Influence of hydrogenation on volume dependence of the Curie temperature and entropy change in La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$

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Abstract. To elucidate the influence of hydrogenation on the volume dependence of the Curie temperature $T_C$ and the entropy change $\Delta S_m$ in La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$, magnetic properties under hydrostatic pressure have been investigated. In the thermomagnetization curves of La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.1}$, the first-order phase transition becomes clearer due to the decrease of volume, as observed before hydrogenation. By hydrogenation, the reduction of the pressure dependence of $T_C$ by about 20% is caused by the magnetovolume contribution to the free energy. Meanwhile, the maximum value of $\Delta S_m$ is increased in magnitude from -9 to -18 J/kgK by applying pressure of 1 GPa. Accordingly, the decrease of volume is also effective to enhance $\Delta S_m$ after hydrogenation.

1. Introduction
The La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds exhibit the itinerant-electron metamagnetic (IEM) transition above the Curie temperature $T_C$ [1, 2], and large magnetocaloric effects (MCEs), such as the magnetic entropy change $\Delta S_m$ [3-5] and the adiabatic temperature change $\Delta T_{ad}$ [3, 4] are brought about by the IEM transition. In addition, $T_C$ is increased by hydrogenation because of the increase of volume by interstitial hydrogen atoms and large MCEs are obtained around room temperature [4]. Accordingly, the present compounds are considered as one of the promising systems of magnetic refrigerants working around room temperature. In La(Fe$_{x}$Si$_{1-x}$)$_{13}$, the IEM transition becomes clear and MCEs become larger with increasing Fe concentration [2-4], while the hysteresis of the IEM transition, which causes loss of efficiency, is increased. Recently, we have demonstrated that the reduction of volume in $x = 0.86$ by applying hydrostatic pressure [2, 6, 7], or partial substitution of Ce [7, 8] or Pr [7, 9] makes the phase transition clearer due to the magnetovolume effect. As a result, the magnetic entropy change $\Delta S_m$ is enhanced to the same magnitude of that with $x = 0.88$, maintaining a small hysteresis associated with relatively low Fe concentrations [7-9]. The control of $T_C$ by hydrogenation is necessary to obtain such advantageous features around room temperature. Meanwhile, it has been pointed out that the magnetovolume effect in $x = 0.88$ is reduced after hydrogenation [10]. Since the magnetovolume effect becomes smaller with decreasing $x$ from 0.88 to 0.86 [2], the volume dependence of $T_C$ and $\Delta S_m$ after hydrogenation is necessary to elucidate for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$. In the present study, the magnetization measurements by applying hydrostatic pressure for
La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.1}$ having $T_C$ close to room temperature are carried out and the volume dependence of $T_C$ and $\Delta S_m$ has been discussed.

2. Experimental
The alloying of La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ was carried out by arc-melting in an Ar gas atmosphere. The homogenization of the specimens was made in an evacuated quartz tube at 1323 K for 10 days. The hydrogenation was made by annealing in H$_2$ atmosphere in a sealed chamber. The magnetization under hydrostatic pressure was measured with a superconducting quantum interference device (SQUID) magnetometer by settling a specimen into a Cu-Ti pressure clamp cell.

3. Results and discussion
Figure 1 shows the temperature $T$ dependence of magnetization $M$ for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.1}$ under various hydrostatic pressures $P$. In the inset, the pressure dependence of $T_C$ for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_y$ ($y = 1.1$) obtained from the $M$-$T$ curve is plotted, together with the data before hydrogenation ($y = 0.0$) [2], for comparison. The magnetization around $T_C$ in $P = 0.0$ GPa shows a continuous variation, although the decrement is much significant compared to the situation in the conventional second-order phase transition. With increasing $P$, $T_C$ shifts to lower values and the discontinuous change of magnetization $\Delta M$ at $T_C$ becomes significant. Similar change of $M$-$T$ curve under hydrostatic pressure has been observed in La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ [6]. Therefore, the influence of the volume change on the phase transition characteristics is scarcely changed by hydrogenation.

From these data, the values of $dT_C/dP$ are evaluated to be -77 for $y = 0.0$ and -68 K/GPa for $y = 1.1$, exhibiting that the magnitude of $dT_C/dP$ is slightly reduced after hydrogenation. It has been reported that the magnitude of $dT_C/dP$ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ becomes smaller from -89 to -59 K/GPa with increasing $y$ from 0.0 to 1.2 [10]. A decrease of $dT_C/dP$ in magnitude of about 30% by hydrogenation has also been observed in La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$H$_{1.64}$ melt-spun ribbon specimen [11]. Compared to these reported results, the reduction rate of $dT_C/dP$ by hydrogenation for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ is relatively small. One may notice that the change of compressibility $\kappa$ by hydrogenation would cause the reduction of $dT_C/dP$ even though the volume dependence of $T_C$ is unchanged. However, it is expected that the change of $\kappa$ by hydrogenation is not so drastically different between $x = 0.88$ and 0.86, and hence the change of volume dependence of $T_C$ against the Fe concentration is essential. According to the theory of the IEM transition based on the Landau expansion including the influence of spin fluctuations and magnetovolume effect, the pressure dependence of $T_C$ around $P$-0 for the second-order transition is given by equation (1) and for the first-order transition by equation (2) [12].

$$
\frac{d^2 \xi(T_C)}{dP} = -\frac{3}{\sqrt{35}} \frac{\kappa C_{\xi}}{|\theta|} \left( 5 \frac{ac}{b^2} \right)^{-1/2}
$$

and
$$\frac{d \xi(T_c)^2}{d P} = - \frac{6 \kappa C_m}{\sqrt{7} |b|} \left( \frac{ac}{b^2} - \frac{5}{28} \right)^{-1/2}$$

where $C_m$ and $\xi(T)^2$ are the magnetovolume coupling coefficient and the mean square amplitude of spin fluctuations. The parameters $a, b$ and $c$ are the coefficient of the Landau expansion of the free energy $F(M)$ as a function of magnetization $M$ given as [12]

$$F(M) = \frac{1}{2} A(T) M^2 + \frac{1}{4} B(T) M^4 + \frac{1}{6} C(T) M^6$$

with

$$A(T) = a + \frac{5}{3} b \xi(T)^2 + \frac{35}{9} c \xi(T)^4 + 2 \kappa C_m P,$$

$$B(T) = b + \frac{14}{3} c \xi(T)^2, \quad C(T) = c$$

Note that the coefficients $A(T)$ and $B(T)$ are modified by the magnetovolume coupling [13], although such contributions are neglected for simplicity [12]. The second- and first-order transition at $T_c$ take place in the range $ac/b^2<5/28$ and $5/28<ac/b^2<3/16$, respectively. From the comparison of phase diagram obtained by equation (3) and experimental data [2], the increase of the Fe concentration qualitatively corresponds to the increase of $ac/b^2$. In this viewpoint, the variation of $dT_c/dP$ against $x$ in the concentration range for the second-order phase transition [14] has been confirmed to be consistent with equation (1). On the other hand, the magnitude of $dT_c/dP$ monotonically increases with increasing $x$ and shows a saturation around $x = 0.89$ [14] unlike with the expected variation from equations (1) and (2) in which the magnitude of $dT_c/dP$ becomes maximum around the boundary between the first- and second-order transition [12,13]. Such discrepancy is explained from the neglected $P$ dependence of $d\xi(T_c)/dP$ in equation (2) for finite values of $P$ [12], and also the concentration dependence of the proportional coefficient between $\xi(T)$ and $T$. What has to be mentioned is that the coefficient $A(T)$ contains the $2\kappa C_m P$ term. Since $\kappa P$ corresponds to the volume change - $\omega (\Delta V/V)$, therefore, the volume expansion caused by hydrogenation gives the negative contribution $-2C_m \omega$ to $A(T)$. This contribution is equivalent to the change given by the decrease of $ac/b^2$. In other words, the hydrogenation brings about the change of $dT_c/dP$ just like a shift to the lower Fe concentration region. Before hydrogenation, the magnitude of $dT_c/dP$ shows a maximum and the concentration dependence becomes steep around $x = 0.89$ [14]. On the other hand, the variation of $dT_c/dP$ in $x \leq 0.86$ becomes moderate. Accordingly, the change of volume dependence of $T_c$ for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ after hydrogenation is much smaller than that for the higher value of $x$.

Before hydrogenation, the reduction of volume by the partial substitution of Ce results in the enhancement of $\Delta S_m$ [7-9]. To verify such a volume dependence of $\Delta S_m$ after hydrogenation, the isothermal magnetizations around $T_c$ are measured at various temperatures around $T_c$ in various values of $P$, and $\Delta S_m$ is evaluated by applying the Maxwell relation. Figure 2 shows the temperature dependence of $\Delta S_m$ of La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.1}$ in a magnetic field change of 2 T under the selected values of $P$. The maximum value $\Delta S_m^{\text{max}}$ is increased with increasing pressure and $\Delta S_m^{\text{max}}$ in $P = 1.0$ GPa is almost twice as that in ambient pressure. The increase of $\Delta S_m^{\text{max}}$ by a factor of two in La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.64}$ has also been reported [11]. Recently, the pressure dependence of $\Delta S_m$ of La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ has been calculated theoretically by the mean-field model based on the 3d band theory, however, the monotonic increase of $\Delta S_m^{\text{max}}$ against $P$ is not realized [15, 16]. The discrepancy is considered to come from the treatment of magnetic excitations such as spin fluctuations in finite temperatures. We should notice that the influence of magnetic excitations to the total entropy is evaded by unnatural treatments of the phonon entropy in these mean-field calculations. From the isothermal magnetizations, the temperature dependence of critical field of the IEM transition, $dBC/dT$, is evaluated to be 0.23~0.24 T/K and shows a slight pressure dependence. From the Clausius-
Clapeyron relation, the entropy change connected with the latent heat is evaluated as the product of $dBc/dT$ and the magnetization change $\Delta M$ at $T_C$. Since $\Delta M$ is prosily increased by $P$ as seen form figure 1, the observed increase of $\Delta S_m^{\text{max}}$ against $P$ is quite expected. As mentioned in Introduction, the partial substitution of Ce or Pr in La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ brings about a volume reduction, resulting in an enhancement of $\Delta S_m^{\text{max}}$ with keeping a small hysteresis of the IEM transition[8, 9]. The enhancement of $\Delta S_m^{\text{max}}$ by $P$ after hydrogenation means that the partial substitution is advantageous to utilize them as magnetic refrigerants working around room temperature.

In summary, the volume dependence of the Curie temperature $T_C$ and the magnetic entropy change $\Delta S_m$ has been investigated for La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$H$_{1.1}$. In thermomagnetization measurements under pressure, the first-order phase transition becomes clearer with decreasing volume, while the pressure dependence $dT_C/dP$ is slightly reduced after hydrogenation. The reduction of volume dependence of $T_C$ is explained by the magnetovolume effect associated with the volume expansion caused by hydrogenation. It is elucidated that the maximal magnetic entropy change $\Delta S_m^{\text{max}}$ is enhanced by a reduction of volume in a similar way as observed before hydrogenation. These results certify that the magnetocaloric effects as well as hysteresis are effectively controlled by the volume change due to the partial substitution together with the increase of $T_C$ up to around room temperature by hydrogenation.

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