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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. [DOI: 10.1063/1.2794412]

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 $Gd_5Si_2Ge_2$.[1] As one of the typical MCE materials, the cubic NaZn13-type $LaFe_{13-x}Si_x$ exhibits many distinctive properties, and is a focus of recent study.[2–14] 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,[15] which results in a large MCE.[2] In general, the MCE of $LaFe_{13-x}Si_x$ enhances with the decrease of Si content,[3] but the decrease of T_C.[15,16] 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 $Gd_5Ge_2Si_2$ with the addition of Fe, which results in a very small hysteresis loss by suppressing the formation of the orthorhombic phase.[17] 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.[4,5] 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.[4,5]

Recently, we have studied the magnetic properties and magnetic entropy change of $La(Fe,Si)_{13}$ 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 $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds, in which a large MCE and a small hysteresis loss are achieved.

The samples with the nominal composition $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ ($x=0$, 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 Kα 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.

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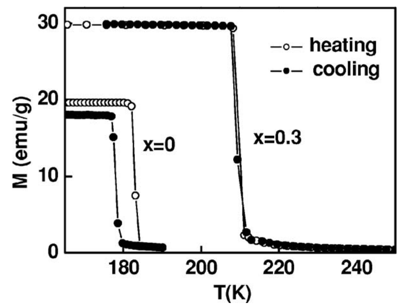

FIG. 1. Thermomagnetization curves for $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds with $x=0$ and 0.3 measured during heating and cooling under a magnetic field of 0.05 T.

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 thermal-induced first-order magnetic transition at T_C. It is very 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,[6–10] while the application of a static pressure leads T_C to decrease due to lattice contraction.[18] 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 $LaFe_{11.7}Si_{1.3}$.[19] 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.

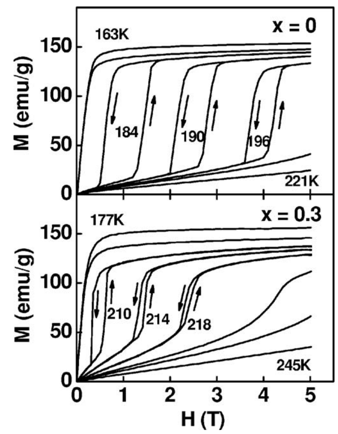

FIG. 3. Magnetization isotherms of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds with $x=0$ and 0.3 measured under increasing and decreasing fields in a range of temperatures around the Curie temperature.

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 $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ 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 ΔS 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 ΔS shifts toward higher temperatures.

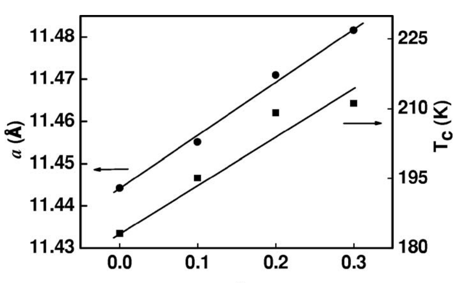

FIG. 2. Crystal lattice parameter and Curie temperature for $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ ($0\leqslant x\leqslant 0.3$) compounds as functions of carbon concentration.

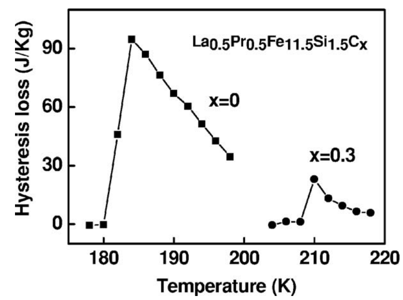

FIG. 4. Temperature dependence of hysteresis loss of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds with $x=0$ and 0.3.

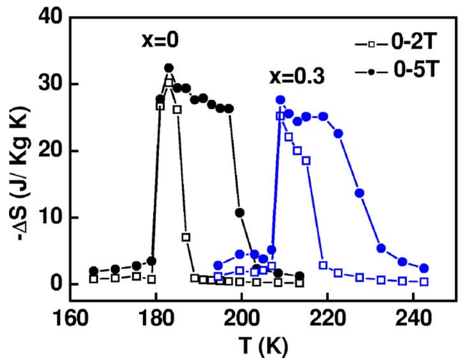

FIG. 5. (Color online) Temperature dependence of the magnetic entropy change of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_x$ compounds with $x=0$ and 0.3 for magnetic field changes from 0 to 2 T and from 0 to 5 T.

Although ΔS exhibits a slight reduction due to the decrease of magnetization caused by interstitial carbon atoms, the maximum ΔS of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_{0.3}$ 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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[1]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2]F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Chen, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[3]S. Fujieda, A. Fujita, and K. Fukamichi, Sci. Technol. Adv. Mater. **4**, 339 (2003).
[4]F. X. Hu, B. G. Shen, J. R. Sun, G. J. Wang, and Z. H. Cheng, Appl. Phys. Lett. **80**, 826 (2002).
[5]X. B. Liu, D. H. Ryan, and Z. Altounian, J. Magn. Magn. Mater. **270**, 305 (2004).
[6]S. Fujieda, A. Fujita, N. Kawamoto, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[7]Y. F. Chen, F. Wang, B. G. Shen, F. X. Hu, Z. H. Cheng, G. J. Wang, and J. R. Sun, Chin. Phys. **11**, 741 (2002).
[8]A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[9]F. Wang, Y. F. Chen, G. J. Wang, J. R. Sun, and B. G. Shen, Chin. Phys. **12**, 911 (2003).
[10]Y. F. Chen, F. Wang, B. G. Shen, J. R. Sun, G. J. Wang, F. X. Hu, Z. H. Cheng, and T. Zhu, J. Appl. Phys. **93**, 6981 (2003).
[11]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[12]D. T. Kim Anh, N. P. Thuy, N. H. Duc, T. T. Nhien, and N. V. Nong, J. Magn. Magn. Mater. **262**, 427 (2003).
[13]S. Fujieda, A. Fujita, and K. Fukamichi, Mater. Trans. **45**, 3228 (2004).
[14]S. Fujieda, A. Fujita, and K. Fukamichi, J. Magn. Magn. Mater. **310**, e1004 (2007).
[15]A. Fujita, Y. Akamatsu, and K. Fukamichi, J. Appl. Phys. **85**, 4756 (1999).
[16]T. T. M. Palstra, J. A. Mydosh, G. J. Nieuwenhuys, A. M. van der Kraan, and K. H. J. Buschow, J. Magn. Magn. Mater. **36**, 290 (1983).
[17]V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).
[18]Y. Sun, Z. Arnold, J. Kamarad, G. J. Wang, B. G. Shen, and Z. H. Cheng, Appl. Phys. Lett. **89**, 172513 (2006).
[19]N. L. Di, Z. H. Cheng, Q. A. Li, G. J. Wang, Z. Q. Kou, X. Ma, Z. Luo, F. X. Hu, and B. G. Shen, Phys. Rev. B **69**, 224411 (2004).