Control of large magnetocaloric effects in metamagnetic La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds by hydrogenation

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Abstract

To obtain large magnetocaloric effects (MCEs) due to the itinerant-electron metamagnetic (IEM) transition in La(Fe$_x$Si$_{1-x}$)$_{13}$, the Curie temperature T_C has been controlled by hydrogen absorption. In La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds, $T_C = 195$ K for $y = 0.0$ increases with increasing hydrogen concentration, resulting in $T_C = 330$ K for $y = 1.6$. Furthermore, the magnetic moment is also stabilized against temperature by hydrogen absorption. Since the IEM transition is preserved after hydrogenation, large MCEs of the magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} have been observed around room temperature. A large value of ΔT_{ad} has been confirmed by a direct measurement in adiabatic magnetic field change for the La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$H$_y$ ($y = 0.0$ and 1.6). Consequently, the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides are promising as high-performance magnetic refrigerants working in a wide range of temperature covering room temperature in relatively low applying magnetic fields.
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1. Introduction

Recently, much attention has been paid to utilization of the magnetic refrigeration, because of its advantages compared with conventional gas-compression refrigerations, such as high environmental safety as against ozone depleting fluorocarbon-based gases, and high energy efficiency [1]. To realize room temperature magnetic refrigerators, it is necessarily to develop new magnetic refrigerants having large magnetocaloric effects (MCS), which are represented by the magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} caused under external magnetic fields [1,2]. Especially, the MCEs are expected to be enhanced in materials having a first-order magnetic transition, which is accompanied by latent heat.

It has been demonstrated that La(Fe$_x$Si$_{1-x}$)$_{13}$ in the concentration range $0.86 \leq x \leq 0.90$ shows a thermally induced first-order magnetic phase transition from the ferromagnetic (F) to the paramagnetic (P) phase at the Curie temperature T_C, as well as the magnetic field induced first-order transition from the P to the F phase, which is known as the itinerant-electron metamagnetic (IEM) transition, just above $T_C \sim 200$ K [3–8]. It has also been estimated that the MCEs are enhanced by the large latent heat of the IEM transition in the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds [9–13]. Therefore, the control of T_C up to room temperature makes the present compounds possible to apply to the magnetic refrigerants showing the large MCEs in relatively low magnetic fields at wide temperature ranges covering room temperature. It has been reported that T_C is increased by hydrogen absorption into La(Fe$_x$Si$_{1-x}$)$_{13}$ up to room temperature with preserving the IEM transition [9,14–17].

In the present paper, the influence of hydrogen absorption on the magnetic properties is investigated in terms of mag-

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netic excitation, and the MCEs together with cooling power of La(Fe$_x$Si$_{1-x}$)$_{13}$ and their hydrides are evaluated from the practical viewpoint. Furthermore, direct measurements of MCEs have been carried out and the results are compared with the values calculated under ideal conditions.

2. Experimental

La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds were prepared by arc-melting in an argon gas atmosphere. To obtain NaZn$_{13}$-type single phase, the heat treatment has been carried out in a vacuum quartz tube at 1323 K for 10 days. Hydrogen absorption in these compounds was carried out by annealing in a hydrogen atmosphere in a sealed chamber. The hydrogen concentration was controlled by hydrogen gas pressure in the chamber. The magnetization was measured with a superconducting quantum interference device magnetometer. Specific heat measurements were carried out by a relaxation method in the range from 4.2 to 300 K. For direct measurements of adiabatic temperature change, the specimens in a quartz holder with glass fibers as inner wrapper were moved quickly between inside and outside of superconducting solenoid.

3. Results and discussion

Fig. 1 shows the temperature dependence of magnetization for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds ($y = 0.0$, 1.1 and 1.6) in a magnetic field of 0.5 T. It has been confirmed that the thermally induced first-order ferromagnetic (F)–paramagentic (P) phase transition occurs at $T_C = 195$ K for $y = 0.0$. Therefore, a steep decrease of magnetization appears at T_C. Furthermore, as shown in the inset in Fig. 1, the magnetic field-induced first-order P–F phase transition, namely the itinerant-electron metamagnetic transition is observed just above T_C. It is noteworthy that the value of T_C is significantly increased by hydrogen absorption as seen in Fig. 1. For the hydrogenated La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds, the volume expansion caused by hydrogen absorbed interstitially has been confirmed [9,17]. The volume dependence of T_C has been discussed in association with the IEM transition [6,18]. According to the theory for the IEM transition, the volume change causes a significant change of T_C due to magnetovolume effect on the thermal variation of free energies in both the F and P states [19,20]. On the other hand, the change of magnetization M is less sensitive to the volume change [19,20]. Actually, as seen from Fig. 1, the increase in low temperatures magnetization by hydrogen absorption is relatively small compared to that in the Curie temperature. However, the decrement of M with increasing temperature is changed by the hydrogen absorption. Consequently, the hydrogen absorption brings about the change not only in the condition of the F–P transition but also in the thermal variation of magnetic moment in the F state.
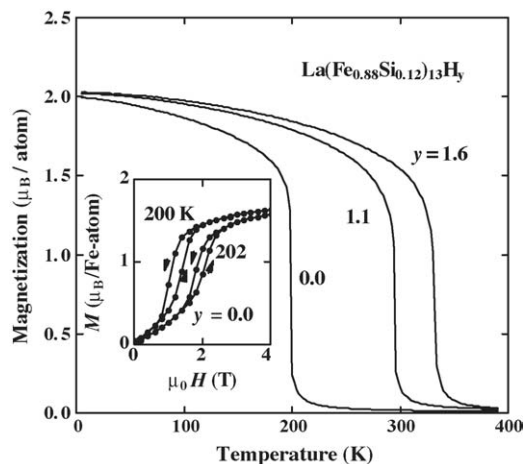

Fig. 1. Thermomagnetization curves of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ ($y = 0.0$, 1.1 and 1.6) compounds. The inset shows the magnetization curves for $y = 0.0$ at 200 and 202 K.

In order to elucidate the influence of the hydrogen absorption on the thermal variation of magnetic moment in the F state, the spin-wave dispersion coefficient D is evaluated by using the following relation [21]:

$$M = M_0 - 5.26\mu_B \left[\frac{4\pi D}{k_B} \right]^{-3/2} T^{3/2} \qquad (1)$$

where μ_B and k_B are the Bohr magneton and the Boltzmann constant, respectively. Shown in Fig. 2 is the hydrogen concentration y dependence of D and T_C for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds. The spin-wave dispersion coefficient D for $y = 0$ is relatively small of 52 meV Å^2. It has been discussed that such small value of D is related to the instability of magnetic moment in connection with a large magnetovolume effect in invar-type alloys such as Fe$_3$Pt [22]. After hydrogen absorption, the value of D as well as T_C increases linearly with hydrogen concentration y, although D of 91 meV Å^2 for $y = 1.6$ is still close to D of 95 meV Å^2 for Fe$_3$Pt invar-type alloy obtained from thermomagnetization curve [22]. Therefore, the hydrogen absorption results in a thermal stabilization of the ferromagnetic moment as well as increase in T_C.

Since the first-order transition is followed by a large latent heat, a large magnetic entropy change ΔS_m is expected in
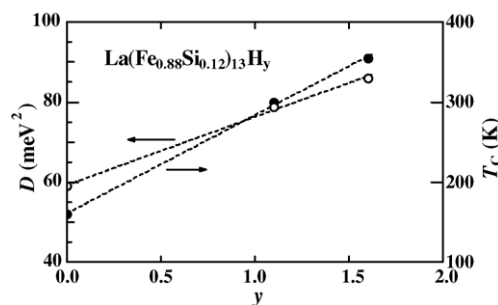

Fig. 2. Hydrogen concentration y dependence of the spin-wave dispersion coefficient D and the Curie temperature T_C for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$.

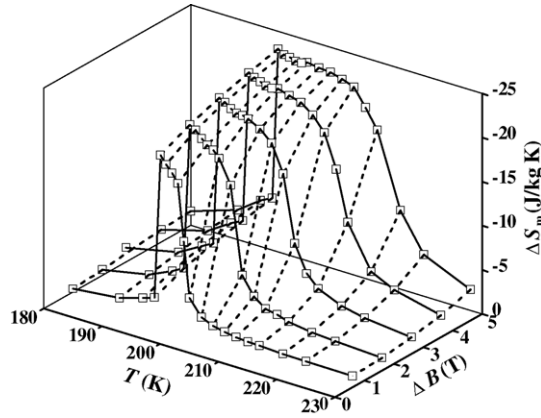Fig. 3. Variation of the entropy change ΔS_m as a function of temperature T and the magnetic field change ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound.

association with the IEM transition. The value of ΔS_m is evaluated from the variation of magnetization as a function of M and H in connection the following Maxwell relation [1]:

$$\Delta S_m = \int_0^{H_{max}} \mu_0 \left(\frac{\partial M}{\partial T} \right) dH \quad (2)$$

As indicated in Eq. (2), a large ΔS_m is obtained because of the large $\partial M / \partial T$, which shows a divergent change at T_C due to the first-order magnetic transition. It should be also noted that the value of ΔS_m is a function of the magnetic field change from 0 to $\mu_0 H_{max} (\Delta B = \mu_0 H_{max})$. In Fig. 3, the variation of ΔS_m is plotted as a function of T and ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound. Because of the thermally induced first-order transition, the peak value of $-\Delta S_m$ steeply increases around $T_C = 195$ K. It is useful to consider that available magnetic flux densities of recent permanent magnets are of about 2 T, therefore, the magnitude of MCEs in $\Delta B = 2$ T is a measure for room-temperature applications. The negative maximum value of the magnetic entropy change, $-\Delta S_m^{max}$ of 18 J/(kg K) for $\Delta B = 2$ T is superior or comparable to data of other candidates for magnetic refrigerants, such as Gd$_5$Ge$_2$Si$_2$ with $-\Delta S_m^{max} = 28$ J/(kg K) [23] and MnFeP$_{0.55}$As$_{0.45}$ with 15 J/(kg K) [24].

The relative cooling power RCP based on the magnetic entropy change ΔS_m is defined by:

$$\text{RCP} = -\Delta S_m^{max} \times \delta T_{FWHM}^S \quad (3)$$

where δT_{FWHM}^S is the full width of half maximum of ΔS_m–T curve [1,25]. By this definition, RCP gives the cooling power indicating how much heat can be transferred between cold and hot end in refrigerators. The values of $-\Delta S_m^{max}$, δT_{FWHM}^S and RCP are plotted against ΔB in Fig. 4. In contrast to the gradual increase in $-\Delta S_m^{max}$, δT_{FWHM}^S continues to increase with ΔB, resulting in a linear increase in RCP. To compare the cooling power with other candidates of the magnetic refrigerants, it is convenient to use the normalized value of RCP/ΔB. In the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$, RCP/ΔB becomes 92 J/(kg T), being comparable to 89 and 93 J/(kg T) for Gd$_5$Ge$_2$Si$_2$ and MnFeP$_{0.65}$As$_{0.35}$, respectively [1].

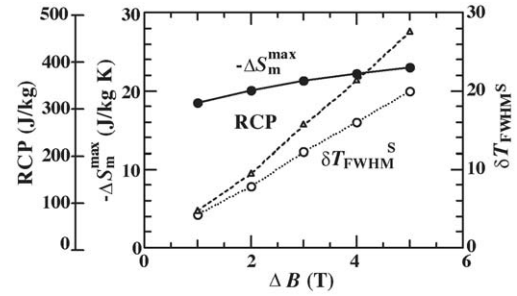

Fig. 4. The negative maximum value of the entropy change $-\Delta S_m^{max}$, the full width of half maximum of ΔS_m–T curve, δT_{FWHM}^S and the relative cooling power RCP as a function of the magnetic field change ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

It has been pointed out that not only the magnetic entropy change ΔS_m but also the adiabatic temperature change ΔT_{ad} should be large for realization of high-efficiency magnetic refrigeration. The value of ΔT_{ad} is evaluated from the following relation [1]:

$$\Delta T_{ad} = [T(S)_{\mu_0 H_{max}} - T(S)_0]_S \quad (4)$$

The temperature as a function of entropy, $T(S)$, is calculated from the S–T curve obtained from the heat capacity measurements. Fig. 5 shows the variation of ΔT_{ad} as a function of T and ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound. What has to be mentioned is that $\Delta T_{ad} = 6.5$ K at relatively low magnetic field of 2 T is comparable to $\Delta T_{ad} = 7.2$ K for Gd$_5$Ge$_2$Si$_2$ [23] and larger than $\Delta T_{ad} = 4.7$ K for MnAs [26]. In Fig. 6, ΔT_{ad}^{max} and FWHM of ΔT_{ad}–T curve, δT_{FWHM}^T, are plotted against ΔB. The change in ΔT_{ad}^{max} against ΔB is similar to that in ΔS_m but the increment in low value region of ΔB is more significant. The value of ΔT_{ad} is proximate to $\Delta S_m/(TC_H)$ by using total heat capacity C_H. Since anomaly in C_H appears at T_C, the magnetic field dependence of T_C is reflected by ΔT_{ad}. The value of δT_{FWHM}^T increases almost linearly against ΔB but its increment is about a half of that of δT_{FWHM}^S, due to the non-magnetic contribution of C_H mainly coming from phonon.

As seen from Fig. 1, T_C is increased up to room-temperature by hydrogen absorption. For the hydrogenated specimens, the change in magnetization at T_C is sharp in analogy with that of $y = 0$. Accordingly, almost the same large values of $-\Delta S_m$ and RCP are kept after controlling T_C between 195 and 320 K. The point to be noticed is that both $-\Delta S_m^{max}$ and RCP for La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_y$, respectively, become about 1.4 and 1.2 times larger than those for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ in whole temperature range. Therefore, the increase in Fe concentration in the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides gives rise to the larger cooling powers. The maximum of the adiabatic temperature change ΔT_{ad}^{max} also keeps their large values after elevating T_C by hydrogen absorption, and then ΔT_{ad}^{max} of 6.5 K is obtained in a temperature range between 195 and 320 K for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ hydrides. The phonon contribution as a main part of C_H is less sensitive to the Fe concentra-

tion, compared to ΔS_m [14,17], resulting in a larger value of ΔT_{ad}^{max} of about 8 K for La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_y$.

In an adiabatic process related to the first-order phase transition, the time scale is dominated by propagation speed of the nucleation and growth of the phase derived by the magnetic field change [6,23]. To confirm a smooth adiabatic process, the direct measurement of ΔT_{ad} is necessarily [27]. Fig. 7 illustrates the time τ dependence of temperature for La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$ compound. The specimen was settled in a magnetic field of 2 T produced by a superconducting magnet at $\tau = 0$, and moved to the outside of the magnet at $\tau = \tau_1$, then inserted again into the magnet bore at $\tau = \tau_2$. As a response to the adiabatic magnetic field change, the change in the specimen temperature of about 4.5 K was observed. These adiabatic temperature changes occur within a few seconds and no delay is confirmed.

Fig. 8 shows the temperature dependence of the directly measured adiabatic temperature change ΔT_{ad}^d for La(Fe$_{0.89}$Si$_{0.12}$)$_{13}$. For comparison, the indirectly obtained value of ΔT_{ad}^{ind} from the specific heat measurements is also shown in the same figure. Although the maximum value is slightly small due to the incomplete thermal insulation in the present experiment, the maximum value of ΔT_{ad}^d in $\Delta B = 2$ T
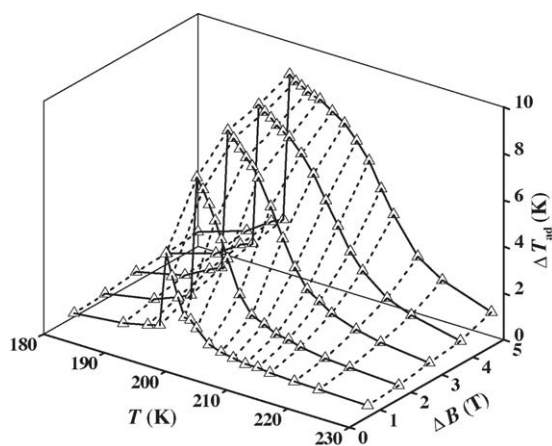

Fig. 7. Time dependence of the temperature change for La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$.

is 5.4 K, being large enough for practical applications. As shown in the inset in Fig. 8, ΔT_{ad}^d in $\Delta B = 2$ T is also directly observed for La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$H$_{1.6}$ in the temperature range around 310–330 K. Since the present specific heat measurements are restricted below room-temperature, we could not calculate the indirect value of ΔT_{ad}^{ind}, however, it is apparent that large ΔT_{ad}^d of about 4 K in $\Delta B = 2$ T is available even above room-temperature in the present hydrides. Note that a slight decrease of ΔT_{ad}^{ind} after hydrogen absorption is caused by a larger heat leak arising from an incomplete insulation, because thermal conductivity of the specimen becomes larger in higher temperatures [28]. Therefore, it is concluded that there is no dissipative effect coming from the IEM transition in adiabatic magnetic field changes after controlling T_C by hydrogen absorption.

It has been discussed that the candidate for magnetic refrigerants should have not only large MCEs but also sufficient thermal conductivity κ and stability against thermal cycles [1]. We have confirmed that κ in 200–330 K for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides is comparable with that of Gd metal, while the values of Gd$_5$Ge$_2$Si$_2$ and MnAs are much lower in this temperature range [28]. Furthermore, other candidates having large MCEs related

Fig. 5. Variation of the adiabatic temperature change ΔT_{ad} as a function of temperature T and the magnetic field change ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound.
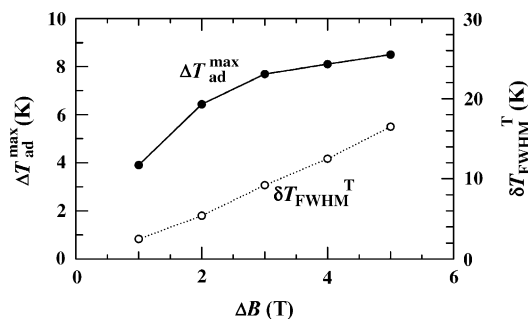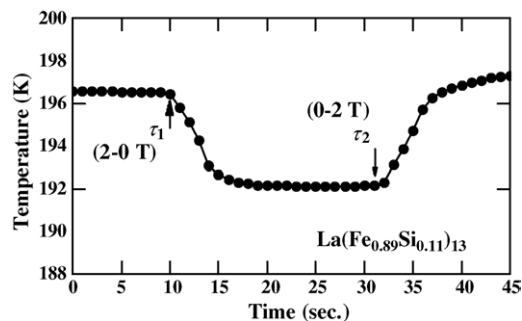

Fig. 6. The maximum value of the adiabatic temperature change ΔT_{ad}^{max} and the full width of half maximum of $\Delta T_{ad}-T$ curve, δT_{FWHM}^T as a function of the magnetic field change ΔB for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.
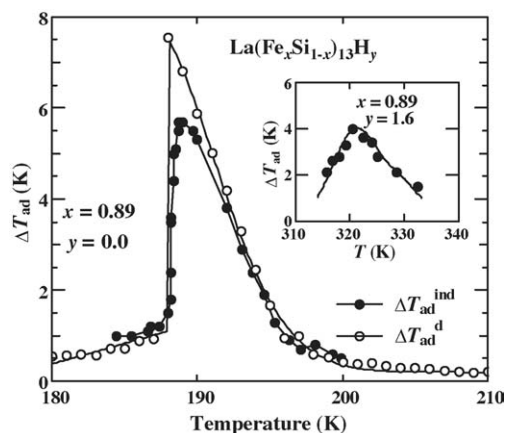

Fig. 8. Temperature dependence of the direct measured adiabatic temperature change ΔT_{ad}^d, together with that of the indirectly obtained adiabatic temperature change ΔT_{ad}^{ind}. The inset shows the temperature dependence of ΔT_{ad}^d for La(Fe$_{0.89}$Si$_{0.11}$)H$_{1.6}$.

to the crystallographic structural transformation exhibit an irreversible decay in the MCEs and/or shift in the transition temperature against thermal cycles [29,30]. There is no such disadvantage in the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides, because the IEM transition is followed by no crystallographic change. In addition, it is also stressed that all constituent elements of the present compounds have low cost and no toxicity against human body and environments.

4. Conclusion

Influences of hydrogen absorption on the magnetic properties and magnetocaloric effects represented by the magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} have been investigated for the La(Fe$_x$Si$_{1-x}$)$_{13}$ itinerant-electron metamagnetic compounds and their hydrides. For the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds, the Curie temperature T_C is increased from 195 K for $y = 0$ to 330 K for $y = 1.6$. By evaluating the spin-wave dispersion coefficient, it is revealed that the thermal stabilization of ferromagnetic moment is also brought about by the hydrogen absorption. After controlling T_C by hydrogen absorption, the IEM transition is preserved, resulting in large MCEs as well as the relative cooling power even in the relatively low magnetic field of 2 T at temperature ranges of 180–330 K. From the direct measurements of MCEs, a large value of ΔT_{ad} is expected to be effectively available in practical cooling cycles. Consequently, the La(Fe$_x$Si$_{1-x}$)$_{13}$H$_y$ compounds are one of the most practical candidates for magnetic refrigerants working in a wide temperature range.

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