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Anti-invar behaviour due to spin fluctuations in $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds

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Abstract

The thermal expansion and low-temperature specific heat measurements for $Y_6(Mn_{1-x}Fe_x)_{23}$ 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. This behaviour, the so-called anti-invar characteristic, is attributed to a remarkable increase of the amplitude of spin fluctuations in paramagnetic temperature regions. The anti-invar characteristic becomes weaker with increasing x. The temperature dependence of the thermal expansion coefficient of the magnetic term α_{mag} is convex upward in the paramagnetic temperature range, which is explained within the framework of spin fluctuations.

1. Introduction

It is well known that the longitudinal amplitude of local magnetic moments $\langle M_{Loc}^2 \rangle$ varies with temperature due to spin fluctuations in itinerant-electron magnetic systems. The thermal variation of $\langle M_{Loc}^2 \rangle$ contributes to the thermal expansion anomaly as the magnetovolume effect [1]. Magnetic properties of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds have been investigated extensively and it has been reported that a ferrimagnetic state appears in Mn-rich concentration ranges [2–14]. An anomalous thermal expansion caused by a spontaneous volume magnetostriction below the Curie temperature has been confirmed by x-ray diffraction [13–16]. In a previous paper, an anomalous thermal expansion in a wide paramagnetic temperature range, several hundred centigrade, was attributed to a short-range magnetic order [14]. However, in general, it is considered that such a short-range magnetic order cannot remain over a wide temperature range after the collapse of a long-range magnetic order. Therefore, such an anomalous enhancement of the thermal expansion coefficient should be explained by another mechanism.

The invar effect is closely correlated with a large magnetovolume effect and the thermal expansion becomes invariant against temperature below the Curie temperature. The invar effect

in fcc $Fe_{65}Ni_{35}$ alloy was investigated more than a century ago and a number of experimental and theoretical studies have been carried out to date; it has been reported that various alloys and compounds exhibit the invar effect [17–24]. The large spontaneous volume magnetostriction mentioned above is explained by a large temperature variation of the amplitude of the local magnetic moment, which is discussed in several ways such as thermal spin excitations, i.e. spin fluctuations [25, 26] and/or the two-γ-state model [27–30]. Moreover, the two-γ-state model was adopted for explanation of the anti-invar behaviour in Mn. In this model, there are two different magnetic states: the low-spin γ_1 state, having a small magnetic moment with a small volume, and the high-spin γ_2 state, having a large magnetic moment with a large volume [27–30]. When the energy difference between two states is small, a magnetic moment instability is liable to occur [29]. It is considered that the anti-invar behaviour is developed when the thermal activation from the γ_1 state to the γ_2 state increases above the magnetic transition temperature and the thermal expansion becomes anomalously large [29]. This phenomenological model is adopted for explanations of the invar and anti-invar effects in the $Fe_{100-x}Ni_x$ alloy system [30]. However, it would be difficult to explain the transition from the invar at low temperatures to the anti-invar effects at high temperatures in $Fe_{70}Ni_{30}$ alloy [20], because the transition should occur in the sequence $\gamma_2 \rightarrow \gamma_1 \rightarrow \gamma_2$ in this model. On the other hand, it is well known that the magnetovolume effect is caused by the thermal amplitude of the magnetic moment. In well defended local magnetic moment systems, the amplitude of spin fluctuations also reflects the amplitude of the local magnetic moment [1]. The spin fluctuations originate from the thermal excitation of spins, and hence increase with increasing temperature. When the amplitude of spin fluctuations is large, the magnetovolume effect will appear even in paramagnetic temperature regions.

Available results of the thermal expansion characteristics for $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds have been obtained from x-ray powder diffraction data [14–16], so the detailed temperature dependence is not clear, especially in the vicinity of the Curie temperature. Therefore, the precise thermal expansion measurements are necessary for more detailed discussions. In the present study, the low-temperature specific heat and the thermal expansion anomaly over a wide paramagnetic temperature region are discussed in terms of the spin fluctuations without any assumption of thermally activated transition between the different states in ferrimagnetic $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds.

2. Experimental details

$Y_6(Mn_{1-x}Fe_x)_{23}$ 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, they were annealed in an evacuated quartz tube at 873 K for 2 days and subsequently quenched into ice water. The DC magnetic susceptibility measurement was carried out with a SQUID magnetometer below 400 K, and with a vibration sample magnetometer above 400 K. The specific heat was measured from 4.2 to 300 K by a relaxation method. The thermal expansion measurements were carried out with a differential transfer-type dilatometer from 300 to 900 K in addition to x-ray powder diffraction measurements from 10 to 300 K.

3. Results and discussion

The thermomagnetization curves in the magnetic field of 0.2 T for $Y_6(Mn_{1-x}Fe_x)_{23}$ ferrimagnetic compounds are shown in figure 1. The Curie temperature T_C conventionally determined from the inflection point of the curves decreases with decreasing x as shown by

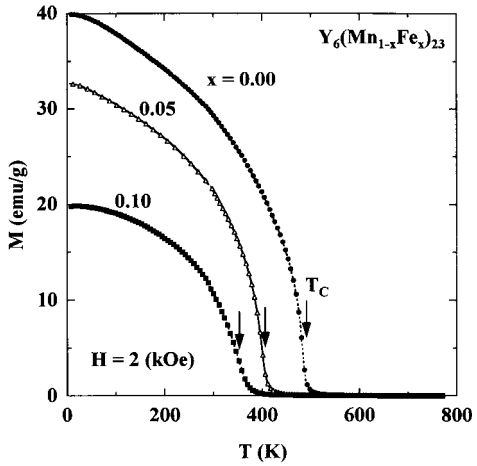

Figure 1. Thermomagnetization curves measured in a magnetic field of 0.2 T for $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10. The arrows indicate the Curie temperature T_C.

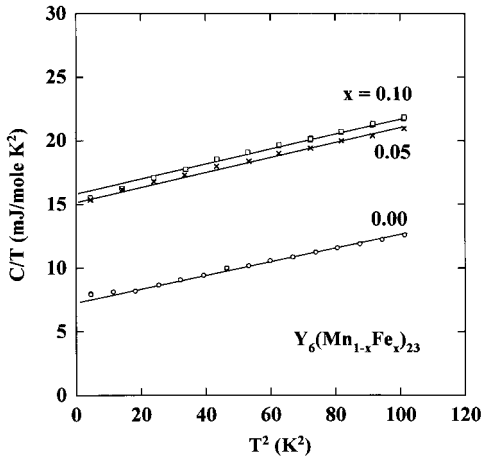

Figure 2. The specific heat in the form of C/T versus T^2 for $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds.

the arrows. It is well known that the low-temperature specific heat reflects the value of the density of states at Fermi level as well as the enhancement effect by spin fluctuations [31]. To observe the spin-fluctuation behaviour, the low-temperature specific heat measurement was carried out. The specific heat data in the form of C/T versus T^2 show straight lines as shown in figure 2. The value of the electronic specific heat data coefficient γ, that is, the value of C/T at $T = 0$ K, shows a significant concentration dependence, and the values of γ for $x = 0.05$ and 0.10 are rather large for 3d-element systems [31]. Such a remarkable enhancement of γ may be caused by the change of spin fluctuations characteristics. The value of γ enhanced by spin fluctuations γ_{SF} is expressed by

$$\gamma_{SF} = \frac{3\pi N_0}{\Gamma_0 q_B^2}, \tag{1}$$

where Γ_0 is the spectrum width of spin fluctuation excitations against energy, q_B is the magnitude of the effective zone boundary and N_0 is the number of atoms [31]. In the case

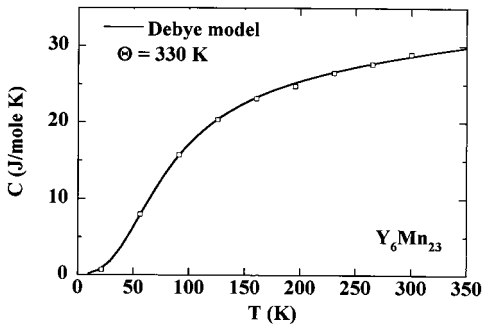

Figure 3. Temperature dependence of the specific heat of the Y_6Mn_{23} compound. The solid curve is obtained by using the Debye model.

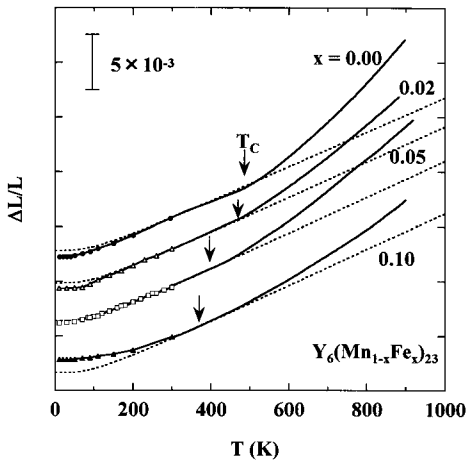

Figure 4. Thermal expansion curves of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00, 0.05$ and 0.10. The arrows indicate the Curie temperatures T_C determined from the thermomagnetization curves in figure 1.

of a small γ_{SF} for the compound with $x = 0.00$, Γ_0 is large and the spectrum is broad and the frequency of low-energy excitations becomes low. On the other hand, for a large γ_{SF}, Γ_0 becomes small and the low-energy spin-fluctuation excitation becomes frequent in the case of the compounds with $x = 0.05$ and 0.10. Therefore, the spin-fluctuation excitations appear from low temperatures. The variation of γ with increasing x suggests a change in the characteristics of spin fluctuations. The spin-fluctuation characteristics would also be reflected in the thermal expansion. The Debye temperature Θ determined from these plots is not so sensitive to x, being about $\Theta = 330 \pm 10$ K.

The temperature dependence of the specific heat C for the Y_6Mn_{23} compound measured under zero magnetic field is shown in figure 3. The excellent fitted solid curve was obtained from the Debye model by using the Debye temperature $\Theta = 330 \pm 10$ K determined from figure 2.

The linear thermal expansion curves $\Delta L/L$ from 300 to 900 K are shown by the solid curves in figure 4, together with the solid and open symbols obtained by x-ray powder diffraction measurements. The arrows represent T_C determined from figure 1. The dashed curves denote a phonon term estimated from figure 3. The slope of the expected curve above

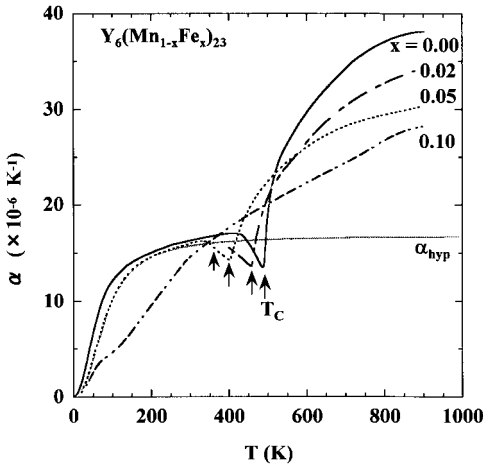

Figure 5. Temperature dependence of the thermal expansion coefficient curves of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10. The thin dotted curve is a hypothetic non-magnetic thermal expansion coefficient.

T_C is much larger than that of the phonon term due to anti-invar behaviour. It should be emphasized that a slight negative magnetovolume effect is observed below T_C in the compound with $x = 0.00$. With increasing x, the negative magnetovolume effect is diminished and no magnetovolume effect is observed in the specimen with $x = 0.05$. Ultimately a positive magnetovolume effect appears in the compound with $x = 0.10$. That is, a gradual change from negative to positive for the magnetovolume effect is observed with increasing x. 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 4 is depicted in figure 5. The pronounced decrease of α at T_C occurs in the compounds with $x = 0.00$, 0.02 and 0.05, and α exhibits a steep increase with a positive curvature above T_C. Such peculiar temperature dependence is observed in all the specimens and the value of α at high temperatures, say around 900 K, decreases with increasing x. For the compound with $x = 0.00$ ($\equiv Y_6Mn_{23}$), the value of α goes up to about 40×10^{-6} K^{-1}, being more than twice as large as the value below T_C. Such a significantly large value of α over a wide paramagnetic temperature range would be difficult to attribute to a short-range magnetic order [14]. Consequently, this anomalously large thermal expansion can be connected with the so-called anti-invar behaviour.

We explain this anomalous thermal expansion characteristic by taking the spin fluctuations in the paramagnetic temperature range into consideration. The thermal expansion coefficient α is expressed by

$$\alpha = \alpha_{ph} + \alpha_{el} + \alpha_{mag}, \tag{2}$$

where α_{ph}, α_{el} and α_{mag} are respectively the phonon, electron and magnetic terms. When the magnetic contribution to the thermal expansion is small in paramagnetic temperature regions, the phonon term α_{ph} should follow the Dulong–Petit law up to high-temperature regions, i.e. above the Debye temperature, and then converge to a constant value. With increasing temperature, generally, α_{el} increases linearly with the order of 10^{-9}–10^{-8} K^{-2} [32]. The value of α of the present compounds does not show such a characteristic temperature dependence but an extremely large increase. These results strongly imply a large magnetic contribution to the thermal expansion anomaly even in paramagnetic temperature ranges. Therefore, it is

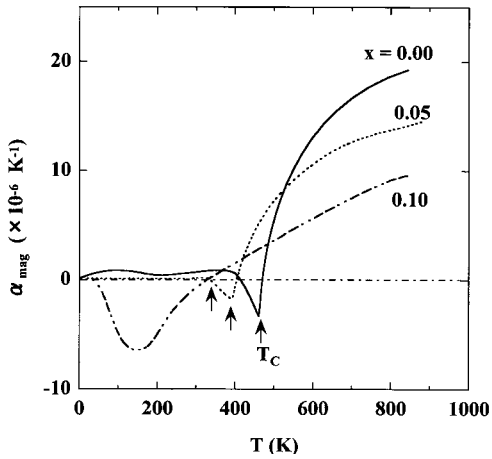

Figure 6. Temperature dependence of the magnetic term α_{mag} for the thermal expansion coefficient of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds.

necessary to separate the α_{mag} term from the others. The hypothetic nonmagnetic coefficient α_{hyp} is expressed as follows:

$$\alpha_{hyp} = \alpha_{ph} + \alpha_{el} \propto (C_v^{ph} + C_v^{el}), \tag{3}$$

where C_v^{ph} and C_v^{el} are the specific heats of the phonon and electron terms, respectively. The temperature dependence of α_{mag} can be estimated from equations (2) and (3). The value of α_{hyp} in figure 5 is estimated from the specific heat data shown in figure 3.

The temperature dependence of α_{mag} for the compounds with $x = 0.00$, 0.05 and 0.10 is shown in figure 6. The value of α_{mag} decreases with increasing x above T_C. On the other hand, α_{mag} of the compound with $x = 0.00$ becomes positive below T_C, where the negative magnetovolume effect was observed in figure 4. The value of α_{mag} is nearly zero below T_C for the compounds with $x = 0.05$, and with 0.10 it becomes negative where the positive magnetovolume effect is observed in figure 4. The behaviour below T_C suggests a gradual change of the magnetic contribution to the thermal expansion anomaly, which is also observed in the low-temperature specific heat as shown in figure 3. In the two-γ-state model, the anti-invar effect is explained as the change of the energy minimum from the low-spin γ_1 state to the high-spin γ_2 state with increasing temperature [30]. Therefore, the invar effect is explained in the opposite way; that is, the thermal activation occurs from the γ_2 state to the γ_1 state [30]. For the compound with $x = 0.10$ in figure 4, however, α_{mag} shows a negative value below T_C, and a positive value above T_C. In other words, the invar effect below T_C and the anti-invar effect above T_C are observed. To explain both the effects within the two-γ-state model, unrealistic transitions, $\gamma_2 \rightarrow \gamma_1 \rightarrow \gamma_2$, should be presumed with increasing temperature.

In a system with 3d electron number nearly $N = 5$, corresponding to Mn and its alloys and compounds, the antiferromagnetic correlation between the nearest atoms become stable [33,34]. In such metals and alloys, the local electron correlation plays a crucial role [35]. Both charge and spin fluctuations are due to thermal excitations of electrons. With enhancement of the local electron correlation, the charge fluctuations decrease, whereas the spin fluctuations increase [35]. Since the local electron correlation restricts the charge transfer between atoms, the charge fluctuations are suppressed and the wavevector component of spin fluctuations should have a limited distribution around a certain wavevector. This behaviour is observed in paramagnetic compounds such as the $Y(Sc)Mn_2$ system [36]. Due to the existence of the intra-

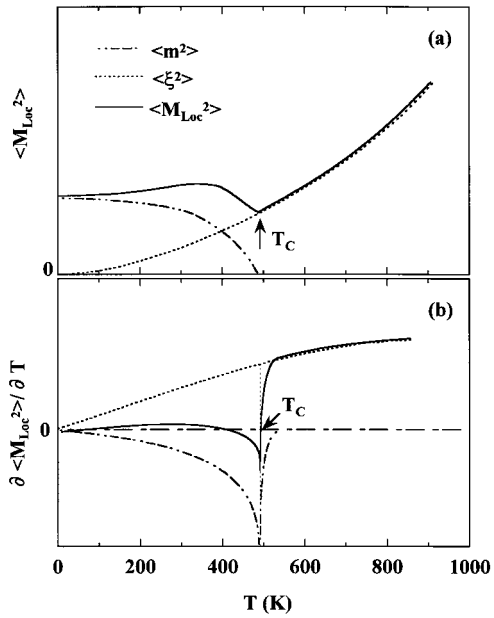

Figure 7. (a) Schematic thermal variations of the amplitude of local magnetic moment $\langle M_{Loc}^2 \rangle$ (solid curve), the spin fluctuations $\langle \xi^2 \rangle$ (dotted curve) and the uniform magnetization due to the magnetic order $\langle m^2 \rangle$ (broken curve) under the condition of a large thermal increase of $\langle \xi^2 \rangle$. (b) Temperature dependence of the partial derivative of $\langle M_{Loc}^2 \rangle$, $\langle \xi^2 \rangle$ and $\langle m^2 \rangle$.

atomic exchange interaction, the local electron correlations cause the formation of localized magnetic moment even in the paramagnetic phase [33]. The amplitude of local magnetic moments $\langle M_{Loc}^2 \rangle$ increases with increasing thermal spin excitations. With increasing x, the 3d electron number diverges from $N = 5$ and the reduction of the local electron correlations occurs [35]. Consequently, the charge fluctuations become large, resulting in the reduction of thermal spin fluctuations. In the magnetic ordered phase, the charge fluctuations make the local magnetic moment unstable [33], reducing the tendency of the formation of local magnetic moment. The nature of the spin fluctuations in the present system can be characterized in terms of the large amplitude of local magnetic moment and the incollective thermal spin excitations, because the large temperature variation of spin-fluctuation amplitude originates from the formation of local magnetic moment.

The spin-fluctuation characteristic is reflected in the spontaneous volume magnetostriction ω_{mag}. The value of ω_{mag} is related to the following expression:

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

where $\langle\ \rangle$ is the thermal average of the amplitude of local magnetic moment [1]. The following expression gives the relation between the thermal expansion coefficient of the magnetic term α_{mag} and the differential of $\langle M_{Loc}^2 \rangle$ [1].

$$\alpha_{mag} \propto \frac{\partial \langle M_{Loc}^2 \rangle}{\partial T}, \tag{5}$$

$$\langle M_{Loc}^2 \rangle = \langle m^2 \rangle + \langle \xi^2 \rangle, \tag{6}$$

where $\langle \xi^2 \rangle$ and $\langle m^2 \rangle$ are the mean-squared amplitude of spin fluctuations and uniform magnetization, respectively. We consider the thermal variations of $\langle M_{Loc}^2 \rangle$, $\langle m^2 \rangle$ and $\langle \xi^2 \rangle$ for the compounds with $x = 0.00$ and 0.10, which is schematically given in figures 7

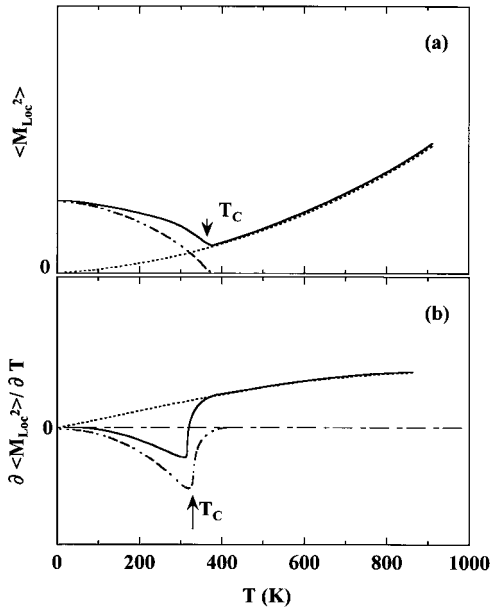

Figure 8. Schematic thermal variations for three parameters given in figure 7 in the case of a small increase of $\langle \xi^2 \rangle$.

and 8, respectively. With increasing temperature, the term $\langle m^2 \rangle$ decreases, whereas the term $\langle \xi^2 \rangle$ increases. To explain the behaviour of α_{mag} for the compound with $x = 0.00$, the thermal increase of $\langle \xi^2 \rangle$ should be very large, rather than the decrease of $\langle m^2 \rangle$ as shown in figure 7(a). Accordingly, the temperature range where $\partial \langle M_{Loc}^2 \rangle / \partial T$ becomes positive, which is proportional to α_{mag}, appears below T_C, and hence $\partial \langle M_{Loc}^2 \rangle / \partial T$ becomes extremely large in the paramagnetic temperature region as shown in figure 7(b). On the other hand, if the thermal increase of $\langle \xi^2 \rangle$ is smaller than the thermal decrease of $\langle m^2 \rangle$ as shown in figure 8(a), $\partial \langle M_{Loc}^2 \rangle / \partial T$ becomes negative below T_C as shown in figure 8(b). If the thermal increase of $\langle \xi^2 \rangle$ and decrease of $\langle m^2 \rangle$ is comparable, the thermal variation of $\langle M_{Loc}^2 \rangle$ will be negligibly small and almost no magnetovolume effect below T_C is observed, which corresponds to the data for $x = 0.05$ given in figures 4 and 5. Note that the thermal expansion curve of $x = 0.05$ coincides with the Debye function of $\Theta = 330 \pm 10$ K below $T = 400$ K, and the marked decrease of α is observed around T_C. Therefore, the thermal decrease of $\langle m^2 \rangle$ occurs but it is cancelled out by the thermal increase of $\langle \xi^2 \rangle$ below $T = 400$ K. Since $\langle m^2 \rangle$ decreases rapidly near T_C, a sharp minimum of α_{mag} is observed in the compounds with $x = 0.00$ and 0.05 as shown in figure 6. The behaviour of α_{mag} shown in figure 6 can be explained by a gradual decrease of the amplitude of the thermal spin fluctuations $\langle \xi^2 \rangle$ with increasing x. Moreover, the thermal decrease of $\langle M_{Loc}^2 \rangle$ below T_C in $x = 0.10$, which corresponds to figure 8(b), suggests the appearance of the effect of low-energy excitations of spin fluctuations, observed in the large value of γ given in figure 3.

4. Conclusion

The thermomagnetization, the thermal expansion characteristics and the low-temperature specific heat of $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds with $x = 0.00$, 0.05 and 0.10 have been

investigated. A pronounced large thermal expansion coefficient above the Curie temperature as well as the magnetovolume effect has been discussed in terms of the spin fluctuations. The main results are summarized as follows.

(a) A notable increase of the electronic specific heat coefficient takes place with increasing x.

(b) The sign of the magnetovolume effect below the Curie temperature T_C changes from negative to positive with increasing x.

(c) The significant increase of the thermal expansion coefficient α above T_C, that is, the anti-invar behaviour for $Y_6(Mn_{1-x}Fe_x)_{23}$ compounds, is explained by the effect of spin fluctuations.

(d) The anti-invar behaviour is explained within the framework of spin fluctuations sensitive to the Fe concentration x and becomes less remarkable with increasing x.

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