Reduction of hysteresis loss and large magnetic entropy change in the NaZn$_{13}$-type LaPrFeSiC interstitial compounds

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Magnetic properties and magnetic entropy change of the NaZn$_{13}$-type La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_{x}$ compounds have been investigated. Both the lattice parameter and the Curie temperature increase linearly with increasing carbon concentration. The maximum hysteresis loss at $T_C$ reduces remarkably from 94.8 J/kg for $x=0$ to 23.1 J/kg for $x=0.3$ because of the weakening of the itinerant electron metamagnetic transition. However, the magnetic entropy change remains at the large values of 32.4 J/kg K for $x=0$ and 27.6 J/kg K for $x=0.3$ under a field change of 0–5 T, which implies that a large magnetocaloric effect and a small hysteresis loss have been simultaneously achieved in the La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_{x}$ carbides. © 2007 American Institute of Physics.

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Because of its great potential in magnetic refrigeration, magnetocaloric effect (MCE) in materials with first-order phase transition have attracted much attention since the discovery of the large magnetic entropy change in Gd$_5$Si$_2$Ge$_2$. As one of the typical MCE materials, the cubic NaZn$_{13}$-type LaFe$_{13-x}$Si$_x$ exhibits many distinctive properties, and is a focus of recent study. It has been found that the LaFe$_{13-x}$Si$_x$ undergoes a field-induced itinerant electron metamagnetic (IEM) transition above the Curie temperature $T_C$, which results in a large MCE. In general, the MCE of LaFe$_{13-x}$Si$_x$ enhances with the decrease of Si content, but the decrease of $T_C$. Meanwhile, a concomitant enhancement of hysteresis loss, which happens inevitably in materials having an IEM transition, occurs around the magnetic transition. Therefore, the depression of hysteresis loss, which lowers the efficiency of magnetic refrigeration, becomes important in the practical application of materials with first-order magnetic transition. Up to now, few quantitative evaluations of the hysteresis loss have been reported. A reduction of the hysteresis loss is found in the Gd$_6$Ge$_2$Si$_2$ with the addition of Fe, which results in a very small hysteresis loss by suppressing the formation of the orthorhombic phase. Previous investigations have revealed that appropriate substitution of Co for Fe in LaFe$_{13-x}$Si$_x$ compounds can cause an increase of the Curie temperature and weakening of the first-order character of the magnetic transition. As a result, the magnetization is nearly reversible against the variation in temperature and magnetic field. This means that a small hysteresis loss can be realized, but the substitution of Co also leads to a decrease of magnetic entropy change.

Recently, we have studied the magnetic properties and magnetic entropy change of La(Fe$_{13}$Si)$_{13}$ compounds by partially replacing La with Pr. A remarkable enhancement of magnetic entropy change is observed. However, the feature of first-order phase transition becomes prominent by the substitution of Pr, which leads to a large hysteresis loss. In this paper, we report the effect of the interstitial carbon atoms on the magnetic properties and magnetic entropy change of La$_{0.3}$Pr$_{0.7}$Fe$_{11.5}$Si$_{1.5}$C$_x$ compounds, in which a large MCE and a small hysteresis loss are achieved.

The samples with the nominal composition La$_{0.3}$Pr$_{0.7}$Fe$_{11.5}$Si$_{1.5}$C$_x$ ($x=0, 0.1, 0.2$, and $0.3$) were prepared by arc-melting in a high-purity argon atmosphere. The purity of starting materials is 99% for Pr, 99.9% for La, Fe, and FeC alloy, and 99.999% for Si. The resulting ingots were wrapped by molybdenum foil, sealed in a quartz tube under high vacuum, and annealed at 1373 K for 40 days to improve the crystallization of the samples, which were then quenched in liquid nitrogen. Powder x-ray diffraction (XRD) measurements were performed using Cu K$_\alpha$ radiation to identify phase purity and crystal structure. It is shown that all the samples are single-phase compounds with cubic NaZn$_{13}$-type structure. Magnetization measurements were carried out as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer. The magnetic entropy change was calculated from the magnetization data by the Maxwell relation.
Figure 1 shows the thermomagnetic M-T curves of La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ compounds with $x=0$ and 0.3, measured during heating and cooling under a magnetic field as low as 0.01 T. For the sample with $x=0$, a thermal hysteresis of 5 K is observed for the magnetic transitions in heating and cooling modes, indicating the presence of a strong thermally induced first-order magnetic transition at $T_C$. It is interesting to note that almost no thermal hysteresis is observed in the La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_{0.3}$ interstitial compound. This implies that the introduction of interstitial carbon atoms can weaken thermal-induced first-order magnetic transition at $T_C$.

Figure 2 shows the carbon concentration dependence of the crystal lattice parameter $a$ and the Curie temperature $T_C$ for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ compounds. Here, $T_C$ is determined from the heating M-T curves measured in a field of 0.05 T. $T_C$ is found to increase linearly with increasing carbon concentration from 183 K for $x=0$ to 211 K for $x=0.3$. The crystal lattice parameter is obtained from the room-temperature XRD patterns, and it is found to increase from 11.444 to 11.482 Å as $x$ increases from 0 to 0.3. Previous studies have demonstrated that the introduction of interstitial hydrogen or carbon atoms in La(Fe,Si)$_{13}$ compounds can cause $T_C$ to increase due to lattice expansion, while the application of a static pressure leads $T_C$ to decrease due to lattice contraction. The lattice expansion generally enhances the magnetic coupling in La(Fe,Si)$_{13}$ systems. Thus, the increase of $T_C$ with increasing $x$ for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ can be attributed to the lattice expansion caused by the introduction of interstitial carbon atoms.

Figure 3 shows the typical magnetization isotherms for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ ($x=0$ and 0.3) measured around the Curie temperature in the field increasing and decreasing processes. It can be seen from Fig. 3 that the magnetization curves for the sample of $x=0$ exhibit an obvious magnetic hysteresis loop, indicative of the coexistence of the ferromagnetic and paramagnetic phases near $T_C$ and a characteristic of the IEM transition above $T_C$, as has been found in LaFe$_{11.7}$Si$_{1.3}$. It proves that the nature of magnetic transition in La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$ is first order. For the compound with $x=0.3$, however, a small magnetic hysteresis is observed. It is indicated that the feature of the first-order magnetic transition becomes weak or is restrained by introducing carbon atoms, which is very useful for magnetic refrigeration applications.

Figure 4 shows the temperature dependence of hysteresis loss, defined as the area enclosed by the ascending and descending branches of magnetization curve, for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ with $x=0$ and 0.3. It can be seen that, for both compounds, the hysteresis loss in a ferromagnetic state below $T_C$ is close to zero, and grows rapidly to reach a maximum around $T_C$, then decreases with further increase of temperature in the paramagnetic state above $T_C$. The maximum hysteresis losses are 94.8 and 23.1 J/kg for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_{0.3}$ with $x=0$ and 0.3, respectively. It is obvious that the first-order magnetic transition is weakened by the introduction of carbon atoms, which leads to the reduction of hysteresis losses.

Figure 5 shows the magnetic entropy change as a function of temperature for different magnetic field changes for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ ($x=0$ and 0.3) compounds. The maximum $\Delta S$ values for magnetic field change from 0 to 2 T and from 0 to 5 T are found to be 30.2 and 32.4 J/kg K and 25.2 and 27.6 J/kg K for samples with $x=0$ and 0.3, respectively. The introduction of carbon atoms leads to an increase of $T_C$; as a result, the peak of $\Delta S$ shifts toward higher temperatures.
Although $\Delta S$ exhibits a slight reduction due to the decrease of magnetization caused by interstitial carbon atoms, the maximum $\Delta S$ of La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ still attains 27.6 J/kg K for a field change of 0–5 T, which is significantly larger than that of the Pr- and C-free compounds.\(^{10}\)

In conclusion, we have found that the introduction of interstitial carbon atoms causes almost no change in the maximum magnetic entropy change, but the Curie temperature is elevated as compared with that without introducing the interstitial carbon atoms. Furthermore, the first-order nature of phase transition is weakened, which leads to the reduction in temperature hysteresis and field hysteresis. The maximum hysteresis loss drops from 94.8 to 23.1 J/kg for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ with $x$ varying from 0 to 0.3. In other words, the efficiency of magnetic refrigeration is greatly improved by introducing interstitial carbon atoms into the La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$ compounds.

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FIG. 5. (Color online) Temperature dependence of the magnetic entropy change of La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_x$ compounds with $x=0$ and 0.3 for magnetic field changes from 0 to 2 T and from 0 to 5 T.