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Reduction of hysteresis loss and large magnetocaloric effect in the C- and H-doped La(Fe, Si)$_{13}$ compounds around room temperature

H. Zhang,[1,a)] B. G. Shen,[1] Z. Y. Xu,[1] X. Q. Zheng,[1] J. Shen,[2] F. X. Hu,[1] J. R. Sun,[1] and Y. Long[3]

[1]*State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, People' Republic of China*

[2]*Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China*

[3]*School of Materials Science and Engineering, University of Science and Technology of Beijing, 100083, People's Republic of China*

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The effects of the interstitial C and H atoms on the phase formation, the hysteresis loss, and magnetocaloric effects of the $NaZn_{13}$-type La(Fe, Si)$_{13}$ compounds are investigated. It is found that the annealing time to obtain a 1:13 structure is significantly reduced from 40 days for $LaFe_{11.7}Si_{1.3}$ to a week for $LaFe_{11.7}Si_{1.3}C_{0.2}$. The introduction of C and H atoms can adjust Curie temperature to around room temperature and leads to the decrease in magnetic entropy change (ΔS_M) and magnetic hysteresis loss due to the weakening of itinerant-electron metamagnetic transition. Large $-\Delta S_M$ of 19.0 J/kg K at room temperature without hysteresis loss for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ is obtained for a field change of 5 T. © *2012 American Institute of Physics*. [doi:10.1063/1.3670608]

In recent years, much attention has been paid to materials with a large magnetocaloric effect (MCE) due to their potentialities for magnetic refrigeration.[1–3] Giant MCE around the transition temperature has been found in many magnetic refrigerants with a first-order phase transition. In these materials, La(Fe, Si)$_{13}$-based compounds with the cubic $NaZn_{13}$-type (1:13) structure, exhibiting itinerant electron metamagnetic (IEM) transition, have been suggested as potential candidates for magnetic refrigeration materials.[3] However, there are still some serious issues, such as prolonged preparation, low working temperature, and large thermal and magnetic hysteresis, preventing this kind of materials from practical applications. In most reports on La(Fe, Si)$_{13}$ compounds,[4,5] a prolonged heat treatment (~several weeks to two months) at high temperature (~1353–1473 K) is necessary to develop the 1:13 phase in bulk alloys. It has been reported that the homogenization time can be reduced significantly by using melt spinning technique.[6,7] However, melt spun La(Fe, Si)$_{13}$ ribbons are usually thinner than the minimum size (~0.2 mm) of practical magnetic refrigerants,[8] thus hindering the utilization of these materials. On the other hand, it has been pointed out that the partial substitution of Fe by Co atoms leads to an increase in the Curie temperature (T_C) and a remarkable decrease in hysteresis loss. Meanwhile, the MCE is also lowered drastically because of the weakening of the first-order magnetic transition (FOMT).[9,10] In contrast, the introduction of interstitial H and C atoms gives rise to a considerable increase in T_C, while it is found that the MCE still maintains at a high value after carbonization and hydrogenation.[11–13] In this paper, we report on the phase formation, the hysteresis loss and magnetocaloric effects in the C- and H-doped La(Fe, Si)$_{13}$ compounds, which exhibit large magnetic entropy change (ΔS_M) with low hysteresis loss around room temperature.

The $LaFe_{11.7}Si_{1.3}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}$ samples were prepared by arc-melting appropriate proportions of constituent components with the purity better than 99.9 wt. %. The heat treatment was carried out in a quartz tube of high vacuum at 1373 K for 40 days for $LaFe_{11.7}Si_{1.3}$ and 7 days for $LaFe_{11.7}Si_{1.3}C_{0.2}$. The hydrogen absorption was carried out by annealing the compound at 523 K in a hydrogen atmosphere of ~0.6 MPa for a long time until saturation. The hydrogen concentration y of $LaFe_{11.7}Si_{1.3}C_{0.2}H_y$ was determined to be ~1.7 by weighing the mass before and after hydrogenation. Powder X-ray diffraction (XRD) measurements were performed at room temperature by using Cu $K\alpha$ radiation. Magnetizations were measured as functions of temperature and magnetic field by employing a commercial superconducting quantum interference device (SQUID) magnetometer from Quantum Design Inc.

Figure 1 shows the observed and refined powder XRD patterns of $LaFe_{11.7}Si_{1.3}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}$. The Rietveld refinement confirms that these compounds crystallize in a cubic $NaZn_{13}$-type structure with a minor amount of α-Fe phase. It is interesting to note that the annealing time is 40 and 7 days at 1373 K for $LaFe_{11.7}Si_{1.3}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}$, respectively, indicating that the introduction of interstitial C atoms promotes the formation of 1:13 phase in La(Fe, Si)$_{13}$-based compounds.

Figure 2 shows the temperature (T) dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations (M) under a magnetic field of 0.05 T. The Curie temperature T_C, defined by the minimum of the dM/dT versus T curves, is found to be 189 K, 212 K, and 320 K for $LaFe_{11.7}Si_{1.3}$,

a)Author to whom correspondence should be addressed. Fax: +86-10-82649485. Electronic mail: zhanghuxt@aphy.iphy.ac.cn.

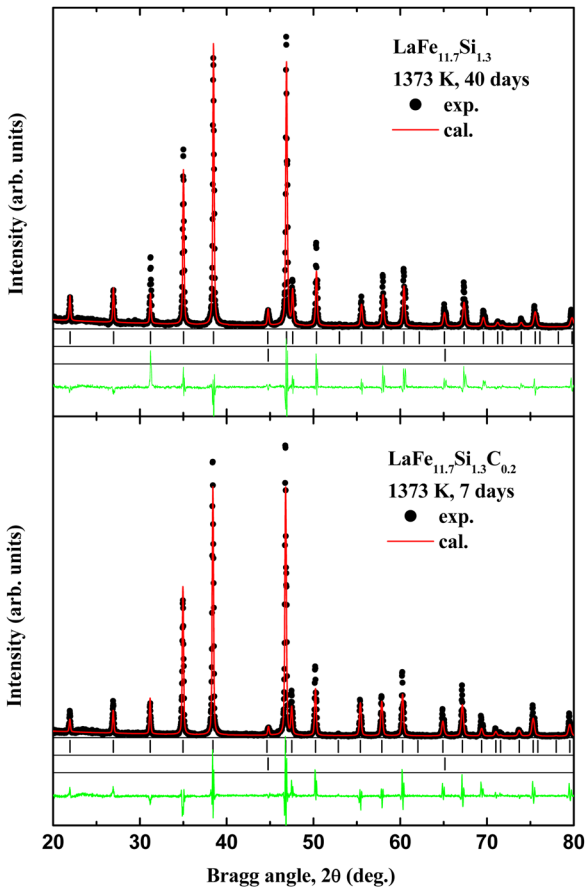

FIG. 1. (Color online) The observed (dots) and refined profile (line drawn through the data points) of the refined powder diffraction patterns of the $LaFe_{11.7}Si_{1.3}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}$ compounds. The upper set of vertical bars indicates the calculated positions of the Bragg peaks for the La(Fe, $Si)_{13}$ (1:13) phase, while the lower set of bars corresponds to the calculated positions of the Bragg peaks of the α-Fe phase. The curve at the bottom of the plot is the difference between the observed and calculated intensities.

$LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$, respectively. The lattice parameter a, determined by using the Rietveld refinement, is 11.4764 Å for $LaFe_{11.7}Si_{1.3}$, 11.5003 Å for $LaFe_{11.7}Si_{1.3}C_{0.2}$, and 11.6076 Å for $LaFe_{11.7}$ $Si_{1.3}C_{0.2}H_{1.7}$, respectively. It is suggested that the increase of T_C results from the lattice expansion caused by the introduction of C and H atoms, which reduces the overlap of the Fe 3d wave functions and enhances the Fe-Fe exchange interactions, as observed in other previous studies.[13–16] In addition, it is observed that the $LaFe_{11.7}Si_{1.3}$ compound exhibits a thermal hysteresis of 2 K between the ZFC and FC M-T curves around T_C, indicating the presence of a thermal-induced FOMT. However, almost no thermal hysteresis is observed for $LaFe_{11.7}Si_{1.3}C_{0.2}$, revealing that the introduction of C atoms can weaken the thermal-induced FOMT.

Figures 3(a)–3(c) show the isothermal magnetization curves measured with field increasing and decreasing around T_C for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}$ $Si_{1.3}C_{0.2}H_{1.7}$, respectively. It can be seen from Fig. 3(a) that $LaFe_{11.7}Si_{1.3}$ exhibits a notable hysteresis loop and a sharp change in magnetization above a critical field, indicating the nature of a typical first-order IEM transition above T_C. However, both $LaFe_{11.7}Si_{1.3}C_{0.2}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ show a nearly reversible change of magnetization during the field increasing and decreasing processes (Figs. 3(a) and 3(b)), which is beneficial to the practical applications of magnetic refrigeration. It is found that the maximum value of

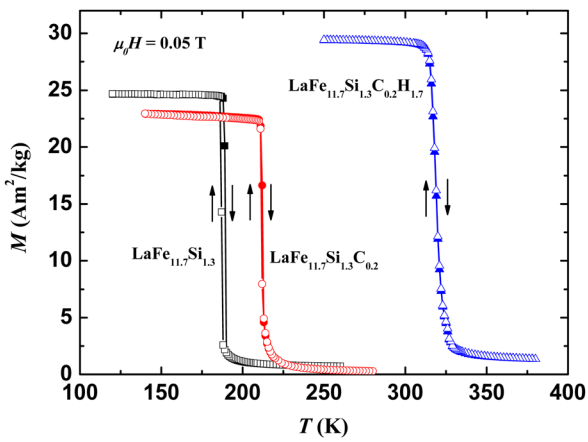

FIG. 2. (Color online) The temperature (T) dependence of magnetizations (M) for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}$ $Si_{1.3}C_{0.2}H_{1.7}$ under a magnetic field of 0.05 T.

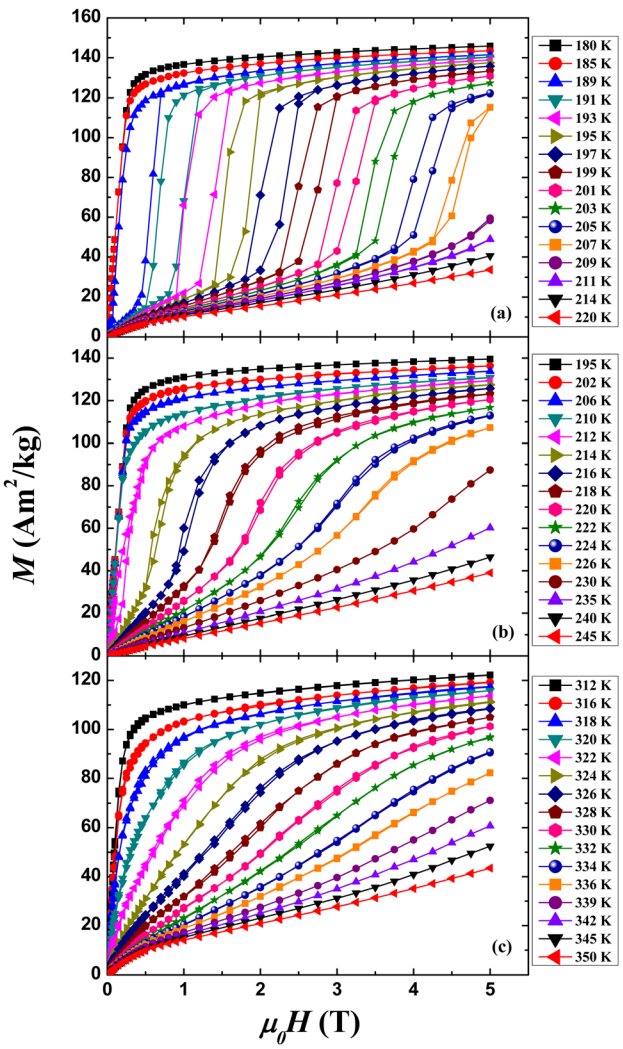

FIG. 3. (Color online) The isothermal magnetization curves measured with field increasing and decreasing around T_C for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}$ $Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$, respectively.

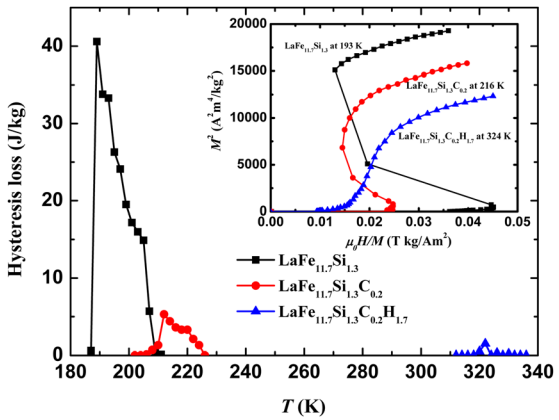

FIG. 4. (Color online) Temperature dependence of the hysteresis loss under a magnetic field change of 5 T for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$, respectively. The inset shows the Arrott plots of these compounds just above their respective T_C.

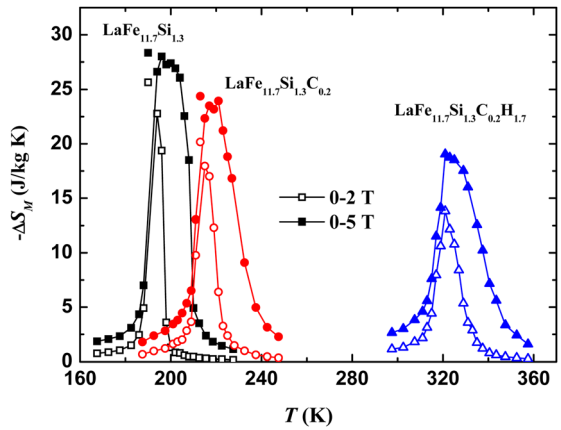

FIG. 5. (Color online) Temperature dependence of the magnetic entropy changes for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}$ $Si_{1.3}C_{0.2}H_{1.7}$ compounds under magnetic field changes of 2 T and 5 T, respectively.

hysteresis loss of $LaFe_{11.7}Si_{1.3}$, defined as the enclosed area between the ascending and descending magnetization curves, is obtained to be 41 J/ kg at T_C as shown in Fig. 4. In contrast, the maximum hysteresis loss is found to be 5.3 J/kg for $LaFe_{11.7}Si_{1.3}C_{0.2}$ and 1.5 J/kg for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ (see Fig. 4), respectively. It suggests that the FOMT is strongly suppressed after carbonization and hydrogenation, resulting in a much smaller hysteresis loss. The inset of Fig. 4 shows the Arrott plots of these compounds just above their respective T_C. For $LaFe_{11.7}Si_{1.3}C_{0.2}$ and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$, the negative curvatures of the slopes are lessened, proving again that the characteristic of FOMT becomes weak by doping the C and H atoms.

Figure 5 presents the ΔS_M as functions of temperature and magnetic field obtained by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. It should be noticed that the spike-like peaks just above T_C for $LaFe_{11.7}Si_{1.3}$ and $LaFe_{11.7}$ $Si_{1.3}C_{0.2}$ are artifacts as discussed in previous studies and are not considered here.[17–19] The maximum values of $-\Delta S_M$ for a field change of 5 T are 28.0, 23.9, and 19.0 J/ kg K for $LaFe_{11.7}Si_{1.3}$, $LaFe_{11.7}Si_{1.3}C_{0.2}$, and $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$, respectively. The introduction of C and H atoms leads to a reduction in ΔS_M by weakening the first-order IEM transition. However, it is worthwhile to note that the $LaFe_{11.7}$ $Si_{1.3}C_{0.2}H_{1.7}$ still retains a relatively large ΔS_M of −19.0 J/kg K around room temperature, which is much larger than those of some magnetocaloric materials with similar transition temperature. In particular, a large reversible ΔS_M of −13.8 J/ kg K for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ is obtained at T_C under a low field change of 2 T, which is advantageous to practical applications since a magnetic field of 2 T can be provided by a permanent magnet.

Introducing C atoms into the La(Fe, $Si)_{13}$-based compounds results in a significant shortening of the annealing time to form 1:13 phase. The addition of C and H atoms can tune T_C to around room temperature and leads to a decrease in thermal/magnetic hysteresis. Although the ΔS_M of the samples with doping C and H atoms decreases due to the weakening of IEM transition, the values of $-\Delta S_M$ for $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.7}$ still reach 13.8 and 19.0 J/kg K at $T_C = 320$ K under the magnetic field changes of 2 T and 5 T, respectively.

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