# Itinerant-electron metamagnetic transition and large magnetocaloric effects in $La(Fe_xSi_{1-x})_{13}$ compounds and their hydrides

A. Fujita,* S. Fujieda, Y. Hasegawa, and K. Fukamichi
*Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan*
(Received 1 October 2002; published 20 March 2003)

The itinerant-electron metamagnetic (IEM) transition and magnetocaloric effects (MCE's) in the $La(Fe_xSi_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}H_y$ compounds have been investigated. The $La(Fe_xSi_{1-x})_{13}$ compounds exhibit large values of both the isothermal entropy change $\Delta S_m$ and the adiabatic temperature change $\Delta T_{ad}$ around the Curie temperature $T_C$ in relatively low magnetic fields. Such large MCE's are explained by a large magnetization change at $T_C$ and a strong temperature dependence of the critical field $B_C$ for the IEM transition. By hydrogen absorption into the compounds, $T_C$ is increased up to about 330 K, keeping the metamagnetic transition properties. Accordingly, the extension of the working temperature range having the large MCE's in relatively low magnetic fields is demonstrated by controlling $y$ in the $La(Fe_xSi_{1-x})_{13}H_y$ compounds. The correlation between the increase of $T_C$ and the large MCE's in the $La(Fe_xSi_{1-x})_{13}H_y$ compounds is discussed by taking the magnetovolume effects into consideration.

DOI: 10.1103/PhysRevB.67.104416 PACS number(s): 75.30.Sg, 75.50.Bb

## I. INTRODUCTION

The itinerant-electron metamagnetic (IEM) transition is the field-induced first-order transition from the paramagnetic (P) to the ferromagnetic (F) state, which relates to the change in the band structure of $3d$ electrons by applying a magnetic field. Therefore, the origin of the IEM transition is associated with a special $3d$ band structure which exhibits a sharp peak of the density of states (DOS) just below the Fermi level.[1] The IEM transitions of Co-based Laves phase and pyrite compounds have been investigated theoretically and experimentally.[1–8] Recently, it has been demonstrated that the cubic $NaZn_{13}$-type $La(Fe_xSi_{1-x})_{13}$ compounds exhibit the IEM transition.[9–11] The $La(Fe_xSi_{1-x})_{13}$ compounds in the ground state are ferromagnetic in the concentration range $0.81 \leqslant x \leqslant 0.89$.[12] For the compound with $x=0.88$, a discontinuous change of the thermomagnetization curve due to the thermal-induced first-order transition is observed at the Curie temperature $T_C=195$ K.[9–11] Since the $La(Fe_{0.88}Si_{0.12})_{13}$ compound exhibits the IEM transition in the P state, the magnetization curves above $T_C=195$ K exhibit an S-shape behavior with a clear hysteresis. This IEM transition is accompanied by a large volume magnetostriction of about 1.5% at 200 K just above $T_C$. Such a large magnetovolume effect has been investigated from both the fundamental and practical viewpoints.[9–11,13–15]

Materials having large magnetocaloric effects (MCE's) are utilized as magnetic refrigerants because of their energy efficiency and environmental safety. To obtain a high performance of magnetic refrigeration, it is necessary to investigate magnetic refrigerants having large MCE's in relatively low magnetic fields. Large MCE's in some magnetic materials have been reported.[16–26] The rare earth elements and their compounds such as Gd (Ref. 18) and $(Dy_{0.5}Er_{0.5})Al_2$ (Ref. 19) having a second-order transition exhibit large MCE's. By changing the magnetic field from 0 to 5 T, Gd exhibits the isothermal entropy change $\Delta S_m=-9$ J/kg K and the adiabatic temperature change $\Delta T_{ad}=11.6$ K at the second-order magnetic transition temperature 294 K. Recently, large MCE's have been observed in compounds having the first-order transition such as $Gd_5(Si_2Ge_2)$ (Ref. 20) and $ErCo_2$ (Ref. 21). For example, $Gd_5(Si_2Ge_2)$ exhibits the values of $\Delta S_m=-18$ J/kg K and $\Delta T_{ad}=15.3$ K at the first-order crystallographic transition temperature 278 K by changing the magnetic field from 0 to 5 T. These values are larger than those of Gd. Such large MCE's have also been observed in transition-metal compounds having a first-order crystallographic transition such as MnAs (Ref. 22) and $Fe_{49}Rh_{51}$ (Refs. 23 and 24). Furthermore, a large value of $\Delta S_m$ has been reported for $La(Fe_{0.86}Si_{0.09}Co_{0.05})_{13}$ (Ref. 25) and $MnFeP_{0.45}As_{0.55}$ (Ref. 26). Therefore, materials having the first-order transition are attractive for magnetic refrigerants.

A large value of $\Delta S_m=-14$ J/kg K in the magnetic field change from 0 to 2 T has been observed in the $La(Fe_{0.877}Si_{0.123})_{13}$ compound containing $\alpha$-Fe impurity of 8 wt % around $T_C=208$ K by a magnetic measurement.[27] However, the magnetic transition characteristics of the $La(Fe_xSi_{1-x})_{13}$ compounds are sensitive to $x$,[9–12] and hence the IEM transition becomes obscure by compositional heterogeneity.[28] In addition, $\Delta T_{ad}$ is necessary to evaluate the MCE's for magnetic refrigerants as well as $\Delta S_m$, because a large value of $\Delta S_m$ does not always bring about a large value of $\Delta T_{ad}$.[29,30] Recently, to discuss the MCE's for magnetic refrigerants, both $\Delta S_m$ and $\Delta T_{ad}$ due to the IEM transition for the $La(Fe_xSi_{1-x})_{13}$ compounds have been investigated.[31,32] It has been reported that the $La(Fe_xSi_{1-x})_{13}$ compounds exhibit large MCE's in relatively low magnetic fields. Additionally, $T_C$ of the $La(Fe_{0.88}Si_{0.12})_{13}$ compound can be increased up to 336 K by hydrogen absorption.[14,15] An extension of the working temperature range having large MCE's in relatively low magnetic fields is expected by controlling $y$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds. Already, the large values of both $\Delta S_m$ and $\Delta T_{ad}$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ compound have been confirmed above $T_C=274$ K.[31,32] Accordingly, investigations of the magnetocaloric properties for the $La(Fe_xSi_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}H_y$ compounds are meaningful for the magnetic refrigerants.

 

In the present study, in order to discuss the magnetocaloric properties of the $La(Fe_xSi_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}H_y$ compounds, $\Delta S_m$, $\Delta T_{ad}$, and the IEM transition have been investigated. Section III A describes the features of the IEM properties for the $La(Fe_xSi_{1-x})_{13}$ compounds. Section III B presents the magnetocaloric properties for the $La(Fe_xSi_{1-x})_{13}$ compounds, and the relationship between the IEM transition and the MCE's is discussed. The increase of $T_C$ by hydrogen absorption into the $La(Fe_xSi_{1-x})_{13}$ compounds is given in Sec. III C. Section III D explains the correlation between the increase of $T_C$ and the large MCE's for the $La(Fe_xSi_{1-x})_{13}H_y$ compounds. The extension of the working temperature range with the large MCE's in relatively low magnetic fields is demonstrated by controlling $y$ in the $La(Fe_xSi_{1-x})_{13}H_y$ compounds.

## II. EXPERIMENTS

The $La(Fe_xSi_{1-x})_{13}$ compounds with the nominal compositions of $x=0.87$, 0.88, 0.89, and 0.90 were prepared by arc melting in an Ar gas atmosphere. The subsequent heat treatment was carried out in a vacuum quartz tube at 1323 K for 10 days. The x-ray powder diffraction patterns of all the specimens identified as a $NaZn_{13}$-type single phase. The hydrogen absorption in the $La(Fe_xSi_{1-x})_{13}$ compounds was carried out by annealing under hydrogen gas atmosphere. The control of the hydrogen concentration $y$ in the $La(Fe_xSi_{1-x})_{13}H_y$ compounds was made by changing both the hydrogen gas pressure and the annealing temperature. The hydrogen concentration was determined by both gas chromatograph and gas fusion analyses. The magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer and the heat capacity measurements were carried out by a relaxation method.[33]

## III. RESULTS AND DISCUSSION

### A. Metamagnetic transition in $La(Fe_xSi_{1-x})_{13}$ compounds

Figure 1 shows the temperature dependence of magnetization for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound in various magnetic fields. All the thermomagnetization curves except for the curve in 0.2 T represent the heating process. For both the heating and cooling processes in the magnetic field of 0.2 T, a discontinuous magnetization change is observed around the Curie temperature $T_C$, accompanied by a small hysteresis of about 1 K. Therefore, a thermal-induced first-order transition between the ferromagnetic and the paramagnetic states takes place at $T_C$. The magnitude of the magnetization change around $T_C$ is large of about $1.5\mu_B$ and $T_C$ significantly increases with increasing magnetic field. Such a discontinuous large magnetization change due to the thermal-induced first-order transition is observed around $T_C$ to an extent of 5 T.

The temperature dependence of the heat capacity $C_H$ for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound in the various magnetic fields is given in Fig. 2. By applying a magnetic field of 1 T, the heat capacity exhibits a distinct peak and this position agrees with $T_C$ in Fig. 1. It is apparent that a clear λ-type peak of the heat capacity is caused by the thermal-induced first-order transition, resulting in a large entropy change.

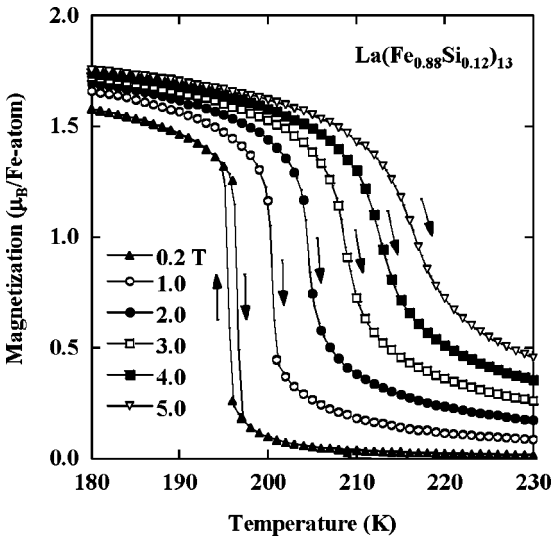


FIG. 1. Thermomagnetization curves of the cooling process for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound in various magnetic fields. Thermomagnetization curves in the magnetic field of 0.2 T are the heating and cooling processes as given by the arrows.

Since $T_C$ increases with the magnetic field, the peak position shifts toward higher-temperature ranges. The thermal-induced first-order transition having a large entropy change of the phase transition is maintained up to the magnetic field of 5 T.

An itinerant-electron metamagnetism at finite temperatures has been discussed by taking the renormalization effect of spin fluctuations on the Landau-Ginzburg theory into account.[2–4] The onset of the itinerant-electron metamagnetic transition means that the free energy as a function of magnetization $f(M)$ has a double minimum in the P state with zero value of $M$ and in the F state with $M$ equal to the spontaneous magnetization $M_S$, and these two states are separated by the energy barrier.[1–4] In the ground state, $f(M)$ depends on the density of states curve around the Fermi level. Recently, band calculations of the $La(Fe_{0.88}Si_{0.12})_{13}$

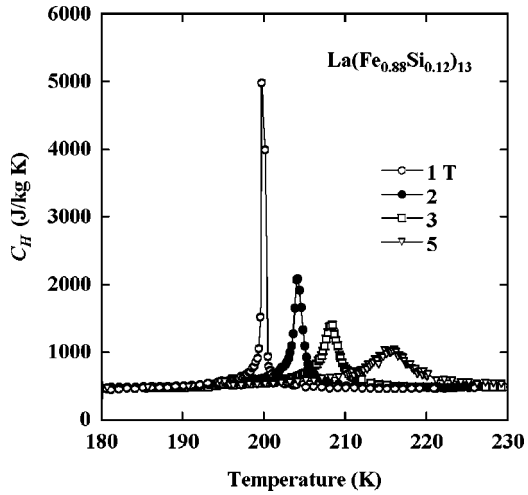


FIG. 2. Temperature dependence of the heat capacity $C_H$ for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound in various magnetic fields.

compound have been carried out.[34] The DOS curves have characteristic features of both strong ferromagnetism in the F state and the magnetic instability in the P state for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound. Therefore, the DOS curve in the F state for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound has the feature of the first-order magnetic phase transition materials. The ground state of the present compounds is ferromagnetic[9–12]; thus, the energy level of the minimum in the F state $f(M_S)$ is lower than that in the P state $f(0)$. It is well known that the thermodynamical properties of itinerant-electron magnets are influenced by spin fluctuations.[2] The local free energy density is a function of local magnetization and local spin fluctuations.[2] Accordingly, not only $M$ but also the amplitude of spin fluctuations dominates the thermal equilibrium conditions at finite temperatures. In other words, $f(M)$ is renormalized by spin fluctuations at finite temperatures.[2] Therefore, $f(M_S)$ is increased by the renormalization effect, and hence the minimum in the F state becomes shallower with increasing temperature. The thermal-induced first-order transition between the F and P states occurs at $T_C$ when $f(M_S)$ exceeds the maximum value of the energy barrier $f(M_b)$. In the P state, the IEM transition is induced by applying the magnetic field $H$, because both $f(M_S)$ and $f(M_b)$ become lower than $f(0)$ due to the Zeeman energy $-MH$. Since the entropy in the P state increases faster than that in the F state, the magnetic flux density of the critical field $B_C=\mu_0 H_C$ ($\mu_0$, permeability of vacuum; $H_C$, the critical magnetic field) for the IEM transition becomes higher with increasing temperature above $T_C$. When the energy barrier is eliminated by the renormalization effect, the IEM transition disappears at the critical temperature $T_0$ where the hysteresis of the magnetization curves disappears (see Sec. III C). The renormalization effect is suppressed due to the Zeeman energy, and hence $T_C$ is increased up to $T_0$ by applying a magnetic field. Consequently, the thermal-induced first-order transition in the magnetic fields originates from the IEM transition in the P state.

Figure 3 indicates the temperature dependence of the critical field $B_C$ of the IEM transition for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90. The critical field $B_C$ is defined as the average of the inflection point in the ascendant and descendent magnetization curves. According to the theoretical consideration, $B_C$ as a function $T$ is expressed by using the amplitude of spin fluctuations $\xi(T)$ as[8]

$$B_C(T)=AM_{T_C}^3[\xi(T)^2-\xi(T_C)^2], \tag{1}$$

where $A$ is the constant obtained from the DOS curve around the Fermi level in the ground state and $M_{T_C}$ is the thermal-induced magnetic moment at $T_C$. The temperature dependence of $B_C$ for $x=0.88$ is slightly curved. On the other hand, $B_C$ for the compound with $x=0.89$ and 0.90 increases linearly with temperature at a rate of $dB_C/dT\sim 0.25$ T/K. The temperature dependence of $B_C$ corresponds to that of $\xi(T)^2$ as given in Eq. (1). Strictly speaking, from the theoretical discussion, $\xi(T)^2$ is proportional to $T^2$ at low temperatures and gradually changes to be proportional to $T$ with increasing temperature.[2–4] For the Co-based Laves phase and pyrite compounds in which the IEM transition appears at low

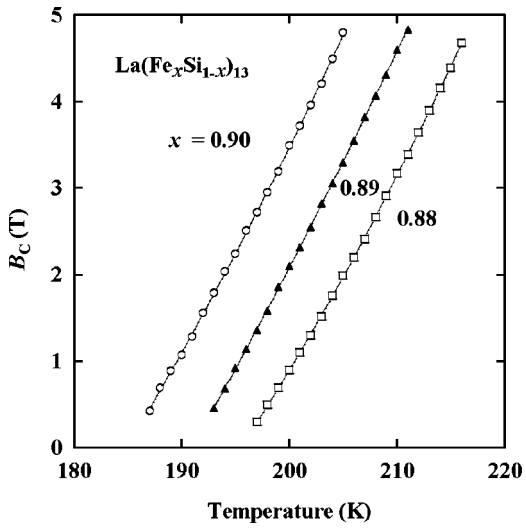


FIG. 3. Average critical field $B_C$ of the itinerant-electron metamagnetic transition as a function of temperature for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90.

temperatures, the $T^2$ dependence of $B_C$ results from the increase of $\xi(T)^2$ proportional to $T^2$ (Refs. 5 and 8). On the other hand, the linear increase of $B_C$ against $T$ originates from the increase of $\xi(T)^2$ proportional to $T$ above $T_C=188$ K for the compound with $x=0.89$. Such a dependence of $B_C$ on $T$ is a characteristic feature of the $La(Fe_xSi_{1-x})_{13}$ compounds having the IEM transition in relatively high temperatures in comparison with both the Co-based Laves phase and pyrite compounds. Although the temperature dependence of $B_C$ for $x=0.88$ is slightly curved, the power $\beta$ of $T^\beta$ is determined to be 1.2 by using a least-squares fitting, much closer to linear rather than quadratic dependence. It should be noted that $M_{T_C}$ is reflected in the slope of $B_C(T)$ from Eq. (1). For all the specimens, $B_C$ sensitively increases with temperature because the magnitude of the magnetization change around $T_C$ is very large as seen from Fig. 1. Since the $B_C-T$ line corresponds to the $B-T_C$ line in the $B-T$ phase diagram, $T_C$ of the present compounds increases with the magnetic field.

It has been reported that the value of $T_C$ decreases while the critical temperature $T_0$ for the disappearance of the IEM transition increases with increasing $x$.[9,11] Namely, the temperature range having an IEM transition becomes wider with increasing $x$. The values of $T_C$ for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90 are 195, 188, and 184 K, respectively. The magnetization curves at temperatures higher than $T_C$ by 5 K for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90 are depicted in Fig. 4. A characteristic S-shape curve with a hysteresis is observed, because the IEM transition takes place above $T_C$. Note that the magnitude of magnetization change due to the IEM transition becomes larger with increasing $x$. In addition, both the magnetic susceptibility in the P state and the high-field magnetic susceptibility in the F state become smaller and the IEM transition becomes sharper with increasing $x$. From the thermodynamical relation, the magnetization $M$ equals the first derivative of the magnetic free energy by the magnetic

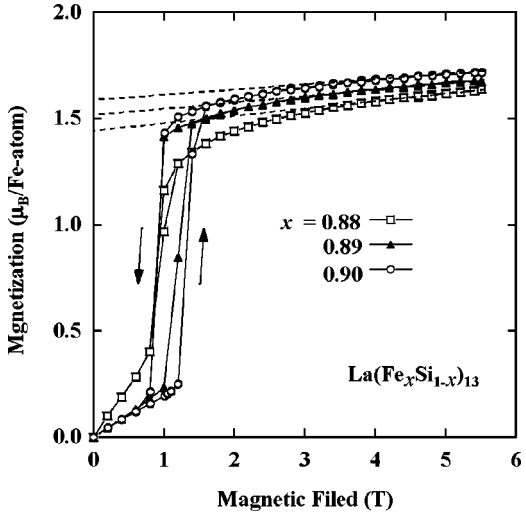


FIG. 4. Magnetization curves at a temperature higher than the Curie temperature $T_C$ by 5 K for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $x=0.88$, 0.89, and 0.90.

field, $df(M)/dH$; therefore, the sharper IEM transition indicates that the energy barrier separating the P and F states in the free energy curve becomes higher with increasing $x$. Accordingly, the concentration change affects the band structure because the onset of the IEM transition and the energy barrier height are clearly correlated with the DOS curve around the Fermi energy.

### B. Magnetocaloric effects in La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds

The value of the isothermal magnetic entropy change $\Delta S_m(T)$ is given by the following expression associated with the Maxwell relationship:

$$\Delta S_m = \int_0^H (\partial M/\partial T) dH. \tag{2}$$

Figure 5 illustrates the temperature dependence of $\Delta S_m$ in the magnetic field change from 0 to 2 T ($\Delta H=2$ T) and from 0 to 5 T ($\Delta H=5$ T) obtained by using Eq. (2) for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $x=0.88$, 0.89, and 0.90. For the compound with $x=0.88$, $\partial M/\partial T$ exhibits a large value around $T_C$ because of the thermal-induced first-order transition, and $T_C$ is increased by the magnetic field, keeping a large value of $\partial M/\partial T$ as presented in Figs. 1 and 2. Therefore, a large value of $\Delta S_m$ above $T_C$ is expected for the present compounds. For the compound with $x=0.88$, $\Delta S_m$ in $\Delta H=5$ T has a negative maximum value of $-23$ J/kg K at $T_C=195$ K and exhibits a plateau of almost the same value against temperature. Since $T_C$ decreases with increasing $x$ in the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds, the large value of $\Delta S_m$ appears at lower-temperature ranges. Furthermore, the negative maximum value of $\Delta S_m$ becomes larger with increasing $x$ because the magnitude of magnetization change due to the IEM transition becomes larger as shown in Fig. 4. For the compound with $x=0.90$, therefore, the negative maximum value of $\Delta S_m$ at $T_C=184$ K becomes $-30$ J/kg K in $\Delta H=5$ T.

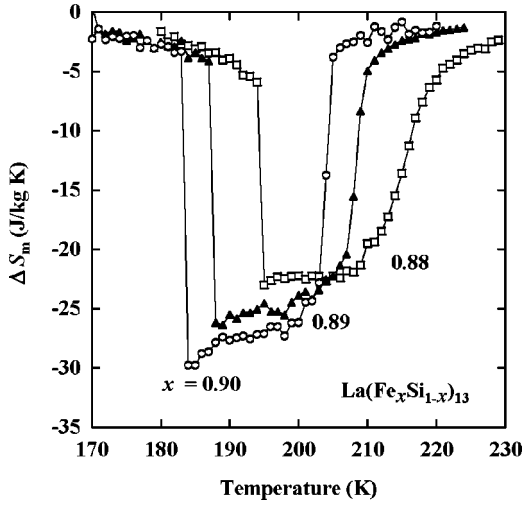


FIG. 5. Temperature dependence of the isothermal magnetic entropy change $\Delta S_m$ for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $x=0.88$, 0.89, and 0.90.

To investigate details of the relation between $\Delta S_m$ and $\Delta H$, Fig. 6 represents $\Delta S_m$ and the rate of its change, $\Delta S_m/\Delta H$, for the compound with $x=0.88$ at 195 K as a function of $\Delta H$. Because the IEM transition is the field-induced first-order phase transition, the discontinuous change of the entropy is caused by the latent heat. Accordingly, $\Delta S_m$ shows a large change around $\Delta H$ corresponding to $B_C$. It should be noted that the value of $\Delta S_m$ gradually increases in higher-field ranges. As mentioned in Sec. III A, the magnetic free energy is renormalized by spin fluctuations. In the F state, the temperature dependence of magnetization $M$ is dominated by the renormalization effect of the free energy. It is well known that the spin fluctuations are suppressed by the magnetic field; therefore, the temperature dependence of $M$ is changed by the magnetic field. As seen from Eq. (2), $\partial M/\partial T$ is closely correlated to $\Delta S_m/\Delta H$. Therefore, the gradual decrease in magnitude of $\Delta S_m/\Delta H$ in higher-field ranges above $B_C$ is related to the suppression of spin fluctuations by magnetic field.

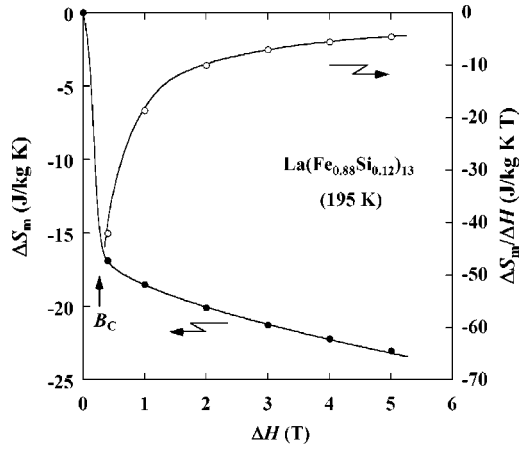


FIG. 6. Isothermal magnetic entropy change $\Delta S_m$ and the rate of its change $\Delta S_m/\Delta H$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound at 195 K as a function of the magnetic field change $\Delta H$ from 0 to $H$.

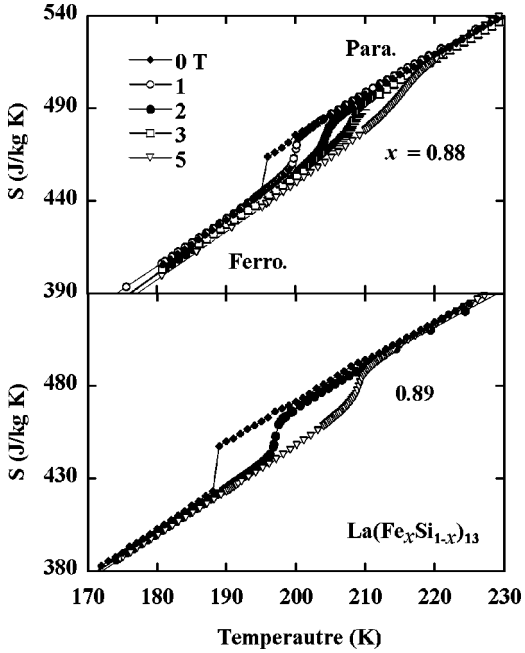


FIG. 7. Temperature dependence of the total entropy $S$ for the $La(Fe_xSi_{1-x})_{13}$ compound with $x=0.88$ and 0.89 in various magnetic fields.

As expected from Eq. (2), the large value of $\Delta S_m$ due to the large magnetization change by the IEM transition is actually confirmed. Accordingly, a significant change of the total entropy $S$ by the magnetic field is expected. By using the thermodynamical relation, the total derivative of $S$ is expressed as

$$dS=(\partial S/\partial T)_H dT+(\partial S/\partial H)_T dH. \tag{3}$$

For an adiabatic process where $dS=0$, the temperature change is given by

$$dT=-T/C_H(\partial S/\partial H)_T dH, \tag{4}$$

where $C_H$ is the sum of the lattice term $C_l$, the electron term $C_e$, and the magnetic term $C_m$ of heat capacities in the magnetic field. Therefore, the adiabatic temperature change $\Delta T_{ad}(T)=\int dT$ becomes also significant when $C_H$ is not so large. For brevity, the value of $\Delta T_{ad}(T)$ is obtained from the heat capacity measurement by using the following relation:

$$\Delta T_{ad}(T)_{\Delta H}=[T(S)_H-T(S)_0]_S. \tag{5}$$

The total entropy $S$ is the sum of the electronic $S_e$, the lattice $S_l$, and the magnetic $S_m$ entropies. The temperature dependence of $S$ in various magnetic fields for the compound with $x=0.88$ and 0.89 is given in Fig. 7. The values of $T(S)_H$ in the magnetic field are obtained from the heat capacity $C_H$ by using $S(T)_H=\int(C_H/T)_H\,dT$. The significant difference in $S$ between the P and F states due to the IEM transition is observed around $T_C$ in the magnetic filed. In an external magnetic field, the divergence of the heat capacity at $T_C$ has a finite value because the growth of the correlation length is suppressed by the magnetic field. Accordingly, the change of $S$ at $T_C$ becomes smooth with increasing magnetic field. It has been reported that $S_e$ is decreased by applying a magnetic field, because the electronic heat capacity decreases due to the suppression of spin fluctuations.[35] The change of $S$ by the magnetic field, $\Delta S$, is in agreement with the magnitude of $\Delta S_m$ obtained from magnetization in Fig. 5, suggesting that the changes of both $S_e$ and $S_l$ in the IEM transition are negligible. For the $S-T$ curve in zero magnetic field, the total divergence of the heat capacity cannot be obtained from the heat capacity measurement due to the first-order transition. Hence, the $S-T$ diagram in zero magnetic field is estimated by subtracting $\Delta S_m$ from $S(T)_H$ as given by the following expression:

$$S(T)_0=[S(T)_H-\Delta S_m(T)_{\Delta H}]_T. \tag{6}$$

Since $T_C$ becomes higher with increasing magnetic field, a significant jump of $S$ around $T_C$ shifts toward higher temperature ranges. Therefore, it is expected that the $La(Fe_xSi_{1-x})_{13}$ compounds exhibit a large value of $\Delta T_{ad}$ around $T_C$.

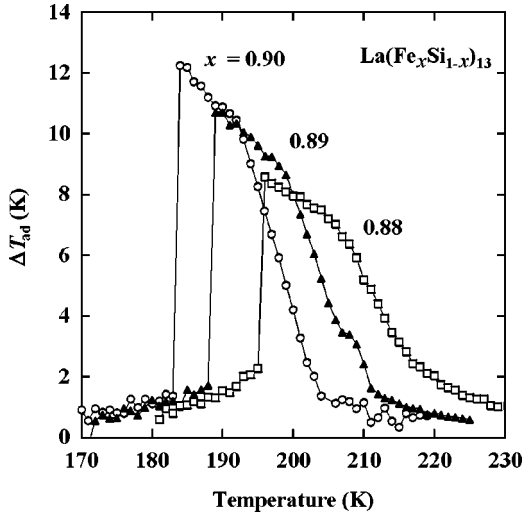


FIG. 8. Temperature dependence of the adiabatic temperature change $\Delta T_{ad}$ for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90.

Figure 8 shows the temperature dependence of $\Delta T_{ad}$ in $\Delta H=5$ T for the $La(Fe_xSi_{1-x})_{13}$ compounds with $x=0.88$, 0.89, and 0.90. The value of $\Delta T_{ad}$ exhibits a large peak above $T_C$. For the compound with $x=0.88$, the maximum value of $\Delta T_{ad}$ is 8.6 K in $\Delta H=5$ T at 195 K. In order to obtain detailed behavior of $\Delta T_{ad}$ against $\Delta H$, the values of $\Delta T_{ad}$ and $\Delta T_{ad}/\Delta H$ for the compound with $x=0.88$ at 195 K as a function of $\Delta H$ are depicted in Fig. 9. First, the value of $\Delta T_{ad}$ steeply increases and then its magnitude gradually increases with $\Delta H$. In lower magnetic fields, the shift of $T_C$ toward higher temperatures is directly reflected in $\Delta T_{ad}$. With increasing $T_C$, the total entropy in the F state just below $T_C$ in the magnetic field, $S(T_C)_H^F$, becomes larger due to the thermal growth of $S_e$ and $S_l$. When $S(T_C)_H^F$ exceeds the value of the total entropy in the P state just above $T_C$ in zero magnetic field, $S(T_C)_0^P$, the rate of $\Delta T_{ad}/\Delta H$ tends to decrease. With increasing $x$ in the $La(Fe_xSi_{1-x})_{13}$ compounds,

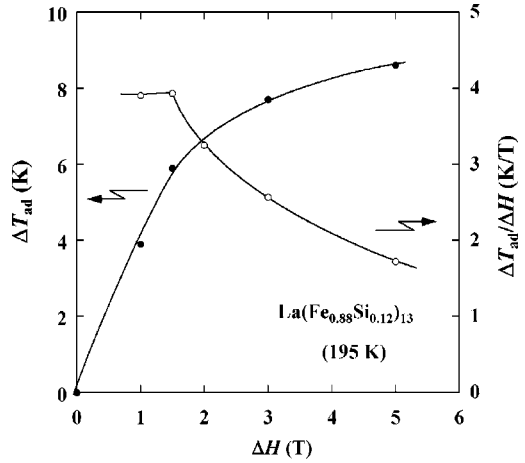


FIG. 9. Adiabatic temperature change $\Delta T_{ad}$ and the rate of its change $\Delta T_{ad}/\Delta H$ for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound at 195 K as a function of the magnetic field change $\Delta H$ from 0 to $H$.

the peak of $\Delta T_{ad}$ shifts toward lower-temperature ranges as a result of the decrease of $T_C$. Moreover, the maximum value of $\Delta T_{ad}$ becomes larger with increasing $x$, because the negative maximum value of $\Delta S_m$ and accordingly $S(T_C)_0^p$ becomes larger while the temperature dependence of $B_C$ is the same rate as that of the compound with $x=0.88$. For the compound with $x=0.90$, therefore, the maximum value of $\Delta T_{ad}$ becomes 12.1 K in $\Delta H=5$ T.

Figure 10 indicates the concentration dependence of the negative maximum value of $\Delta S_m$ and the maximum value of $\Delta T_{ad}$ in $\Delta H=5$ T for the $La(Fe_xSi_{1-x})_{13}$ compounds, together with the results reported in Refs. 27 and 36. Both the negative maximum value of $\Delta S_m$ and the maximum value of $\Delta T_{ad}$ become larger with increasing $x$. It has been reported that $x=0.84$ is very close to the concentration of tricritical point where the transition at $T_C$ changes from second to first

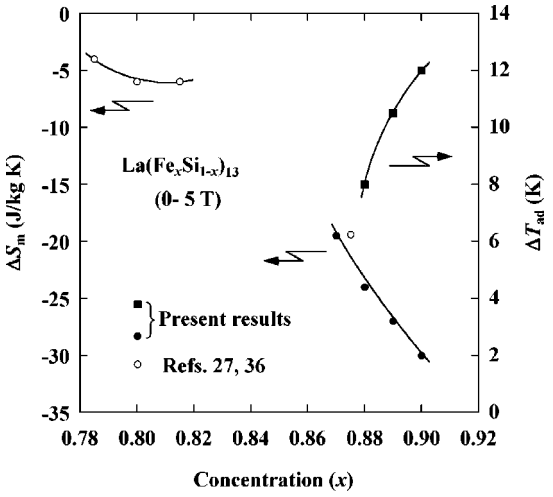


FIG. 10. Concentration dependence of the negative maximum value of the isothermal magnetic entropy change $\Delta S_m$ and the maximum value of the adiabatic temperature change $\Delta T_{ad}$ in the magnetic field change from 0 to 5 T ($\Delta H=5$ T) for the $La(Fe_xSi_{1-x})_{13}$ compounds. The present data are given by the solid symbols. The open symbols are from the Refs. 27 and 36.

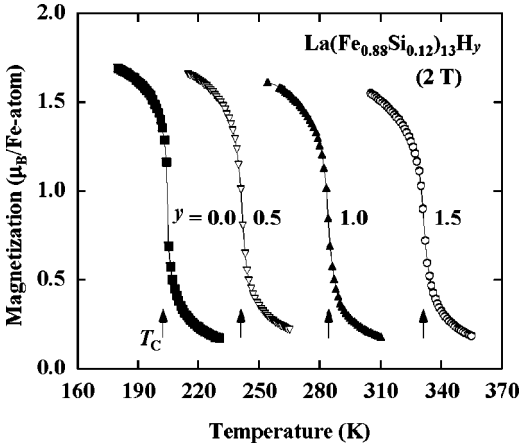


FIG. 11. Thermomagnetization curves of the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds in a magnetic field of 2 T. The arrows indicate the Curie temperature $T_C$.

order and $T_C$ almost coincides with the critical temperature $T_0$ where the IEM transition disappears.[11] In the concentration range $x \leqq 0.84$, therefore, the phase transition at $T_C$ is of second order, accompanied by no IEM transition. As a result, $\Delta S_m$ is relatively small in $x<0.82$ as seen from Fig. 10. Therefore, it is confirmed that the large values of $\Delta S_m$ and $\Delta T_{ad}$ are the intrinsic behaviors of the IEM transition in the present compounds with $x \geqq 0.88$.

### C. Increase of the Curie temperature by hydrogen absorption into the $La(Fe_xSi_{1-x})_{13}$ compounds

The value of $T_C$ is increased significantly by hydrogen absorption, accompanied by a marked volume expansion.[14,15] The cubic $NaZn_{13}$-type structure of the $La(Fe_xSi_{1-x})_{13}$ compounds is kept after hydrogen absorption. The thermomagnetization curves for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds in the magnetic field of 2 T are presented in Fig. 11. The pronounced change in the magnetization curve at $T_C$ is observed up to room temperature. To put it another way, the thermomagnetization curves still exhibit a significant magnetization change around $T_C$ given by the arrows, because the thermal-induced first-order transition is maintained after hydrogen absorption.[14,15] The magnitude of $\partial M/\partial T$ around $T_C=323$ K for the compound with hydrogen concentration $y=1.5$ is almost the same as that of the compound with $y=0.0$. After annealing at about 400 K, $T_C$ is hardly changed, and hence the desorption of the hydrogen for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds scarcely proceeds below 400 K, because $T_C$ is significantly sensitive to $y$.

Figure 12 shows the temperature dependence of the heat capacity $C_H$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds in a magnetic field of 2 T. By using the Debye function, the Debye temperature $\Theta_D$ is estimated to be about 350 K, insensitive to the concentration $y$. The heat capacity exhibits a sharp peak due to the thermal-induced first-order transition at $T_C$. Since $T_C$ increases with $y$ as seen from Fig. 11, the peak position of heat capacity shifts toward a higher temperature range. Apparently, the thermal-induced first-order transition having similar entropy changes is sustained after hydrogen absorption.

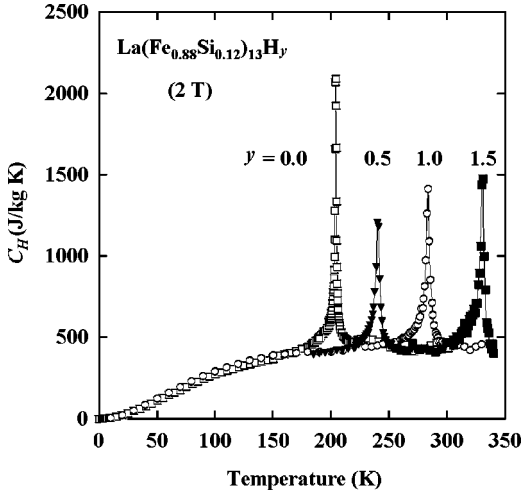


FIG. 12. Temperature dependence of the heat capacity $C_H$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds in a magnetic field of 2 T.

The magnetization curves at 4.2 K for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds with $y=0.0$, 1.0, and 1.6 are depicted in Fig. 13. The value of $M_S$ at 4.2 K increases with $y$. It is noteworthy that the increase of $T_C$ is significant in comparison with that of $M_S$. A significant decrease of $T_C$ contrast to a small decrease of $M_S$ has been observed by applying hydrostatic pressure for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound[11] Such a different pressure dependence of both $T_C$ and $M_S$, that is, the magnetovolume effects, has been discussed theoretically by taking the renormalization effect of spin fluctuations into consideration.[3,4] The decrease of $M_S$ under hydrostatic pressure is attributed to the change of the DOS curve in the ground state, because the bandwidth becomes wider under pressure. On the other hand, the decrease of $T_C$ with hydrostatic pressure is caused by the enhancement of the renormalization effect due to the decrease of volume through the magnetovolume effects. Therefore, $T_C$ can be significantly changed by hydrostatic pressure, although the change of $M_S$ is relatively small. The relation

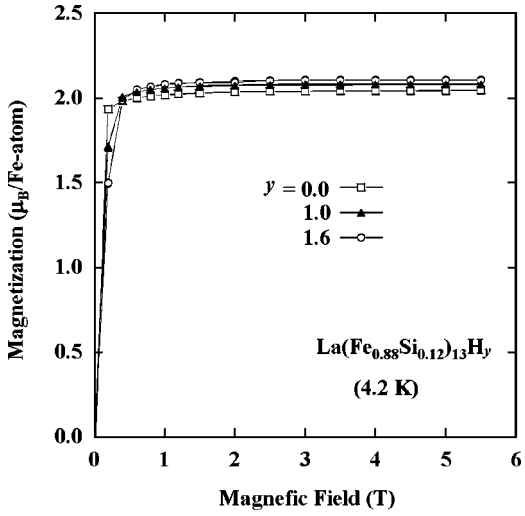


FIG. 13. Magnetization curves at 4.2 K for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds with $y=0.0$, 1.0, and 1.6.

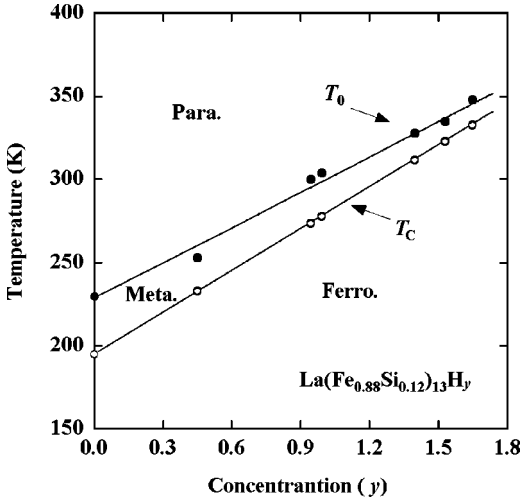


FIG. 14. Magnetic phase diagram of the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds for the hydrogen concentration $y$ and temperature $T$. The temperatures of $T_C$ and $T_0$ denote the Curie temperature and the critical temperature where the itinerant-electron metamagnetic (IEM) transition disappears, respectively. Below the $T_C$ line, the ferromagnetic state appears. The IEM transition occurs in the paramagnetic state between the $T_C$ and $T_0$ lines.

between $y$ and the room-temperature volume of the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds is linear regardless in the P or F state, though the magnetic state at room temperature depends on $y$.[15] The pressure dependence of both the experimental and the theoretical results for the $La(Fe_{0.88}Si_{0.12})_{13}$ compound would qualitatively correspond to the volume dependence of both $T_C$ and $M_S$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds.

Taking into account the enhancement of the renormalization effect due to the magnetovolume effects, the phase diagrams for the itinerant-electron metamagnets for pressure and temperature have been obtained by the theoretical discussions.[3,4] The decrease of $T_0$ with hydrostatic pressure is also caused by the enhancement of the renormalization effect due to the decrease of volume through the magnetovolume effects. It has been pointed out that the pressure dependence of $T_0$ is smaller than that of $T_C$, resulting in an extension of the temperature range between $T_0$ and $T_C$ where the IEM transition appears. A similar phase diagram has been demonstrated by an experiment on pressure effect.[37] The magnetic phase diagram of the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds for $y$ and temperature is presented in Fig. 14. According to the Landau theory for the IEM transition with renormalization effects of spin fluctuations, the appearance of three characteristic temperatures $T_0$, $T_{max}$, and $T_b$ is expected.[2] The temperatures $T_{max}$ and $T_b$ are, respectively, the temperature where the paramagnetic susceptibility shows a maximum and the inflection point of the Arrott plot disappears. The temperature $T_0$ is defined as the disappearance temperature of hysteresis in the magnetization curves. There is the following relation among them, that is, $T_0 < T_{max} \leqq T_b$. The temperature dependence of the paramagnetic susceptibility of the present system shows no maximum and exhibits a Curie-Weiss-like behavior, in analogy with $Co(S_{0.9}Se_{0.1})_2$ which also exhibits the IEM transition above

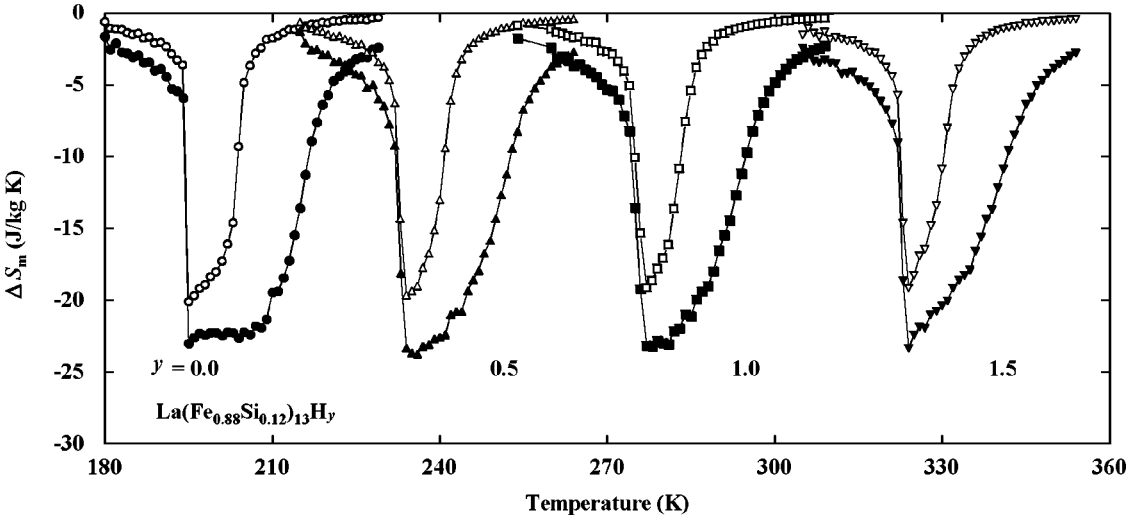


FIG. 15. Temperature dependence of the isothermal magnetic entropy change $\Delta S_m$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds. The values of $\Delta S_m$ in the magnetic field change from 0 to 2 T ($\Delta H=2$ T) and from 0 to 5 T ($\Delta H=5$ T) are given by the open and solid symbols, respectively.

$T_C$.[8] However, the relation $T_0<T_b$ is held in the present systems. The temperature of $T_0$ also increases with $y$ as well as $T_C$. The increment of $T_0$ with $y$ is smaller than that of $T_C$. In the figure, the IEM transition takes place in the wide temperature range between $T_C$ and $T_0$. The phase diagram for the hydrogen content $y$ and temperature $T$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds would qualitatively correspond to the phase diagram for pressure $P$ and temperature $T$ of both the experimental and the theoretical results for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound, because hydrogen absorption is accompanied by a marked volume expansion. Namely, the volume dependence of $T_0$ is smaller than that of $T_C$. Accordingly, it is suggested that the renormalization effect of spin fluctuations is affected by the significant volume expansion with increasing $y$ in the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds. To discuss quantitatively the relation of the volume dependence of the IEM transition under pressure and that for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds, further information such as compressibility is necessary.

The increase of $T_C$ for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds has been investigated by substituting Co for Si, and confirmed that $T_C$ increases up to 250 K of the La(Fe$_{0.88}$Si$_{0.09}$Co$_{0.03}$)$_{13}$ compound.[13] However, the IEM transition becomes obscure, and hence the magnetization change around $T_C$ becomes sluggish. In contrast, the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds clearly exhibit the IEM transition above $T_C$. The origin of the IEM transition is associated with the DOS curve just below the Fermi level where the magnetic free energy curve has a double-minimum structure,[1–4] and hence it is considered that the DOS curve around the Fermi level is hardly modified after hydrogen absorption. Consequently, the suppression of the renormalization effect due to the volume expansion of the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds through the magnetovolume effects is dominant influence of hydrogen absorption on the IEM transition.

### D. Magnetocaloric effect in La(Fe$_x$Si$_{1-x}$)$_{13}$H$_y$ compounds

Figure 15 shows the temperature dependence of $\Delta S_m$ as a function of $y$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds. The data in $\Delta H=2$ and 5 T are given by the open and solid symbols, respectively. A significant large negative peak is observed above $T_C$ after hydrogen absorption. For the compound with $y=1.5$, the negative maximum value of $\Delta S_m$ is $-19$ J/kg K around room temperature in $\Delta H=2$ T, because a large magnetization change at $T_C$ retains after hydrogen absorption as seen from Fig. 11. Since $T_C$ increases with the magnetic field, the larger value of $\Delta S_m$ is obtained in the wide temperature range in $\Delta H=5$ T. All these behaviors are similar to $\Delta S_m$ for the compound with $y=0.0$, which exhibits $\Delta S_m=-20$ J/kg K in $\Delta H=2$ T and $-23$ J/kg K in $\Delta H=5$ T at $T_C=195$ K. Accordingly, the large value of $\Delta S_m$ is obtained in the temperature range between 195 and 336 K in

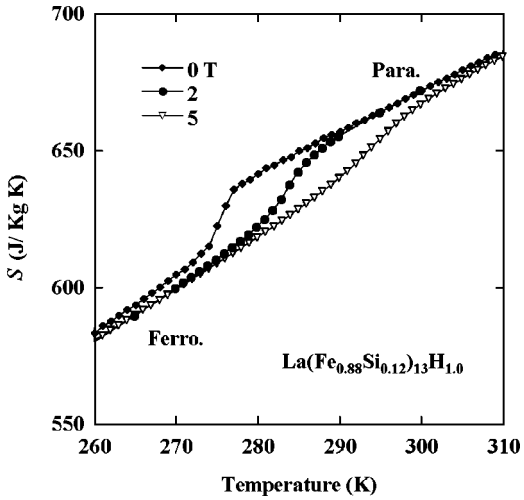


FIG. 16. Temperature dependence of the total entropy $S$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_{1.0}$ compound as a function of magnetic field.

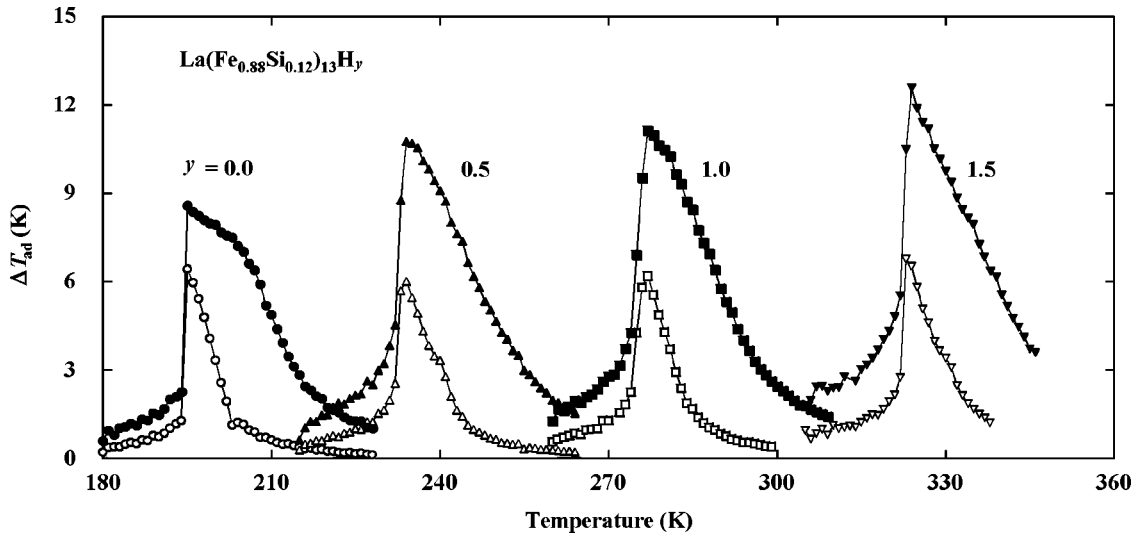


FIG. 17. Temperature dependence of the adiabatic temperature change $\Delta T_{ad}$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds. The values of $\Delta T_{ad}$ in the magnetic field change from 0 to 2 T ($\Delta H=2$ T) and from 0 to 5 T ($\Delta H=5$ T) are given by the open and solid symbols, respectively.

relatively low magnetic fields by controlling $y$ in the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds.

The representative data of the total entropy $S$ after hydrogen absorption are given in Fig. 16, which are the temperature dependence of $S$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ compound in the applied magnetic fields. The significant difference between $S$ in the P and F states due to the IEM transition is kept after hydrogen absorption. The increasing rate of $T_C$ against the magnetic field is the same as that in the compound with $y=0.0$ (see Fig. 7). Therefore, a large value of $\Delta T_{ad}$ is expected in relatively low magnetic fields around $T_C$ for the $La(Fe_xSi_{1-x})_{13}H_y$ compounds.

Shown in Fig. 17 is the temperature dependence of $\Delta T_{ad}$ for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds. The data in $\Delta H=2$ and 5 T are plotted by the open and solid symbols, respectively. The large peak of $\Delta T_{ad}$ is observed around $T_C$ and the maximum value of $\Delta T_{ad}$ at $T_C=323$ K is 6.8 K in $\Delta H=2$ T for the compound with $y=1.5$. This value of $\Delta T_{ad}$ is the same as the maximum value of $\Delta T_{ad}$ for the compound with $y=0.0$, which exhibits $\Delta T_{ad}=6.5$ K in $\Delta H=2$ T. With increasing magnetic field, the maximum value of $\Delta T_{ad}$ becomes larger and the maximum value of $\Delta T_{ad}$ is 12.6 K in $\Delta H=5$ T. This value is larger by about 50% than that of the compound with $y=0.0$, which exhibits $\Delta T_{ad}=8.6$ K in $\Delta H=5$ T at $T_C=195$ K. The value of $T_C$ increases with $y$ up to 336 K, keeping the large value of $\Delta S_m$. The value of $T_C$ becomes close to the Debye temperature $\Theta_D$ as increasing $y$ in the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds, because $\Theta_D$ is insensitive to $y$ as pointed out in connection with Fig. 12. Therefore, the lattice heat capacity at $T_C$, $C_l/T_C$, decreases with increasing $y$. The value of $\Delta T_{ad}$ becomes larger with decreasing $C_H/T$ in line with Eq. (4). As a result, the maximum value of $\Delta T_{ad}$ at $T_C$ becomes larger with increasing $y$ in $\Delta H=5$ T, though the magnitude of $\Delta S_m$ is insensitive to $y$ in the same $\Delta H$. Accordingly, the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds exhibit a large value of $\Delta T_{ad}$ in the temperature range between 195 and 336 K as well as $\Delta S_m$.

From Figs. 15 and 17, it is concluded that the extension of the working temperature range having large MCE's in relatively low magnetic fields can be obtained by controlling $y$ in the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds. It should be noted that the MCE's are enhanced remarkably by increasing $x$ of the $La(Fe_xSi_{1-x})_{13}$ compounds as described in Sec. III B. For the $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound, the values of $\Delta S_m$ at 287 K become $-28$ and $-31$ J/kg K in $\Delta H=2$ and 5 T, respectively. Moreover, the maximum values of $\Delta T_{ad}$ at 287 K are attained 7.1 and 15.4 K in the $\Delta H=2$ and 5 T, respectively. The concentration $y$ dependence of $\Delta S_m$ and $\Delta T_{ad}$ is shown in Figs. 18(a) and 18(b), respectively, for the com-

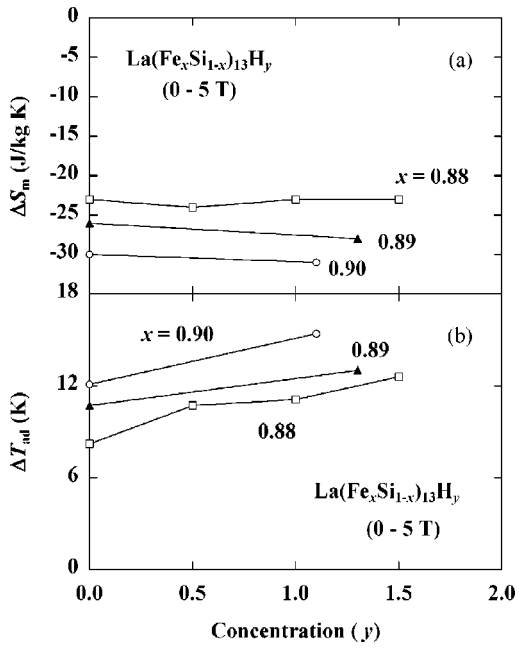


FIG. 18. Concentration $y$ dependence of (a) the isothermal magnetic entropy change $\Delta S_m$ and (b) the adiabatic temperature change for the $La(Fe_xSi_{1-x})_{13}H_y$ compounds with $x=0.88$, 0.89, and 0.90 in the magnetic field change from 0 to 5 T ($\Delta H=5$ T).

TABLE I. The magnetic (a) and crystallographic (b) transition temperatures $T_t$, the isothermal entropy change $\Delta S_m$, the adiabatic temperature change $\Delta T_{ad}$ for $La(Fe_xSi_{1-x})_{13}$ ($x=0.877$, 0.880, 0.890, 0.900), $La(Fe_{0.88}Si_{0.12})_{13}H_y$ ($y=0.5$, 1.0, 1.5), $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$, $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$, and $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$, together with those for $La(Fe_{0.86}Si_{0.09}Co_{0.05})_{13}$, $MnFeP_{0.45}As_{0.55}$, Gd, $Fe_{51}Rh_{49}$, $Gd_5(Si_2Ge_2)$, and MnAs in the magnetic field changes from 0 to 2 T ($\Delta H=2$ T) and from 0 to 5 T ($\Delta H=5$ T).

| | | $\Delta S_m$ (J/kg K) | | $\Delta T_{ad}$ (K) | | |
|---|---|---|---|---|---|---|
| Material | $T_t$ | 0–2 T | 0–5 T | 0–2 T | 0–5 T | Reference |
| $La(Fe_xSi_{1-x})_{13}$ | | | | | | |
| $x=0.877$ | 208[a] | −14 | ··· | ··· | ··· | 27 |
| $x=0.880$ | 195[a] | −20 | −23 | 6.5 | 8.6 | †Present data |
| $x=0.890$ | 188[a] | −24 | −26 | 7.5 | 10.7 | † |
| $x=0.900$ | 184[a] | −28 | −30 | 8.1 | 12.1 | † |
| $La(Fe_{0.88}Si_{0.12})_{13}H_y$ | | | | | | |
| $y=0.5$ | 233[a] | −20 | −24 | 6.0 | 10.7 | † |
| $y=1.0$ | 274[a] | −19 | −23 | 6.2 | 11.1 | † |
| $y=1.5$ | 323[a] | −19 | −23 | 6.8 | 12.6 | † |
| $La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$ | 291[a] | −24 | −28 | 6.9 | 12.8 | † |
| $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ | 287[a] | −28 | −31 | 7.1 | 15.4 | † |
| $La(Fe_{0.86}Si_{0.09}Co_{0.05})_{13}$ | 274[a] | −12 | −20 | ··· | ··· | 25 |
| $MnFeP_{0.45}As_{0.55}$ | 302[a] | −15 | −18 | ··· | ··· | 26 |
| Gd | 294[a] | −5 | −9 | 5.7 | 11.6 | 18 |
| $Fe_{49}Rh_{51}$ | 313[b] | −22 | ··· | 12.9 | ··· | 23 |
| $Fe_{49}Rh_{51}$ | 316[b] | −12 | ··· | 8.4 | ··· | 24 |
| $Gd_5(Si_2Ge_2)$ | 278[b] | −14 | −18 | 7.3 | 15.3 | 20 |
| MnAs | 318[b] | −31 | −32 | 4.7 | 12.8 | 22 |

[a]Curie temperature.

[b]Crystallographic transition temperature.

pound with $x=0.88$, 0.89, and 0.90 in $\Delta H=5$ T. The magnitudes of both $\Delta S_m$ and $\Delta T_{ad}$ become larger with increasing $x$ after hydrogen absorption. Accordingly, the MCE's are enhanced after hydrogen absorption with increasing $x$ for the $La(Fe_xSi_{1-x})_{13}H_y$ compounds.

Collected in Table I are the magnetic and crystallographic transition temperatures $T_t$ and the magnetocaloric properties $\Delta S_m$ and $\Delta T_{ad}$ in the magnetic field changes from 0 to 2 T and from 0 to 5 T for the $La(Fe_xSi_{1-x})_{13}H_y$ compounds, together with those of candidates reported as magnetic refrigerants, $La(Fe_{0.86}Si_{0.09}Co_{0.05})_{13}$,[25] $MnFeP_{0.45}As_{0.55}$,[26] Gd,[18] $Fe_{49}Rh_{51}$,[23,24] $Gd_5(Si_2Ge_2)$,[20] and MnAs.[22] The MCE's for the $La(Fe_xSi_{1-x})_{13}$ compounds are sensitive to $x$ as given in Fig. 10, because the magnetic transition characteristics of the $La(Fe_xSi_{1-x})_{13}$ compounds are sensitive to $x$,[9–12] and hence the IEM transition becomes obscure by compositional heterogeneity with $\alpha$-Fe.[27] Therefore, $\Delta S_m$ for the homogeneous compound with a similar concentration of the $La(Fe_{0.88}Si_{0.12})_{13}$ compound is larger than that for the heterogeneous $La(Fe_{0.877}Si_{0.123})_{13}$ compound. For the $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound, both $\Delta S_m$ and $\Delta T_{ad}$ are larger than those of Gd having a second-order magnetic transition. The value of $\Delta S_m$ for the $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound is larger than that of the $La(Fe_{0.86}Si_{0.09}Co_{0.05})_{13}$ and $MnFeP_{0.45}As_{0.55}$, respectively. In addition, since a large value of $\Delta S_m$ does not always result in a large value of $\Delta T_{ad}$, it is necessary to evaluate $\Delta T_{ad}$ for these compounds.[29,30] In $\Delta H=2$ T, the value of $\Delta T_{ad}$ for the $Fe_{49}Rh_{51}$ and $Gd_5(Si_xGe_{4-x})$ is larger than that of the $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound, although their values of $\Delta S_m$ are not so large. However, the MCE's in $Fe_{49}Rh_{51}$ disappear after several thermal cycles around $T_C$ because this alloy is accompanied by a crystallographic structure change at the same time,[23] and $Gd_5(Si_xGe_{4-x})$ cause a gradual change in $T_t$ after thermal cycles because of crystallographic structure change.[20,38] In other words, $Fe_{49}Rh_{51}$ and $Gd_5(Si_xGe_{4-x})$ are thermally unstable. Furthermore, the MCE's for $Fe_{49}Rh_{51}$ are extremely sensitive to the process of heat treatment.[24] Therefore, different data for the same composition of $Fe_{49}Rh_{51}$ have been reported by the same authors.[23,24] In contrast, the IEM transitions of the $La(Fe_xSi_{1-x})_{13}H_y$ compounds are accompanied by no crystallographic structural changes[10,11,15] and no apparent decay of the magnetocaloric effects is confirmed after repeating

thermal cycles, and hence the present compounds are thermally stable. As seen from the table, $\Delta T_{ad}$ for the $La(Fe_{0.90}Si_{0.10})_{13}H_{1.1}$ compound is larger than that of MnAs in $\Delta H = 2$ T, though $\Delta S_m$ for the former is almost the same as that for the latter. In consequence, the $La(Fe_xSi_{1-x})_{13}H_y$ compounds are one of the most promising magnetic refrigerants working in relatively low magnetic fields.

## IV. CONCLUSION

The relation between the itinerant-electron metamagnetic transition and the magnetocaloric effects of the $La(Fe_xSi_{1-x})_{13}$ and $La(Fe_xSi_{1-x})_{13}H_y$ compounds has been investigated. The $La(Fe_{0.88}Si_{0.12})_{13}$ compound exhibits a large value of the isothermal entropy change $\Delta S_m$ in relatively low magnetic fields, because a significant magnetization change of about $1.5\mu_B$ occurs at the Curie temperature $T_C = 195$ K due to the thermal-induced first-order transition between the ferromagnetic (F) and paramagnetic (P) states. Furthermore, the $La(Fe_{0.88}Si_{0.12})_{13}$ compound exhibits a large value of adiabatic temperature change $\Delta T_{ad}$ in relatively low magnetic fields, because the critical field of the IEM transition $B_C$ strongly increases with a rate of $dB_C/dT \sim 0.25$ T/K with temperature due to the large magnetization change at $T_C$. That is to say, large MCE's in the $La(Fe_{0.88}Si_{0.12})_{13}$ compound are observed in relatively low magnetic fields at $T_C = 195$ K, which originate from the IEM transition. The MCE's are enhanced by increasing $x$ in the $La(Fe_xSi_{1-x})_{13}$ compounds because the magnetization change due to the IEM transition becomes larger with increasing $x$ and the large temperature dependence of $B_C$ is insensitive to $x$. As a result, both the values of $\Delta S_m$ and $\Delta T_{ad}$ for the $La(Fe_{0.90}Si_{0.10})_{13}$ compound are $-30$ J/kg K and 12.1 K, respectively, in the magnetic field change from 0 to 5 T at $T_C = 184$ K.

By hydrogen absorption into the present compounds, the increase of $T_C$ is significant compared with that of the spontaneous magnetization $M_S$. In addition, the IEM transition takes place above $T_C$ because of the increase of the critical temperature $T_0$ where the IEM transition disappears. These behaviors reflect the suppression of the renormalization effect due to the volume expansion of the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds through magnetovolume effects. Therefore, the MCE's, both $\Delta S_m$ and $\Delta T_{ad}$, for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds are large, almost the same values as those of $y = 0.0$ in the temperature range between 195 and 336 K. Consequently, the $La(Fe_xSi_{1-x})_{13}H_y$ compounds are one of the most promising magnetic refrigerants working in wide temperature ranges in relatively low magnetic fields.

## ACKNOWLEDGMENT

The present work was partly supported by a Grant-Aid for Science Research (A), No. 14702050, from the Japan Society for the Promotion of Science.

*Electronic address: afujita@material.tohoku.ac.jp

[1] H. Yamada, J. Inoue, and M. Shimizu, J. Phys. F: Met. Phys. **15**, 169 (1985).
[2] H. Yamada, Phys. Rev. B **47**, 11 211 (1993).
[3] H. Yamada, J. Magn. Magn. Mater. **139**, 162 (1995).
[4] H. Yamada, K. Fukamichi, and T. Goto, Phys. Rev. B **65**, 024413 (2002).
[5] K. Murata, K. Fukamichi, T. Sakakibara, T. Goto, and H.A. Katori, J. Phys.: Condens. Matter **5**, 2582 (1993).
[6] H. Saito, T. Yokoyama, K. Fukamichi, K. Kamishima, and T. Goto, Phys. Rev. B **59**, 8725 (1999).
[7] K. Fukamichi, T. Yokoyama, H. Saito, T. Goto, and H. Yamada, Phys. Rev. B **64**, 134401 (2001).
[8] T. Goto, K. Fukamichi, and H. Yamada, Physica B **300**, 167 (2001).
[9] A. Fujita, Y. Akamatsu, and K. Fukamichi, J. Appl. Phys. **85**, 4756 (1999).
[10] K. Fukamichi and A. Fujita, J. Mater. Sci. Technol. **16**, 167 (2000).
[11] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, Phys. Rev. B **65**, 014410 (2002).
[12] T.T.M. Palstra, J.A. Mydosh, G.J. Nieuwenhuys, A.M. Van der Kraan, and K.H.J. Buschow, J. Magn. Magn. Mater. **36**, 290 (1983).
[13] A. Fujita and K. Fukamichi, IEEE Trans. Magn. **35**, 3796 (1999).
[14] A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki, and Y. Iijima, Trans. Mater. Res. Soc. Jpn. **26**, 219 (2001).
[15] S. Fujieda, A. Fujita, K. Fukamichi, Y. Yamazaki, and Y. Iijima, Appl. Phys. Lett. **79**, 653 (2001).
[16] A. M. Tishin, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 1999), Vol. 12, p. 395.
[17] V.K. Pecharsky and K.A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).
[18] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, and K.A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
[19] K.A. Gschneidner, Jr., H. Takeya, J.O. Moorman, and V.K. Pecharsky, Appl. Phys. Lett. **64**, 253 (1994).
[20] V.K. Pecharsky and K.A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[21] H. Wada, S. Tomekawa, and M. Shiga, Cryogenics **39**, 915 (1999).
[22] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[23] M.P. Annaorazov, K.A. Asatryan, G. Myalikgulyev, S.A. Nikitin, A.M. Tishin, and A.L. Tyurin, Cryogenics **32**, 867 (1992).
[24] M.P. Annaorazov, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, and A.Kh. Dovletov, J. Appl. Phys. **79**, 1689 (1996).
[25] F.X. Hu, B.G. Shen, J.R. Sun, G.J. Wang, and Z.H. Cheng, Appl. Phys. Lett. **80**, 826 (2002).
[26] O. Tegus, E. Brück, K.H.J. Buschow, and F.R. de Boer, Nature (London) **415**, 150 (2002).
[27] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, G.H. Rao, and X.X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[28] T. Yokoyama, H. Saito, K. Fukamichi, K. Kamishima, T. Goto, and H. Yamada, J. Phys.: Condens. Matter **13**, 9281 (2001).
[29] V.K. Pecharsky and K.A. Gschneidner, Jr., J. Appl. Phys. **90**, 4614 (2001).
[30] V.K. Pecharsky, K.A. Gschneidner, Jr., A.O. Pecharsky, and A.M.

Tishin, Phys. Rev. B **64**, 144406 (2001).
[31] A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki, and Y. Iijima, Mater. Trans., JIM **43**, 1202 (2002).
[32] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[33] J.S. Hwang, K.J. Lin, and C. Tien, Rev. Sci. Instrum. **68**, 94 (1997).
[34] A. Fujita, K. Fukamichi, J. T. Wang, and Y. Kawazoe (unpublished).
[35] K. Ikeda and K.A. Gschneidner, Jr., Phys. Rev. Lett. **45**, 1341 (1980).
[36] G.H. Wen, R.K. Zheng, X.X. Zhang, W.H. Wang, J.L. Chen, and G.H. Wu, J. Appl. Phys. **91**, 8537 (2002).
[37] A. Fujita, K. Fukamichi, M. Yamada, and T. Goto, J. Appl. Phys. (to be published).
[38] E.M. Levin, A.O. Pecharsky, V.K. Pecharsky, and K.A. Gschneidner, Jr., Phys. Rev. B **63**, 064426 (2001).