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Large magnetocaloric effects enhanced by partial substitution of Ce for La in $La(Fe_{0.88}Si_{0.12})_{13}$ compound

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Abstract

The itinerant-electron metamagnetic (IEM) transition and magnetocaloric effects (MCEs) in cubic $NaZn_{13}$-type $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ with $z = 0.0$, 0.1, 0.2 and 0.3 have been investigated. By partial substitution of Ce for La, the Curie temperature T_C decreases with decreasing the lattice constant. In addition, the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} due to the IEM transition are enhanced because of the increase of the entropy change caused by the latent heat. Therefore, the partial substitution of Ce for La in $La(Fe_xSi_{1-x})_{13}$ is highly effective in the enhancement of MCEs.

Keywords: Magnetic refrigeration; Itinerant-electron metamagnetic transition

1. Introduction

Materials having large magnetocaloric effects (MCEs) such as the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} are utilized as magnetic refrigerants for magnetic refrigeration. To obtain a high performance of magnetic refrigeration, it is necessary to develop the magnetic refrigerants having large MCEs in relatively low magnetic fields. Recently, we have demonstrated that $NaZn_{13}$-type $La(Fe_xSi_{1-x})_{13}$ exhibit large values of ΔS_m [1–5] and ΔT_{ad} [2–6] just above the Curie temperature T_C because of the itinerant-electron metamagnetic (IEM) transition, that is, the field-induced first-order magnetic transition from the paramagnetic to ferromagnetic state [7–9]. Since T_C is increased up to about 340 K by controlling y in hydrogenated $La(Fe_xSi_{1-x})_{13}H_y$ [4,10,11], large MCEs are obtainable in the temperature range between 190 and 340 K [2–6]. In addition, their excellent thermal conductivity in the vicinity of room temperature for magnetic refrigerants has been confirmed [12]. Therefore, $La(Fe_xSi_{1-x})_{13}$ and their hydrides are one of the most promising magnetic refrigerants working in a wide temperature range covering room temperature. Further improvements such as the enhancement of MCEs and extension of working temperature range toward a lower temperature side for $La(Fe_xSi_{1-x})_{13}$ are of particular interest.

Recently, we have found that MCEs for $La(Fe_{0.90}Si_{0.10})_{13}$ are enhanced by a partial substitution of Ce for La [13]. Furthermore, this enhancement is maintained in the vicinity of room temperature after hydrogen absorption into the Ce substituted compounds. Therefore, the effect of the partial substitution of Ce for La in $La(Fe_xSi_{1-x})_{13}$ needs to be examined in detail. In the present study, the enhancements of MCEs due to the partial substitution of Ce have been discussed in terms of change in the lattice constant, the Curie temperature and the latent heat of the IEM transition of $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$.

2. Experiments

$La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ compounds were arc-melted by using 99.9 mass% pure La, Ce and Fe and 99.999 mass%

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pure Si in an argon gas atmosphere. The subsequent heat-treatments were carried out in a vacuum quartz tube. The annealing temperature and duration were 1323 K and 10 days for the compound with $z = 0.0$, 1323 K and 14 days for the compound with $z = 0.1$ and 1373 K and 14 days for the compound with $z = 0.2$ and 1423 K and 10 days for the compound with $z = 0.3$. The crystal structure and the lattice constant were determined by x-ray diffraction measurements with Cu Kα radiation. The magnetization was measured with a SQUID magnetometer and the heat capacity measurements in magnetic field were carried out by a relaxation method. By using the Maxwell relation, the isothermal magnetic entropy change ΔS_m was estimated from the magnetization data. The adiabatic temperature change ΔT_{ad} was evaluated from the magnetic and heat capacity data in the magnetic field [4].

3. Results and discussion

Fig. 1 displays the Ce concentration dependence of the lattice constant for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$. The structure of $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ is identified as the cubic $NaZn_{13}$-type single phase in the concentration range $0.0 \leq z \leq 0.3$. The lattice constant decreases linearly with increasing z. For $La(Fe_{0.88}Si_{0.12})_{13}$, several studies have been made on the relation between the volume and the Curie temperature T_C. The value of T_C for $La(Fe_{0.88}Si_{0.12})_{13}$ is decreased significantly by applying hydrostatic pressure, namely, T_C decreases with decreasing the volume [9]. On the other hand, the increase of T_C for $La(Fe_{0.88}Si_{0.12})_{13}H_y$ is brought about by the volume expansion due to hydrogen absorption [4,10,11]. From these results, it is expected that T_C is decreased by partial substitution of Ce due to the decrease of the lattice constant.

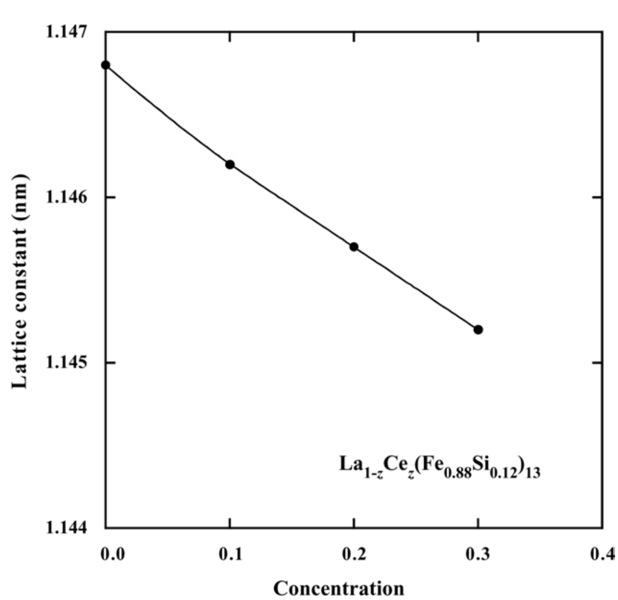

Fig. 1. Concentration dependence of the lattice constant for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$.

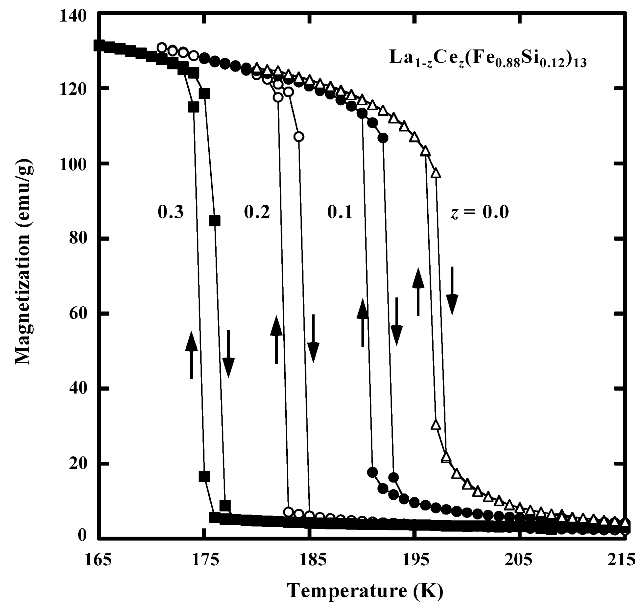

Fig. 2. Thermomagnetization curves in a magnetic field of 0.4 T for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ with $z = 0.0$, 0.1, 0.2 and 0.3.

The thermomagnetization curves in a magnetic field of 0.4 T for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ with $z = 0.0$, 0.1, 0.2 and 0.3 are given in Fig. 2. All the thermomagnetization curves were measured in both the heating and cooling processes as given by the arrows. The thermomagnetization curve for the compound with $z = 0.0$ exhibits a discontinuous change with a hysteresis because of a thermal-induced first-order magnetic transition at T_C. The value of T_C decreases with increasing z. Since the thermomagnetization curves for the compounds with $z = 0.1$, 0.2 and 0.3 are also accompanied by a hysteresis, a thermal-induced first-order magnetic transition is maintained. With increasing z, the paramagnetic susceptibility just above T_C becomes smaller and the magnetization just below T_C becomes larger. Therefore, the discontinuous magnetization change at T_C becomes larger with increasing z. According to the theoretical discussion of itinerant-electron metamagnets, a significant decrease of T_C due to the magnetovolume effects takes place without the marked decrease of magnetization at 0 K [14]. From the magnetization measurements at 4.2 K, the magnetization is hardly changed by partial substitution of Ce. Therefore, the decrease of the lattice constant is merely reflected in T_C for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ due to the magnetovolume effects.

By applying magnetic field, an S-shape behavior of the magnetization curve was observed just above T_C for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ with $z = 0.1$, 0.2 and 0.3, and hence the present compounds exhibit the itinerant-electron metamagnetic (IEM) transition. Fig. 3 presents the temperature dependence of the critical field B_c of the IEM transition for $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ with $z = 0.0$, 0.1, 0.2 and 0.3. The value of B_c is defined as the average of the inflection points in the ascendant and descendant magnetization curves. The value of B_c increases linearly with increasing temperature.

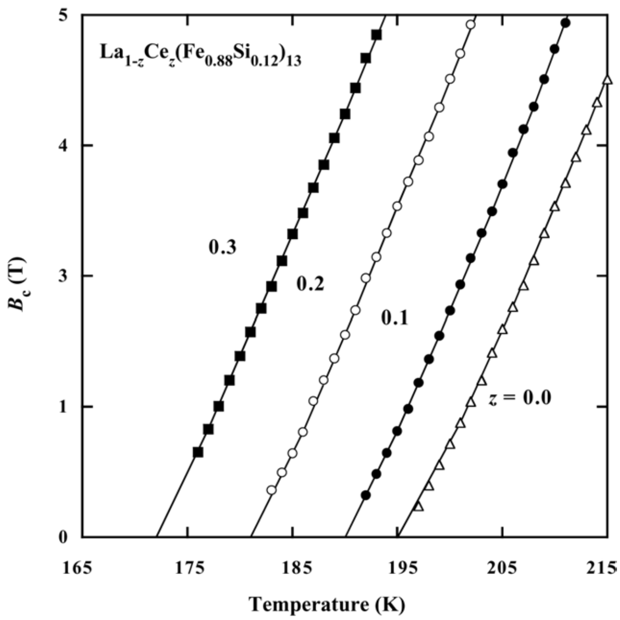

Fig. 3. Temperature dependence of the critical field B_c of the itinerant-electron metamagnetic transition for La$_{1-z}$Ce$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ with $z = 0.0$, 0.1, 0.2 and 0.3.

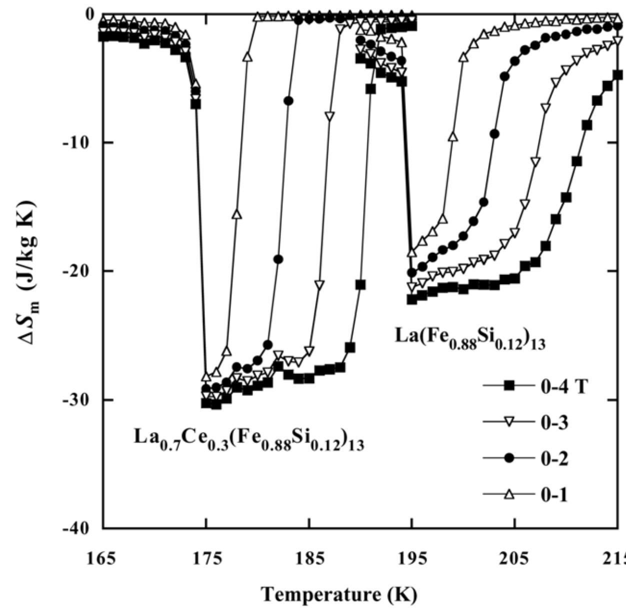

Fig. 4. Temperature dependence of the isothermal magnetic entropy change ΔS_m for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in various magnetic field changes.

From the least-square method, dB_c/dT for the compound with $z = 0.0$ is determined to be 0.23 T/K, insensitive to concentration z. For the first-order magnetic transition, the entropy change $\Delta Q/T$ due to the latent heat ΔQ is related to both the discontinuous magnetization change ΔM at T_C and dB_c/dT, as given by the following Clausius–Clapeyron equation:

$$\frac{\Delta Q}{T\Delta M} = \frac{dB_c}{dT}. \quad (1)$$

From the data in Figs. 2 and 3, it is revealed that the entropy change $\Delta Q/T$ increases with increasing z.

Fig. 4 displays the temperature dependence of ΔS_m in various magnetic field changes ΔB from 0 to B for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. Since T_C decreases with increasing z, the negative peak of ΔS_m is shifted toward a lower temperature range by partial substitution of Ce. In addition, the increase of ΔS_m due to the partial substitution of Ce is observed in all the curves of ΔB. The value of ΔS_m in $\Delta B = 1$ T for La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is about -28 J/kg K, which is about 50% larger than $\Delta S_m = -19$ J/kg K for the compound without Ce. By using Eq. (1), the values of ΔQ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ are calculated to be 3.4 kJ/kg at 197 K and 4.4 kJ/kg at 176 K, respectively, from data in Figs. 2 and 3. Note that the difference between ΔS_m of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is almost the same in magnitude as that in the entropy change $\Delta Q/T$. Accordingly, it is concluded that the enhancement of ΔS_m due to the partial substitution of Ce comes from the increase of the entropy change $\Delta Q/T$.

The temperature dependence of ΔT_{ad} for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in $\Delta B = 1$, 2, 3 and 4 T is illustrated in Fig. 5. The value of ΔT_{ad} becomes larger with increasing ΔB. From the analysis of ΔT_{ad} just above T_C for materials with a first-order transition, ΔT_{ad} in relatively low ΔB is expressed as [15]

$$\Delta T_{ad} = T_C(B) - T_C(0). \quad (2)$$

The B_C–T line in Fig. 3 corresponds to the B–T_C line. Therefore, ΔT_{ad} for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in $\Delta B = 1$ T is determined to be about 4 K by using Eq. (2). Similar value is

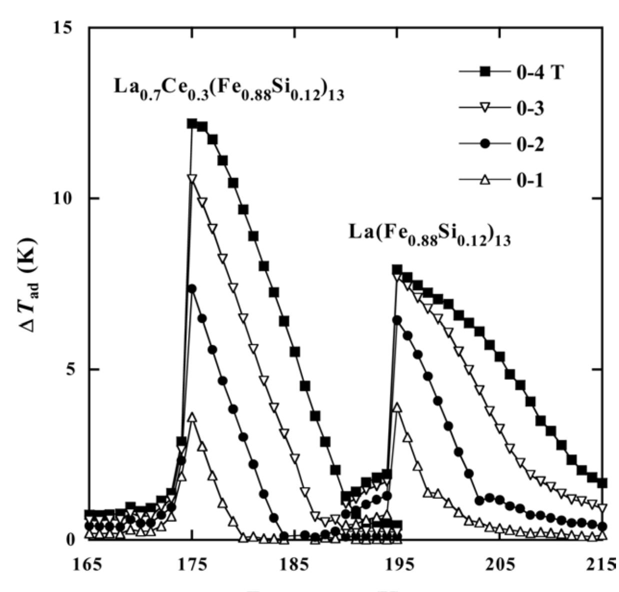

Fig. 5. Temperature dependence of the adiabatic temperature change ΔT_{ad} for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{0.7}$Ce$_{0.3}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in various magnetic field changes.

observed in $\Delta T_{ad} = 3.9$ K in $\Delta B = 1$ T for $La(Fe_{0.88}Si_{0.12})_{13}$. Apparently, ΔT_{ad} in $\Delta B \leq 1$ T for $La(Fe_{0.88}Si_{0.12})_{13}$ depends on only the magnetic field dependence of T_C. Since dT_C/dB is hardly changed by a partial substitution of Ce, $\Delta T_{ad} = 3.6$ K in $\Delta B = 1$ T for $La_{0.7}Ce_{0.3}(Fe_{0.88}Si_{0.12})_{13}$ is almost the same value as that for $La(Fe_{0.88}Si_{0.12})_{13}$. On the other hand, the value of $\Delta T_{ad} = 12.2$ K in $\Delta B = 4$ T for $La_{0.7}Ce_{0.3}(Fe_{0.88}Si_{0.12})_{13}$ is about 50% larger than $\Delta T_{ad} = 7.9$ K for $La(Fe_{0.88}Si_{0.12})_{13}$. When the total entropy just above $T_C(0)$ is smaller than that just below $T_C(B)$, ΔT_{ad} just above T_C in Eq. (2) is rewritten as [15]

$$\Delta T_{ad} = -\frac{T}{C}\Delta S_m, \tag{3}$$

where C is the heat capacity. It has been reported that the total entropy just below $T_C(B)$ for $La(Fe_{0.88}Si_{0.12})_{13}$ in $B \geq 2$ T is larger than that just above $T_C(0)$ [4]. Namely, ΔT_{ad} in $\Delta B \geq 2$ T for $La(Fe_{0.88}Si_{0.12})_{13}$ is affected by ΔS_m. Therefore, ΔT_{ad} in $\Delta B \geq 2$ T for $La(Fe_{0.88}Si_{0.12})_{13}$ is enhanced by the partial substitution of Ce because of the enhancement of ΔS_m as seen in Fig. 4. Consequently, the increase of entropy change due to the latent heat caused by the partial substitution of Ce for La in $La(Fe_xSi_{1-x})_{13}$ is important to enhance the MCEs from the practical viewpoint.

Recently, several candidates for almost the same temperature range have been reported. For example, large values of ΔS_m have been observed in $Dy(Co_{0.95}Si_{0.05})_2$ and $MnFeP_{0.75}As_{0.25}$, though no values of ΔT_{ad} for these compounds have been reported. That is, the $Dy(Co_{0.95}Si_{0.05})_2$ compound shows $\Delta S_m = -3.3$ J/kg K in $\Delta B = 1$ T at $T_C = 167$ K [16]. The value of ΔS_m for $MnFeP_{0.75}As_{0.25}$ is -11 J/kg K in $\Delta B = 2$ T at $T_C = 168$ K [17]. These values are much smaller than the data of $La_{0.7}Ce_{0.3}(Fe_{0.88}Si_{0.12})_{13}$ shown in Fig. 4. More recently, it has been demonstrated that T_C of $La_{1-z}Ce_z(Fe_{0.90}Si_{0.10})_{13}$ can be increased up to around room temperature without appreciable decrease of ΔS_m [13]. The value of $\Delta S_m = -28$ J/kg K in $\Delta B = 1$ T of $La_{0.7}Ce_{0.3}(Fe_{0.88}Si_{0.12})_{13}$ is larger than the value of $\Delta S_m = -11$ J/kg K of $Gd_5Si_2Ge_2$ [18] proposed as a candidate in the vicinity of room temperature. In consequence, the $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ compounds are one of the considerable candidates as magnetic refrigerants to obtain high-performance of magnetic refrigeration in relatively low magnetic fields.

4. Conclusion

The cubic $NaZn_{13}$-type single phase is formed in $La_{1-z}Ce_z(Fe_{0.88}Si_{0.12})_{13}$ in the concentration range $0.0 \leq z \leq 0.3$. By partial substitution of Ce for La, the Curie temperature T_C decreases with decreasing the lattice constant because of the magnetovolume effects. The magnetization change at T_C becomes larger with increasing concentration z, whereas the temperature dependence of the critical field B_c of the itinerant-electron metamagnetic (IEM) transition hardly changes. Therefore, the entropy change due to the latent heat becomes larger with increasing z. As a result, the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} due to the IEM transition for $La(Fe_{0.88}Si_{0.12})_{13}$ are enhanced by partial substitution of Ce. Consequently, the partial substitution of Ce for La in $La(Fe_xSi_{1-x})_{13}$ is highly effective in the enhancements of magnetocaloric effects.

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