Reduction of Hysteresis Loss in Itinerant-Electron Metamagnetic Transition of La$_{1-x}$Ce$_x$(Fe$_x$Mn$_y$Si$_{1-x-y}$)$_{13}$ Magnetic Refrigerants at Low Temperatures

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Since La$_{0.75}$Ce$_{0.25}$(Fe$_0.8$Mn$_{0.2}$Si$_{0.12}$)$_{13}$ magnetocaloric effects (MCEs) are remarkably reduced from 78 to 31 kJ/kg by a slight adjustment of compositions, that is, the increase of the Ce concentration up to $z = 0.35$ and the decrease of the Fe concentration down to $x = 0.84$. What is important is that such improvement is achieved without a striking decrease of the isothermal magnetic entropy change $\Delta S_m$ at low temperatures.

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1. Introduction

Magnetic refrigerators have attracted much attention as an alternate refrigeration technology because of the environmental safety and high-efficiency. Remarkable developments have been achieved in various researches.$^{1,2}$ To be concrete, the rotary magnetic refrigerator by using a permanent magnet has been demonstrated at room temperature.$^{3}$ In addition, the hydrogen liquefaction has been realized with a high efficiency by the magnetic refrigeration at low temperatures.$^{4,5}$ For further improvement of the efficiency, the development of high-performance magnetic refrigerants is required.

Magnetization curves of La$_8$(Fe$_2$Si$_{1-x}$)$_{13}$ ($0.90 \geq x \geq 0.86$) cubic NaZn$_{13}$-type compounds exhibit an S-shape behavior with a remarkable hysteresis just above the Curie temperature $T_C$ because of the field-induced first-order transition from the paramagnetic (P) to the ferromagnetic (F) state, that is, the itinerant-electron metamagnetic (IEM) transition.$^{5,6}$ Recently, we have demonstrated that the IEM transition just above $T_C$ is accompanied by the large magnetocaloric effects (MCEs) such as the isothermal magnetic entropy change $\Delta S_m$ and the adiabatic temperature change $\Delta T_{ad}$. The value of $T_C$ is increased from about 180 to 330 K by hydrogen absorption.$^{12}$ Furthermore, $T_C$ is decreased below 180 K by the partial substitutions of Ce and Mn.$^{13,14}$ Since the IEM transition is kept in La$_{1-x}$Ce$_x$(Fe$_x$Mn$_{0.2}$Si$_{1-x-y}$)$_{13}$, large MCEs are obtained in a wide range of temperature below room temperature. However, the calorification due to the energy loss associated with the intrinsic hysteresis in the first-order transition reduces the efficiency in the cycles of magnetic refrigeration, though its quantitative definition is not established. In addition, the energy barrier between the P and F states in the magnetic free energy for the IEM transition is concerned with the decrease of $\Delta T_{ad}$. Therefore, the reduction of hysteresis loss in the La$_8$(Fe$_2$Si$_{1-x}$)$_{13}$ compounds is necessary for the increase in performance of magnetic refrigerators.

Recently, we have investigated the hysteresis loss estimated from the enclosed area between the ascendant and descendant magnetization curves for the La$_8$(Fe$_2$Si$_{1-x}$)$_{13}$, La$_{1-x}$Ce$_x$(Fe$_0.8$Si$_{1.4}$)$_{13}$, and La$_{1-x}$Pr$_x$(Fe$_0.8$Si$_{1.4}$)$_{13}$. The MCEs in La$_8$(Fe$_0.8$Si$_{1.2}$)$_{13}$ are enhanced by the increase of the Fe concentration, enhancing the hysteresis loss. In addition, the partial substitution of a rare earth element such as Ce, Pr, and Nd causes the decreases of both hysteresis loss and MCEs. However, the hysteresis loss in La$_{0.7}$(Ce$_{0.3}$)$_{13}$ and La$_{0.7}$(Pr$_{0.3}$)$_{13}$ is smaller than that of La$_8$(Fe$_0.8$Si$_{1.2}$)$_{13}$, though the MCEs are almost the same among them.$^{16,18}$ In other words, the hysteresis loss in La$_8$(Fe$_{1-x}$)$_{13}$ is decreased by the decrease of the Fe concentration, while the MCEs are maintained by the partial substitution of Ce or Pr.

In the present study, we have investigated the reduction of hysteresis loss when $T_C$ of La$_8$(Fe$_{1-x}$)$_{13}$ is decreased to low temperatures by the partial substitutions of Ce and Mn. We have selected La$_{0.75}$Ce$_{0.25}$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ as the basic compound, because it exhibits large MCEs and a large hysteresis above 19 K because of the IEM transition. From the previous works on the reduction of hysteresis loss in La$_{1-x}$Ce$_x$(Fe$_0.8$Si$_{1-x}$)$_{13}$, it is expected that the hysteresis loss in La$_{0.75}$Ce$_{0.25}$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ is decreased by the increase of the Ce concentration, together with the decrease of the Fe concentration. In this paper, therefore, the hysteresis loss in La$_{1-x}$Ce$_x$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ has been examined.

2. Experiments

The La$_{1-x}$Ce$_x$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ compounds with $z = 0.00, 0.10, 0.20, 0.30$ and $0.35$ and La$_{0.75}$Ce$_{0.25}$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ were arc-melted in an argon gas atmosphere and the heat-treatments were carried out in a vacuum quartz tube. The annealing temperature of La$_{1-x}$Ce$_x$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ increased from 1323 to 1423 K with increasing $z$ from 0.00 to 0.35, and the annealing duration was 10 days. The annealing temperature and duration for La$_{0.75}$Ce$_{0.25}$(Fe$_0.8$Mn$_{0.2}$Si$_{1.2}$)$_{13}$ were 1423 and 10 days, respectively. The crystal structure was identified by powder X-ray diffractions with Cu Kα radiation. The magnetization was measured with a SQUID magnetometer.
3. Results and Discussion

Figure 1 shows the powder X-ray diffraction patterns of La$_{1-x}$Ce$_x$(Fe$_{0.84}$Mn$_{0.03}$Si$_{0.13}$)$_{13}$ with $z = 0.00$, 0.10, 0.20, 0.30 and 0.35. The vertical thin short bars below the diffraction patterns stand for the positions of all the possible Bragg reflections from a cubic NaZn$_{13}$-type structure with the $Fm\bar{3}c$ space group. All the diffraction peaks are identified as the peaks for the cubic NaZn$_{13}$-type structure. The solubility of Ce in the higher Fe concentration La$_{1-x}$Ce$_x$(Fe$_{0.83}$Mn$_{0.03}$Si$_{0.12}$)$_{13}$ has been reported to be about $z = 0.25$.\cite{22} It should be noted that the decrease of the Fe concentration allows us to prepare the single phase with the higher concentration of Ce, namely, La$_{0.05}$Ce$_{0.35}$(Fe$_{0.84}$Mn$_{0.03}$Si$_{0.13}$)$_{13}$.

Shown in Fig. 2 is the Ce concentration dependence of the lattice constant $a$ of the La$_{1-x}$Ce$_x$(Fe$_{0.84}$Mn$_{0.03}$Si$_{0.13}$)$_{13}$ system. The value of $a$ linearly decreases with increasing $z$, because the ionic radius of Ce atom is smaller than that of La atom due to the lanthanide contraction. It has been reported that the La(Fe,Si$_{1-x}$)$_{13}$ compounds exhibit the significant decrease of the Curie temperature $T_C$ by applying hydrostatic pressure.\cite{20} In other words, $T_C$ of La(Fe$_{1-x}$Si$_x$)$_{13}$ sensitively decreases with decreasing the unit cell volume because of magnetovolume effects. Therefore, the partial substitution of Ce for La in La(Fe$_{1-x}$Si$_x$)$_{13}$ results in the decrease of $T_C$ because of the volume contraction.\cite{20} As can be seen from the thermomagnetization curves under a magnetic field of 0.4 T in Fig. 3, $T_C$ of La$_{1-x}$Ce$_x$(Fe$_{0.84}$Mn$_{0.03}$Si$_{0.13}$)$_{13}$ also decreases with increasing $z$. Since the thermomagnetization curve exhibits continuous change without a thermal hysteresis, no IEM transition takes place in the compound with $z = 0.00$, showing the second-order transition. On the other hand, the significant magnetization change with a very week thermal hysteresis takes place around $T_C = 27$ K for the compound with $z = 0.35$. Therefore, the thermal-induced first-order transition at $T_C$ is obtained by the partial substitution up to $z = 0.35$.

The magnetization curves at various temperatures for $\text{La}_{0.05}\text{Ce}_{0.35}(\text{Fe}_{0.84}\text{Mn}_{0.03}\text{Si}_{0.13})_{13}$ and $\text{La}_{0.75}\text{Ce}_{0.25}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ are presented in Figs. 4(a) and (b), respectively. The increasing and decreasing magnetic field processes are indicated by the arrows. The magnetization curve above $T_C$ of the compound with $z = 0.35$ exhibits the distinct magnetization change with a weak hysteresis associated with the IEM transition. The point to be noted is that the hysteresis accompanied by the IEM transition for the compound with $z = 0.35$ is obviously smaller than that for the compound with $z = 0.25$. Such hysteresis becomes smaller with increasing temperature and disappears around 57 K. On the other hand, the hysteresis of the compound with $z = 0.25$ is large even at a high temperature of 80 K. Namely, the hysteresis of the former is drastically reduced at much lower temperatures, compared with that of the latter.

The isothermal magnetic entropy change $\Delta S_m$ caused by the IEM transition contains the entropy change $\Delta S_I$ due to the latent heat. It has been reported that $\Delta S_m$ just above $T_C$ of La(Fe$_{0.84}$Si$_{0.12}$)$_{13}$ is dominated by the $\Delta S_I$ term.\cite{23} According to the following Clausius-Clapeyron equation, $\Delta S_I$ is related to both the critical field $B_c$ and the magnetization change $\Delta M$ for the IEM transition.
The magnitude of thermal magnetic entropy change $S_m$ for the compounds with $z = 0.35$ and 0.25. The value of $S_m$ was obtained from the Maxwell relation given by

$$\Delta S_m = \int_0^R \left( \frac{\partial M}{\partial T} \right)_B dB. \quad (2)$$

The value of $\Delta S_m$ for the compound with $z = 0.35$ exhibits a peak in the similar temperature range as that for the compound with $z = 0.25$. The values of $\Delta S_m$ for the both compounds are almost the same. As a measure of the energy loss caused by hysteresis in magnetic refrigeration cycles, we show the temperature dependence of hysteresis loss $E_h$ estimated from the enclosed area between the ascendent and descendant magnetization curves in Fig. 7. What have to be noted is that $E_h$ of the compound with $z = 0.35$ is much smaller than that of the compound with $z = 0.25$ in the working temperature range of $\Delta S_m$ given in Fig. 6. For example, the maximum value of $E_h$, $E_h^\text{MAX}$, for the compound with $z = 0.35$ corresponds to only about 4% of that for the compound with $z = 0.25$. Clearly, the reduction of $E_h$ for La$_{0.75}$Ce$_{0.25}$(Fe$_{0.85}$Mn$_{0.03}$Si$_{0.13}$)$_{13}$ is realized without the striking decrease of $\Delta S_m$ by the adjustment of compositions, that is, the increase of the Ce concentration up to $z = 0.35$, together with the decrease of the Fe concentration down to $x = 0.84$. Accordingly, the adjustment of compositions mentioned above is useful to improve the efficiency in the cycles of magnetic refrigeration.

When the IEM transition takes place, the free energy curve against magnetization has two minima in the P state with zero value of magnetization and in the F state with a finite value of magnetization.
magnetization. Namely, the P state is separated from the F state by an energy barrier. The hysteresis caused by the IEM transition in La_{0.75}Ce_{0.25}(Fe_{0.85}Mn_{0.03}Si_{0.12})_{13} is mainly attributed to the energy barrier of magnetic free energy, because the IEM transition takes place without a crystallographic transition. On the basis of the Landau-Ginzburg theory for the itinerant-electron metamagnets, the free energy has been discussed by taking the renormalization effect of spin fluctuations and the magnetovolume effects into account. According to the theoretical discussion, the free energy is expanded up to the $M^6$-term by using hydrostatic pressure and the Landau coefficients associated with the density of state (DOS) around the Fermi level. Accordingly, the hysteresis loss is influenced by both hydrostatic pressure and the DOS. Note that the partial substitution of Ce has the same effect on hydrostatic pressure because of the volume contraction. Therefore, the reduction of hysteresis loss by the slight adjustment of compositions in La_{0.75}Ce_{0.25}(Fe_{0.85}Mn_{0.03}Si_{0.12})_{13} allows us to conclude that the volume contraction induced by the increase of the Ce concentration is effective to obtain large $\Delta S_m$ with small hysteresis loss in comparison with the change of DOS associated with the increase of the Fe concentration. The bottom line described above is consistent with the recent report that $E_h^{\text{MAX}}$ against the maximum value of $\Delta S_m$ for La$_{1-x}$Ce$_x$(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ and La$_{1-x}$Pr$_x$(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ is smaller than that of La$_x$(Fe$_{0.75}$Si$_{0.25}$)$_{13}$ with $0.86 \leq x \leq 0.88$.

4. Conclusion

La$_{0.75}$Ce$_{0.25}$(Fe$_{0.85}$Mn$_{0.03}$Si$_{0.12}$)$_{13}$ exhibits large hysteresis and large magnetocaloric effects (MCEs) above 19 K because of the itinerant-electron metamagnetic (IEM) transition. To reduce the hysteresis loss without the lowering the isostructural magnetic entropy change $\Delta S_m$, La$_{1-x}$Ce$_x$(Fe$_{0.84}$Mn$_{0.03}$Si$_{0.12}$)$_{13}$ have been investigated. In the compound system, the Ce concentration can be controlled up to $z = 0.35$. The Curie temperature $T_C$ decreases down to about 27 K with increasing $z$ up to 0.35. Additionally, the second-order transition at $T_C$ of the compound with $z = 0.00$ changes to the first-order transition in the compound with $z = 0.35$, showing the IEM transition above $T_C$. The hysteresis due to the IEM transition of the compound with $z = 0.35$ is much smaller than that of the basic compound with $z = 0.25$, that is, La$_{0.75}$Ce$_{0.25}$(Fe$_{0.85}$Mn$_{0.03}$Si$_{0.12}$)$_{13}$. To put it another way, the hysteresis loss estimated from the enclosed area between the ascendant and descendant magnetization in the basic compound is significantly reduced by the increase of the Ce concentration up to $z = 0.35$, together with the decrease of the Fe concentration down to $x = 0.84$. Favorably, such reduction of the hysteresis loss is scarcely accompanied by striking decrease of $\Delta S_m$. Consequently, the adjustment of compositions, the increase of the Ce concentration and the simultaneous decrease of the Fe concentration, is effective to reduce the hysteresis loss induced by the IEM transition at low temperatures.

REFERENCES

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