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Published in:
Journal of Applied Physics

Link to article, DOI:
10.1063/1.2829035

Publication date:
2008

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Shen, J., Li, Y.-Z., Zhang, J., Gao, B., Hu, F.-X., Zhang, H.-W., Chen, Y., Rong, C.-B., & Sun, J.-R. (2008). Large magnetic entropy change and low hysteresis loss in the Nd- and Co-doped $La(Fe,Si)_{13}$ compounds. *Journal of Applied Physics*, *103*(7), Article 07B317. https://doi.org/10.1063/1.2829035

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Citation: Journal of Applied Physics **103**, 07B317 (2008); doi: 10.1063/1.2829035
View online: http://dx.doi.org/10.1063/1.2829035
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/103/7?ver=pdfcov
Published by the AIP Publishing

Large magnetic entropy change and low hysteresis loss in the Nd- and Co-doped La(Fe,Si)$_{13}$ compounds

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(Presented on 6 November 2007; received 10 September 2007; accepted 1 October 2007; published online 31 January 2008)

The effect of Nd and Co substitution on magnetic entropy changes and hysteresis losses has been investigated for the cubic NaZn$_{13}$-type LaFe$_{13-x}$Si$_x$ compounds. Partially replacing La with Nd leads to a decrease of the Curie temperature T_C and an increase of the magnetic entropy change ΔS. Substitution of Co for Fe in La$_{0.7}$Nd$_{0.3}$Fe$_{10.5}$Si$_{1.5}$ can adjust T_C to around room temperature. A large ΔS of 15 J/Kg K at T_C=280 K for a field change from 0 to 5 T and a small hysteresis loss close to zero near T_C have been obtained in La$_{0.7}$Nd$_{0.3}$Fe$_{10.7}$Co$_{0.8}$Si$_{1.5}$. The Co-doped NaZn$_{13}$-type LaNdFeSi compounds may be a suitable candidate for magnetic refrigerant near room temperature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2829035]

Recently, many investigations have been carried out on the magnetocaloric effect (MCE) of the LaFe$_{13-x}$Si$_x$ based compounds because of their potential application in magnetic refrigeration.[1,2] It was found that the LaFe$_{13-x}$Si$_x$ compounds with a low Si concentration show a large magnetic entropy change due to the itinerant electron metamagnetic (IEM) transition.[3–6] Although the MCE of LaFe$_{13-x}$Si$_x$ enhances with the decrease of Si content x, the Curie temperature T_C reduces, and it is usually much lower than the room temperature.[7,8] In order to work as a magnetic refrigerant near the ambient temperature, it is needed to adjust T_C to room temperature while retaining its large magnetic entropy change. Magnetic hysteresis loss is inevitable for the materials experiencing a first-order transition. To improve the efficiency of magnetic refrigeration, it is necessary to depress the hysteresis loss. A recent study has indicated that partially replacing La with Ce, Pr, and Nd in the LaFe$_{13-x}$Si$_x$ compounds can enhance remarkably the MCE effect,[9–11] but also leads to a large hysteresis loss. In this paper, we report the effect of Nd and Co substitution on the magnetic entropy change ΔS and hysteresis loss in the La(Fe,Si)$_{13}$ compounds. A large magnetic entropy change and a low hysteresis loss can be obtained in the Co-doped NaZn$_{13}$-type LaNdFeSi compounds.

Samples of LaFe$_{11.5}$Si$_{1.5}$, LaFe$_{11.2}$Si$_{1.8}$, La$_{0.7}$Nd$_{0.3}$Fe$_{11.5}$Si$_{1.5}$, La$_{0.7}$Nd$_{0.3}$Fe$_{11.2}$Si$_{1.8}$, and La$_{0.7}$Nd$_{0.3}$Fe$_{10.7}$Co$_{0.8}$Si$_{1.5}$ were prepared by arc melting in an argon atmosphere of high purity. The purity of starting materials is 99% for Nd, 99.9% for La, Fe, and Co, and 99.999% for Si. The as-prepared ingots were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1373 K for 40 days, and then quenched to room temperature. X-ray diffraction (XRD) measurements on powder samples were performed using Cu $K\alpha$ radiation to identify the phase structure and the crystal lattice parameter. Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device magnetometer. The isothermal magnetic entropy change was calculated from the magnetization data by using the Maxwell relation.

Figure 1 shows the room-temperature powder XRD patterns of LaFe$_{11.5}$Si$_{1.5}$, LaFe$_{11.2}$Si$_{1.8}$, La$_{0.7}$Nd$_{0.3}$Fe$_{11.5}$Si$_{1.5}$, La$_{0.7}$Nd$_{0.3}$Fe$_{11.2}$Si$_{1.8}$, and La$_{0.7}$Nd$_{0.3}$Fe$_{10.7}$Co$_{0.8}$Si$_{1.5}$. These compounds crystallized in a very clean single phase of a cubic NaZn$_{13}$-type structure. The lattice parameter a ob-

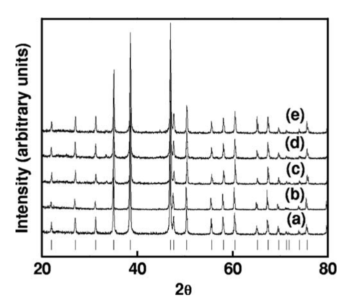

FIG. 1. Room-temperature powder XRD patterns of LaFe$_{11.5}$Si$_{1.5}$ (a), LaFe$_{11.2}$Si$_{1.8}$ (b), La$_{07}$Nd$_{0.3}$Fe$_{11.5}$Si$_{1.5}$ (c), La$_{07}$Nd$_{0.3}$Fe$_{11.2}$Si$_{1.8}$ (d), and La$_{07}$Nd$_{0.3}$Fe$_{10.7}$Co$_{0.8}$Si$_{1.5}$ (e). Bragg reflections (small vertical lines) are also shown.

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TABLE I. The lattice parameter *a*, Curie temperature T_C, and magnetic entropy change ΔS for the magnetic field changes of 0–2 and 0–5 T, and the magnetic hysteresis losses for $LaFe_{11.5}Si_{1.5}$, $LaFe_{11.2}Si_{1.8}$, $La_{07}Nd_{0.3}Fe_{11.5}Si_{1.5}$, $La_{07}Nd_{0.3}Fe_{11.2}Si_{1.8}$, and $La_{07}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$.

Compounds	*a* (Å)	T_C (K)	ΔS (0–2 T) (J/kg K)	ΔS (0–5 T) (J/kg K)	Hysteresis loss (J/kg)
$LaFe_{11.5}Si_{1.5}$	11.4686	194	20.9	23.7	21.2
$LaFe_{11.2}Si_{1.8}$	11.4635	216	7.8	13.7	No
$La_{07}Nd_{0.3}Fe_{11.5}Si_{1.5}$	11.4502	188	29.3	32.0	78.1
$La_{07}Nd_{0.3}Fe_{11.2}Si_{1.8}$	11.4426	207	10.5	15.2	3.5
$La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$	11.4533	280	7.9	15.0	No

tained from the XRD patterns is listed in Table I. It is found that the substitution of Nd leads to a contraction of the lattice, as has been observed in $La_{1-x}Ce_xFe_{13-y}Si_y$ compounds.[9]

Figure 2 shows the thermomagnetic *M-T* curves for $LaFe_{11.5}Si_{1.5}$, $LaFe_{11.2}Si_{1.8}$, $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$, and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ compounds measured in the heating and cooling processes under a magnetic field of 0.01 T. For $LaFe_{11.5}Si_{1.5}$ and $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, an obvious temperature hysteresis is observed between the transition on heating and cooling, indicating that two samples have a thermal-induced first-order magnetic transition at T_C. A nearly reversible change of magnetization with temperature is observed for $LaFe_{11.2}Si_{1.8}$, $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$, and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$, which is a characteristic of second-order magnetic transition or a weak first-order magnetic transition. It can be seen from Fig. 2 that the substitution of Si and/or Co for Fe drives the magnetic transition from first order to second order. The Curie temperature T_C is determined from the thermomagnetic *M-T* curves obtained in an external magnetic field *H* =0.01 T. Table I summarizes the values of T_C. One can find that substitution of Nd for La downward shifts T_C, while the substitution of Co for Fe drives T_C upward. The small decrease of T_C with increasing Nd content is due to the lattice contraction, as observed in the Ce-doped $LaFe_{13-x}Si_x$ compounds.[9] A compound $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ with T_C=280 K is obtained. The obvious enhancement of T_C may result from the contributions of the strong Fe-Co interactions. Our study shows that in $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ compounds, properly replacing Fe with Co can adjust T_C to around room temperature, which is essential for room-temperature magnetic refrigeration application.

As an example, Fig. 3 shows the isothermal magnetization curves for $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ in a wide temperature range around the Curie temperature with different temperature steps in magnetic fields up to 5.0 T. The temperature step of 2 K is chosen in the vicinity of T_C and steps of 5 K for the regions far away from T_C. It can be seen from Fig. 3(a) that an obvious magnetic hystersis loop is observed for $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, indicating a characteristic of the IEM transition and the nature of a first-order magnetic transition, as found in $LaFe_{11.7}Si_{1.3}$.[3–6,12] For $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$, however, no magnetic hystersis is observed, as shown in Fig. 3(b); that is, the Co-doped $NaZn_{13}$-type LaNdFeSi compounds show a reversible change of the magnetization with temperature and magnetic field. This is very favorable to the magnetic refrigeration application since a completely reversible MCE requires that there exists no hysteresis as the magnetization varies with temperature and magnetic field.

Figure 4 shows the temperature dependences of hysteresis loss for $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$, respectively. The hysteretic loss is defined as the enclosed area between the ascending and descending branches of magnetization curve. Table I lists the maximum values of hysteresis loss for $LaFe_{11.5}Si_{1.5}$,

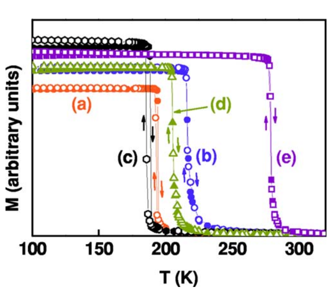

FIG. 2. (Color online) Temperature dependence of the magnetization measured on heating and cooling in a magnetic field of 0.01 T for $LaFe_{11.5}Si_{1.5}$ (a), $LaFe_{11.2}Si_{1.8}$ (b), $La_{07}Nd_{0.3}Fe_{11.5}Si_{1.5}$ (c), $La_{07}Nd_{0.3}Fe_{11.2}Si_{1.8}$ (d), and $La_{07}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ (e).

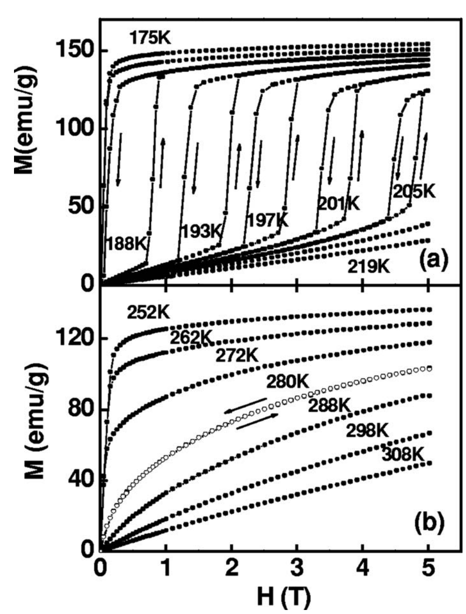

FIG. 3. Isothermal magnetization curves of $La_{07}Nd_{0.3}Fe_{11.5}Si_{1.5}$ (a) and $La_{07}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ (b) on field increase and decrease around the Curie temperature.

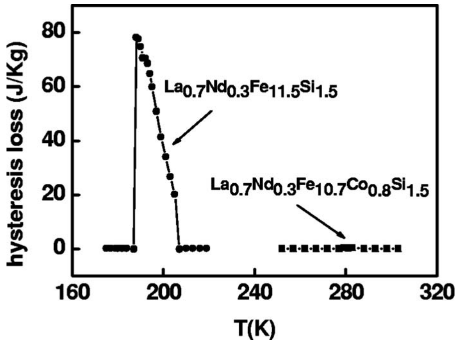

FIG. 4. Temperature dependence of the hysteresis loss of $La_{07}Nd_{0.3}Fe_{11.5}Si_{1.5}$ and $La_{07}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$.

$LaFe_{11.2}Si_{1.8}$, $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$, and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$. For $La_{0.7}Nd_{0.3}Fe_{11.5}Si_{1.5}$, a large hysteresis loss of 78.1 J/kg is observed, while the $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ exhibits a hysteresis loss close to zero. It is clear that the magnetic first-order phase transition is suppressed by the substitution of Co for Fe, leading to the disappearance of hysteresis losses.

The magnetic entropy change ΔS is calculated from magnetization data by using the following equation:

$$\Delta S(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH,$$

which is based on the Maxwell relation. The ΔS for $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ compounds as a function of temperature for different magnetic field changes are shown in Fig. 5. Table I lists the maximum values of ΔS for the magnetic field changes from 0 to 2 T and 0 to 5 T at T_C. It is found that substitution of Nd for La in $LaFe_{13-x}Si_x$ leads to a remarkable increase of magnetic entropy change. The enhancement of ΔS is attributed to the strengthening of IEM transition above T_C caused by the substitution of Nd, similar to the case of Ce-doped LaFeSi.[9] Figures 6(a) and 6(b) show the Arrott plots of $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$ and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ compounds, respectively. An obvious inflection point in the Arrott plots at T_C for $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$ is the signature of the IEM transition from paramagnetic to ferromagnetic order

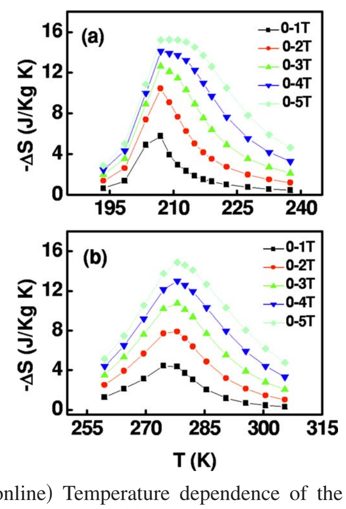

FIG. 5. (Color online) Temperature dependence of the magnetic entropy change of $La_{07}Nd_{0.3}Fe_{11.2}Si_{1.8}$ (a) and $La_{07}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ (b) for the magnetic field changes of 0–1, 0–2, 0–3, 0–4, and 0–5 T.

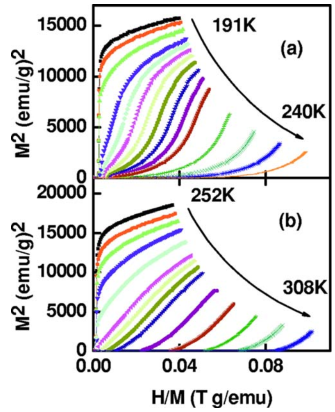

FIG. 6. (Color online) Arrott plots of $La_{0.7}Nd_{0.3}Fe_{11.2}Si_{1.8}$ (a) and $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ (b).

above T_C. For $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$, a characteristic of second-order transition is observed, as shown in Fig. 6(b). The maximum value of ΔS for $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$ is 15 J/kg K at T_C for a field change of 0–5 T, which is larger than that of Gd.[13] Since the highest magnetocaloric effect involving a second-order magnetic transition near room temperature is produced by Gd, the Co-doped $La_{1-x}Nd_xFe_{11.5}Si_{1.5}$ compounds are attractive candidates for magnetic refrigerants in an extended high temperature range even at room temperature.

We have studied the magnetic entropy change ΔS and the magnetic hysteresis loss in the Nd- and Co-doped cubic $NaZn_{13}$-type $La(Fe,Si)_{13}$ compounds. It is found that substitution of Nd for La downward shifts T_C, while the substitution of Co for Fe upward shifts T_C. The substitution of Nd for La enhances the characteristic of the IEM transition above T_C, resulting in a large ΔS. For $La_{0.7}Nd_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$, the maximum value of ΔS is 15 J/kg K at T_C=280 K for a field change of 0–5 T, which is larger than that of Gd. A remarkable result is that the magnetic behavior of the Co-doped compounds is nearly reversible for the field and temperature increase-decrease cycling, and no hysteresis loss near T_C is observed. We believe that the Co-doped $NaZn_{13}$-type LaNdFeSi compounds may be a suitable candidate for magnetic refrigerant near room temperature.

The present work has been supported by the National Basic Research Program of China, the National Natural Science Foundation of China, and the Basic Research Program of the Chinese Academy of Sciences.

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