Journal of the Physical Society of Japan
Vol. 62, No. 4, April, 1993, pp. 1329-1336

Spin Liquid Behavior of Highly Frustrated Y(Sc)Mn_2 and Effects of Nonmagnetic Impurity

Masayuki SHIGA, Koji FUJISAWA* and Hirofumi WADA

Department of Metal Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-01

(Received October 30, 1992)

The roles of geometrical spin frustration in magnetic and thermodynamic properties of YMn_2 and Y(Sc)Mn_2 are studied. It is shown that the ground state of Y(Sc)Mn_2, which exhibits heavy fermion like behavior, may be regarded as a quantum spin liquid realized through the frustration. To confirm this idea, magnetic, thermal and electrical properties of the $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ pseudobinary system have been studied. The substitution of Al for Mn causes a spin liquid to spin glass transition as a result of partial raise of spin configurational degeneracy.

[Laves phase compound, YMn_2, spin liquid, spin glass, frustration, spin fluctuations, heavy fermion]

§1. Introduction

The ground state properties of magnetically frustrated spin systems such as a 2-dimensional triangular antiferromagnet or a 2-dimensional square lattice are now being intensively studied in connection with the mechanism of high T_c superconductor. Anderson[1] and coworkers[2] introduced the concept of quantum spin liquid (QSL) or the resonating valence bond (RVB) state as a nonmagnetic ground state of the frustrated system, which is characterized by a strong antiferromagnetic short-range correlation as well as an absence of long range order. So far, candidates for QSL have been searched in quasi low dimensional ionic compounds including high T_c oxides. The fully frustrated system may be found in 3-dimensional crystals such as the spinel lattice with magnetic ions on B sites only.[3] Candidates for this type of lattice have been searched in pyrochlore compounds[4,5] However, in most of these materials, a magnetically ordered state or a spin-glass state is formed at a low temperature by secondary mechanisms. On the other hand, metallic magnetic systems have not been intensively studied from the view point of frustration.

The Mn sub-lattice of YMn_2 with C15 structure is equivalent to the B sites on spinel lattice and, therefore, the antiferromagnetic YMn_2 can be regarded as a fully frustrated system. This compound undergoes a first order transition to an antiferromagnetic state at T_N of 100 K, of which magnetic structure is shown in Fig. 1. Open and closed circles represent Mn atoms with up and down spins respectively.[6] The antiferromagnetism of YMn_2, however, exhibits many anomalies probably due to the effects of frustration. The Mn moment is estimated as 2.7 μ_B by neutron diffraction.[6] Pre-

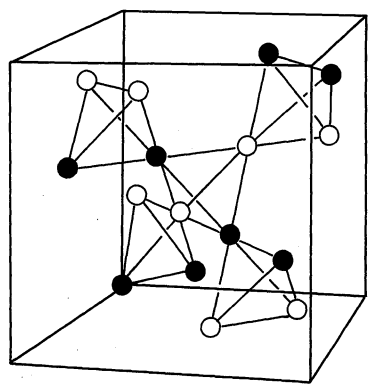

Fig. 1. Spin structure of YMn_2. Only Mn sites are shown. Open and closed circles represent up and down spins, respectively. Spin directions are not colinear each other and helically modulated.

* Present address: IBM Japan Ltd., Yasu-gun, Shiga 520-23.

cise neutron diffraction measurements using long wave length neutron have revealed that the spin alignment is not simply colinear antiferromagnetic but has a canted structure and is, furthermore, helically modulated with the period of 400 Å[7])} or doubly modulated with different wave vectors.[8] The exact spin structure has not yet been established.

Paramagnetic state of YMn_2 is quite interesting, because it exhibits giant spin fluctuations.[9-11] By giving positive chemical pressure through the substitution of a small amount of Sc for Y, the paramagnetic state is stabilized down to the lowest temperature.[12] The absence of static Mn moments was confirmed by NMR down to 70 mK for $Y_{0.97}Sc_{0.03}Mn_2$.[13] Paramagnetic $Y(Sc)Mn_2$ exhibits really striking characteristics. The γ value of low temperature specific heat is enormously large for a 3d metal, being 150 mJ/K^2 mol, which is about 15 times as large as that expected from the bare density of states.[14] The temperature dependence of electrical resistivity at low temperatures is approximately given by $\rho=\rho_0+AT^2$ with a large A value of 0.25 $\mu\Omega$ cm K^{-2}.[15] At high temperatures, ρ increases with increasing temperature and shows a trend of saturation as observed in 5f heavy fermion systems such as UPt_3.[16] Both γ and A values are comparable to those of moderately mass-enhanced heavy fermion systems. The A/γ^2 ratio of 1.1×10^{-5} ($\mu\Omega$ cm mJ^{-2} mol^2) is nearly the same as other heavy fermion compounds.[17] The thermoelectric power also exhibits similar temperature dependence to that of UPt_3, having a sharp peak at low temperatures and negative values in the intermediate temperature range.[18] It is likely that these heavy fermion like characters may be caused by strong spin fluctuations in this system. In order to detect the spin fluctuations directly, paramagnetic neutron scattering experiments was carried out on $Y_{0.97}Sc_{0.03}Mn_2$ using polarized neutrons at 8 K, 120 K and 330 K.[19] A huge scattering centered around $Q=1.5$ Å^{-1} was observed at each temperature, indicating giant spin fluctuations with a strong antiferromagnetic correlation. The amplitude of the scattering increases with increasing temperature, suggesting that spin fluctuations are thermally excited. It should be noted that the strong scattering is observed even at the lowest temperature of 8 K. By integrating the spectrum, the local spin amplitude on Mn atoms has been roughly estimated to be 1.3 μ_B.[19] These observations and the absence of static magnetic moments even at 70 mK indicate the existence of giant quantum spin fluctuations with a strong antiferromagnetic correlation. In this sense, the ground state of this system can be regarded as in the QSL state.

§2. Spin Frustration as the Origin of Giant Spin Fluctuations

So far, we considered that the $Y_{1-x}Sc_xMn_2$ system is an itinerant electron paramagnet with giant spin fluctuations. The reason why this particular system shows such distinct spin fluctuations has not been elucidated. In this study, we propose an alternative approach from the strong correlation limit for the interpretation of remarkable behavior of this system by assuming that Mn atoms carry local moments at high temperatures.

Usually, in strongly correlated metallic systems, each atom possesses a local moment and a certain magnetically ordered state appears at a low temperature except some special cases such as dense Kondo lattice and possibly geometrically frustrated systems. Villain has shown that classical vector spins on the B site of spinel structure, which is equivalent to the Mn site of the present system, can be regarded as a fully frustrated system,[3] having an infinite number of ground states with respect to spin configurations and that any stable spin structure can not be formed. At the lowest temperature, this degeneracy should be lifted by: (1) through 2nd. or longer distant interactions, a complicated spin structure is formed, (2) by a structural deformation, a simple antiferromagnetic structure is stabilized and (3) through quantum effects, the frustrated spin system condenses into a singlet ground state. The complicated spin structure of YMn_2 may originate in the first mechanism as pointed out by Ballou *et al.*[7] We consider that the QSL state of $Y(Sc)Mn_2$ may be explained by the third mechanism. The Sc doping, which shortens the Mn–Mn distance, may enhance the quantum effects through the increase of transfer integrals. Thus, $Y(Sc)Mn_2$ may be re-

garded as a highly correlated electron system with strong intra- and inter-atomic interaction enough to form an antiferromagnet with large local moments but the formation of any magnetic order is suppressed due to the frustration.

The ground state degeneracy of frustrated systems can also be removed by lattice defects, for instance, non-magnetic substitutional impurities. Villain has also shown that in this particular lattice, the substitution of a small amount of magnetic atoms by non-magnetic ones gives rise to a transition from spin liquid to a spin glass state.[3] To confirm this prediction, we have studied effects of substitution of a non-magnetic atom for Mn on magnetic and other properties for the $Y(Sc)(Mn_{1-x}Al_x)_2$ system. A part of this study has been published elsewhere.[20]

§3. Experimentals

The $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ samples were prepared in an argon arc furnace. As-cast samples were used for each measurement. No other phase than C15 was detected by X-ray diffraction. The magnetic susceptibility was measured by a magnetic torsion balance from 4.2 K up to room temperature. The low temperature specific heat was measured by a conventional adiabatic calorimeter between 1.4 K and 9.5 K. The thermal expansion was measured by a differential transformer type dilatometer from 4.2 K up to 300 K. The temperature dependence of electrical resistivity was measured by a standard 4 terminal method.

§4. Results

Figure 2 shows the temperature dependence of the susceptibility. The susceptibility increases with increasing x and approaches a Curie-Weiss type at high temperatures. For $x \geq 0.05$, a maximum is observed in χ-T curves at low temperatures for zero field cooled samples but not for field cooled samples, suggesting spin glass freezing.

Figure 3 shows the temperature dependence of specific heat in the form of C/T versus T^2 plots. For $x=0$ and $x=0.01$ small upturn was observed below around 2 K. Neglecting this upturn, the γ values were estimated by extrapolation of the linear part at high temperatures.

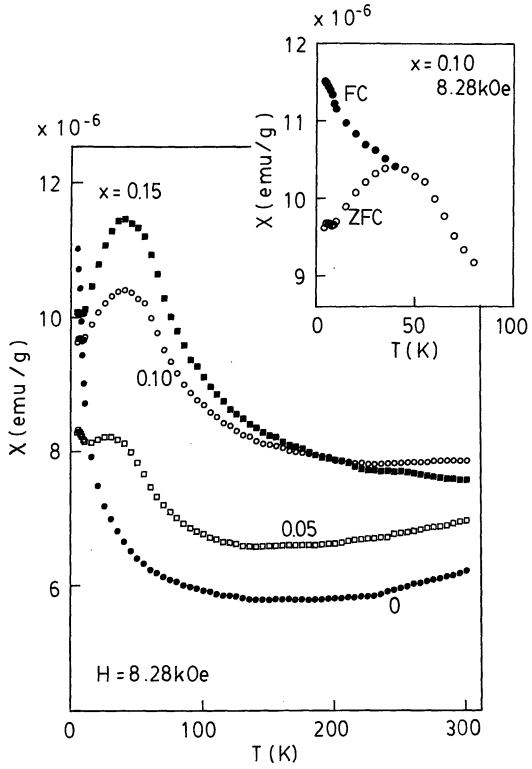

Fig. 2. Temperature dependence of the susceptibility of $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ under an applied field of 8.3 kOe. An inset indicates the susceptibility of zero field cooled and field cooled processes for $x=0.1$.

The γ values thus estimated are plotted as a function of x in Fig. 4. It should be noted that the large γ value observed for $x=0$ and $x=0.01$ rapidly decrease with increasing x and becomes a normal value in the spin glass region.

The profile of thermal expansion curves changes remarkably by substitution of Al for Mn as shown in Fig. 5. For $x=0$ and $x=0.01$, the expansion curves look normal but its coefficient is as large as 40×10^{-6}/K at room temperature. In the spin glass region, the coefficient at room temperature decreases to a normal value of about 20×10^{-6}/K. For $x=0.05$ and $x=0.1$, a volume expansion was observed below 100 K but it disappears for $x=0.15$.

Figure 6 shows the temperature dependence of electrical resistivity of $Y(Sc)(Mn_{1-x}Al_x)_2$ normalized at 300 K. The absolute value of the resistivity scatters around $100\sim200\,\mu\Omega$ cm at 300 K, probably due to the presence of

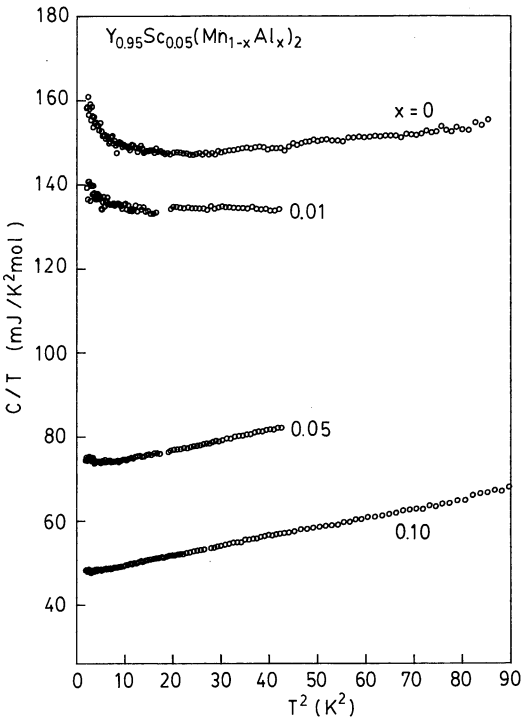

Fig. 3. Low temperature specific heats of $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ plotted in a form of C/T vs T^2.

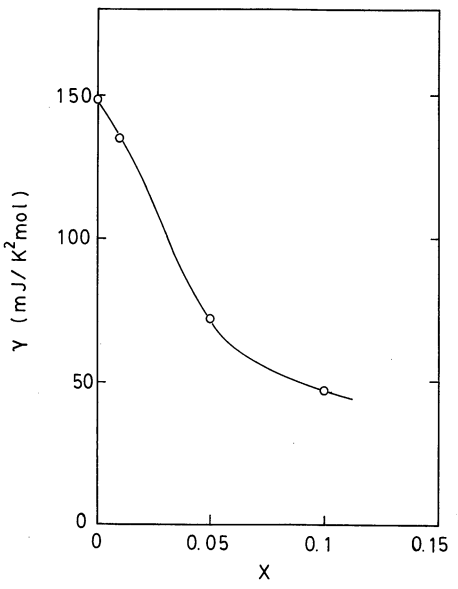

Fig. 4. The electronic specific heat coefficient, γ, of $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ as a function of Al content, x.

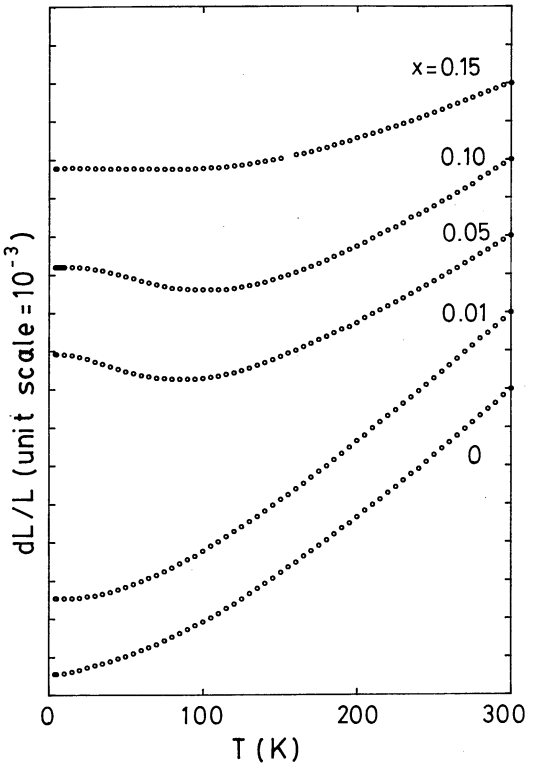

Fig. 5. The thermal expansion curves of $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$.

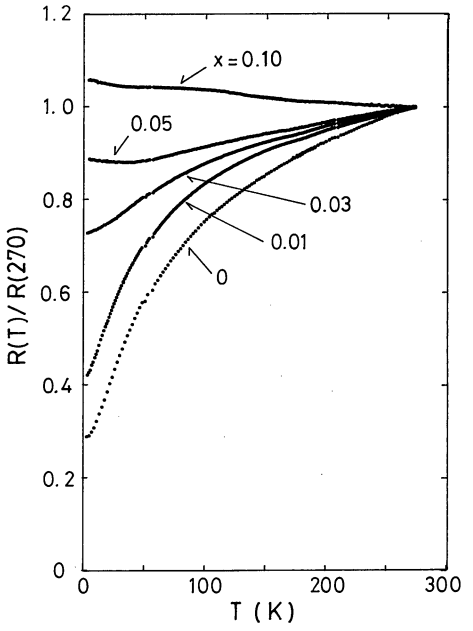

Fig. 6. Temperature dependence of electrical resistivity of $Y_{0.95}Sc_{0.05}(Mn_{1-x}Al_x)_2$ normalized at $T=270$ K.

microcracks in the samples. The profile of ρ-T curves also changes remarkably by substitution of Al. For $x=0$, ρ increases rapidly at low temperature proportionally to T^2 and tends to saturate at high temperatures similarly to UPt_3.[16] With increasing x, ρ becomes less sensitive to temperature and exhibits a minimum for $x \geq 0.05$.

§5. Discussion

We have shown that the ground state of Y(Sc)Mn_2 may be regarded as a QSL realized through the spin frustration and that by substituting Al for Mn the system transfers to a spin glass state due to partial raising of spin configurational degeneracy of the frustrated system. We observed drastic changes in thermodynamic and electric properties when the system transfers from the QSL state to the spin-glass state. Since there is no comprehensive theory to treat the thermodynamic properties of the QSL state in a metallic system, we discuss the present results on the basis of the spin fluctuation theory developed by Takahashi,[21,22] who stresses the importance of zero-point spin fluctuations. In terms of spin fluctuation theory, the QSL state can be described as a state where giant zero-point spin fluctuations with strong antiferromagnetic correlation exist. According to his theory, the squared local spin fluctuation amplitude, $\langle S_L^2 \rangle_{TOT}$, can be given by the sum of the average squared amplitude of zero-point spin fluctuations, $\langle S_L^2 \rangle_{ZP}$, thermal spin fluctuations, $\langle S_L^2 \rangle_{TH}$, and the squared static local moment, $\langle S_L^2 \rangle_{ST}$, induced by a molecular field as,

$$\langle S_L^2 \rangle_{TOT} = \langle S_L^2 \rangle_{ZP} + \langle S_L^2 \rangle_{TH} + \langle S_L^2 \rangle_{ST}. \quad (1)$$

Furthermore, he assumed that the total amplitude is almost constant against temperature. For pure local moments, $\langle S_L^2 \rangle_{TOT}$ corresponds to $S(S+1)$. In the present system, the total amplitude should reach to $S=3/2$ because the Mn moment in antiferromagnetic YMn_2 is $2.7\mu_B$. For paramagnetic state of Y(Sc)Mn_2, the Mn moment, m_{Mn} ($=2\sqrt{\langle S_L^2 \rangle_{OBS}}$, was estimated by energy integrated neutron scattering.[19] The results are shown in Fig. 7 by open circles. The estimated value of m_{Mn} is somewhat smaller than the maximum value of $3\,\mu_B$ and is temperature dependent. However, as discussed in Ref. 19, the energy window of neutron scattering of about 25 meV is not wide enough to detect all of the fluctuations and therefore the observed value of m_{Mn} gives the lower limit of the total spin fluctuations. It is possibly that the total amplitude approaches the maximum value by taking account of the contribution of higher frequency fluctuations, which are not detected by neutron scattering. The increase of m_{Mn} with increasing temperature may be explained as that the thermal excitation of low frequency fluctuations gives rise to the increase in observable fluctuations within the limited energy window. The amplitude of thermal spin fluctuation can be estimated by integrating the intensity for energy gain scattering as proposed by Ishikawa.[23] The results are also shown in Fig. 7 by closed circles. It should be noted that a large value of m_{Mn} at the lowest temperature is purely due to zero-point fluctuations.

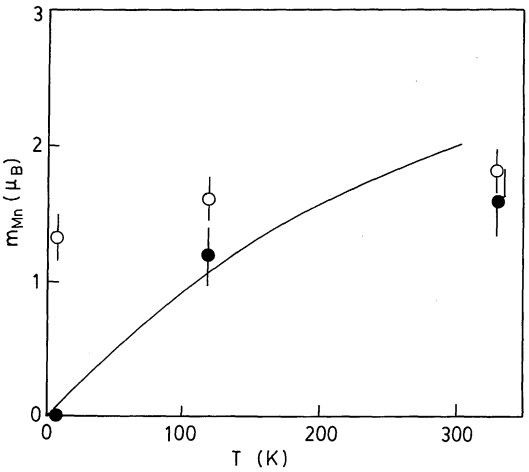

Fig. 7. Temperature dependence of paramagnetic Mn moment, m_{Mn} of $Y_{0.97}Sc_{0.03}Mn_2$. Open circles represent m_{Mn} calculated from the observed spin fluctuations, ($2\sqrt{\langle S_L^2 \rangle_{OBS}}$) and closed circles from thermal spin fluctuations, ($2\sqrt{\langle S_L^2 \rangle_{TH}}$). A solid line was estimated by the analysis of the thermal expansion curve.[9]

It is clear that zero point fluctuations do not involved in the magnetic entropy, S_{mag}, but only thermal fluctuations contribute to S_{mag}. Figures 8(a) and (b) represent a schematic feature of the temperature dependence of local spin amplitude and the magnetic entropy, S_{mag}, for $x=0$. The magnetic entropy as well as

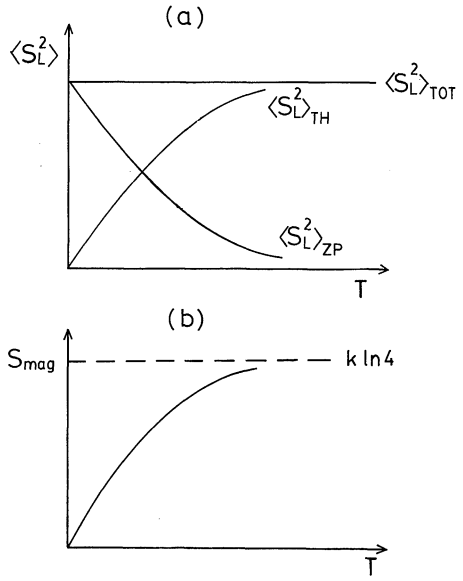

Fig. 8. (a) Schematic representation of temperature dependence of the local amplitude of longitudinal spin fluctuations in Y(Sc)Mn_2. $\langle S_L^2 \rangle_{TOT}$: total amplitude. $\langle S_L^2 \rangle_{TH}$: thermal spin fluctuations. $\langle S_L^2 \rangle_{ZP}$: zero-point spin fluctuations. (b) Temperature dependence of magnetic entropy in Y(Sc)Mn_2.

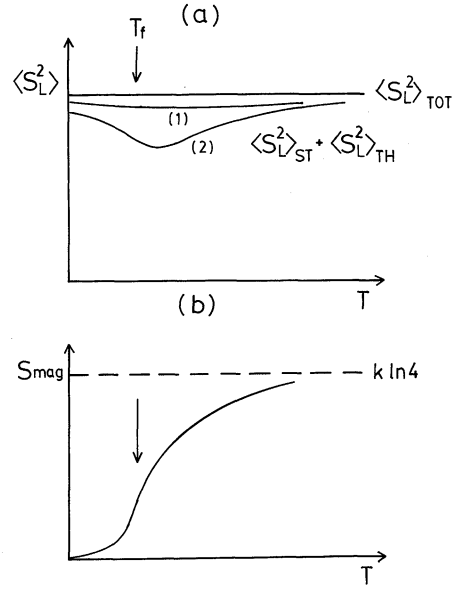

Fig. 9. (a) Schematic representation of temperature dependence of the local amplitude of longitudinal spin fluctuations in Y(Sc)$(Mn_{1-x}Al_x)_2$. $\langle S_L^2 \rangle_{TOT}$: total amplitude. $\langle S_L^2 \rangle_{ST}$: static local moment. $\langle S_L^2 \rangle_{TH}$: thermal spin fluctuations. (1) and (2) correspond to $x=0.05$ and 0.1, respectively. (b) Temperature dependence of magnetic entropy in Y(Sc)$(Mn_{1-x}Al_x)_2$.

$\langle S_L^2 \rangle_{TH}$ increases rapidly with increasing temperature associated with thermal excitations of low-energy spin fluctuations. At the high temperature limit, the magnetic entropy should approach to $S_{mag}=k_B \ln(2S+1) \approx k_B \ln 4$, where k_B is the Boltzmann constant. The large low temperature specific heat can be ascribed to the rapid increase of S_{mag}. On the other hand, the temperature dependence of $\langle S_L^2 \rangle$ and S_{mag} for Al substituted systems may be schematically given as Figs. 9(a) and 9(b). At low temperatures, $\langle S_L^2 \rangle_{ST}$ is induced and the magnetic entropy is reduced by spin glass freezing. Thus, the γ value decreases rapidly with increasing x.

The thermal expansion and the electrical resistivity are also explained on the basis of the present model by assuming that the zero-point fluctuations contribute neither to magnetovolume effects nor to resistivity. The enhanced thermal expansion coefficient for $x=0$ can be ascribed to the rapid increase in $\langle S_L^2 \rangle_{TH}$, as discussed in ref. 9. The volume expansion observed at low temperatures for $0.05 \leq x \leq 0.1$ can be explained by the increase of $\langle S_L^2 \rangle_{ST}$ due to spin glass freezing. An absence of the thermal expansion anomaly and a small (normal) expansion coefficient for $x \geq 0.15$ may be understood as the result of stabilized Mn moment as discussed in ref. 9. The temperature dependence of resistivity can be also elucidated in the same context. The rapid raise of ρ at low temperatures can be ascribed to a rapid increase of collision rate with thermal spin fluctuations. At high temperatures, $\langle S_L^2 \rangle_{TH}$ saturates to the upper limit value and hence the resistivity too. If $\langle S_L^2 \rangle_{TH}$ and $\langle S_L^2 \rangle_{ST}$ contribute to electron scattering with the same cross section, it is reasonable that the magnetic resistivity becomes nearly constant for $x \geq 0.10$.

Next, we refer to the temperature dependence of susceptibility. Usually, a constant susceptibility or a positive derivative of χ-T curves observed in Y(Sc)Mn_2 and YMn_2 above T_N is regarded as the evidence of itinerant electron magnetism in conflict to the present model. However, the existence of the strong antiferromagnetic correlation even at 700 K[11] implies Curie-Weiss-like behavior in the stag-

gered susceptibility $\chi(Q)$ but not in the uniform susceptibility, $\chi(0)$. The increase of static susceptibility with increasing temperature has been experimentally[24] and theoretically[25,26] studied for low dimensional insulators with antiferromagnetic pair interactions. If any long range antiferromagnetic order is not formed due to dimensionality[25] or frustration[26] effects, the static susceptibility shows a broad maximum at around a characteristic temperature for the exchange energy. The increase of static susceptibility with increasing temperature in the present system with $x=0$ may be explained in this context. If it is the case, the antiferromagnetic exchange energy between nearest neighbor Mn pairs is so strong as several hundred Kelvin. Strong antiferromagnetic correlations observed at high temperatures[11] support this interpretation. It is indicative to note the trend of forming a maximum in static susceptibility of YMn_2 at around 700 K.[27]

As we have pointed out in section 2, the present system with $x=0$ exhibits similarity to so-called heavy fermion systems, particularly those of actinide compounds, in many respects. Can we call Y(Sc)Mn_2 a heavy fermion system? We consider that in the present system, the spin freedom remains finite at low temperatures without forming an antiferromagnetic order due to frustration and finally condenses into a singlet state through some quantum effects. Such a mechanism should give rise to mass enhancement. In this sense, there is similarity to a dense Kondo system. However, the mechanism to form the singlet state may be different from 4f heavy fermion compounds. In this case, inter-site exchange interactions play an important role possibly forming a RVB-like state. The original concept of the RVB state was proposed for purely localized spin systems. In this case, the singlet state, which is described by an appropriate linear combination of spin wave-functions, is stabilized by the second order perturbation effect of exchange interactions. On the other hand, the present system is metallic and 3d electrons move from atom to atom through the transfer integral, which may also help the formation of the RVB-like state. Recently, Lacroix and Pinettes[28] discussed on the effect of frustration in itinerant antiferromagnetism on the basis of the Hubbard model. One of characteristic results of their theory is the existence of a mixed phase consisting of magnetic and nonmagnetic atoms. Such a mixed phase has been actually found in $DyMn_2$,[29,30] $Tb_{1-x}Sc_xMn_2$[31] and $TbMn_2$ under pressure[32] but not in $Y_{1-x}Sc_xMn_2$ system.[12] Instead, we found the QSL state in the latter system. Since their theory does not take into account of the effects of dynamical spin fluctuations, the existence of a RVB-like state in itinerant electron systems with frustration seems theoretically open for question.

Acknowledgements

The authors are indebted to Mr. H.Nakamura for discussions, to Mr. R. Iehara for his technical support. This work is partially supported by a Grand-in-Aid for Scientific Research given by the Ministry of Education, Science and Culture (No. 02452038).

References

1) P. W. Anderson: Mater. Res. Bull. **8** (1973) 153.
2) P. Fazekas and P.W. Anderson: Philos. Mag. **30** (1974) 423.
3) J. Villain: Z. Phys. B **33** (1979) 31.
4) J. N. Reimers, J. E. Greedan, R. K. Kremer, E. Gmelin and M. A. Subramanian: Phys. Rev. B **43** (1991) 3387.
5) J. N. Reimers, J. R. Greedan, C. V. Stager, M. Bjorgvinnsen and M. A. Subramanian: Phys. Rev. B **43** (1991) 5692.
6) Y. Nakamura, M. Shiga and S. Kawano: Physica B **120** (1983) 212.
7) R. Ballou, J. Deportes, R. Lemaire, Y. Nakamura and B. Ouladdiaf: J. Magn. Magn. & Mater. **70** (1987) 129.
8) R. Cywinski, S. H. Kilcoyne and C.A. Scott: J. Phys. Condens. Matter **3** (1991) 6473.
9) M. Shiga, H. Wada, H. Nakamura, K. Yoshimura and Y. Nakamura: J. Phys. F **17** (1987) 1781.
10) J. Deportes, B. Ouladdiaf and K. R. A. Ziebeck: J. Phys. (paris) **48** (1987) 1029.
11) T. Freltoft, P. Böni, G. Shirane and K. Motoya: Phys. Rev. B **37** (1988) 3454.
12) H. Nakamura, H. Wada, K. Yoshimura, M. Shiga, Y. Nakamura, J. Sakurai and Y. Komura: J. Phys. F **18** (1988) 981.
13) H. Nakamura, Y. Kitaoka, K. Yoshimura, Y. Kohori, K. Asayama, M. Shiga and Y. Nakamura: J. Phys. (paris) **49** (1988) C8-257.
14) H. Wada, M. Shiga and Y. Nakamura: Physica B **161** (1989) 197.

15) M. Shiga, H. Wada, Y. Nakamura, J. Deportes and K. R. A. Ziebeck: J. Phys. (Paris) **49** (1988) C8-241.
16) J. J. M. Franse, A. Menovsky and A. de Visser: Z. Phys. B **59** (1985) 15.
17) K. Kadowaki and S. B. Woods: Solid State Commun. **58** (1986) 507.
18) H. Kamimura, J. Sakurai, K. Komura, H. Nakamura, M. Shiga and Y. Nakamura: J. Magn. & Magn. Mater. **70** (1987) 145.
19) M. Shiga, H. Wada, Y. Nakamura, J. Deportes and K. R. A. Ziebeck: J. Phys. Soc. Jpn. **57** (1988) 3141.
20) M. Shiga, K. Fujisawa and H. Wada: J. Magn. & Magn. Mater. **90–91** (1990) 331.
21) Y. Takahashi: J. Phys. Condens. Matter **2** (1990) 8405.
22) Y. Takahashi: J. Phys. Soc. Jpn. **55** (1986) 3553.
23) Y. Ishikawa: J. Magn. & Magn. Mater. **31–34** (1983) 309.
24) Y. Nakazawa and M. Ishikawa: Physica C **158** (1989) 381.
25) S. Katsura, T. Horiguchi and M. Suzuki: Physica **46** (1970) 67.
26) D. Poilblanc: Phys. Rev. B **42** (1990) 4049.
27) M. Shiga: Physica B **149** (1988) 293.
28) C. Lacroix and C. Pinettes: J. Magn. & Magn. Mater. **104–107** (1992) 751.
29) K. Yoshimura, M. Shiga and Y. Nakamura: J. Phys. Soc. Jpn. **55** (1986) 3585.
30) C. Ritter, S. H. Kilcoyne and R. Cywinski: J. Phys. Condens. Matter **3** (1991) 727.
31) M. Shiga, J. Hirokawa, H. Wada and Y. Nakamura: J. Phys. Soc. Jpn. **59** (1990) 1410.
32) S. Mondel, R. Cywinski, S. H. Kilcoyne, B. D. Rainford and C. Ritter: Physica B **180** (1992) 108.