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# Specific heat and thermal expansion characteristics related to spin fluctuations in antiferromagnetic $\beta$-MnOs alloys

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**Abstract**

The temperature dependences of magnetic susceptibility, the specific heat and the thermal expansion of $\beta$-Mn$_{1-x}$Os$_x$ alloys have been investigated. The electronic specific heat coefficient $\gamma$ is significantly large and drastically decreases with increasing $x$. The specific heat peak associated with the Néel temperature $T_N$ is clearly observed in high Os concentration regions. On the other hand, in low Os concentration regions, the peak is not clear and a linear relation between $\gamma$ and $T_N^{3/4}$ is observed. Therefore, it is concluded that $\beta$-Mn$_{1-x}$Os$_x$ alloys with low $x$ are weak itinerant-electron antiferromagnets. The thermal expansion coefficient $\alpha$ in the paramagnetic state is remarkably large in the low Os concentration regions and becomes smaller with increasing $x$; that is, the larger the electronic specific heat coefficient $\gamma$, the larger the value of $\alpha$ in the paramagnetic regions.

## 1. Introduction

Pure Mn has four kinds of crystallographic phase as the temperature increases [1]. From NMR [2] and neutron diffraction [3] studies, it has been reported that $\beta$-Mn shows no magnetic ordering down to low temperatures, although $\alpha$- and $\gamma$-Mn phases are antiferromagnetic [4, 5]. The electronic specific heat coefficient $\gamma$ of $\beta$-Mn is extremely large value at 70 mJ mol$^{-1}$ K$^{-2}$ in contrast to the calculated value of 8 mJ mol$^{-1}$ K$^{-2}$ [6, 7]. Therefore, $\beta$-Mn is regarded as an enhanced Pauli paramagnet. $\beta$-Mn consists of two inequivalent Mn sites (site 1 and site 2) which bring different effects on the magnetic properties. According to NMR study of $\beta$-Mn, the longitudinal nuclear spin–lattice relaxation rate $1/T_1$ satisfies a $T^{1/2}$ dependence, showing an antiferromagnetic correlation [8]. Moreover, the value of $1/T_1$ at site 2 is about 20 times larger than that at site 1, namely, the electronic state of the Mn at site 2 is more magnetic than that at site 1 [2]. The magnetic state in $\beta$-Mn alloys is affected by the substitutional atoms occupying site 1 or site 2. For example, $\beta$-MnFe, $\beta$-MnCo, $\beta$-MnNi alloys in which the substitutional atoms almost occupy site 1 become weak itinerant-electron antiferromagnets and their magnetic properties are discussed within the framework of the SCR theory [9, 10]. On the other hand, $\beta$-MnAl alloy in which the substitutional atoms almost occupy site 2 shows a spin-glass-like behaviour [11]. In recent years, it has been pointed out that the Mn atoms at site 2 form a geometrical triangular lattice, accompanied by a highly frustrated magnetic state, which is a reason why $\beta$-Mn has no magnetic ordering although antiferromagnetic correlation exists between the Mn moments [11, 12].

In our previous paper, the phase diagram of the Mn–Os system was reported for the first time and it was shown that the Os atom is almost substituted at site 1 in $\beta$-Mn and the large $\gamma$ value due to the effect of spin fluctuations tends to decrease with increasing Os concentration [13]. Moreover, a notable change is observed in the concentration dependence of the Néel temperature $T_N$. That is, $T_N$ increases with increasing Os concentration and a steeper increase takes place around $x = 0.13$ Os concentration, although the crystal structures with the space group $P4_132$ containing 20 atoms are preserved in a wide range of composition below $x = 0.36$. In this concentration range, the lattice constant increases linearly with increasing Os concentration. Such a clear change in $T_N$ occurs in none of the other $\beta$-Mn alloys, showing that the antiferromagnetic interaction is enhanced above $x = 0.13$. The magnetic properties of itinerant-electron antiferromagnetic systems such as $\beta$-Mn would be affected by spin fluctuations. To understand the magnetic state of $\beta$-MnOs alloys, it is meaningful to investigate the specific heat and the thermal expansion characteristics which are closely related to spin fluctuations. In the present study, we have carried out the specific heat and the thermal expansion measurements of $\beta$-MnOs alloys. The results are discussed within the framework of the SCR theory.

## 2. Experiment

The specimens were prepared by arc-melting and quenching into ice water from 1273 K after annealing for 0.5 h. No extra phase was detected by x-ray powder diffraction measurement with Cu K$\alpha$ radiation. The alloy compositions were determined by EDXS (energy dispersive x-ray spectroscopy). The temperature dependence of the magnetic susceptibility was measured with a SQUID magnetometer. The specific heat measurement was carried out by a relaxation method. The thermal expansion curves were obtained with a conventional differential transformer-type dilatometer, and the temperature dependence of the lattice constant was measured by x-ray powder diffraction.

## 3. Results and discussion

Figure 1 shows the temperature dependence of magnetic susceptibility $\chi(T)$ of $\beta$-Mn$_{1-x}$Os$_x$ alloys for the specific heat and thermal expansion measurements. A small peak or an inflection point in these curves indicates the Néel temperature $T_N$. With increasing $x$, the value of $\chi(T)$ decreases and the small peak smears away and then the inflection becomes clear above $x = 0.15$. Moreover, $T_N$ increases and a steep increase takes place around $x = 0.15$ with increasing $x$ [13].

Figures 2 and 3 show the temperature dependence of the specific heat of $\beta$-Mn$_{1-x}$Os$_x$ alloys with low and high Os concentrations, respectively. The arrows in the figure indicate the Néel temperature $T_N$ decided from the temperature dependence of the magnetic susceptibility. Above $x = 0.15$, a clear peak is observed at $T_N$ and becomes larger with increasing $x$. On the other hand, below $x = 0.06$, no peak is observable at $T_N$ and a very broad anomaly is observed around $T_N$ for $\beta$-Mn$_{0.87}$Os$_{0.13}$ alloy. In weak itinerant-electron ferromagnets

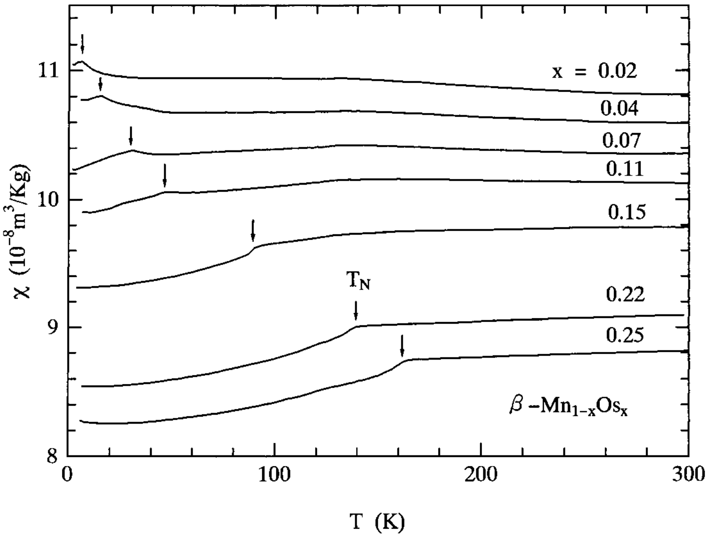

**Figure 1.** Temperature dependence of the magnetic susceptibility $\chi$ of $\beta$-$Mn_{1-x}Os_x$ alloys. The arrows indicate the Néel temperature $T_N$.

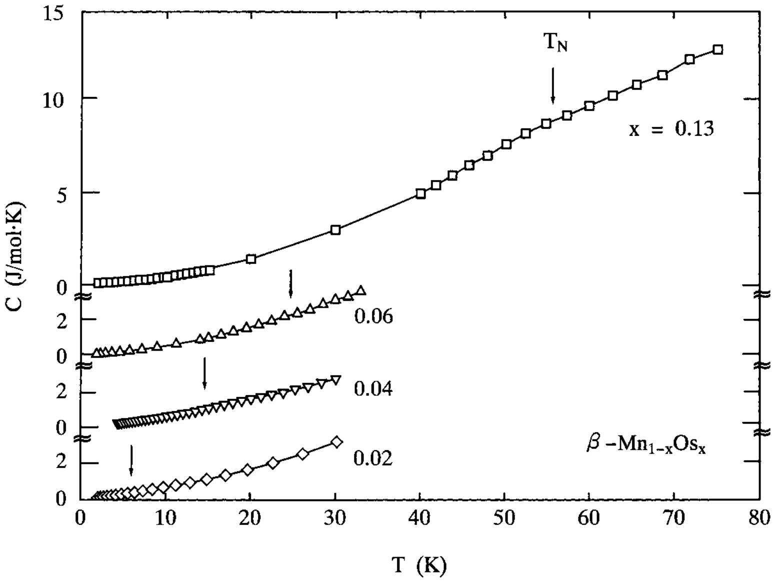

**Figure 2.** Temperature dependence of the specific heat of $\beta$-$Mn_{1-x}Os_x$ alloys with $x \leqslant 0.13$. The arrows indicate the Néel temperature $T_N$.

such as $Sc_3In$, the peak at the Curie temperature is hardly observed from the specific heat measurement [14]. Similar behaviour is also observed in $\beta$-MnFe, $\beta$-MnCo, $\beta$-MnNi alloys [6]. In the SCR calculation of the specific heat for weak itinerant-electron ferromagnets, the effect of spin fluctuations is widely enhanced around the Curie temperature $T_C$ and the anomaly corresponding to the peak at $T_C$ becomes smaller with decreasing $T_C$ [15]. In weak itinerant-electron antiferromagnets, the contribution to the anomaly at $T_N$ is small, compared to

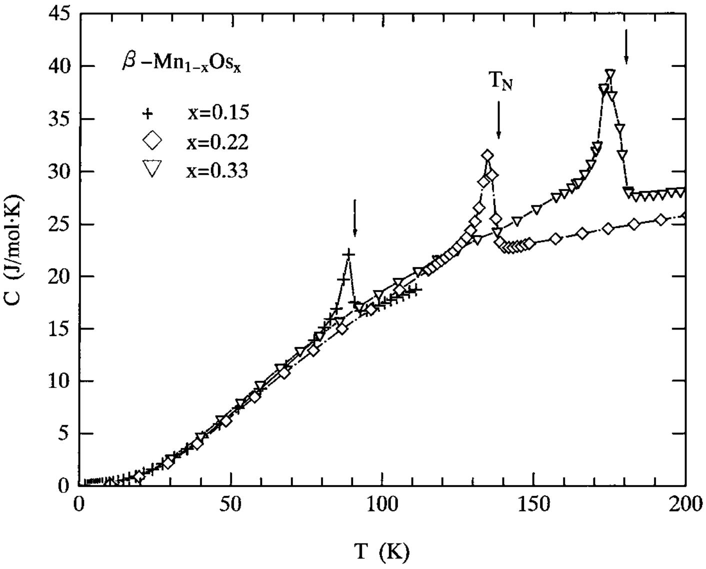

**Figure 3.** Temperature dependence of the specific heat of β-$Mn_{1-x}Os_x$ alloys with $x \geqslant 0.15$. The arrows indicate the Néel temperature $T_N$.

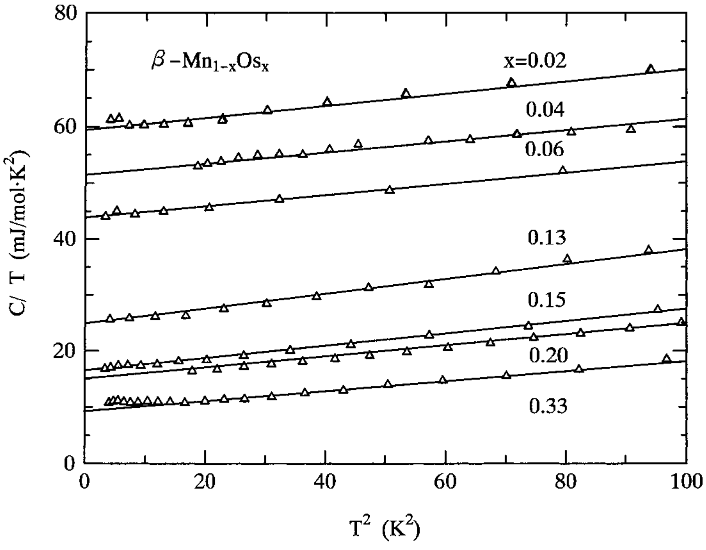

**Figure 4.** Temperature dependence of the low-temperature specific heat in the form of $C/T$–$T^2$ for β-$Mn_{1-x}Os_x$ alloys.

that at $T_C$ for weak ferromagnets [16], showing no clear anomaly at $T_N$. Consequently, β-MnOs alloys are regarded as weak itinerant-electron antiferromagnets in low Os concentrations.

Figure 4 shows the temperature dependence of the specific heat in the form of $C/T$ versus $T^2$ for β-$Mn_{1-x}Os_x$ alloys. All the plots are well fitted by straight lines below 10 K. The electronic specific heat coefficient $\gamma$ can be obtained by a linear extrapolation. In the low Os concentration range, the $\gamma$ value is large and decreases with increasing $x$. β-Mn is well known as nearly an antiferromagnet and the $\gamma$ value is quite large at about 70 mJ $\text{mol}^{-1}$ $\text{K}^{-2}$, associated with the spin fluctuations. For the present $\beta$-MnOs alloys, it is considered that the contribution from the spin fluctuations decreases with increasing $x$.

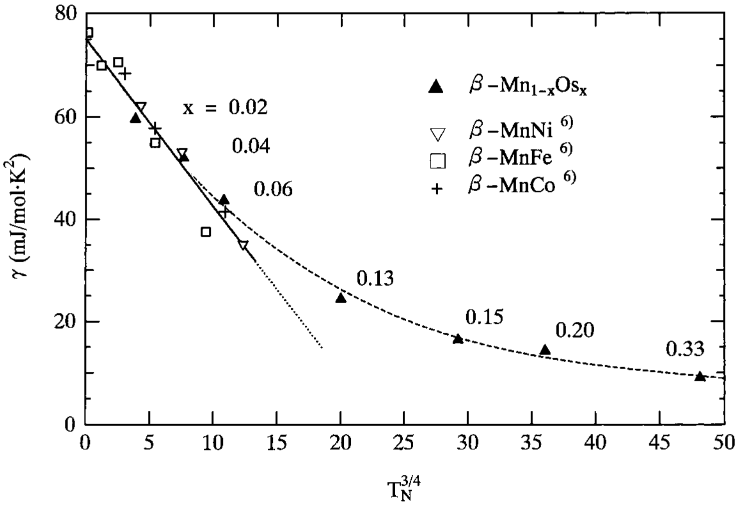

**Figure 5.** The relationship between the electronic specific heat coefficient $\gamma$ and the Néel temperature $T_N$ in the form of $\gamma$–$T_N^{3/4}$ of $\beta$-$\text{Mn}_{1-x}\text{Os}_x$ alloys, together with that of other $\beta$-Mn alloy systems.

The relationship between the Néel temperature $T_N$ and the electronic specific heat coefficient $\gamma$ of $\beta$-$\text{Mn}_{1-x}\text{Os}_x$ alloys is shown in figure 5, together with that of $\beta$-MnFe, $\beta$-MnCo, $\beta$-MnNi [6], in which the substitutional atoms preferentially occupy site 1 of $\beta$-Mn. According to the SCR calculation by Hasegawa, the $\gamma$ value is proportional to $T_N^{3/4}$ in weak itinerant-electron antiferromagnets. As shown in the figure, $\beta$-MnFe, $\beta$-MnCo, $\beta$-MnNi alloys satisfy the linear relationship as weak itinerant-electron antiferromagnets [6]. Below $x = 0.1$ for $\beta$-$\text{Mn}_{1-x}\text{Os}_x$ alloys, the linear relationship between $\gamma$ and $T_N^{3/4}$ is also observed. In the $\beta$-MnFe, $\beta$-MnCo alloys, it has been pointed out from Mössbauer spectroscopy that Fe and Co atoms have no localized moment [17]. Therefore, it is considered that substitution of Fe or Co atoms for Mn atoms is the same as the substitution of non-magnetic atom such as Os, and the difference in the spin fluctuations between the substitutional atoms which preferentially occupy site 1 is scarcely confirmed. With increasing $x$, the deviation from the linear relationship becomes clear, showing that these alloys are no longer weak itinerant-electron antiferromagnets. It should be noted that a steeper increase in the concentration dependence of the Néel temperature is observed above about $x = 0.13$ [13]. Furthermore, the clear peak due to the magnetic phase transition is observed above this Os concentration in the temperature dependence of the specific heat as seen from figure 3. In the theory, by taking the effect of the localized electron on the itinerant-electron system into consideration, the peak becomes larger with increasing intra-atomic electron–electron interaction [18]. The lattice expansion of $\beta$-Mn alloys leads to longitudinal spin fluctuations, resulting in an increasing localization of the itinerant Mn moments [19]. Therefore, it is suggested that Mn atoms have more or less a localized moment in the range of high Os concentrations, showing an intermediate state between the itinerant-electron and the localized-electron state. It should be noted that the alloys with high concentration of Os are not in the completely localized-electron state because the $\chi(T)$ curves do not show a Curie–Weiss type behaviour and exhibit a monotonic increase in the paramagnetic regions as seen from figure 1. From these discussions, it is concluded that the magnetic state in $\beta$-MnOs alloys changes from the weak itinerant-electron antiferromagnetic to the intermediate state with increasing $x$.

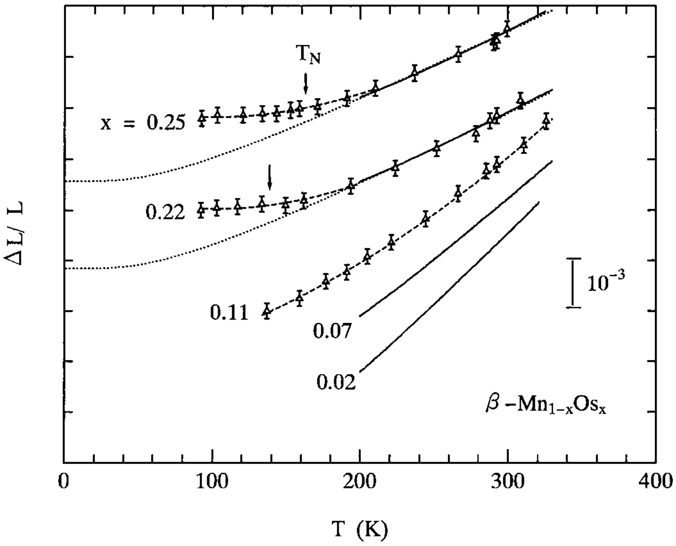

**Figure 6.** Temperature dependence of the thermal expansion of $\beta$-Mn$_{1-x}$Os$_x$ alloys. The open circles and the solid lines indicate the results obtained by the x-ray powder diffraction and conventional dilatometry, respectively. The arrows indicate the Néel temperature $T_N$.

Figure 6 shows the thermal expansion curves of $\beta$-Mn$_{1-x}$Os$_x$ alloys. The open circles indicate the results from x-ray powder diffraction and the solid lines the results obtained by a conventional transformer-type dilatometer. The arrows show the Néel temperature $T_N$ determined from the temperature dependence of magnetic susceptibility. These curves gradually increase with increasing temperature and the slope becomes more sluggish with increasing $x$. In the curves for $\beta$-Mn$_{0.78}$Os$_{0.22}$ and $\beta$-Mn$_{0.75}$Os$_{0.25}$ alloys, the slope changes around $T_N$. In general, the total thermal expansion curve of magnetic materials consists of the lattice and the magnetic contributions. Therefore, subtracting the lattice contribution from the total thermal expansion curve, the magnetic contribution is estimated. The lattice contribution is calculated from the Grüneisen relation with the Debye temperature obtained from the low temperature specific heat data. The resultant Debye temperature is about 260 K, almost independent of the Os concentration. The lattice contribution using the Debye temperature of 260 K is indicated by the dotted line in figure 6. A clear positive magnetovolume effect is observed below the Néel temperatures above $x = 0.22$.

Figure 7 shows the temperature dependence of the thermal expansion coefficient $\alpha$ in the paramagnetic state for $\beta$-Mn$_{1-x}$Os$_x$ alloys. On the basis of the SCR theory, the mean square local amplitude of spin fluctuations $S_L^2$ indicates a marked temperature dependence and reflects the thermal expansion [20]. In weak itinerant-electron antiferromagnets, it is expected that the $\alpha$ value in the paramagnetic region will be large. It is clear that the sample with the larger value of the electronic specific heat coefficient $\gamma$ indicates a larger value of $\alpha$ in the paramagnetic region. With increasing Os concentration, $\alpha$ becomes smaller and scarcely depends on $x$ above 0.22 as seen from the figure. The value of the alloy with $x = 0.22$ is about half the value of $30 \times 10^{-6}$ K$^{-1}$ for $\beta$-Mn at room temperature [11]

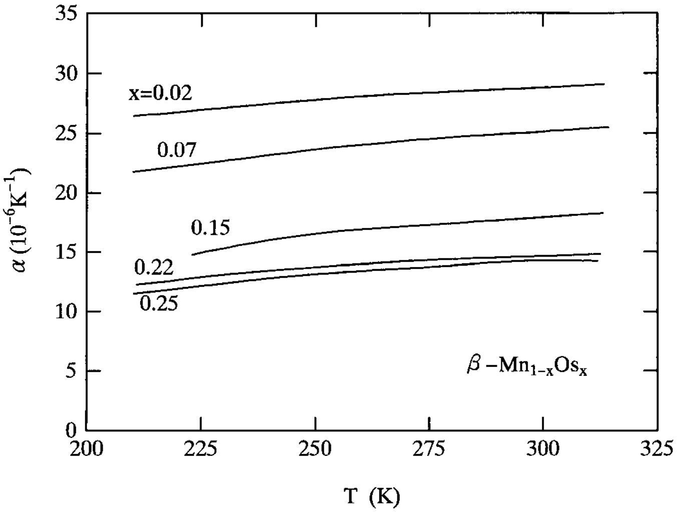

**Figure 7.** Temperature dependence of the thermal expansion coefficient $\alpha$ in the paramagnetic state for $\beta$-Mn$_{1-x}$Os$_x$ alloys.

and the temperature dependence of $\alpha$ around room temperature becomes weak, tending to saturation of spin fluctuations.

## 4. Conclusion

In order to discuss the spin fluctuation effects in $\beta$-Mn$_{1-x}$Os$_x$ alloys, the magnetic susceptibility, the specific heat and the thermal expansion have been investigated over a wide temperature range. The main results are summarized as follows.

(a) The linear relation between the electronic specific heat coefficient $\gamma$ and the Néel temperature $T_N$ in the form of $\gamma$ versus $T_N^{3/4}$ for weak itinerant-electron antiferromagnets is satisfied in the low Os concentration range.

(b) In the temperature dependence of the specific heat, a clear peak is observed at the Néel temperature above $x = 0.13$ and becomes clearer with increasing $x$. On the other hand, no peak is observed in the low Os concentration regions, showing weak itinerant-electron antiferromagnetic characteristics.

(c) Related to spin fluctuations in the low Os concentrations, the $\gamma$ value is markedly large and decreases with increasing $x$.

(d) In the paramagnetic state, the thermal expansion coefficient $\alpha$ is enhanced by the spin fluctuations and reduced with increasing $x$.

(e) A positive magnetovolume effect is observed below the Néel temperature for the alloys with higher concentrations of Os.

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## References

[1] Shull C G and Wilkinson M K 1953 *Rev. Mod. Phys.* **25** 100
[2] Kohori Y, Noguchi Y and Kohara T 1993 *J. Phys. Soc. Japan* **62** 447
[3] Masuda Y, Asayama K, Kobayashi S and Itoh J 1964 *J. Phys. Soc. Japan* **19** 460
[4] Yamada T, Kunitomi N, Nakai Y, Cox D E and Shirane G 1970 *J. Phys. Soc. Japan* **28** 615
[5] Krén E 1966 *Phys. Lett.* **21** 383
[6] Shinkoda T, Kumagai K and Asayama K 1979 *J. Phys. Soc. Japan* **46** 1754
[7] Mori N, Ukai T and Sasaki K 1980 *Physics of Transition Metals (Institute of Physics Conference Series 55)* ed P Rhoden (Bristol: Institute of Physics) p 21
[8] Katayama M, Akimoto S and Asayama K 1977 *J. Phys. Soc. Japan* **46** 97
[9] Oyamatsu H, Nakai Y and Kunitomi N 1989 *J. Phys. Soc. Japan* **58** 3606
[10] Hasegawa H 1975 *J. Phys. Soc. Japan* **38** 1780
[11] Nakamura H, Yoshimura K, Shiga M, Nishi M and Kakurai K 1997 *J. Phys.: Condens. Matter* **9** 4701
[12] Nakamura H and Shiga M 1997 *Physica* B **237/238** 453
[13] Yamauchi R, Miyakawa M, Sasao K and Fukamichi K 2000 *J. Alloys Compounds* **311** 124
[14] Takeuchi J and Masuda Y 1979 *J. Phys. Soc. Japan* **46** 468
[15] Makoshi K and Moriya T 1975 *J. Phys. Soc. Japan* **38** 10
[16] Takahashi Y 1999 *J. Phys.: Condens. Matter* **11** 6439
[17] Nishihara Y, Ogawa S and Waki S 1977 *J. Phys. Soc. Japan* **42** 845
[18] Hasegawa H 1980 *J. Phys. Soc. Japan* **49** 178
[19] Stewart J R and Cywinski R 1999 *Phys. Rev.* B **59** 4305
[20] Moriya T 1985 *Spin Fluctuation in Itinerant Electron Magnetism* (Berlin: Springer)