Large Isotropic Volume Change due to Thermal-induced First-order Transition in La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$

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Abstract NaZn$_{13}$-type La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ exhibits an isotropic volume change associated with the thermal-induced first-order transition at the Curie temperature $T_C$ = 186 K. The magnitude of the isotropic volume change at $T_C$ of La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is about 1.3 %, larger than that of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. As a result, the enhancement in the local magnetic moment of Fe at $T_C$ is caused by the partial substitution of Pr. The volume change around $T_C$ of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is comparable in magnitude to that of La$_{1-z}$Ce$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ having the same $T_C$. Accordingly, the enhancement in the local magnetic moment of Fe at $T_C$ for La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is closely related with the decrease of $T_C$ without the marked decrease of thermal stability of Fe moment.

1. Introduction
NaZn$_{13}$-type 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 ferromagnetic (F) to the paramagnetic (P) states at the Curie temperature $T_C$ [1]. The thermal-induced first-order transition at $T_C$ is accompanied by a marked volume change [2, 3]. Since the cubic NaZn$_{13}$-type structure of the Fm3c space group is kept after the thermal-induced first-order transition, the volume change at $T_C$ is isotropic [2, 3]. Furthermore, $T_C$ is sensibly decreased with decreasing the unit cell volume by applying the hydrostatic pressure, though the decrease of saturation magnetization $M_s$ is not so significant [2]. Such magnetovolume effects in La(Fe$_x$Si$_{1-x}$)$_{13}$ are discussed in terms of Landau-type expansion of magnetic free energy by taking the effects of spin fluctuations and the magnetoelastic energy into account [2, 4-6]. Recently, it has been reported that La in La(Fe$_x$Si$_{1-x}$)$_{13}$ is replaced by other rare earth elements such as Ce [7], Pr [8] and Nd [9, 10]. The NaZn$_{13}$-type single phase is obtained in La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ with $z \leq 0.5$ [8]. Since the unit cell volume decreases with increasing $z$ because of the lanthanide contraction, $T_C$ is decreased from 195 K to 186 K by a partial substitution of $z = 0.5$ with keeping the thermal-induced first-order transition. In addition, $M_s$ increases with increasing $z$, and hence the magnetic moment per Pr atom is estimated to be about 3.3 $\mu_B$, very close to that of a free Pr$^{3+}$ ion, indicating that the magnetic moment of Pr is regarded as the parallel to that of Fe. As a result, the magnetization change at $T_C$ in the thermomagnetization curve becomes larger with increasing $z$. The amplitude of local magnetic moment is closely related with the volume change [11, 12]. In the present study, therefore, the volume change associated with the thermal-induced first-order transition at $T_C$ of
$La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ has been evaluated in order to investigate the influence of the partial substitution of Pr on the local magnetic moment change of Fe.

2. Experimental

NaZn$_{13}$-type $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}$ compounds were prepared by arc-melted in an argon gas atmosphere and the heat-treatments for homogenization were carried out in a vacuum quartz tube. The annealing temperature and duration were 1173 K and 10 days for $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ and 1323 K for 10 days for $La(Fe_{0.88}Si_{0.12})_{13}$. The powder x-ray diffraction measurements were made by using CuK$\alpha$ radiation. The magnetization was measured with a SQUID magnetometer.

3. Results and discussion

Figure 1 presents the temperature dependence of x-ray diffraction patterns in the 2$\theta$ region between 99 and 105° with a step interval of 0.02° for $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ with $T_C = 186$ K. Since the diffraction patterns below $T_C$ is almost the same as that at 220 K, the cubic NaZn$_{13}$-type structure is kept after the thermal-induced first-order transition. A significant shift of the pattern toward a lower angle side is observed with increasing temperature form 180 to 185 K. Accordingly, $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ exhibits an isotropic volume change associated with the thermal-induced first-order transition at $T_C$ in analogy with $La(Fe_{0.88}Si_{0.12})_{13}$[2].

Figure 2 shows the temperature dependence of the relative volume change $\Delta V/V$ evaluated from x-ray diffraction data of $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}$. The value of $T_C$ is indicated by the arrow. A marked change of $\Delta V/V$ in the vicinity of $T_C$ is observed in $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$. By using the local magnetic moment $M$ and the mean-squared amplitude of thermal spin fluctuations $\xi_2$, the contribution of the magnetism to the volume as a function of the temperature $\omega(T)$ is given as [12]

$$\omega(T) = \kappa C_{mv}\{M^2(T) + \xi_2^2(T)\}, \quad (1)$$

where $\kappa$ and $C_{mv}$ are the compressibility and the magnetovolume coupling constant, respectively. The value of $\xi_2$ increases with increasing temperature [12]. In contrast, $M$ decreases with increasing temperature and becomes zero in the P state. Therefore, the volume change associated with the thermal-induced first-order transition at $T_C$, $\Delta \omega(T_C)$, is expressed as [12];

$$\Delta \omega(T_C) = \kappa C_{mv}\{M^2(T)_{F} + \xi_2^2(T)_{P}\}, \quad (2)$$

![Fig.1 Temperature dependence of X-ray diffraction patterns in the 2$\theta$ region between 99 and 105° with a step interval of 0.02° for $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}$ with $T_C = 185$ K.](image)
Recently, we have investigated the temperature dependence of the enhancement of isotropic volume change associated with the thermal-induced first-order transition of Fe results in the large volume change at $T_C$ where $z' = 0.3$.  The volume dependence of $V/T$ for La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is mainly attributed to the increase in $M$ of Fe.  Accordingly, the enhancement of isotropic volume change associated with the thermal-induced first-order transition of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is increased by the partial substitution of Ce, although the saturation magnetization at 5 K is hardly changed [14].  In other words, the partial substitution of Ce brings about the increase in $M$ of Fe because of the decrease of the unit cell volume [14].  The magnitude of the volume change in the vicinity of $T_C$ is similar to that of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ under hydrostatic pressure.  However, the value of the spin-wave dispersion coefficient is slightly increased by the partial substitution of Ce, although the value of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ under hydrostatic pressure decreases with decreasing $T_C$ [13].  Therefore, $T_C$ of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is decreased without the marked decrease of thermal stability of Fe moment.  As a result, the magnetization change at $T_C$ is enhanced by the partial substitution of Ce, although the saturation magnetization at 5 K is hardly changed [14].  In other words, the partial substitution of Ce brings about the increase in $M$ of Fe at $T_C$, resulting in the enhancement of volume change associated with the thermal-induced first-order transition.  It should be noted that the relation between $\Delta V/V(T_C)$ and $T_C$ of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is similar to that of La$_{1-z}$Ce$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$, indicating that $M$ of Fe in the former is almost the same as that in the latter having the same $T_C$.  Therefore, it is concluded that the increase in $M$ of Fe due to the partial substitution of Pr is caused by.

where $M(T_C)$ is $M$ at $T_C$ in the F state and $\xi^2(T_C)$ is $\xi^2$ at $T_C$ in the P state.  Thus the large value of $M$ of Fe results in the large volume change at $T_C$.  Note that the magnitude of the volume change around $T_C$ of La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is about 1.3 %, clearly larger than that of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.  Accordingly, the enhancement of isotropic volume change associated with the thermal-induced first-order transition of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is given in Fig. 3, together with the data of La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

Note that the magnitude of the volume change around $T_C$ of La$_{1-z}$Ce$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is decreased without the marked decrease of thermal stability of Fe.

![Fig. 2](image-url)  Fig. 2. Temperature dependence of the relative volume change $\Delta V/V$ evaluated from X-ray diffraction data of La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.

![Fig. 3](image-url)  Fig. 3. The value of $\Delta V/V(T_C)$ associated with the thermal-induced first-order transition as a function of $T_C$ for La$_{1-z}$Pr$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ and La$_{1-z}$Ce$_z$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$.
the decrease of $T_C$ without the marked decrease of thermal stability of Fe moment.

4. Conclusion

The relative volume $\Delta V/V$ change associated with the thermal-induced first-order transition at the Curie temperature $T_C$ of La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ has been investigated. La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ exhibits an isotropic volume change at $T_C = 186$ K in a similar way of La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. The magnitude of $\Delta V/V$ at $T_C$ of La$_{0.5}$Pr$_{0.5}$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is about 1.3 $\%$, which is larger than that for La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. The value of $\Delta V/V$ associated with the thermal-induced first-order transition as a function $T_C$ of La$_{1-x}$Pr$_x$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ is comparable with that of La$_{1-x}$Ce$_x$(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. Therefore, it is concluded that the increase in the local magnetic moment of Fe at $T_C$ is connected with the decrease of $T_C$ caused by the partial substitution of Pr.

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