Abstract. The pressure dependence of the Curie temperature $T_C$ has been investigated up to 1GPa for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ itinerant-electron metamagnet. The magnetization change at the thermally induced first-order transition at $T_C$ becomes sluggish with increasing $y$. On the other hand, the magnitude of the pressure coefficient of $T_C$, $|d\ln T_C/dP|$, is enhanced by the partial substitution of Al for Si. From the relation between the thermal variation of the spin fluctuations and the critical magnetic field of the metamagnetic transition, the change of thermal variation of spin fluctuation is closely related with the enhancement of $|d\ln T_C/dP|$ after partial substitution of Al.

1. Introduction
La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $0.86 \leq x \leq 0.90$ exhibit the thermal induced first-order transition between the paramagnetic and the ferromagnetic states at the Curie temperature $T_C$ [1, 2]. The itinerant-electric metamagnetic (IEM) transition, that is, the first-order transition from the paramagnetic to the ferromagnetic state above $T_C$ is induced by applying magnetic field [1-3]. This compound exhibits the magnetocaloric effects: the isothermal magnetic entropy change $\Delta S_m$ and adiabatic temperature change $\Delta T_{ad}$ due to IEM transition [4-7]. Enlargement of temperature range for the large $\Delta S_m$ is established by the decrease of the thermal variation of IEM critical field, $\mu_0 dH_c/dT$, after the partial substitution of Al for Si in La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$, although the decrease of $\mu_0 dH_c/dT$ results in a slight decrease of the maximum of $\Delta S_m$. It has been pointed out that the IEM transition of La(Fe$_x$Si$_{1-x}$)$_{13}$ becomes sharper on applying pressure $P$, accompanied by an increase of the magnetization change $\Delta M$ at the transition temperature [8, 9]. Since $\Delta S_m$ is enhanced by increase of $\Delta M$, an application of pressure is one of the convenient methods to enhance $\Delta S_m$. However, the large pressure-induced change of the IEM transition is originated from the influence of spin fluctuations, and the change of $\mu_0 dH_c/dT$ means the change of thermal variation of spin fluctuations after the partial substitution of Al. The pressure effect of $T_C$ is a subtle measure for the relation between spin fluctuations and influence of pressure on the magnetic states. In the present study, therefore, the pressure effect on $T_C$ has been investigated for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ with $y = 0.01, 0.02$ and $0.03$. 

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2. Experimental details

La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ were prepared by arc-melting by using 99.9 mass% pure La, Fe and Al and 99.999 mass% pure Si in an argon gas atmosphere. The ingots were re-melted several times, and subsequent heat-treatment for homogenization was carried out in an evacuated quartz tube. The annealing temperature and duration were 1323 K and 10 days, respectively. The crystal structure and the lattice constant were determined by powder x-ray diffraction measurements with Cu Kα radiation at room temperature. The magnetization under hydrostatic pressure was measured with a SQUID magnetometer setting up with a Cu-Ti nonmagnetic pressure clamp cell. The pressure medium was a Daphne 7373 oil. Hydrostatic pressures were calibrated by measuring the shift of the superconducting transition temperature of Pb at low temperatures. By considering the pressure drift due to the solidification and volume contraction of the Daphne oil at temperatures around 100-200 K [10], the pressure calibration has been carried out by referring the available data for compounds such as Lu(Co$_{1-x}$Ga$_x$)$_2$ [11].

3. Results and discussion

Shown in Fig. 1 are the thermomagnetization curves for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ with $y$ = 0.01, 0.02 and 0.03 in a magnetic field of 0.3 T under hydrostatic pressures $p$ = 0.00, 0.25, 0.50, 0.75 and 1.00 GPa. At ambient pressure, the compounds exhibit the first-order magnetic phase transition from a ferromagnetic to paramagnetic transition at $T_C$, exhibiting a drastic change of magnetization. With increasing $y$, the magnetization change at $T_C$ becomes sluggish. The value of $T_C$ for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ has been reported to be 195 K [2], and after partial substitution, $T_C$ becomes 194, 192 and 189 K for $y$ = 0.01, 0.02 and 0.03, respectively. Note that the itinerant-electron metamagnetic transition just above $T_C$ is confirmed after partial substitution of Al up to $y$ = 0.03. With increasing hydrostatic pressures, a discontinuous change of thermomagnetization curves at $T_C$ becomes clear as seem from Fig.1. In addition, a significant decrease in $T_C$ is observed by applying hydrostatic pressure.

![Figure 1. Thermomagnetization curves at various pressures for La(Fe$_{0.88}$Si$_{0.12}$-$y$Al$_y$)$_{13}$ with $y$ = 0.01, 0.02 and 0.03 in a magnetic field of 0.3 T.](image-url)
where $P_C$ is the critical pressure at which $T_c$ becomes 0 K, and the square-root $P$ dependence in Eq.(1) is explained by the spin fluctuation theory of the IEM transition based on the Landau expansion. According to the theory, free energy $F(M)$ as a function of magnetization $M$ is given as \[ F(M) = \frac{1}{2} A(T) M^2 + \frac{1}{4} B(T) M^4 + \frac{1}{6} C(T) M^6 \] (2)

with \[ A(T) = a + \frac{2}{3} b \xi(T)^2 + \frac{35}{9} c \xi(T)^4 + 2 \kappa_{mv} P, \]
\[ B(T) = b + \frac{14}{3} c \xi(T)^2, \quad C(T) = c \] (3)

where $\kappa_{mv}$ and $\xi(T)^2$ are the magnetovolume coupling coefficient and the mean square amplitude of spin fluctuations, respectively. The parameters $a$, $b$ and $c$ are related to the 3d band structures. Note that the coefficients $A(T)$ and $B(T)$ are modified by the magnetovolume coupling [8], although such contributions are neglected for simplicity. The first-order transition at $T_c$ takes place in the range $5/28 < ac/b^2 < 3/16$ [15, 16]. From the comparison of the phase diagrams obtained by theory and our experiments, the increase of the Fe concentration is associated with the increase of $ac/b^2$, resulting in a clear first-order transition. For La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ at higher Fe concentrations, in addition, the clearer the first-order transition, the larger the pressure effect of $T_c$ and the value of $d\ln T_c/dP$ with $x = 0.86, 0.88$ and 0.89 were reported to be -0.31, -0.46 and -0.54 GPa$^{-1}$, respectively [8, 9]. After partial substitution of Al, the change of thermomagnetization curve at $T_c$ becomes vague with increasing $y$, namely, the phase transition of La(Fe$_{0.88}$Si$_{0.12-y}$Al$_y$)$_{13}$ comes gradually closer to the second-order. On the other hand, the initial slope in low $P$ ranges and curvature in high $P$ ranges become larger with increasing $y$ as shown in Fig. 2.

To reveal the change of the pressure effect of $T_c$, the Al concentration dependence of $d\ln T_c/dP$ and $\beta$ is displayed in Fig. 3. For comparison, the data of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ [8] before partial substitution is also shown. After partial substitution of Al, the value of $|d\ln T_c/dP|$ decreases for the compound with $y = 0.01$. Such a change is advisable in terms of the distinctness of the IEM transition and the magnitude of $d\ln T_c/dP$ in La(Fe$_{v.88}$Si$_{0.12}$)$_{13}$ [3, 9]. However, the concentration dependence of $|d\ln T_c/dP|$ turns into an increasing tendency above $y = 0.01$. The concentration dependence of $\beta$ is similar to that of $|d\ln T_c/dP|$. This similarity is quite expected because the root function in Eq. (1) becomes
asymptotical when a value of \( P \) departs from \( P_C \). Accordingly, we focus on the variation of \( \beta \) to explain the influence of Al on the pressure effect of \( T_C \). From Eqs. 1 and 2, \( \beta \) is derived as [9]

\[
\beta \propto \left( \kappa C_{mv} / (b \delta) \right)^{1/2}
\]  

(4)

The parameter \( \delta \) is the proportional coefficient of the relation \( \xi(T)^2 = \delta T^2 \) [17]. What has to be noticed is that the value of \( \delta \) is related to the energy distribution of spin-fluctuation spectrum. Accordingly, it is apparent that \( \beta \) governs the interrelation between the temperature and pressure scales. The value of \( \kappa C_{mv} \) of La(Fe\(_{1-x}\)Si\(_{1.2}\))\(_{13}\) is about 0.5 \%/\( \mu_0 \) for \( x = 0.86 \) and 0.7 \%/\( \mu_0 \) for \( x = 0.88 \) [2]. Since the reported value of \( \kappa C_{mv} \) for La(Fe\(_{0.88}\)Al\(_{0.12}\))\(_{13}\) is about 0.5 \%/\( \mu_0 \) [18], the influence of partial substitution of Al up to \( y = 0.03 \) on \( \kappa C_{mv} \) is expected to become small. Direct observation of the thermal variation of \( \xi(T)^2 \) is difficult, however, the following relation between the temperature dependence of the critical field \( \mu_0 H_C \) of the IEM transition and the thermal variation of \( \xi(T)^2 \) is useful [19].

\[
\mu_0 H_C \propto \Delta M b \left\{ \xi(T)^2 - \xi(T_C)^2 \right\} = \Delta M \left(b \delta\right) \left| T^2 - T_C^2 \right|^{1/2}
\]  

(5)

where \( \Delta M \) is the magnetization change at the IEM transition. Note that the \( T^2-T_C^2 \) term is approximated as \( T \) around \( T_C \), therefore, \( \mu_0 H_C \) is proportional to \( \Delta M(b \delta) = \lambda T \). From the magnetization measurements, the value of \( \lambda \) is found to be smaller with increasing \( y \). The magnitude of \( \mu_0 dH_C/dT \) becomes smaller with increasing Al concentration and the value for \( y = 0.00, 0.01, 0.02, 0.03 \) is evaluated to be about 0.23, 0.21, 0.20 and 0.19 T/K, respectively. Although, \( \Delta M \) slightly decreases against \( y \), the change is not so drastic because the IEM transition is kept even at \( y = 0.03 \). Accordingly, the increase of \( y \) brings about the decrease of the magnitude of \( b \delta \). As a result, the magnitude of \( \beta \) shown by Eq. (4) is enhanced, turning out the larger \( |d\ln T_C/dP| \). In our previous results, the change of \( b \) is sensitively induced by change of Fe concentration or the partial substitution of Ce for La(Fe\(_{1-x}\)Si\(_{1.2}\))\(_{13}\) [19, 20], while the value of \( \lambda \) is almost the same as that of the partial substitution of Ce and also the hydrogenation [21]. Namely, the change of \( \lambda \) is mainly dominated by the change of \( \delta \).

Consequently, the enhancement in the pressure effect on \( T_C \) is closely associated with the decrease of the thermal variation of \( \xi(T)^2 \) with a small \( \delta \) after the partial substitution of Al.

One may notice that not only \( \beta \) but also \( P_C \) influences the variation of \( T_C \) at high \( P \) ranges. Actually, the decrease of \( P_C \) with increasing \( y \) is confirmed by extrapolating the \( T_C-P \) line by using Eq. (1). This tendency is also opposite to that of La(Fe\(_{1-x}\)Si\(_{1.2}\))\(_{13}\), in which a broader first-order transition corresponds to the larger value of \( P_C \). Furthermore, the Landau expansion theory gives no straightforward explanation for decrease of \( P_C \) followed by a broadening of the IEM transition. To this issue, further investigations such as direct determination of \( P_C \) are necessary.

Figure 3. The Al concentration dependence of the coefficient \( \beta (\bullet) \) and the magnitude of \( |d\ln T_C/dP| (\bigcirc) \) for La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\) with \( y = 0.01, 0.02 \) and 0.03.
4. Conclusion
The influence of partial substitution of Al on the pressure effect on the Curie temperature $T_C$ has been investigated for itinerant-electron metamagnetic La$(Fe_{0.88}Si_{0.12}Al_y)_{13}$. The pressure $P$ dependence of $T_C$ shows a linear variation at low pressures, and gradually deviates from the linear variation with increasing $P$, following a line of the square-root dependence, $T_C = \beta (P_{c} - P)^{1/2}$, where $P_c$ is the critical pressure. Although the phase transition comes close to the second-order type after partial substitution, the value of $\beta$ becomes larger. In addition, the magnitude of the pressure coefficient $|d\ln T_C/dP|$ is also enhanced with increasing the Al concentration $y$. From the spin fluctuation theory of itinerant-electron metamagnetic transition, both the value of $d\ln T_C/dP$ and the thermal variation of the critical field of the itinerant-electron metamagnetic transition $\mu_0 dH_c/dT$ are highly associated with the change of thermal variation of $\xi(T)^2$. Since the decrease of $\mu_0 dH_c/dT$ with increasing $y$ indicates the small thermal variation of $\xi(T)^2$, the enhancement of pressure effect on $T_C$ of La$(Fe_{0.88}Si_{0.12}Al_y)_{13}$ is explained in terms of the change of thermal variation of $\xi(T)^2$.

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