Control of Working Temperature of Large Isothermal Magnetic Entropy Change in La(Fe_xTM_ySi_{1-x-y})_{13} (TM = Cr, Mn, Ni) and La_{1-z}Ce_z(Fe_xMn_ySi_{1-x-y})_{13}

Shun Fujieda1, Naoyuki Kawamoto2, Asaya Fujita1 and Kazuaki Fukamichi2

1 Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
2 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

The Curie temperature $T_C$ of La(Fe$_x$Si$_{1-x}$)$_{13}$ is increased by a partial substitution of Ni for Fe. On the contrary, $T_C$ is decreased by a partial substitution of Cr or Mn. In addition, a partial substitution of Ce for La in La(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ causes the further decrease of $T_C$. As a result, La$_{0.85}$Ce$_{0.15}$(Fe$_{0.85}$Mn$_{0.15}$Si$_{1.13}$)$_{13}$ exhibits a thermal-induced first-order transition at $T_C = 60$ K. This result means that $T_C$ of the La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ is tunable in the temperature range between 60 and 180 K by adjusting composition with keeping the itinerant-electron metamagnetic transition. In the magnetic field change from 0 to 4 T in the vicinity of $T_C = 60$ K, the La$_{0.85}$Ce$_{0.15}$(Fe$_{0.85}$Mn$_{0.15}$Si$_{1.13}$)$_{13}$ shows the isothermal magnetic entropy change $\Delta S_m = -131$ J kg$^{-1}$ K$^{-1}$ and the relative cooling power $RCP = 458$ J kg$^{-1}$. Consequently, the La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ compounds are useful for magnetic refrigerants working in a temperature range between 60 and 180 K.

(Received September 20, 2005; Accepted November 24, 2005; Published March 15, 2006)

Keywords: magnetocaloric effect, itinerant-electron metamagnetic transition, magnetic refrigeration, relative cooling power

1. Introduction

Magnetic refrigerations and magnetocaloric effects (MCEs) have been investigated extensively. Magnetic refrigerations are free from environmentally-unfriendly gases such as hydrochlorofluorocarbon and hydrofluorocarbon. In addition, it has been pointed out that the magnitude of energy loss incurred in the refrigeration cycle of magnetic refrigerators is smaller than that of vapor-cycle refrigerators. Therefore, magnetic refrigerations are expected to be useful for refrigeration technologies such as freezers and air-conditioners in the vicinity of room temperature and the liquefaction of gases at low temperatures. To realize such applications with high performance in various temperature ranges, the research and development of magnetic refrigerants are important.

Above the Curie temperature $T_C$, La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds exhibit the itinerant-electron metamagnetic (IEM) transition2–4) which is accompanied by a large isothermal magnetic entropy change $\Delta S_m$5–9) as well as a large adiabatic temperature change $\Delta T_{ad}$6–10) Such large MCEs are obtained in relatively low magnetic fields just above $T_C$, because the critical field of the IEM transition becomes smaller when the temperature comes close to $T_C$. The La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds also exhibit large magnetovolume effects such as a remarkable pressure effect411) and a large thermal expansion anomaly.4) The value of $T_C$ for the La(Fe$_x$Si$_{1-x}$)$_{13}$ decreases remarkably by applying hydrostatic pressure. On the contrary, the hydrogen absorption into the La(Fe$_x$Si$_{1-x}$)$_{13}$ causes a volume expansion of about 3%, resulting in the increase of $T_C$ up to about 340 K.12,13) Furthermore, the IEM transition is maintained after hydrogen absorption. As a result, by controlling hydrogen concentration, the La(Fe$_x$Si$_{1-x}$)$_{13}$H$_y$ compounds exhibit large MCEs in relatively low magnetic fields in a temperature range between about 180 and 340 K.6–10) Therefore, the La(Fe$_x$Si$_{1-x}$)$_{13}$ and their hydrides are promising as magnetic refrigerants working between about 180 and 340 K. The magnetic refrigeration below 180 K is also important. For example, new electronics devices for high-transition temperature ($T_C$) superconductor such as noise filters and high sensitive antennas can be operated in these temperatures. The transition temperature of high-$T_C$ superconductors is located lower than about 140 K.14) Therefore, high-performance magnetic refrigerants working below the temperature mentioned above is necessary in the field of superconducting technologies. However, development research of magnetic refrigerators around such temperature ranges have not been so active, in comparison with that around room temperature range.15) Therefore, we try to reduce $T_C$ below 180 K for La(Fe$_x$Si$_{1-x}$)$_{13}$. It is considered two kinds of feasible methods to decrease of $T_C$. The onset of the IEM transition means that magnetic free energy has two minima in the paramagnetic and ferromagnetic states. On the basis of the Landau–Ginzburg theory, such magnetic free energy has been discussed by using the Landau coefficients associated with the density of state (DOS) around the Fermi level.16) Since $T_C$ is influenced by the balance between two minima in the paramagnetic and ferromagnetic states, $T_C$ is correlated with the Landau coefficients.16) It is expected that $T_C$ can be controlled by a partial substitution of 3d elements for Fe, because the Landau coefficients are changed by the shift of the Fermi level. Already, it has been reported that $T_C$ is increased by a partial substitution of Co17) and a partial substitution of Mn causes the decrease of $T_C$.18) The other method is a partial substitution of rare earth elements for La, because the lanthanoid contraction decreases volume. We have reported that a partial substitution of Ce for La causes the decrease of $T_C$, which mainly attributes to the volume contraction.19–21) Therefore, the investigation of the effect of the partial substitution on $T_C$ is useful to control the working temperature range. In the present study, to obtain large MCEs in lower temperature ranges, we try to control $T_C$ and $\Delta S_m$ for in La(Fe$_x$TM$_y$Si$_{1-x-y}$)$_{13}$ (TM = Cr, Mn, Ni) and La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ compounds adjusting the partial substitution rate.
2. Experiments

Several kinds of compounds of La(Fe_{0.88-\gamma}TM, Si_{0.12})_{13} (TM = Cr, Mn), La(Fe_{0.87-\gamma}TM, Si_{0.13})_{13} (TM = Ni) and La_{0.65}Ce_{0.35}(Fe_{0.95}Mn_{0.05}, Si_{0.12})_{13} were arc-melted in an argon gas atmosphere. The subsequent heat-treatments were carried out in vacuum quartz tubes. The annealing temperature and duration were 1323 K and 10 days for the La(Fe_{0.88-\gamma}TM, Si_{0.12})_{13} and La(Fe_{0.87-\gamma}TM, Si_{0.13})_{13} compounds and 1423 K and 14 days for the La_{0.65}Ce_{0.35}(Fe_{0.95}Mn_{0.05}, Si_{0.12})_{13} compound. The crystal structure was confirmed by x-ray powder diffraction with Cu Kα radiation. The magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer. The isothermal magnetic entropy change $\Delta S_m$ was obtained from the Maxwell relation.

3. Results and Discussion

The occurrence of the IEM transition of the La(Fe, Si)_{13} is limited in the concentration range $x \geq 0.86$, and the transition characteristics is very sensitive to the composition.\(^4\) Therefore, the important point of investigation for the influence of the partial substitution is to prepare compositionally homogeneous specimens. The La(Fe_{0.88-\gamma}Cr, Si_{0.12})_{13} with $y \leq 0.2$, La(Fe_{0.88-\gamma}Mn, Si_{0.12})_{13} with $y \leq 0.3$ and La(Fe_{0.87-\gamma}Ni, Si_{0.13})_{13} with $y \leq 0.2$ are identified as the single phase of a cubic NaZn_{13}-type structure with $Fd\overline{3}c$ space group. Figure 1 shows the concentration $y$ dependence of the Curie temperature $T_C$ for La(Fe_{0.88-\gamma}Cr, Si_{0.12})_{13}, La(Fe_{0.88-\gamma}Mn, Si_{0.12})_{13} and La(Fe_{0.87-\gamma}Ni, Si_{0.13})_{13}. The value of $T_C$ was determined from the thermomagnetization curve of heating process in a magnetic field of 0.01 T. The value of $T_C$ is increased by the partial substitution of Ni for Fe. Contrary, $T_C$ is decreased by the partial substitution of Cr or Mn. The influence of the partial substitution of Mn on the decrease of $T_C$ is much larger than that of Cr. To be more precise, $T_C$ of the La(Fe_{0.88}Si_{0.12})_{13} is decreased from 195 to 136 K by the substitution of $y = 0.03$ of Mn.

It is important to control the working temperature range with keeping large magnetocaloric effects (MCEs). Therefore, we should pay notice to the influence of partial substitution on not only $T_C$ but also the magnetization change in the vicinity of $T_C$. According to the Maxwell relation, the isothermal magnetic entropy change $\Delta S_m$ is expressed by

$$\Delta S_m = \int_0^B \frac{\partial M}{\partial T} dB,$$

where $M$, $T$ and $B$ are the magnetization, temperature and magnetic field. Therefore, a large $\partial M/\partial T$ is important to obtain a large $\Delta S_m$. Shown in Figs. 2(a) and (b) are the thermomagnetization curves in a magnetic field of 1 T for (a) La(Fe_{0.88-\gamma}Cr, Si_{0.12})_{13} and (b) La(Fe_{0.88-\gamma}Mn, Si_{0.12})_{13}. All the curves were measured in both the heating and cooling processes. The thermomagnetization curve without TM for the La(Fe_{0.88}Si_{0.12})_{13} exhibits a remarkable change with hysteresis at $T_C$ because of the thermal-induced first-order transition. Such behavior becomes obscure with increasing Cr or Mn concentration. In particular, by substituting Mn, the magnetization change at $T_C$ remarkably becomes broader. Additionally, the thermal hysteresis at $T_C$ disappears after the substitution of $y = 0.03$ of Mn. In other words, the magnetic transition at $T_C$ changes from the first-order to the second-order, and the IEM transition above $T_C$ disappears after the substitution of $y = 0.03$ of Mn.
Figure 3 shows the temperature dependence of $\Delta S_m$ obtained by using eq. (1) in a magnetic field change from 0 to 4 T ($\Delta B = 4$ T) for $\text{La(Fe}_{0.88-}\text{x} \text{TM}_{x}\text{Si}_{0.12})_{13}$ ($\text{TM} = \text{Cr, Mn}$). Since $T_C$ decreases with increasing Cr or Mn concentration, the negative peak of $\Delta S_m$ for $\text{La(Fe}_{0.88} \text{Si}_{0.12})_{13}$ is shifted toward a lower temperature range. In addition, the maximum value of $\Delta S_m$, $\Delta S_m^{\text{MAX}}$ is decreased especially for the $\text{La(Fe}_{0.88-}\text{x} \text{Mn}_{x}\text{Si}_{0.12})_{13}$, whereas the full width of the half maximum $\delta T$ becomes wider with increasing Mn concentration. Recently, it has been pointed out that the relative cooling power ($RCP$) is also important to magnetic refrigerants, because $RCP$ is one of the measures of heat quantity transferred by magnetic refrigerants.22) The value of $RCP$ is defined by the following expression:22)

$$RCP = -\frac{\Delta S_m^{\text{MAX}}}{\delta T}.$$  

(2)

The values of $RCP$ calculated from Fig. 3 for $\text{La(Fe}_{0.88}\text{Si}_{0.12})_{13}$, $\text{La(Fe}_{0.86}\text{Co}_{0.02}\text{Si}_{0.12})_{13}$ and $\text{La(Fe}_{0.86}\text{Mn}_{0.02}\text{Si}_{0.12})_{13}$ are 370, 361 and 327 J kg$^{-1}$, respectively. Therefore, $RCP$ is also decreased by the partial substitution of Mn or Cr. Accordingly, it is clear that the further decrease of $T_C$ due to the partial substitution of Cr or Mn is undesirable from the practical viewpoint.

Recently, it has been reported the partial substitution of Ce for La in the $\text{La(Fe}_{y}\text{Ce}_{1-y}\text{Si}_{0.12})_{13}$ brings about not only the decrease of $T_C$ but also the significant enhancement of MCEs.19-21) Therefore, both the further decrease of $T_C$ and enhancement of $\Delta S_m$ for the $\text{La(Fe}_{0.86}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ are expected by the partial substitution of Ce for La. The thermomagnetization curves in a magnetic field of 1 T for the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.05}\text{Si}_{0.12})_{13}$ are given in Fig. 4. The value of $T_C$ is decreased from 136 to 60 K by the substitution of 35% Ce for La in $\text{La(Fe}_{0.85}\text{Mn}_{0.05}\text{Si}_{0.12})_{13}$. It should be noted that the thermomagnetization curve is accompanied by a hysteresis. The IEM transition at finite temperature has been discussed in the terms of the phenomenological Landau–Ginzburg theory with the magnetic free energy expanded up to the sixth order, by taking the renormalization effect of spin fluctuations on the Landau–Ginzburg coefficient and the magnetovolume effects into account.23,24) According to the theoretical investigation, the negative sign of the forth order of the Landau–Ginzburg coefficient means the negative mode–mode couplings among spin fluctuations is necessary to induce the IEM transition. In addition, it has been indicated that the magnetic transition at $T_C$ of the itinerant-electron ferromagnets with negative mode–mode coupling among spin fluctuations changes from the second-order to the first-order by applying hydrostatic pressure and the IEM transition takes place above $T_C$ of the first-order.22,24) In fact, such behaviors were obtained for $\text{Co(Se}_{0.65}\text{S}_{0.35})$ Ref. 25), $\text{Lu(Co}_{0.12}\text{Al}_{0.88})$ Ref. 26) which show the IEM transition. Furthermore, the thermal-induced first-order transition of the $\text{La}_{1-0.2}\text{Ce}_{0.2}(\text{Fe}_{0.85}\text{Mn}_{0.05}\text{Si}_{0.12})_{13}$ becomes clear with increasing Ce concentration because of the volume contraction.19-21) Therefore, $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.05}\text{Si}_{0.12})_{13}$ exhibits clearly the thermal-induced first-order magnetic transition with the IEM transition, though the $\text{La(Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ without Ce exhibits the second-order transition at $T_C$. Accordingly, $T_C$ of the $\text{La}_{1-0.2}\text{Ce}_{0.2}(\text{Fe}_{0.85}\text{Mn}_{0.05}\text{Si}_{0.12})_{13}$ is tunable in the temperature range between 60 and 180 K, with keeping the IEM transition by adjusting the composition.

The temperature dependence of $\Delta S_m$ in $\Delta B = 4$ T is given in Fig. 5 for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$. The values of $\Delta S_m^{\text{MAX}}$ and $RCP$ for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ in $\Delta B = 4$ T are about $-13$ J kg$^{-1}$ K$^{-1}$ and 458 J kg$^{-1}$, respectively. Therefore, the values of $\Delta S_m^{\text{MAX}}$ and $RCP$ become larger by substituting Ce for La in the $\text{La(Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$. In addition, the value of the $RCP$ of the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ is much larger than that of the $\text{La(Fe}_{0.88}\text{Si}_{0.12})_{13}$, though $\Delta S_m^{\text{MAX}}$ of the former is smaller than that of the latter. This result means that such large values of $\Delta S_m$ and $RCP$ are obtained in the temperature range between 60 and 180 K by adjusting the composition in
La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$. Consequently, the La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ compounds are promising as magnetic refrigerants working in the temperature range between 60 and 180 K.

4. Conclusion

To obtain large magnetocaloric effects (MCEs) in temperature ranges much lower than room temperature, we have investigated the change of $T_C$ for the La($\text{Fe}$_{1-x}\text{Si}$_{1-\gamma}$)$_{13}$ by the partial substitution. The value of $T_C$ for La($\text{Fe}$_{1-x}\text{Si}$_{1-\gamma}$)$_{13}$ is increased by the partial substitution of Ni for Fe and decreased by the partial substitution of Cr or Mn. In addition, the partial substitution of Ce for La in La($\text{Fe}$_{1-x}\text{Mn}$_y$Si$_{1-x-y}$)$_{13}$ causes the further decrease of $T_C$. As a result, a large isothermal entropy change is obtained in the temperature range between 60 and 180 K by adjusting the composition of La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$. Consequently, it is concluded that the La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ compounds are promising as magnetic refrigerants working in the temperature range between 60 and 180 K.

Acknowledgements

The present work has been supported by the Grant-in-Aids for Scientific Research (B) (No. 17360333) from the Japan Society for Promotion of Science. The present authors wish to thank Mr. Y. Morita for his experimental support. One of the authors (S. Fujieda) acknowledges the support of the JSPS Research Fellowships for Young Scientists.

REFERENCES