbides under a magnetic field of 0.01 and 1.0 T, respectively. The Curie temperatures, determined from the $M$–$T$ curves, are $\sim 195$, $\sim 225$, and $\sim 241$ K for $y = 0$, 0.2, and 0.5, respectively, increasing from $\sim 195$ to $\sim 240$ K with the increase of carbon concentration. The intrusion of the interstitial C atoms into the lattice leads to lattice expansion, which makes the Fe 3$d$ band narrow and bring about the increase in $T_C$ by reducing the overlap of the Fe 3$d$ wave functions.

Magnetization isotherms of the LaFe$_{11.5}$Si$_{1.5}$C$_y$ compounds for $y = 0$, 0.2, and 0.5 are measured in a wide temperature range. The temperature step is 2 K in the vicinity of $T_C$ and 5 or 10 K for the range far away from $T_C$. The sweep rate of the field is slow enough to ensure that the $M$–$H$ curves are recorded in an isothermal process. Figures 3(a) and 3(b) show the magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$, the magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$ was shown elsewhere. 3

The magnetic entropy change $|\Delta S|$ was obtained from the Maxwell relation $\Delta S(T,H) = \int_0^H \langle \partial M/\partial T \rangle dH$ using the collected isothermal magnetization data. 15–17 Figure 4 shows the $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ under a magnetic field change of 0–2 and 0–5 T. Results for LaFe$_{11.5}$Si$_{1.5}$ and Gd$^2$ are also presented for comparison. The maximal $|\Delta S|$ values of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ at respective $T_C$ under 0–5 T are $\sim 22.8$ and $\sim 12.7$ J/kg K, respectively, while the corresponding values of LaFe$_{11.5}$Si$_{1.5}$ and Gd are 24.6 and 9.8 J/kg K, respectively.

It is noted that the $|\Delta S|$ of LaFe$_{11.5}$Si$_{1.5}$C$_y$ are very large, notably exceeding that of Gd. Compared with the parent alloy, $|\Delta S|$ decreases slightly for LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$, while for LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$, $|\Delta S|$ is only half of that of the parent alloy. Figure 5 shows Arrott plots of LaFe$_{11.5}$Si$_{1.5}$C$_y$ just above $T_C$. The appearance of obvious negative slope in the Arrott plots of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ just above $T_C$, like that of the parent alloy LaFe$_{11.5}$Si$_{1.5}$, confirms the occurrence of a first-order field-induced IEM transition, 1,18–20 which should be responsible for the giant magnetic entropy change in both compounds (Fig. 5). However, a second magnetic transition caused by a large number of interstitial carbon atoms occurs in LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$, which results in a lower $|\Delta S|$. 

FIG. 2. Temperature dependence of magnetization of LaFe$_{11.5}$Si$_{1.5}$C$_y$ ($y = 0, 0.2, 0.5$). Magnetic field is 0.01 T for $y = 0$ (see inset), and 1.0 T for $y = 0.2$ and 0.5.

FIG. 3. Magnetization isotherms of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ (a) and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ (b). Temperature step is 2 K in the vicinity of $T_C$, and 5 or 10 K for the range far from $T_C$. 

FIG. 4. Magnetic entropy changes of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ and LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ in comparison with those of the parent alloy LaFe$_{11.5}$Si$_{1.5}$ and Gd for magnetic field changes of 0–2 and 0–5 T.
IV. CONCLUSION

In summary, the $T_C$ of LaFe$_{11.5}$Si$_{1.5}$C$_y$ carbides increases monotonously with increasing carbon concentration. The nature of magnetic-phase transition in LaFe$_{11.5}$Si$_{1.5}$C$_y$ can be changed from first order to second order with increasing carbon concentration, which is crucial for the magnetic entropy change. LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ exhibits giant magnetic entropy change due to the occurrence of a typical first-order IEM transition, while the $\mu_D S$ of LaFe$_{11.5}$Si$_{1.5}$C$_{0.5}$ decreases significantly in accordance with a second-order magnetic transition. The large $\mu_D S$, convenient adjustment of $T_C$ and low cost make the LaFe$_{11.5}$Si$_{1.5}$C$_y$ interstitial compounds promising candidates for magnetic refrigerants in the corresponding temperature range.

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