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著者	Fujieda S., Fujita A., Fukamichi K.
journal or publication title	Applied Physics Letters
volume	81
number	7
page range	1276-1278
year	2002
URL	http://hdl.handle.net/10097/51822

doi: 10.1063/1.1498148

Large magnetocaloric effect in La$(Fe_xSi_{1-x})_{13}$ itinerant-electron metamagnetic compounds

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(Received 18 February 2002; accepted for publication 9 June 2002)

The magnetocaloric effect (MCE) originated from the itinerant-electron metamagnetic transition for La$(Fe_xSi_{1-x})_{13}$ compounds has been investigated. With increasing Fe concentration, the MCE is enhanced and both the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} for the compound with $x=0.90$ are -28 J/kg K and 8.1 K, respectively, by changing the magnetic field from 0 to 2 T. Similar large MCE values are achieved around room temperature by controlling the Curie temperature by means of hydrogen absorption. Consequently, La$(Fe_xSi_{1-x})_{13}$ compounds are promising as magnetic refrigerant materials working in relatively low magnetic fields. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1498148]

Recently, a large MCE was discovered in first-order transition materials.[1–4] By changing the magnetic field from 0 to 5 T, for example, $Gd_5(Si_2Ge_2)$ exhibits the isothermal magnetic entropy change $\Delta S_m = -18$ J/kg K and the adiabatic temperature change $\Delta T_{ad} = 15$ K at the first-order crystallographic transition temperature 278 K. These two values are larger than the values of $\Delta S_m = -9$ J/kg K and $\Delta T_{ad} = 12$ K of Gd, which exhibit a second-order magnetic transition temperature at 294 K.[5] Therefore, materials having a first-order transition are considered to be attractive for magnetic refrigerant materials.

Cubic $NaZn_{13}$-type La$(Fe_xSi_{1-x})_{13}$ compounds have a ferromagnetic ground state in the concentration range $0.81 \leqslant x \leqslant 0.89$.[6] For the compound with $x=0.88$, a discontinuous volume change indicative of a first-order transition around Curie temperature $T_C = 195$ K has also been measured by x-ray diffraction.[7,8] A Mössbauer spectrum change from a ferromagnetic (F) sextet to a paramagnetic (P) doublet also occurs in the narrow temperature range of $T_C \pm 2$. In addition, the coexistence of both F and P spectra due to the supercooling phenomenon has been confirmed just at $T_C = 195$ K.[7] In the P state, the magnetization curves exhibit an S-shape behavior, accompanied by a clear hysteresis.[7–9] All these behaviors of the La$(Fe_{0.88}Si_{0.12})_{13}$ compound are consistent with there being in these materials an itinerant-electron metamagnetic (IEM) transition, that is, a field-induced first-order magnetic transition from the P to the F state, which occurs above $T_C = 195$ K.[7–9]

Recently, a large value of ΔS_m around $T_C = 208$ K for the La$(Fe_{0.877}Si_{0.123})_{13}$ compound containing α-Fe impurity of 8 wt % has been reported.[10] It should be noted that the magnetic transition characteristics of La$(Fe_xSi_{1-x})_{13}$ compounds are sensitive to x,[7–9] and hence, the IEM transition becomes obscure by compositional heterogenity.[11] In addition, both the values of ΔS_m and ΔT_{ad} are necessary for us to evaluate the refrigerant properties, because a large ΔS_m does not always correspond to a large ΔT_{ad}.[12] In the present study, in order to discuss the MCE in homogeneous La$(Fe_xSi_{1-x})_{13}$ compounds due to the IEM transition, both ΔS_m and ΔT_{ad} have been investigated. Details of the experimental conditions and magnetic properties have been reported elsewhere.[7–9]

When the electronic and lattice entropies are independent of the magnetic field, both the values of ΔS_m and ΔT_{ad} as a function of temperature T are given by

$$\Delta S_m(T)_{\Delta H} = [S(T)_H - S(T)_0]_T, \quad (1)$$

$$\Delta T_{ad}(T)_{\Delta H} = [T(S)_H - T(S)_0]_S, \quad (2)$$

where S is the total entropy and ΔH is the magnetic field change from 0 to H. Figure 1 shows the temperature dependence of the total entropy in various magnetic fields for the La$(Fe_{0.88}Si_{0.12})_{13}$ compound. The value of $S(T)_H = \int (C/T)_H dT$ is calculated from the specific heat measurement carried out by a relaxation method.[13] With increasing magnetic field, a significant jump of S due to the IEM transition shifts to a higher temperature range. The value of ΔS_m is also related to the magnetization M as functions of T and H, which is given by the following equation related to the Maxwell relationship:

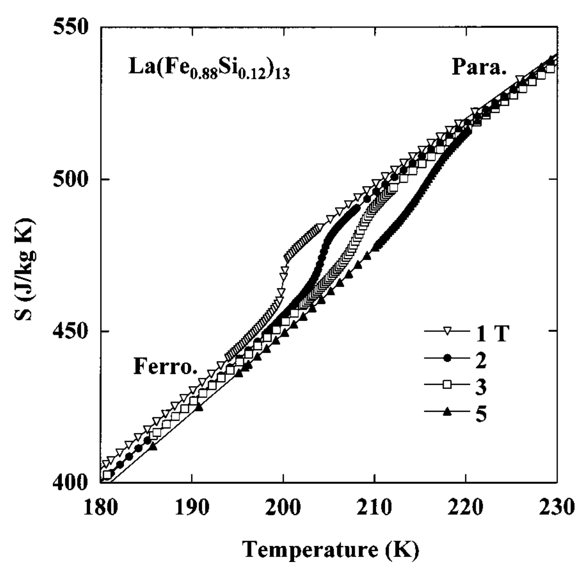

FIG. 1. Temperature dependence of the total entropy S in various magnetic fields for the La$(Fe_{0.88}Si_{0.12})_{13}$ compound.

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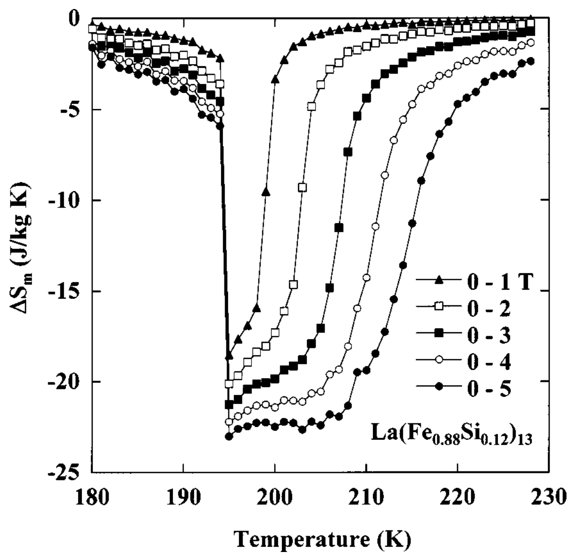

FIG. 2. Temperature dependence of the isothermal magnetic entropy change ΔS_m for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound.

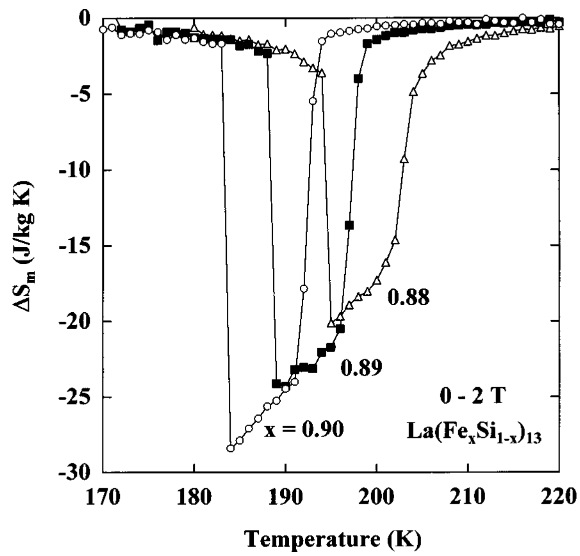

FIG. 4. Temperature dependence of the isothermal entropy change ΔS_m in the magnetic field change from 0 to 2 T ($\Delta H = 2$ T) for $La(Fe_xSi_{1-x})_{13}$ compounds with $x = 0.88$, 0.89, and 0.90.

$$\Delta S_m(T)_{\Delta H} = \int_0^H (\partial M/\partial T)_H dH. \tag{3}$$

The temperature dependence of ΔS_m obtained from Eq. (3) for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound is given in Fig. 2. The value of M exhibits a drastic change of about 1.5 μ_B due to the IEM transition,[7–9] resulting in a significant large negative maximum value of ΔS_m. The magnitude of the peak of ΔS_m is in agreement with the difference in S between the P and F states shown in Fig. 1, which suggests that the electronic and lattice entropy changes due to the IEM transition are negligibly small. It should be noted that such a large ΔS_m is obtained even in relatively low magnetic fields, because the IEM transition field becomes lower as the temperature comes close to $T_C = 195$ K. That is to say, as seen from Fig. 2, the negative maximum value of ΔS_m under the magnetic field change from 0 to 2 ($\Delta H = 2$ T) is -20 J/kg K.

For magnetic refrigerant materials, a small heat capacity per unit mass and a large value of ΔS_m in a wide temperature range are desirable. Otherwise, ΔT_{ad} is not so large even though ΔS_m is large enough,[12] therefore, ΔT_{ad} should be evaluated.

The temperature dependence of ΔT_{ad} as a function of magnetic field change for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound is presented in Fig. 3. The value of $T(S)_H$ was obtained from Fig. 1 and $T(S)_0$ was estimated by subtracting $\Delta S_m(T)_{\Delta H}$ from $S(T)_H$ by using Eq. (1). The value of ΔT_{ad} exhibits a sharp peak at 195 K. The maximum value of ΔT_{ad} becomes 6.5 K under $\Delta H = 2T$. From Figs. 2 and 3, it is clear that the $La(Fe_{0.88}Si_{0.12})_{13}$ compound has a large MCE due to the IEM transition.

Figure 4 shows the temperature dependence of ΔS_m under $\Delta H = 2T$ for $La(Fe_xSi_{1-x})_{13}$ compounds with $x = 0.88$, 0.89, and 0.90. The negative value of ΔS_m becomes larger with increasing x. For the compound with $x = 0.90$, the negative maximum value of ΔS_m becomes -28 J/kg K under

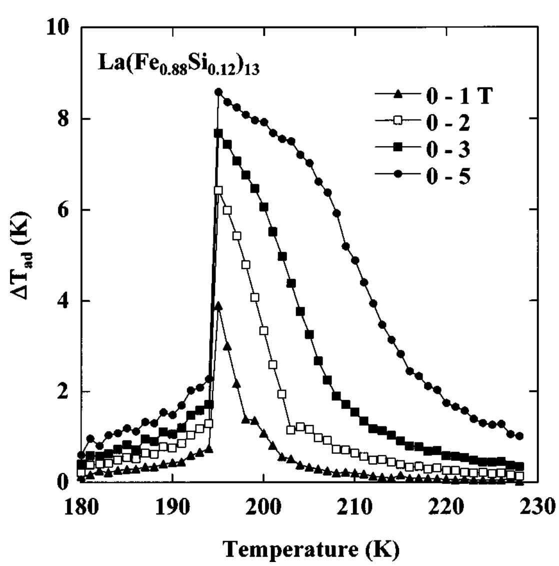

FIG. 3. Temperature dependence of the adiabatic temperature change ΔT_{ad} for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound.

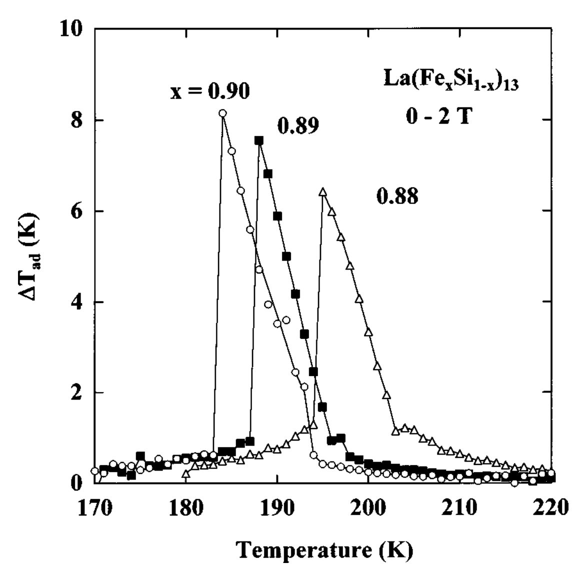

FIG. 5. Temperature dependence of the adiabatic temperature change ΔT_{ad} in the magnetic field change from 0 to 2 T ($\Delta H = 2$ T) for $La(Fe_xSi_{1-x})_{13}$ compounds with $x = 0.88$, 0.89, and 0.90.

TABLE I. Transition temperature T_t; isothermal entropy change ΔS_m; and adiabatic temperature change ΔT_{ad} of $La(Fe_xSi_{1-x})_{13}$ ($x=0.877$, 0.880, 0.890, 0.900), $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$, $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$, together with those for MnAs, $Gd_5(Si_2Ge_2)$, and Gd in the magnetic field change from 0 to 2 T ($\Delta H=2$ T).

Material	T_t (K)	ΔS_m (J/kg K)	ΔT_{ad} (K)	Reference
$La(Fe_xSi_{1-x})_{13}$				
$x=0.877$	208[a]	−14	⋯	10
$x=0.880$	195[a]	−20	6.5	Present results
$x=0.890$	188[a]	−24	7.5	Present results
$x=0.900$	184[a]	−28	8.1	Present results
$La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$	274[a]	−19	6.2	Present results
$La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$	291[a]	−24	6.9	Present results
MnAs	318[b]	−31	4.7	3
$Gd_5(Si_2Ge_2)$	278[b]	−14	7.3	4
Gd	294[a]	−5	5.7	5

[a]Curie temperature.
[b]Crystallographic transition temperature.

$\Delta H=2$ T, which increases about 40%, compared with the value for the compound with $x=0.88$. The temperature dependence of ΔT_{ad} is given in Fig. 5 for $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90. The value of ΔT_{ad} becomes larger with increasing x. For the compound with $x=0.90$, the maximum value of ΔT_{ad} reaches 8.1 K under $\Delta H=2$ T. Accordingly, the magnetocaloric properties are enhanced by controlling x in $La(Fe_xSi_{1-x})_{13}$ compounds.

From the practical viewpoint, it is important to control the temperature range of the large MCE. For the $La(Fe_{0.88}Si_{0.12})_{13}$ compound, the Curie temperature T_C can be controlled up to 336 K continuously by hydrogen absorption while still keeping the IEM transition,[14,15] accompanied by its zero-hydrogen comparable value of ΔS_m.[16] As a result, $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ exhibits $\Delta S_m=-19$ J/kg K and $\Delta T_{ad}=6.2$ K under $\Delta H=2$ T at 274 K. Furthermore, $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$ exhibits $\Delta S_m=-24$ J/kg K and $\Delta T_{ad}=6.9$ K under $\Delta H=2$ T at 291 K. Therefore, the large MCE for $La(Fe_xSi_{1-x})_{13}H_y$ compounds is also obtained up to room temperature in relatively low magnetic fields, which can be generated by using permanent magnets.

Collected in Table I are the transition temperature T_t and the magnetocaloric properties under $\Delta H=2$ T for $La(Fe_xSi_{1-x})_{13}$ compounds, $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$, $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$, together with those of MnAs,[3] $Gd_5(Si_2Ge_2)$,[4] and Gd,[5] reported as candidates for magnetic refrigerant materials. The value of ΔS_m for the heterogeneous $La(Fe_{0.877}Si_{0.123})_{13}$ compound is -14 J/kg K under $\Delta H=2$ T.[10] On the other hand, ΔS_m for the homogeneous compound with $x=0.880$ having the IEM transition is -20 J/kg K. The latter value is larger than the former value. For $Gd_5(Si_xGe_{4-x})$ having a large value of ΔT_{ad}, the first-order transition causes a gradual change in the transition temperature after thermal cycling.[4,17] On the other hand, the IEM transition of $La(Fe_xSi_{1-x})_{13}H_y$ compounds is accompanied by no structural changes.[7–9,14,15] As seen from Table I, the values of ΔT_{ad} for the $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ and $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$ compounds are larger than the values for MnAs (Ref. 3) and Gd.[5] Accordingly, $La(Fe_xSi_{1-x})_{13}$ compounds are one of the most promising magnetic refrigerant materials.

In conclusion, the magnetocaloric effect, the isothermal entropy change ΔS_m, and the adiabatic temperature change ΔT_{ad} have been investigated in $La(Fe_xSi_{1-x})_{13}$ itinerant-electron metamagnetic compounds. The MCE is enhanced by increasing x, and hence, ΔS_m and ΔT_{ad} reach -28 J/kg K and 8.1 K, respectively, under $\Delta H=2$ T at 184 K for the compound with $x=0.90$. The large MCE is also obtained around room temperature by controlling the Curie temperature by means of hydrogen absorption. Consequently, $La(Fe_xSi_{1-x})_{13}$ compounds are one of the most promising magnetic refrigerant materials acting in relatively low magnetic fields.

The present work has been supported by the Grant-in-Aids for Scientific Research (B) (2) (No. 13555168) and on Priority Areas (A) (No. 299) from Japan Society for the Promotion of Science. One of the authors (A.F.) would like to acknowledge support by the Industrial Technology Research Grant Program in 2000 (No. 00A26019a) from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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