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Thermal expansion characteristics related to spin fluctuations and the pressure effect on the Néel temperature of β-MnOs alloys

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Abstract

The thermal expansion and the magnetic susceptibility under ambient pressure and the temperature dependence of electrical resistivity under applied pressures for β-$Mn_{1-x}Os_x$ alloys have been investigated. The concentration dependence of the spontaneous volume magneto-striction at 0 K, $\omega_{mag}(0)$, exhibits a broad maximum at about $x = 0.14$. The thermal expansion characteristic is explained qualitatively by the unified model based on the self-consistent renormalization theory. A weak itinerant-electron antiferromagnetic state in the β-$Mn_{1-x}Os_x$ alloys varies with x to an intermediate state. The pressure coefficient of the Néel temperature decreases with increasing x, in accord with the variation of the magnetic state.

1. Introduction

β-Mn shows no magnetic ordering down to low temperatures and the electronic specific heat coefficient γ is extremely large [1–4]. Therefore, β-Mn has been regarded as an enhanced Pauli paramagnet and the magnetic properties have been investigated from the viewpoint of itinerant-electron magnetic systems. From a nuclear magnetic resonance (NMR) study of β-Mn, the temperature dependence of the spin–lattice relaxation rate $1/T_1$ follows a $T^{1/2}$ dependence, which is well explained within the framework of the self-consistent renormalization (SCR) theory for weak itinerant-electron antiferromagnets at the Néel temperature $T_N = 0$ K. This implies the existence of antiferromagnetic correlations even in the paramagnetic state [5, 6]. Therefore, the magnetic state in β-Mn is on the verge of antiferromagnetism.

There are two crystallographically inequivalent Mn sites, namely site 1 (8c) and site 2 (12d), in the β-Mn structure ($P4_132$). The magnetic properties of these sites are extremely different from each other. The value of $1/T_1$ at site 2 is about 20 times larger

than that at site 1, showing that the staggered susceptibility of site 2 is much larger than that of site 1 [1, 7]. The magnetic properties of the β-Mn alloys are affected by the difference in the atomic site. β-MnFe [8], β-MnCo [8], β-MnNi [8] and β-MnRu [9] alloy systems, in which almost all substitutional atoms occupy site 1, become weak itinerant-electron antiferromagnets in low-concentration ranges. On the other hand, β-MnAl alloys [10–12], in which almost all the substitutional atoms occupy site 2, exhibit spin-glass-like behaviour. In recent years, it has been pointed out that site 2 sublattices can be regarded as geometrical triangular lattices, resulting in a highly frustrated magnetic state. This is one of the reasons why β-Mn has no magnetic ordering, although the antiferromagnetic correlation between the Mn moments is clearly present [10, 13].

In the Mn–Os alloy system, the existence of the β-phase has been reported by the present authors [14]. The β-MnOs alloys have been considered to be weak itinerant-electron antiferromagnets, because almost all Os atoms occupy site 1 in the β-Mn lattice [14, 15]. In our previous study of the low-temperature specific heats, we discussed the variation of the magnetic properties with increasing Os concentration x in the β-$Mn_{1-x}Os_x$ alloy system [15]. According to the SCR theory for weak itinerant-electron antiferromagnets, the electronic specific heat coefficient γ is proportional to $T_N^{3/4}$ [16]. This relation is satisfied with the data on β-MnFe, β-MnCo and β-MnNi alloys having the same occupation site as that in the β-MnOs alloy [4]. In the case of the β-$Mn_{1-x}Os_x$ alloy system, the above proportional relationship is satisfied below about $x = 0.10$, but then the data deviate from this relationship above $x = 0.13$. In addition, in the temperature dependence of specific heat of the β-$Mn_{1-x}Os_x$ alloys, a clear peak due to the magnetic phase transition is observed above $x = 0.13$, where the magnetic susceptibility increases with increasing temperature above T_N, in contrast to the temperature dependence of magnetic susceptibility for localized-electron systems. Consequently, it has been concluded that the antiferromagnetic state in the β-MnOs alloy system varies from a weak itinerant-electron state to an intermediate state with increasing x [15].

To make the variation in the magnetic state with composition for the β-MnOs alloy system clear, it is meaningful to investigate the thermal expansion characteristics closely related to the spin fluctuations. In our previous study, a significant concentration dependence of the thermal expansion coefficient in the paramagnetic state was observed [15]. In this study, the thermal expansion measurements have been extended to much lower-temperature regions in order to discuss the magneto-volume effects. By using electrical resistivity data under applied pressures, the pressure dependence of the Néel temperature is discussed in connection with the magneto-volume effects and the variation in the magnetic state with Os concentration.

2. Experiment

The alloying was performed by arc melting. The specimens were quenched in ice water from 1273 K after annealing for 0.5 h. No extra phase was detected by x-ray powder diffraction measurement with Cu Kα radiation. The alloy compositions were determined by energy dispersive x-ray spectroscopy (EDXS). The temperature dependence of the magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer. The temperature dependence of the lattice constant was measured by x-ray powder diffraction from 10 up to 300 K. The temperature dependence of the electrical resistivity under pressure was obtained by a conventional four-probe method, applying up to 1 GPa by using a piston–cylinder method.

3. Results and discussion

From the specific heat measurement [15], the magnetic state in the β-MnOs alloys varies from the weak itinerant-electron antiferromagnetic to the intermediate magnetic state with

increasing x. According to the unified model based on the SCR theory, for the variation from itinerant-electron magnetism to localized-electron magnetism, the important factors for magnetic materials are the thermal average of local magnetic moment, $\langle M_{Loc}(T)^2\rangle$, and its temperature dependence, which are reflected in the magnetic term $\omega_{mag}(T)$ of the thermal expansion [17]. Thus, $\langle M_{Loc}(T)^2\rangle$ and $\omega_{mag}(T)$ are respectively given by the following equations [18, 19]:

$$\langle M_{Loc}(T)^2\rangle = \langle m(T)^2\rangle + \langle \xi(T)^2\rangle \tag{1}$$

and

$$\omega_{mag}(T) = \kappa C \langle M_{Loc}(T)^2\rangle \tag{2}$$

where $\langle \xi(T)^2\rangle$ and $\langle m(T)^2\rangle$ are the mean square local amplitude of spin fluctuations and the magnetic moment respectively, and κ and C are the compressibility and the coupling constant, respectively. For the itinerant-electron ferromagnets and antiferromagnets, $\langle m(T)^2\rangle$ decreases with increasing temperature and disappears at the magnetic transition temperature. On the other hand, $\langle \xi(T)^2\rangle$ increases through the magnetic transition temperature with increasing temperature. For weak itinerant-electron magnets, the temperature dependence of $\langle \xi(T)^2\rangle$ is extremely large, and hence the thermal expansion coefficient α in paramagnetic regions exhibits a large value [17]. On the contrary, decreasing the itinerant-electron features, $\langle \xi(T)^2\rangle$ becomes smaller, reducing the magnitude of α in paramagnetic regions.

Figure 1 shows the thermal expansion curves obtained from low-temperature x-ray diffraction for several kinds of β-$Mn_{1-x}Os_x$ alloys. The arrows indicate the Néel temperature, T_N, determined from the temperature dependence of the magnetic susceptibility shown in the inset. No change in crystallographic structure occurs at T_N. The volume thermal expansivity of magnetic materials, $3\Delta L/L$, is given by the following expression:

$$3\Delta L/L = \omega_{tot} = \omega_{lat} + \omega_{ele} + \omega_{mag} \tag{3}$$

where ω_{lat}, ω_{ele} and ω_{mag} are the lattice, electron and magnetic terms, respectively. It should be noted that electron term is about two orders of magnitude smaller than the lattice term [20], and hence we consider $(\omega_{lat} + \omega_{ele}) \sim \omega_{lat}$. The lattice term is approximated by the Debye function and the Debye temperature is about 260 K, almost independent of the Os concentration [15]. Therefore, the magnitude of the lattice term is regarded as the same in all the alloys. In figure 1, depending on x, the slope above T_N increases gradually with increasing temperature, implying that the effect of $\langle \xi(T)^2\rangle$ is significant. The magnetic term is obtained by subtracting the lattice term from the total thermal expansion curve. The magnetic term is also reflected in the difference of the electronic specific heat coefficient. The large electronic specific heat coefficient at $x = 0.02$, $\gamma = 59$ mJ mol^{-1} K^2, becomes smaller with increasing x, and the value is nearly equal to the band-calculated value of β-Mn at $x = 0.33$ (9 mJ mol^{-1} K^{-2}) [15]. To estimate the magnetic term, the lattice term is given by the dashed curve for each total thermal expansion curve in figure 1, using the lattice term $x = 0.33$, for which it is assumed that the $\langle \xi(T)^2\rangle$ is comparatively small. As seen from the figure, a clear spontaneous volume magnetostriction, ω_{mag}, is observed below T_N, except for the alloy with $x = 0.11$. In contrast, above T_N the so-called anti-invar effect [21] (or the increase in the thermal expansion coefficient) is observed due to the significantly large value of $\langle \xi(T)^2\rangle$. This behaviour is reduced with increasing Os content.

Figure 2 illustrates the concentration dependence of ω_{mag} at 0 K, $\omega_{mag}(0)$, obtained from figure 1. The value of $\omega_{mag}(0)$ shows a broad maximum at $x = 0.14$ and is small at $x = 0.11$. In the β-$Mn_{1-x}Os_x$ alloy systems, $\omega_{mag}(0)$ at $x = 0.11$ is not so large because of their weak itinerant-electron antiferromagnetic state. With increasing x, the magnetic state varies from the weak itinerant-electron antiferromagnetic state to the intermediate antiferromagnetic

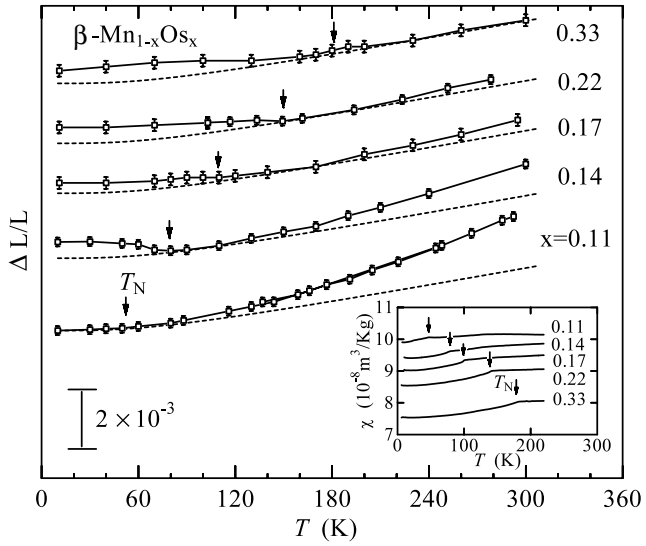

Figure 1. Thermal expansion curves obtained by x-ray powder diffraction for β-$Mn_{1-x}Os_x$ alloys. The inset shows the temperature dependence of the magnetic susceptibility, χ, of the same alloys. The arrows indicate the Néel temperature, T_N. The solid curves are the total thermal expansion curves. The dashed curves are the lattice term.

state around $x = 0.14$. As a consequence of the enhancement of the antiferromagnetic interaction with increasing x, a large spontaneous volume magneto-striction is observed in the alloy with $x = 0.14$. Above this concentration, $\omega_{mag}(0)$ becomes smaller with increasing x, though the antiferromagnetic interaction is enhanced gradually. This implies that the temperature dependence of $\langle M_{Loc}(T)^2\rangle$ is reduced approaching the localized-electron magnetic state, accompanied by a smaller spontaneous magneto-striction below T_N. With increasing x, α at room temperature becomes smaller and scarcely depends on the concentration above $x = 0.22$, as reported in our previous measurement [15] and seen from figure 1. The value of the alloy with $x = 0.22$ is about 15×10^{-6} K^{-1} at room temperature, about half that of a β-Mn [10]. From these results, it is clear that the variations of the spontaneous volume magneto-striction, ω_{mag}, and the thermal expansion coefficient, α, with increasing x in the β-$Mn_{1-x}Os_x$ alloys are reflected in the variation of the magnetic state from the weak itinerant-electron antiferromagnetic state to the intermediate state, in accord with the specific heat data [15].

Since the positive value of ω_{mag} is observed, the negative pressure dependence of the Néel temperature is expected. It is well known that the magneto-volume effect is thermodynamically correlated to the pressure dependence of the Néel temperature, T_N. In the second-order transformation, the Ehrenfest equation is given by

$$\frac{dT_N}{dP} = V T_N \frac{\Delta\alpha_V}{\Delta C_m} \tag{4}$$

where V, $\Delta\alpha_V$ and ΔC_m are the volume, the difference below and above T_N for the volume thermal expansion coefficient, and the difference in specific heat, respectively. In the β-$Mn_{1-x}Os_x$ alloys, $\Delta\alpha_V$ is negative and ΔC_m is positive, and hence dT_N/dP is expected to be negative. Therefore, we have measured the temperature dependence of the electrical resistivity under pressure in order to obtain the shift of T_N under pressure. Theoretical analysis for a antiferromagnet tells us that the temperature derivative of electrical resistivity

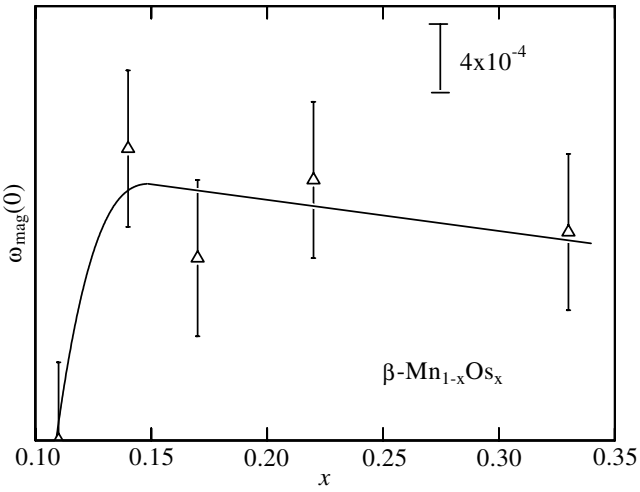

Figure 2. The concentration dependence of the spontaneous volume magneto-striction at 0 K, $\omega_{mag}(0)$, of β-$Mn_{1-x}Os_x$ alloys.

diverges negatively at T_N [22]. The temperature dependence of electrical resistivity, ρ, of the β-$Mn_{1-x}Os_x$ alloys is shown in figure 3. The arrows indicate T_N, corresponding to the temperature determined from the temperature dependence of magnetic susceptibility. On the basis of SCR theory for weak itinerant-electron antiferromagnets at the Néel temperature $T_N = 0$ K, $(\rho - \rho_0)$ is proportional to $T^{3/2}$, where ρ_0 is the residual resistivity [23]. It has been reported that this relation is satisfied below 20 K in β-Mn [24], suggesting that the effect of spin fluctuations is reflected and that the magnetic state is on the verge of antiferromagnetism. The value for the electrical resistivity of the β-$Mn_{1-x}Os_x$ alloys is high. In a previous report, the residual resistivity of β-Mn is about 80 $\mu\Omega$ cm [24], which is almost the same magnitude as for the β-$Mn_{0.98}Os_{0.02}$ alloy, as seen from figure 3. Besides, the high electrical resistivities were attributed to defects and micro-cracks in β-Mn alloys [10]. In the β-$Mn_{1-x}Os_x$ alloys, these effects may be excluded, but apparently the magnitude of ρ increases with increasing x and the temperature coefficient of electrical resistivity in the paramagnetic regions changes from positive to negative. Mooij has pointed out the relation between the electrical resistivity and its temperature coefficient [25], which is that the sign of the temperature coefficient changes from positive to negative around 150–200 $\mu\Omega$ cm with increasing electrical resistivity. This correlation is common to various kinds of crystalline [25] and amorphous alloys [26]. In the β-$Mn_{1-x}Os_x$ alloys, the results are satisfied with Mooij's rule, as explained in the following way. The residual resistivity, ρ_0, versus x for the β-$Mn_{1-x}Os_x$ alloys is given in figure 4. The value of ρ_0 is extrapolated from the curve of the paramagnetic regions and the value increases linearly with increasing x. The present large increase in resistivity seems to be intrinsic, though the existence of defects or micro-cracks is not rigorously excluded. The β-$Mn_{1-x}Os_x$ alloys become more disordered states with increasing x and the electron mean free path is reduced, accompanied by a higher resistivity and the change in the sign of the temperature coefficient, which takes around 150–200 $\mu\Omega$ cm.

Shown in figure 5 is the temperature dependence of electrical resistivity as a function of pressure for the β-$Mn_{1-x}Os_x$ alloys in the concentration region from $x = 0.14$ to 0.33. Similar to the data in figure 4, T_N under applied pressure is defined as the minimum point of the temperature derivative of electrical resistivity. A negative pressure dependence of T_N is observed in all the compositions, as seen from figure 5. The pressure dependence of T_N for the

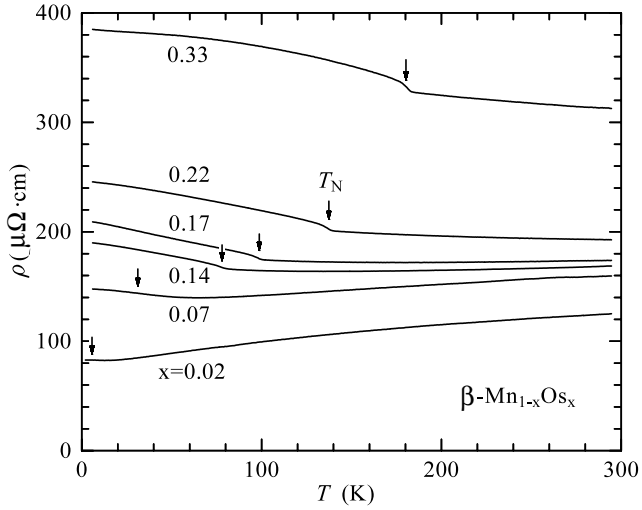

Figure 3. The temperature dependence of the electrical resistivity of β-$Mn_{1-x}Os_x$ alloys. The arrows indicate the Néel temperature, T_N, determined from the temperature dependence of magnetic susceptibility.

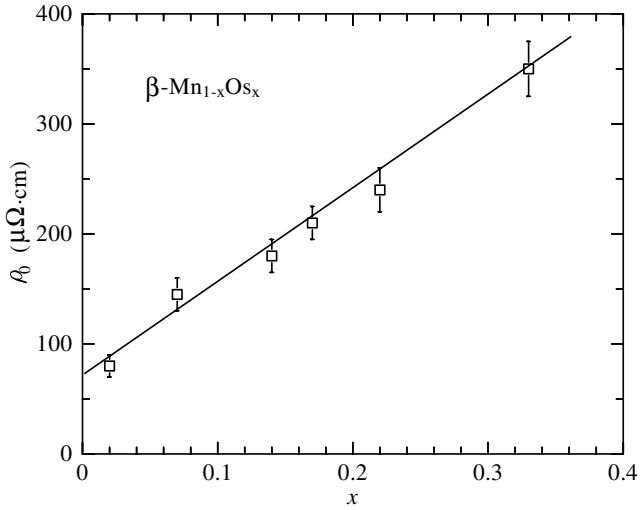

Figure 4. The concentration dependence of the residual resistivity, ρ_0, for β-$Mn_{1-x}Os_x$ alloys.

β-$Mn_{1-x}Os_x$ alloys is given in figure 6. The value of T_N decreases linearly at $x = 0.22$ and 0.33, while the decrease of T_N for $x = 0.14$ and 0.17 becomes more significant with increasing pressure. Figure 7 shows the pressure coefficient of the Néel temperature T_N versus x between 0.14 and 0.33 for the β-$Mn_{1-x}Os_x$ alloys. The pressure coefficient of the initial slope is given in figure 6. The pressure coefficient decreases with increasing x, which is closely correlated to the variation of itinerant-electron features. The magnitude of the spontaneous volume magnetostriction, $\omega_{mag}(0)$, decreases with increasing x from 0.14 to 0.33, in accord with the variation of itinerant-electron features. It is well known that the pressure coefficient is large in weak itinerant-electron magnets. In weak itinerant-electron ferromagnets, the pressure coefficient of the Curie temperature, $d \ln T_C/dP$, is proportional to $-1/T_C^{4/3}$ within the framework of the

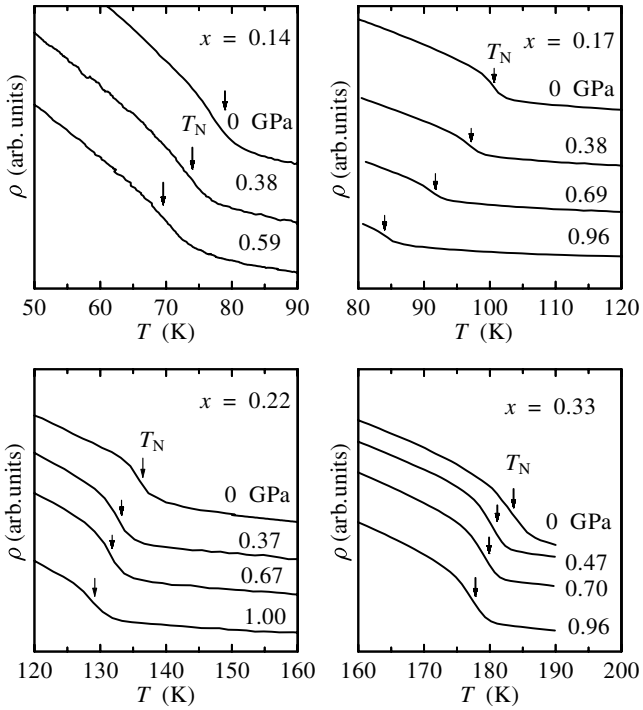

Figure 5. The temperature dependence of the electrical resistivity under pressure for β-$Mn_{1-x}Os_x$ alloys in the concentration region from $x = 0.14$ to 0.33. The arrows indicate the Néel temperature, T_N.

SCR theory [27]. For weak itinerant-electron antiferromagnets, the uniform magnetization and long-wavelength components of spin fluctuations in ferromagnets are replaced, respectively, by the staggered magnetization and the components of spin fluctuations with wavevectors close to the antiferromagnetic vector Q [17]. Therefore, the theory is also essentially valid in weak itinerant-electron antiferromagnets. The β-$Mn_{1-x}Os_x$ alloys with low x concentration are considered to be weak itinerant-electron antiferromagnets, and hence the pressure coefficient is expected to be relatively large. One may notice that $\mathrm{d}\ln T_N/\mathrm{d}P$ of the alloys with $x = 0.14$ and 0.17 is comparable with the pressure coefficient of the Curie temperature $-0.0635\ \mathrm{GPa}^{-1}$ for a typical weak itinerant-electron ferromagnet Ni_3Al [28]. Furthermore, for the alloy with $x = 0.33$, the pressure coefficient is still relatively large, because this alloy is not a complete localized-electron antiferromagnet but an intermediate antiferromagnet in the magnetic state.

4. Conclusion

In order to discuss the magneto-volume effects in the β-$Mn_{1-x}Os_x$ alloys, the thermal expansion and magnetic susceptibility under ambient pressure and the electrical resistivity under high pressures have been investigated. In connection with the variation of the magnetic state, the thermal expansion properties and the pressure dependence of the Néel temperature have been discussed on the basis of the spin fluctuation theory. The main results are summarized as follows.

(a) A clear positive spontaneous volume magneto-striction ω_{mag} is observed, and the value at 0 K, $\omega_{mag}(0)$, decreases above $x = 0.14$ with increasing x.

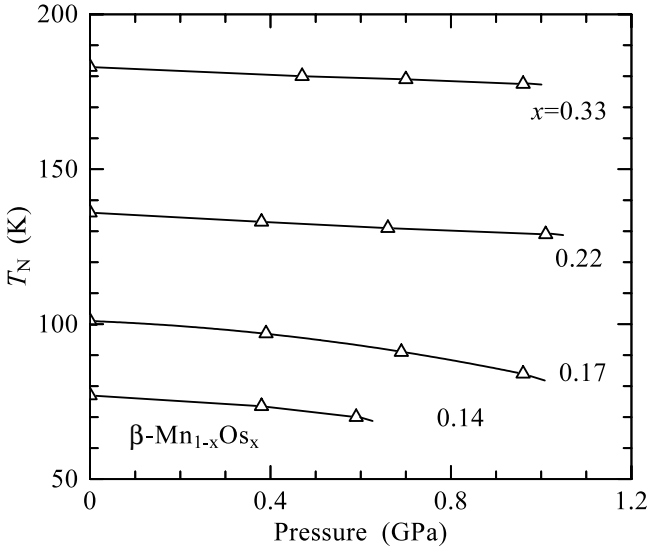

Figure 6. The pressure dependence of the Néel temperature, T_N, for β-$Mn_{1-x}Os_x$ alloys.

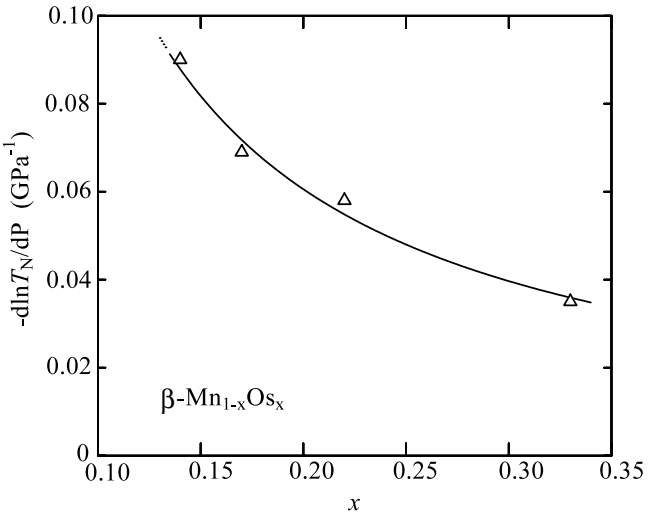

Figure 7. The concentration dependence of the pressure coefficient of the Néel temperature, T_N, for β-$Mn_{1-x}Os_x$ alloys.

(b) The thermal expansion characteristics are explained qualitatively in terms of the spin fluctuations. The magnetic state varies from the weak itinerant-electron antiferromagnetic state to the intermediate state with increasing x.

(c) The pressure dependence of the Néel temperature, T_N, is negative, in harmony with the positive spontaneous volume magneto-striction. The pressure coefficient of T_N decreases with increasing x, reflecting the variation of the magnetic state.

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