Reduction in hysteresis losses and large magnetic entropy change in the B-doped $La(Fe,Si)_{13}$ compounds

Jun Shen,[1,3,a)] Fang Wang,[2] Jin-Liang Zhao,[2,3] Jian-Feng Wu,[1] Mao-Qiong Gong,[1] Feng-Xia Hu,[2] Yang-Xian Li,[3] Ji-Rong Sun,[2] and Bao-Gen Shen[2]
[1]*Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[2]*State Key Laboratory for Magnetism, Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[3]*School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, China*

(Presented 22 January 2010; received 28 October 2009; accepted 23 November 2009; published online 19 April 2010)

The effect of the B-addition on magnetic entropy change ΔS_M and hysteresis loss in $La(Fe,Si)_{13}$ is studied. The maximal values of ΔS_M for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ are found to be 27.0, 26.1, 23.7, and 21.2 J/kg K at Curie temperature T_C for a field change in 0–5 T, respectively. The maximal hysteresis losses around T_C are 43 and 21 J/kg for $LaFe_{11.9}Si_{1.1}$ and $LaFe_{11.5}Si_{1.5}$, respectively, while almost no magnetic hysteresis is observed for the B-doped compounds. Our result reveals that a large ΔS_M and a small hysteresis loss can be simultaneously achieved in $NaZn_{13}$-type $La(Fe,Si)_{13}$ compounds by the addition of B. © *2010 American Institute of Physics*. [doi:10.1063/1.3349325]

Many investigations have demonstrated that the giant magnetocaloric effect (MCE) in materials is closely related to a field-induced first-order phase transition.[1–4] However, the first-order transition is usually accompanied by a magnetic hysteresis, giving rise to hysteresis loss, which leads to a reduction in refrigeration efficiency. A reduction in hysteresis loss becomes important for the application of materials with a first-order magnetic transition. Recently, much attention has been paid mainly to the materials that possess large magnetic entropy change and small hysteresis loss.[5–9] However, the improvement of the hysteresis behavior always accompanies the weakening of the magnetocaloric property of the materials. Reductions in hysteresis associated with the first-order crystallographic transition in some magnetocaloric materials have been reported.[5,6] For example, the addition of Fe in the $Gd_5Ge_2Si_2$ is found to lead to a reduction in the hysteresis loss because small substitution of Fe suppresses the formation of the orthorhombic phase.[5] A reduction in the hysteresis loss is also observed in the Sb-doped MnAs compounds due to the stable NiAs-type structure caused by the substitution of Sb.[6] The cubic $NaZn_{13}$-type $La(Fe,Si)_{13}$ compounds exhibit a large MCE due to its first-order magnetic transition at the Curie temperature T_C, that is, the itinerant-electron metamagnetic (IEM) transition from the paramagnetic to the ferromagnetic state. The IEM transition of $La(Fe,Si)_{13}$ brings also about a large hysteresis loss. Recently, we have demonstrated[7,8] that an appropriate increase in Si and/or Co content in the $NaZn_{13}$-type LaFeSi compounds suppresses strongly the IEM transition, leading to a remarkable reduction in hysteresis loss. A large magnetic entropy change ΔS_M and a low hysteresis loss can be achieved by the partially replacing Fe with Co or adjusting the content of Si and Fe. It is also found that the hysteresis can be significantly depressed by introducing interstitial carbon atoms into the $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}$ compound. The hysteresis loss of $La_{0.5}Pr_{0.5}Fe_{11.5}Si_{1.5}C_\delta$ decreases from 94.8 to 23.1 J/kg when δ increases from 0 to 0.3, while a large value of ΔS_M can be retained.[9] Very recently, the magnetocaloric properties of $LaFe_{11.57}Si_{1.43}B_x$ ($0<x<1.64$) compounds were studied by Pathak *et al.* They observed that the hysteresis loss for the sample of $x=1.64$ is much less than that of the sample of $x=0$.[10] Further investigations on hysteresis of $La(Fe,Si)_{13}$-based compounds are important from the practical viewpoint. In this paper, we report the effect of the substitution of B for Fe on ΔS_M and hysteretic losses in the $La(Fe,Si)_{13}$ compounds. It is found that a large MEC and almost zero hysteresis loss can be simultaneously achieved in $La(Fe,Si)_{13}$ by the addition of B.

$LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ samples were prepared by arc melting in a high-purity argon atmosphere. The purities of the starting materials were 99.9% for La and Fe, 99.5% for B–Fe alloy and 99.999% for Si. Each ingot was turned over and remelted several times to ensure its homogeneity. Ingots obtained by arc melting were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1353–1423 K for 20–40 days, depending on the concentration, and then quenched to room temperature. The crystal structure was identified by room-temperature powder x-ray diffractions (XRDs) with Cu K_α radiation. The magnetization was measured as a function of temperature and magnetic field around the Curie temperature by using superconducting quantum interference device magnetometer from Quantum Design. By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization data.

From the results of powder XRD patterns, it was found

[a)]Author to whom correspondence should be addressed. Electronic mail: sj@g203.iphy.ac.cn.

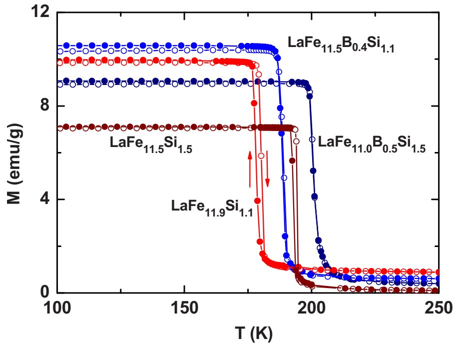

FIG. 1. (Color online) Temperature dependence of magnetization for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ measured in the heating and cooling cycles under a magnetic field of 0.01 T.

that all the annealed samples investigated here exhibit a cubic $NaZn_{13}$-type structure with a few percent of α-Fe phase in $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ samples. Almost no other phases were observed within the limits of powder XRD technique. However, it is possible that small amounts of La-rich phases, up to ~5 vol % could be present. The temperature dependences of the magnetization $M(T)$ measured during heating and cooling under a low magnetic field of 0.01 T are shown in Fig. 1. The T_C of the samples is defined as the temperature at which the dM/dT of the heating M-T curves is a minimum. The lattice parameters a and the Curie temperatures T_C for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ are determined to be 1.1478, 1.1480, 1.1467, and 1.1476 nm, and 179, 188, 194, and 201 K, respectively. It is found that the substitution of B for Fe leads to an increase in both a and T_C for $La(Fe,Si)_{13}$ compounds at constant Si concentration as shown in $LaFe_{11.57}Si_{1.43}B_x$.[10] For the Fe-rich rare-earth (R) iron compounds, T_C depends mainly on Fe–Fe direct exchange interactions. The exchange integral is affected by interatomic distance. The increase in T_C for the B-doped samples is due to the increase in the Fe–Fe exchange interactions, which can be attributed to the increase in Fe-Fe spacing caused by the addition of B.

It is observed from Fig. 1 that the M-T curves of the B-free samples exhibits a remarkable thermal hysteresis, indicating the presence of a thermal-induced first-order magnetic transition at T_C. The thermal hystereses are estimated from the difference in temperature between magnetic transitions in the cooling and the heating cycles to be about 2.0 and 1.4 K for $LaFe_{11.9}Si_{1.1}$ and $LaFe_{11.5}Si_{1.5}$, respectively. However, a very small thermal hysteresis or almost no thermal hysteresis is observed for the B-doped samples. These results reveal that the appropriate addition of B in $La(Fe,Si)_{13}$ compounds can weaken the thermal-induced first-order magnetic transition at T_C.

Figure 2 shows the isothermal magnetization (M-H) curves around T_C for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$. The magnetization curves at temperatures far above T_C show a curvature at low fields, which is caused by the α-Fe phase. It is found that the M-H curves exhibit typical ferromagnetic nature below T_C for all samples. A sharp change in magnetization above T_C takes place at a critical field for each magnetization curves. The

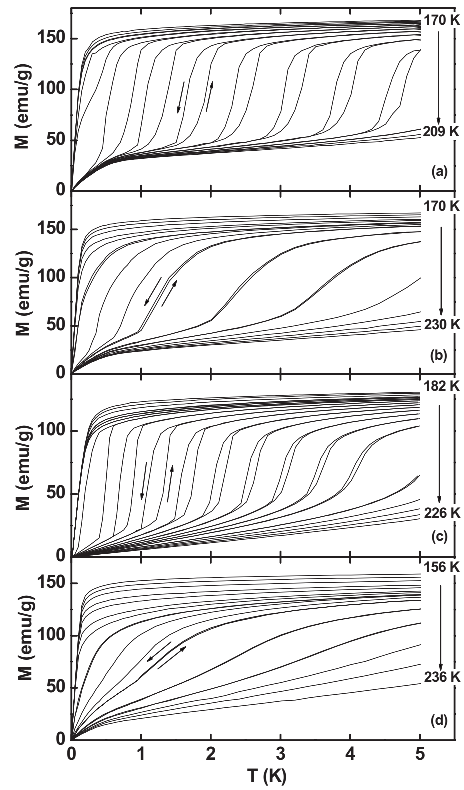

FIG. 2. Magnetization isotherms of (a) $LaFe_{11.9}Si_{1.1}$, (b) $LaFe_{11.5}B_{0.4}Si_{1.1}$, (c) $LaFe_{11.5}Si_{1.5}$, and (d) $LaFe_{11.0}B_{0.5}Si_{1.5}$ measured in the field-ascending and field-descending processes.

increase in the critical field with increasing temperature above T_C exhibits a typical characteristic of the field-induced IEM transition from the paramagnetic to the ferromagnetic state.[11,12] For the B-free sample, the M-H curves measured under increasing and decreasing fields exhibit an obvious

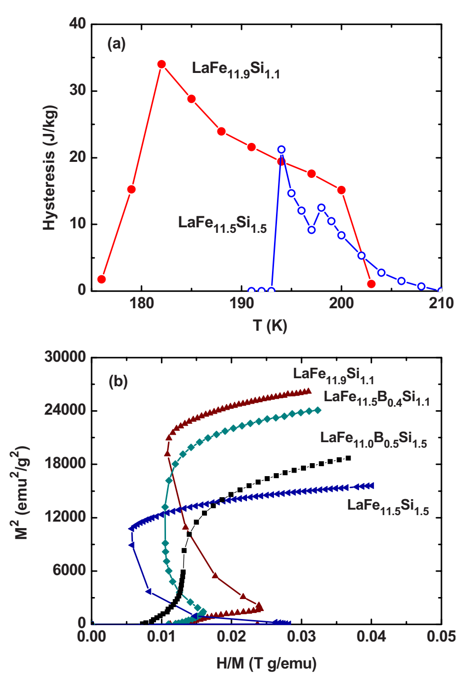

FIG. 3. (Color online) Temperature dependence of hysteresis loss for (a) $LaFe_{11.9}Si_{1.1}$ and $LaFe_{11.5}Si_{1.5}$ and (b) Arrott plots of $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$.

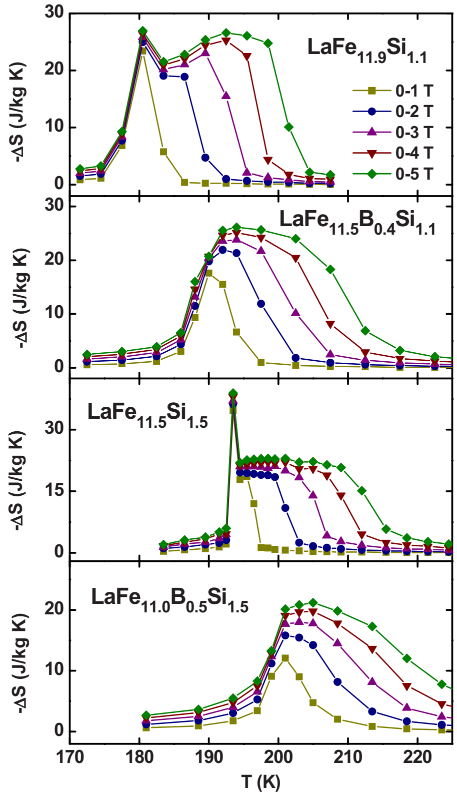

FIG. 4. (Color online) Magnetic entropy change as a function of temperature under different magnetic field changes for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$.

magnetic hysteresis loop, implying that a large magnetic hysteresis occurs. It is very interesting to note that the magnetization of the B-doped compounds is almost reversible in the reverse of temperature and magnetic field change, and the magnetic hysteresis disappears at all temperatures. The maximal hysteresis losses around T_C are 43 and 21 J/kg for $LaFe_{11.9}Si_{1.1}$ and $LaFe_{11.5}Si_{1.5}$ [see Fig. 3(a)], respectively, while they are almost zero for both $LaFe_{11.5}B_{0.4}Si_{1.1}$ and $LaFe_{11.0}B_{0.5}Si_{1.5}$. Similar result was observed in $LaFe_{11.57}Si_{1.43}B_x$.[10] This result indicates that the field-induced first-order magnetic transition from paramagnetic to ferromagnetic state has been weakened by the addition of B.

Figure 3(b) shows the Arrott plots for all samples above their respective T_C. It is found that negative slopes of the Arrott plots still appear even for B-doped samples, indicating that the boron atoms do not seriously influence the shape of the density of states around the Fermi level[13] and a strong IEM behavior is still retained, but the hysteresis loss becomes smaller or almost zero. The strong IEM transition without magnetic hysteresis predicts a large reversible MCE effect. This is considered very favorable for magnetic refrigeration applications.

The magnetic entropy change ΔS_M has been calculated from isothermal magnetization data shown in Fig. 2 by using the Maxwell relation $\Delta S_M=\int_0^H(\partial M/\partial T)_H dH$, which is widely used for evaluating ΔS_M even for the systems with the first-order transition.[1,14,15] Fig. 4 shows the ΔS_M as functions of temperature and magnetic field for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$. An interesting feature is that the ΔS_M peak broadens asymmetrically toward higher temperature with increasing magnetic field, which is a result of the field-induced IEM transition above T_C.[16] The maximal values of ΔS_M for $LaFe_{11.9}Si_{1.1}$, $LaFe_{11.5}B_{0.4}Si_{1.1}$, $LaFe_{11.5}Si_{1.5}$, and $LaFe_{11.0}B_{0.5}Si_{1.5}$ are found to be 27.0, 26.1, 23.7, and 21.2 J/kg K at 181, 194, 194, and 205 K for a field change in 0–5 T, respectively. Although the substitution of B for Fe leads to a small reduction in ΔS_M, the maximal ΔS_M in the B-doped samples is still larger than 20 J/kg K for a field change in 0–5 T. More important is that no magnetic hysteresis loss appears in these samples, indicating that large MCE and almost zero hysteresis loss are simultaneously achieved in the B-doped $La(Fe,Si)_{13}$ compounds.

The substitution of B for Fe in $La(Fe,Si)_{13}$ leads to an increase in T_C due to the increase in Fe–Fe interaction caused by the addition of B. Compared with the B-free samples, the first-order nature of magnetic transition in the B-doped $La(Fe,Si)_{13}$ becomes weaker, leading to a remarkable reduction in both thermal and magnetic hystereses. Although the ΔS_M has a small reduction in the B-doped $La(Fe,Si)_{13}$, the magnetic hysteresis loss is almost zero. Large reversible ΔS_M and very low hysteresis loss indicate the potentiality of the B-doped $La(Fe,Si)_{13}$ as a candidate of magnetic refrigerant in the corresponding temperature range.

The present work was supported by the National Basic Research Program of China, the National Natural Science Foundation of China (Contract No. 50731007), and the Knowledge Innovation Project of the Chinese Academy of Sciences.

[1]V. K. Pecharsky and K. A. Gschneidner, Phys. Rev. Lett. **78**, 4494 (1997).
[2]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[3]E. Brück, in *Handbook of Magnetic Materials*, edited by K. H. J. Bushcow (Elsevier, New York, 2008), Vol. 17, p. 235.
[4]B. G. Shen, J. R. Sun, F. X. Hu, H. W. Zhang, and Z. H. Cheng, Adv. Mater. **21**, 4545 (2009).
[5]V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).
[6]F. Ishikawa, K. Koyama, K. Watanabe, T. Asano, and H. Wada, Mater. Trans. **45**, 311 (2004).
[7]J. Shen, Q. Y. Dong, Y. X. Li, and J. R. Sun, J. Magn. Magn. Mater. **321**, 2336 (2009).
[8]J. Shen, Y. X. Li, F. X. Hu, and J. R. Sun, J. Appl. Phys. **105**, 07A901 (2009).
[9]J. Shen, B. Gao, H. W. Zhang, F. X. Hu, Y. X. Li, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **91**, 142504 (2007).
[10]A. K. Pathak, P. Basnyat, I. Dubenko, S. Stadler, and N. Ali, J. Appl. Phys. **106**, 063917 (2009).
[11]T. Goto, K. Fukamichi, and H. Yamada, Physica B **300**, 167 (2001).
[12]A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[13]S. Fujieda, A. Fujita, K. Fukamichi, Y. Yamazaki, and Y. Iijima, Appl. Phys. Lett. **79**, 653 (2001).
[14]V. K. Pecharsky and K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).
[15]J. R. Sun, F. X. Hu, and B. G. Shen, Phys. Rev. Lett. **85**, 4191 (2000).
[16]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).