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Thermal expansion anomaly and pressure effect on the Curie temperature of $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds

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Abstract

The thermal expansion and specific heat measurements under ambient pressure and the thermomagnetization measurement under applied pressure for new $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds have been carried out in order to discuss the relationship between the thermal expansion anomaly and the spin fluctuations. The thermal expansion coefficient α significantly increases above the Curie temperature T_C. The electronic specific heat coefficient increases with increasing x, accompanied by the decrease of the spin fluctuation spectral width. The value of the pressure dependence of T_C, $\partial T_C/\partial P$, is large at about -50 K GPa^{-1}. The anti-invar effect and the pressure effect of T_C are closely related to a significant thermal variation of the amplitude of spin fluctuations.

1. Introduction

Magnetic properties of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds have been investigated extensively and it is reported that a ferrimagnetic state appears in Mn-rich concentration ranges [1–13]. An anomalously large thermal expansion coefficient in paramagnetic temperature regimes has been confirmed by x-ray diffraction data [12–15] and differential transformer-type dilatometic measurements [16]. This so-called anti-invar effect is observed in other Mn-based compounds such as YMn_{12} [14, 15] and YMn_2 [17].

In itinerant-electron magnetic systems, it is well known that the longitudinal amplitude of local magnetic moments $\langle M^2_{Loc}\rangle$ varies with temperature. The thermal variation of $\langle M^2_{Loc}\rangle$ contributes to the thermal expansion anomaly associated with the magnetovolume effect [18]. The magnetovolume effect has been investigated mainly in magnetically ordered states. In particular, the invar effect is one of the typical phenomena closely correlated with a pronounced magnetovolume effect. In the invar-type alloys, the thermal expansion due to phonon terms is cancelled out by a large spontaneous volume magnetostriction and the total thermal expansion becomes invariant against temperatures below the Curie temperature. It has been reported that various magnetic alloys and compounds exhibit the invar effect [19–26]. The large spontaneous volume magnetostriction is explained by a large thermal variation of the amplitude of the local magnetic moment, which is discussed in several ways such as spin fluctuations [27, 28] and/or a two-γ-states model [29–32]. In addition, the two-γ-states model was applied for an explanation of the anti-invar effect of bcc Mn [30]. In the two-γ-states model, there are two different magnetic states; a low-spin γ_1 state having a small magnetic moment with a small volume, and a high-spin γ_2 state having a large magnetic moment with a large volume [30–32]. When the energy difference between the two states is small, the excitation from a lower energy state to a higher energy one is expected [31]. It is considered that, in the anti-invar type alloys, the γ_1 state is the magnetic ordered state below the magnetic transition temperature and the γ_2 state is the paramagnetic state and the thermal excitation from γ_1 to γ_2 results in the large thermal volume expansion in the paramagnetic state [31]. Therefore, when the volume of the specimen is decreased by applying hydrostatic pressure, the magnetically ordered state γ_1 should become stable, accompanied by an increase in the Curie temperature T_C. Moreover, this phenomenological model has been adopted for explanations of both invar and anti-invar states in the $Fe_{100-x}Ni_x$ alloy system [32]. However, this model does not explain successfully the crossover from the invar effect at low temperatures to the anti-invar effect at high temperatures in a $Fe_{70}Ni_{30}$ alloy, because the thermal excitation should occur from the γ_2 to the γ_1 state at low temperatures, while the reverse occurs at high temperatures.

Recently, the thermal variation of the amplitude of the magnetic moment has been extensively discussed from the microscopic viewpoint of spin fluctuations. The amplitude of the local magnetic moment is influenced by not only exchange splitting of the 3d electron band, but also fluctuation of the local spin density i.e. spin fluctuations [18]. The amplitude of spin fluctuations increases with temperature even in paramagnetic temperature ranges and the magnetovolume effect would appear even though the spontaneous magnetization disappears in paramagnetic temperature regions [27].

In $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds, the significant magnetovolume effect in the paramagnetic state is discussed in relation to the anomalous enhancement of the spin fluctuations in paramagnetic temperatures [16]. However, systematic discussions of the magnetovolume effects below and above the magnetic ordering temperature are still not established, especially in compounds with high Mn concentrations. To investigate the spin fluctuations of itinerant 3d electrons in Mn-based compounds, the systems consisting of Mn and a non-magnetic element, such as Lu and Y, are useful. The Lu_6Mn_{23} compound has an isostructural crystal structure of Y_6Mn_{23} with a Th_6Mn_{23}-type structure and several studies of magnetic properties have been carried out [32–36]. To examine the anti-invar effect from the viewpoint of the itinerant-electron model, the substitution of Mn by other 3d elements, such as Fe, is also effective. Nevertheless, no magnetic properties of the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compound system have been reported. In the present study, for the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds, the thermal expansion anomaly over a wide paramagnetic temperature region and the pressure dependence of the Curie temperature T_C is discussed in terms of the spin fluctuations.

2. Experiment

The $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds were made by arc-melting in an Ar gas atmosphere. The ingots were turned over and re-melted four times. In order to homogenize them, the specimens were cut into sizes of about $10 \times 5 \times 5$ mm^3, and they were annealed in an evacuated-quartz tube at 873 K for 2 days, then subsequently quenched in ice water. The DC magnetic susceptibility measurement below 400 K was carried out for the bulk specimens of 10–20 mg weight with a

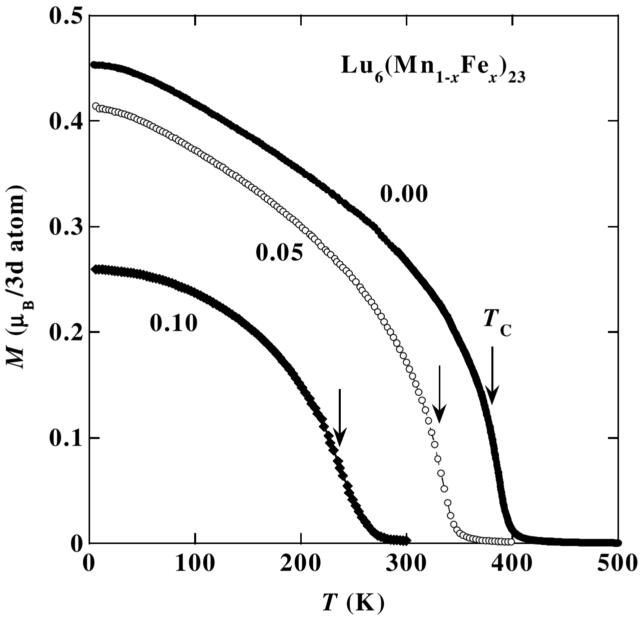

Figure 1. Thermomagnetization curves measured in a magnetic field of 0.2 T for Lu_6 $(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10. The arrows indicate the Curie temperature T_C.

superconducting quantum interference device (SQUID) magnetometer. The thermal expansion measurements were carried out with a differential transformer-type dilatometer from 300 to 900 K for the specimen size of about $8 \times 3 \times 3$ mm^3, in addition to x-ray powder diffraction measurements from 10 to 300 K. The specific heat measurements were made by a relaxation method below 200 K for the same specimen used for the DC susceptibility measurement, and by an AC optical method above 100 K for the plane shape specimen with thickness of about 100–200 μm. The thermomagnetization under pressure was measured with an extraction-type magnetometer below 290 K by using the same specimen as in the DC susceptibility measurement. Pressure up to 1 GPa was applied to the specimen with a nonmagnetic pressure clamp cell made of a Cu-3 wt% Ti alloy. The applied hydrostatic external pressures at low temperatures were calibrated by measuring the shift of the superconducting transition temperature of Pb [37].

3. Results and discussion

The formation of $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds with the Th_6Mn_{23}-type structure below $x = 0.10$ has been confirmed from x-ray powder diffraction patterns. The thermomagnetization curves in a magnetic field of 0.2 T for the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds are shown in figure 1. The Curie temperature T_C, identified as the inflection point of the curves, decreases with increasing x, as shown by the arrows. The inverse magnetic susceptibility $1/\chi$ curves of Lu_6Mn_{23} and $Lu_6(Mn_{0.95}Fe_{0.05})_{23}$ are shown in figure 2 together with that of Y_6Mn_{23}, for comparison. A significant convex curvature of $1/\chi$ as a typical feature of ferrimagnets is observed in all the specimens. Accordingly, it is concluded that the ferrimagnetic structure is also established below T_C in the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds.

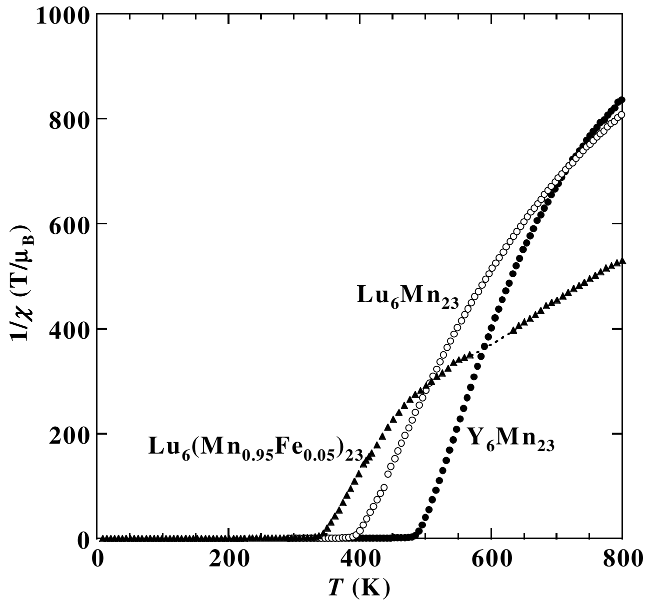

Figure 2. Temperature dependence of the inverse susceptibility for $Lu_6(Mn_{0.95}Fe_{0.05})_{23}$, together with Lu_6Mn_{23} and Y_6Mn_{23} compounds.

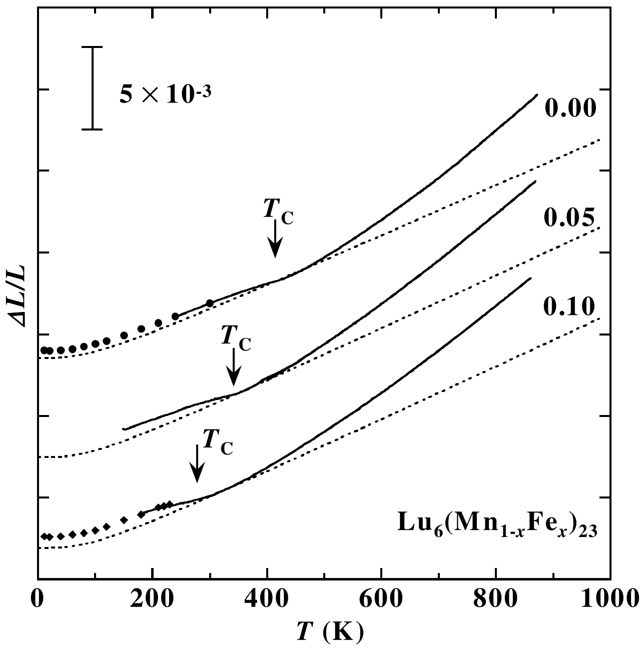

Figure 3. Thermal expansion curves of $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10. The arrows indicate the Curie temperature T_C.

The linear thermal expansion curves from 300 to 900 K are shown by the full curves in figure 3, together with the full symbols obtained by x-ray powder diffraction measurements.

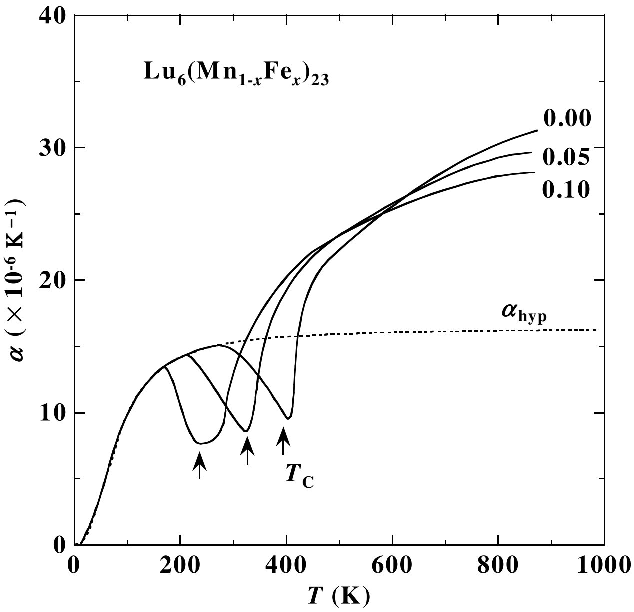

Figure 4. Temperature dependence of the thermal expansion coefficient α for $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10. The thin dotted curve is a hypothetical nonmagnetic thermal expansion coefficient.

The arrows stand for T_C determined from figure 1. The broken curves denote a phonon term obtained from the Debye model using the Debye temperature $\Theta_D = 290$ K determined from the specific heat data discussed in figure 6. The slope of the observed curve above T_C is much larger than that of the phonon term. In order to clarify the thermal expansion anomaly over a wide temperature range, the temperature dependence of the linear thermal expansion coefficient α obtained from figure 3 is depicted in figure 4. The pronounced decrease of α occurs at T_C and α exhibits a steep increase with a positive curvature above T_C. Such a peculiar temperature dependence is observed in all the specimens and the value of α at high temperatures, around 900 K, decreases with increasing x. For the compound with $x = 0.00$ ($\equiv Lu_6Mn_{23}$), the value of α goes up to 32×10^{-6} K^{-1}, being about twice as large as the value below T_C. This anomalously large thermal expansion coefficient can be attributed to the anti-invar effect.

In order to explain the anomaly of thermal expansion characteristics over the whole temperature range, the influence of the spin fluctuations is taken into account. The thermal expansion coefficient α is expressed by

$$\alpha = \alpha_{ph} + \alpha_{el} + \alpha_{mag}, \tag{1}$$

where α_{ph}, α_{el} and α_{mag} are, respectively, the phonon, electron and magnetic terms. With increasing temperature, α_{el} generally increases in proportion to temperature with the rate of the order of 10^{-9} K^{-2}. Therefore, its contribution is smaller than other terms even at high temperatures, such as 900 K. Therefore, the hypothetical nonmagnetic coefficient α_{hyp} is expressed as

$$\begin{aligned}\alpha_{hyp} &\approx \alpha_{ph} \\ &\propto C_v^{ph},\end{aligned} \tag{2}$$

where C_v^{ph} is the specific heat at the constant volume of the phonon term. The result of α_{hyp}

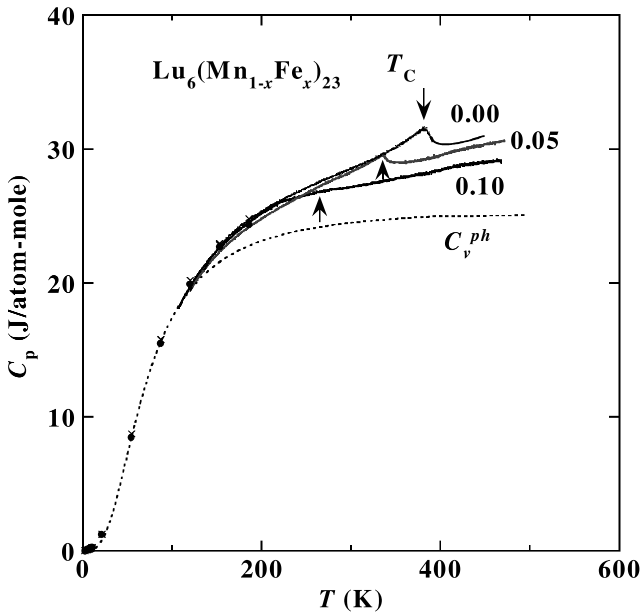

Figure 5. Temperature dependence of the specific heat of $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds. The value at the low temperatures given by the dotted curve is obtained by using the Debye model.

evaluated from the relation (2) is given by the broken curve in figure 4. The curve of the specific heat of the phonon term at constant volume C_v^{ph} is obtained by fitting with the Debye model, using $\Theta_D = 290$, to the data below 120 K as given by the broken curve in figure 5. Note that the Debye temperature depends on temperature, especially for the present system significantly influenced by the magnetic term. Therefore, it is difficult to obtain definitely the Debye temperature, resulting in an error of about ± 10 K. The phonon term α_{ph} follows the Dulong–Petit law above the Debye temperature Θ_D, and hence α_{ph} increases slowly, as shown in figure 4. According to equations (1) and (2), the magnetic term α_{mag} is obtained by subtracting α_{hyp}, given by the broken curve, from the experimental α, given by the full curve in figure 4. At low temperatures, the difference between α and α_{hyp} is hardly observed. However, the value of α_{mag} becomes negative while approaching T_C with increasing temperature. Therefore, the spontaneous volume magnetostriction exists below T_C. On the other hand, a large positive value of α_{mag} at high temperatures above T_C implies the appearance of the anti-invar effect. The thermal expansion and specific heat properties are strongly related to each other. In the present system, a notable thermal expansion anomaly has been observed. In such a system, the magnetic contribution could also be observed in the specific heat data, especially near T_C and also at low temperatures where the influence of spin fluctuations appears in the electronic term.

The temperature dependence of the specific heat in wide temperature regions for the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds is given in figure 5. The symbols denote the data obtained from a relaxation method and the curves denote the data obtained from an AC optical method. The arrows denote T_C obtained from figure 1. At high temperatures, the phonon term C_v^{ph} increases slowly and approaches $3R \approx 25$ J/atom-mol (where R is the gas constant), following the Dulong–Petit law. However, the present data exceed $3R$ even in the temperature range 50–100 K higher than T_C, implying a large contribution of spin fluctuations to the heat capacity

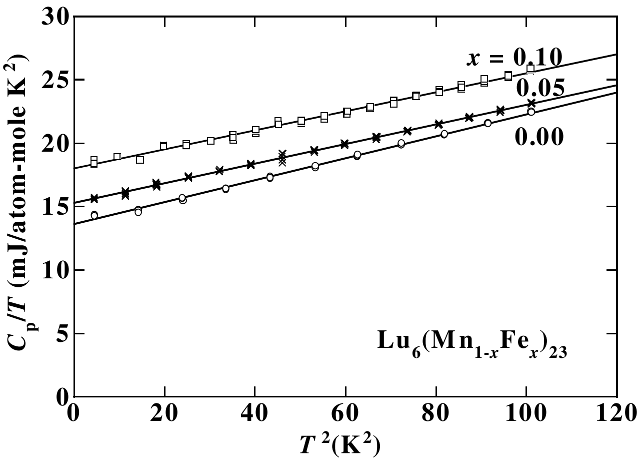

Figure 6. The specific heat in the form of C_p/T versus T^2 for the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds.

at paramagnetic temperatures. The cusp of the second-order phase transition is observed near T_C for $x = 0.00$ and 0.05. The height of the cusp decreases with increasing x. The cusp of the specific heat is related to the increase of the magnetic entropy. In the localized magnetic moment system, the increase of the magnetic specific heat below T_C is related to the value of the magnetic moment and the thermal increase of the transverse fluctuation. In a paramagnetic temperature range, the short wavelength spin fluctuations having the antiferromagnetic correlation attenuate rapidly, and hence the magnitude of discontinuity of the magnetic specific heat at T_C becomes large. On the other hand, in the itinerant-electron magnets, the longitudinal amplitude of local magnetic moment decreases with increasing temperature below T_C, related to the increase of the long wavelength spin fluctuations. Then the short lifetime antiferromagnetic correlation still remains at paramagnetic temperatures. Therefore, the height of the specific heat cusp becomes small in the present system, and the broadening of the cusp at T_C with increasing x implies that a more significant thermal reduction of the longitudinal amplitude of magnetic moment occurs below T_C.

The electronic term of the low temperature specific heat reflects the value of the density of states at the Fermi level as well as the enhancement of spin fluctuations [38]. To observe the contribution from the spin fluctuations, the low temperature specific heat measurements were carried out. The specific heat data in the form of C_p/T versus T^2 indicate straight lines, as given in figure 6. The value of the electronic specific heat coefficient, γ, obtained from the intercept of the C_p/T–T line at $T = 0$ K, increases with increasing x. The values of γ for the present compounds are about twice as large as that of non-magnetic pure 3d elements of about several mJ mol^{-1} K^{-2}. Such a significant enhancement of γ should be attributed to the spin fluctuation excitations. The value of γ enhanced by spin fluctuations γ_{SF} is expressed as

$$\gamma_{SF} = \frac{3\pi N_0}{\Gamma_0 q_B^2}, \tag{3}$$

where Γ_0 is the spectral width of excitations of spin fluctuations against energy, q_B is the wavenumber at the effective zone boundary and N_0 is the number of atoms [38]. For a large Γ_0, the spectral intensity of the higher energy side increases, and hence the low energy excitations decrease and result in a small γ_{SF}, whereas a smaller Γ_0 gives a larger γ_{SF}. Since γ increases with increasing x, Γ_0 decreases systematically, and hence results in the increase

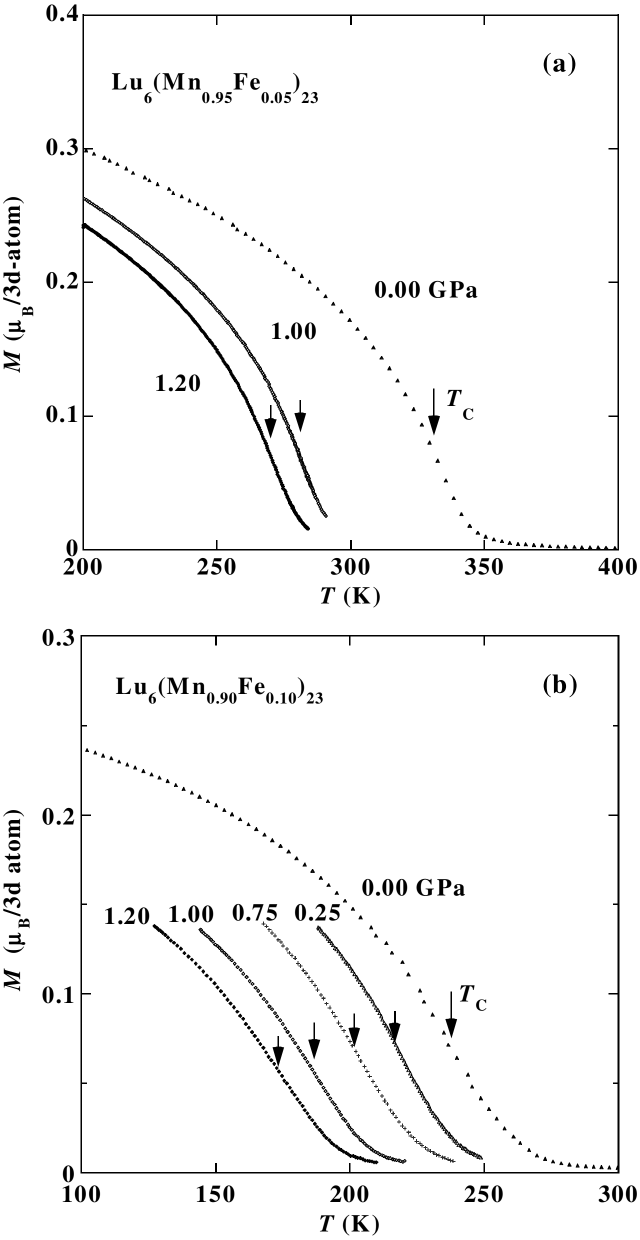

Figure 7. Thermomagnetization curves under different several pressures for $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds. (a) $Lu_6(Mn_{0.95}Fe_{0.05})_{23}$, (b) $Lu_6(Mn_{0.90}Fe_{0.10})_{23}$.

of low energy excitations. The value of α in high temperatures above T_C is more significant in larger Γ_0, implying that the anti-invar effect appears when the low energy excitations of spin fluctuations decrease.

The thermomagnetization curves obtained under different several hydrostatic pressures for $Lu_6(Mn_{0.95}Fe_{0.05})_{23}$ and $Lu_6(Mn_{0.90}Fe_{0.10})_{23}$ compounds are shown in figures 7(a) and (b), respectively. The Curie temperature T_C determined from the inflection point of the curves

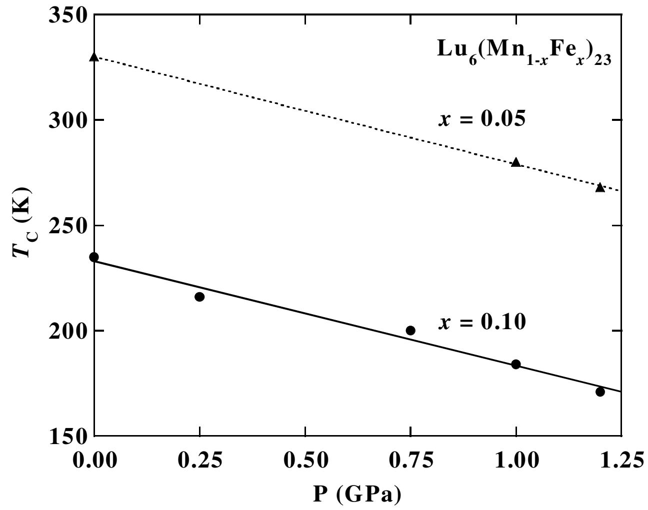

Figure 8. Pressure dependence of T_C for the $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds. The value of $\partial T_C/\partial P$ is estimated to be about -50 K GPa^{-1}.

decreases with increasing pressure, as shown by the arrows. The pressure dependence of T_C is shown in figure 8. As shown in figure, T_C decreases linearly with increasing pressure. The value of $\partial T_C/\partial P$ is estimated to be about -50 K GPa^{-1}, comparable to the value of conventional invar-type alloys having a very large value [29].

In the two-γ-states model, the anti-invar effect is explained as a result of excitation from a low-spin γ_1 state with a small volume to a high-spin γ_2 state with a large volume with increasing temperature [28–31]. When the ferrimagnetic state below T_C is supposed to be the γ_1 state and the paramagnetic state above T_C is supposed to be the γ_2 state, the value of T_C should increase on applying hydrostatic pressure, because the energy minimum of the small volume ferrimagnetic γ_1 state shifts to the lower energy side and becomes more stable than that of a large volume paramagnetic γ_2 state. However, the present dependence of T_C on pressure is contrasted with the two-γ-states model. In the present study, therefore, the anti-invar effect and the pressure effect of T_C are discussed in terms of spin fluctuations.

The thermal variation of the spin fluctuations is reflected in the spontaneous volume magnetostriction $\omega_{mag}(T)$. The value of $\omega_{mag}(T)$ is related to the following expression: given by

$$\omega_{mag}(T) \propto \langle M_{Loc}^2(T)\rangle, \tag{4}$$

where $\langle\ \rangle$ is the thermal average of amplitude of the local magnetic moment [18, 39]. The following expression gives the relation between the thermal expansion coefficient of the magnetic term $\alpha_{mag}(T)$ and the temperature differential of $\langle M_{Loc}^2(T)\rangle$ [18, 39]:

$$\alpha_{mag}(T) = \frac{1}{3}\frac{\partial\omega_{mag}(T)}{\partial T} \propto \frac{\partial\langle M_{Loc}^2(T)\rangle}{\partial T}, \tag{5}$$

with

$$\langle M_{Loc}^2(T)\rangle = m^2(T) + \langle\xi^2(T)\rangle,$$

where $\langle\xi^2(T)\rangle$ and $m^2(T)$ are the mean-square amplitude of spin fluctuations and the square uniform magnetization, respectively. With increasing temperature, $\langle\xi^2(T)\rangle$ increases, whereas $m^2(T)$ decreases. In the paramagnetic state, where $m^2(T) = 0$, the amplitude of local magnetic

Table 1. The values of $\partial T_C/\partial P$ and $\partial \ln T_C/\partial P$ for $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.05$ and 0.10.

Compound	$\partial \ln T_C/\partial P$(K GPa^{-1})	$\partial \ln T_C/\partial P$
$Lu_6(Mn_{0.95}Fe_{0.05})_{23}$	−50	−0.15
$Lu_6(Mn_{0.90}Fe_{0.10})_{23}$	−50	−0.22

moments $\langle M^2_{Loc}(T)\rangle$ increases with increasing $\langle\xi^2(T)\rangle$. When the thermal increase of $\langle\xi^2(T)\rangle$, $\partial\langle\xi^2(T)\rangle/\partial T$, is large, i.e. the local moment is soft in the longitudinal direction, the anti-invar effect is observed. The spin fluctuations are characterized by the longitudinal and the exchange stiffness [27]. In the weakly ferromagnet limit, where collective spin fluctuations are dominant and the exchange interaction depends on the wavevector $\boldsymbol{q}$, the spin fluctuation spectral width Γ_0 is proportional to the inverse of the longitudinal stiffness constant $1/T_0$ [27]. Therefore, in the large Γ_0, the longitudinal stiffness constant $1/T_0$ becomes small, and hence the ratio of $\partial\langle\xi^2(T)\rangle/\partial T$ becomes large. In $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds, the local magnetic moment of about 2 μ_B for $x = 0.00$ is confirmed by a neutron diffraction study [9]. Therefore the single-site spin fluctuations are more dominant, compared with the collective spin fluctuations. It is also expected that in ferrimagnetic $Lu_6(Mn_{1-x}Fe_x)_{23}$, the spin fluctuation should exhibit single-site characteristics. It has been confirmed that a similar relation between $1/T_0$ and Γ_0 holds even for the single-site spin fluctuations with constant exchange interaction in the $\boldsymbol{q}$ space, and hence $\partial\langle\xi^2(T)\rangle/\partial T$ becomes larger in the larger Γ_0 as well as weakly ferromagnetic systems [27]. According to equations (4) and (5), the thermal variation of the spontaneous volume magnetostriction $\Delta\omega_{mag}$ below T_C is obtained as

$$\Delta\omega_{mag} = \omega_{mag}(0) - \omega_{mag}(T_C) \propto m^2(0) - \langle\xi^2(T_C)\rangle. \tag{6}$$

where $m^2(0)$ is m^2 at 0 K and $\langle\xi^2(T_C)\rangle$ is $\langle\xi^2(T)\rangle$ at T_C, respectively [18]. The amplitude of $\langle\xi^2(T_C)\rangle$ becomes larger with increasing T_C and $\partial\langle\xi^2(T)\rangle/\partial T$, namely, when Γ_0 is large as the compound with $x = 0.00$. In the present compound system, T_C and $\partial\langle\xi^2(T)\rangle/\partial T$ decrease, and hence $\langle\xi^2(T_C)\rangle$ decrease with increasing x. On the other hand, the decrease of $m^2(0)$ with increasing x is expected from the analogy of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds, related closely with Hund's rule [9, 16]. Even $m^2(0)$ is small, $\Delta\omega_{mag}$ exhibits a large value when $\langle\xi^2(T_C)\rangle$ is small as the compound with $x = 0.10$. There is the thermodynamical relation between the volume variation due to the phase transition and the pressure effect of T_C as expressed in Ehrenfest's relation such as

$$\frac{\partial \ln T_C}{\partial P} = V\frac{\Delta\alpha}{\Delta C_{mag}}, \tag{7}$$

where V is the volume of the system and ΔC_{mag} is the change of the magnetic specific heat $C_{mag}(T)$ between the phase transition. The value of $C_{mag}(T)$ could be roughly estimated from the difference between the experimental data and $C_v^{ph}(T)$ shown in figure 5. As mentioned above, the thermal reduction of $\langle M^2_{Loc}(T)\rangle$ becomes large, while the height of the cusp at T_C and ΔC_{mag} decrease with increasing x. On the other hand, as shown in figure 4, the change of $\alpha(T)$ between the phase transition $\Delta\alpha$ is almost the same for all specimens, and hence the values of $\Delta\omega_{mag}$ are comparable with each other. Therefore, according to equation (6), the absolute value of the pressure coefficient $\partial \ln T_C/\partial P$ becomes large with increasing x. In the present result, the value of $\partial T_C/\partial P$ for $x = 0.05$ is almost the same as that of $x = 0.10$, though $\partial \ln T_C/\partial P$ becomes −0.15 for the former and −0.22 for the latter, as shown in table 1.

The feature of the spin fluctuations which brings about the anti-invar effect in the present system is characterized by the significant thermal increase of amplitude of the local magnetic moment related to the high energy excitations of spin fluctuations. The thermal increase of amplitude of the local magnetic moment systematically decreases with increasing x, accompanied by the increase of the low energy with long wavelength spin fluctuation excitations.

4. Conclusion

The thermomagnetization, thermal expansion characteristics, specific heat and pressure effects on the Curie temperature T_C of $Lu_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10 have been investigated. A pronounced large thermal expansion coefficient α above T_C and a large magnitude of $\partial \ln T_C/\partial P$ are discussed in terms of the spin fluctuations. The main results are summarized as follows:

(a) The significant increase of the thermal expansion coefficient α above T_C, that is, the anti-invar effect, is explained by means of spin fluctuations.
(b) The electronic specific heat coefficient γ increases with increasing x, suggesting the decrease of the spin fluctuations spectral width Γ_0.
(c) The pressure effect of the Curie temperature, $\partial T_C/\partial P$, is about -50 K GPa^{-1}, comparable with that of conventional invar-type alloys.
(d) The absolute value of the pressure coefficient $\partial \ln T_C/\partial P$ increases with increasing x, suggesting that the itinerant-electron characteristics becomes more significant with increasing x.
(e) The concentration dependences of the anti-invar effect and the value of $\partial \ln T_C/\partial P$ are considered to originate from the variation of the spectral width in spin fluctuations with the concentration.

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