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Effects of Spin Fluctuations on the Specific Heat in YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$

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The specific heat measurements of YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$, which exhibit giant spin fluctuatuions in the paramagnetic state, were carried out in the temperature range of 13 K to 300 K. The spin fluctuation contribution to the specific heat C_m was estimated by subtracting the phonon and electronic parts. The magnetic entropy S_m was deduced from C_m. Above 120 K, where the the effect of the antiferromagnetic transition vanishes, the entropy curves of two compounds coincide each other, indicating that in the paramagnetic state, YMn_2 has the same amplitude of spin fluctuations as $Y_{0.97}Sc_{0.03}Mn_2$. The absolute value of the entropy was also discussed taking account of results of neutron scattering measurements.

[specific heat, spin fluctuations, magnetic entropy, $Y_{1-x}Sc_xMn_2$]

§1. Introduction

Effects of spin fluctuations on the specific heat in itinerant electron magnetism have been of considerable interest from both theoretical and experimental points of view. It is known that spin fluctuations enhance the effective mass of electrons at low temperatures, which was initially pointed out by Doniach and Engelsberg,[1] Berk and Schrieffer.[2] Until now, the enhancement of the low temperature specific heat coefficient, γ, has been extensively investigated for a lot of nearly and weakly ferromagnetic compounds. Recent developments of the spin fluctuation theory enable us to make quantitative comparisons between γ and other physical quantities.[3,4] On the other hand, progress in the investigations above T_C is unsatisfactory from both theoretical and experimental aspects. Beyond the random phase approximation, Murata and Doniach discussed the magnetic specific heat by taking account of mode-mode coupling between spin fluctuations.[5] Subsequently, Makoshi and Moriya have calculated the magnetic specific heat for weakly itinerant ferromagnets on the basis of the self-consistent renomalization theory of spin fluctuations.[6] The latter results indicate the magnetic specific heat increases with increasing temperature above T_C. However, it is not easy to separate the magnetic specific heat at high temperatures experimentally, because it is generally much smaller than the phonon contribution to the specific heat. Difficulties of the correct estimation of the phonon part also make it ambiguous to evaluate the magnetic specific heat above T_C.

For metallic Cr, the presence of the magnetic specific heat due to spin fluctuations was suggested by White *et al.*,[7] by assuming the Debye model for the phonon specific heat. Quite recently, Grimvall *et al.* reanalyzed thermodynamical data of Cr and pointed out the importance of the anharmonic effect on the phonon specific heat.[8] They have shown that the magnetic entropy remarkably increases with increasing temperature above 1000 K due to spin fluctuations.

For further understanding of effects of spin fluctuations on the specific heat, it is strongly desired to study thermal properties of typical examples for spin fluctuators. The Laves phase compound YMn_2 is one of the best candidates for this purpose. This compound is a helimagnet below $T_N = 100$ K with the Mn moment of 2.7 μ_B. The magnetic phase transition is of first order accompanied with the volume change of 5% due to the collapse of Mn local moments. Above T_N, YMn_2 shows remarkable spin fluctuations, which were demonstrated by neutron scattering measurements[9] and magnetovolume effects.[10] The specific heat of YMn_2 was reported by Okamoto *et al.*[11] According to their results, a specific heat anomaly was observed at T_N and the corresponding entropy change is 3.9 J/K mol. Furthermore, they observed the strong temperature dependence of the specific heat above T_N, which is ascribed to giant spin fluctuations. The antiferromagnetism of YMn_2 is easily destroyed by appling the pressure.[12] The substitution of 3% Sc for Y, which reduces the lattice parameter, stabilizes the paramagnetic state down to the lowest temperature.[13] Although no magnetic ordering was observed down to 70 mK,[14] giant spin fluctuations were observed at 8 K in the neutron scattering measurements.[15] Moreover, the paramagnetic scattering intensity increase with increasing temperature, suggesting the thermal growth of spin fluctuations.

Previously, we studied the low temperature specific heat of YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$.[16] The γ value of $Y_{0.97}Sc_{0.03}Mn_2$ is 150 mJ/K^2 mol, which is the largest among 3d transition metal compounds as far as we know. On the other hand, the γ value of the antiferromagnetic state of YMn_2 is 14 mJ/K mol, being comparable to the results from the band calculations.[17] The large enhancement of γ in $Y_{0.97}Sc_{0.03}Mn_2$ is clearly associated with giant spin fluctuations in this system, which may be caused by the geometrical spin frustrations in this particular compounds discussed in a previous paper.[18]

In order to study the effects of spin fluctuations on the specific heat at high temperatures, we extended measurements up to 300 K. In this paper, we report the specific heat of YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$ and discuss the effects of spin fluctuations.

§2. Experimental

Samples were prepared by arc-melting in an argon atmosphere. Used starting materials Y, Sc and Mn, have the purity of 3N. As-cast samples were used for measurements, because the annealed ones are too brittle to be shaped for measurements. Powder X-ray diffraction analyses confirmed that samples were of a single phase with C15 structure. Specific heat measurements were performed by a standard heat-pulse method with a lidded sample cell surrounded by double adiabatic shields in the temperature range of 13 K to 300 K. The detail of apparatus was described elsewhere.[19] The weight of samples was 10 g to 12 g.

§3. Results

The specific heat of YMn_2 (closed circle) and $Y_{0.97}Sc_{0.03}Mn_2$ (open circle) is shown in Fig. 1 as a function of temperature. Data in the low temperature (1.4 K ~ 6.5 K) reported previously[16] are also included. The solid line is the nonmagnetic contribution to the specific heat, which will be described later. As seen in Fig. 1, the Néel temperature is 106 K for YMn_2 and a specific heat anomaly was observed around T_N. This specific heat anomaly consists of a broad peak, and the divergence of the specific heat, which is characteristic of the first order phase transition,was not observed. Similar behavior was also reported by Okamoto *et al.*[11] The absence of a sharp peak in the specific heat curve is may be attributable to the large volume change of this compound at T_N through the mechanism stated below. During heating, a part of the sample transforms into the paramagnetic state, which causes inhomogenity in the internal pressure, giving rise to the distributions of the Néel temperature, and

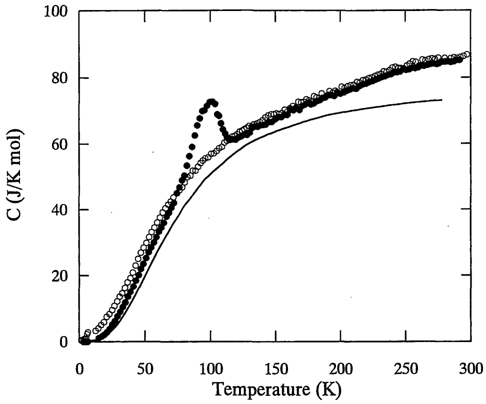

Fig. 1. Specific heat of $Y_{1-x}Sc_xMn_2$. $x=0.0$ (closed circle), $x=0.03$ (open circle). The solid line is the nonmagnetic specific heat for $Y_{1-x}Sc_xMn_2$ estimated by using Debye function with $\Theta_D=304$ K.

the smearing of the transition over a finite temperature range. No anomaly was found for $Y_{0.97}Sc_{0.03}Mn_2$ in the temperature range that we studied. It should be noted that the magnitude of the specific heat of $Y_{0.97}Sc_{0.03}Mn_2$ is larger than that of YMn_2 below 60 K. These results suggest that the effect of spin fluctuations on the specific heat is significant in this temperature range. Above 120 K, the specific heat curves of two samples are nearly the same within experimental errors, indicating that, in the paramagnetic state, YMn_2 has the same amplitude of spin fluctuations as $Y_{0.97}Sc_{0.03}Mn_2$.

§4. Discussion

The total specific heat, C_{total}, of magnetic metals can be written as follows,

$$C_{\text{total}} = C_e + C_{\text{ph}} + C_m$$

where, C_e, C_{ph} and C_m are electronic, phonon and magnetic contributions, respectively. The electronic term is expressed as $\gamma_0 T$, where γ_0 is the unenhanced specific heat coefficient expected from the electron density of states. Since the magnetic contribution is negligibly small in the antiferromagnetic state, the γ_0 value of YMn_2 is estimated as 14 mJ/K mol from the low temperature measurement. While the γ_0 value for the paramagnetic state cannot be determined from experiments because the low temperature specific heat coefficient of $Y_{0.97}Sc_{0.03}Mn_2$ is strongly enhanced by spin fluctuations. Here, we adopt $\gamma_0 = 9$ mJ/K mol for the paramagnetic state, which is evaluated from the result of band calculation.[17]

The phonon part is approximated by the Debye function. The Debye temperature, Θ_D, can be estimated from the slope of C/T vs. T^2 plots at low temperatures. Our previous measurements between 1.4 and 6.5 K give $\Theta_D = 304$ K and 301 K for YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$, respectively. Assuming that Θ_D is independent of the temperature, we use the Debye function with $\Theta_D = 304$ K as the phonon contribution for both YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$.

The magnetic specific heat, C_m, is obtained by subtracting $C_e + C_{\text{ph}}$ from C_{total}. The results are shown in Fig. 2 as functions of the temperature. In the C_m vs T curve of YMn_2, a large peak is observed around T_N, above which it increases with increasing temperature, as pointed out by Okamoto *et al.*[11] previously. On the other hand, C_m of $Y_{0.97}Sc_{0.03}Mn_2$ shows a broad peak around 50 K, followed by an increase with increasing temperature. The temperature variation of C_m above 120 K is identical with that of YMn_2. Below the large peak, the substantial magnetic specific heat was obtained in the antiferromagnetic state. A possible origin may be due to the temperature variation of the sublattice magnetization, as demonstrated by Mössbauer studies.[20,21] However, the estimation of C_m is very sensitive to the choice of Θ_D in this temperature range. If we take a little smaller value of Θ_D, the C_m below T_N is substantially reduced. Therefore, it is difficult to have a definit conclusion for the origin of the hump of C_m just below T_N. The temperature dependence of C_m/T is shown in Fig. 3. At the low temperature limit, C_m/T corresponds to the magnetic contribution to the low temperature specific heat coefficient, γ. $Y_{0.97}Sc_{0.03}Mn_2$ shows a large C_m/T value of 0.14 J/K^2 mol due to strong spin fluctuations. With increasing temperature, C_m/T of $Y_{0.97}Sc_{0.03}Mn_2$ decreases, showing a broad minimum at around 150 K. Above 150 K, it gradually increases as well as C_m/T of YMn_2.

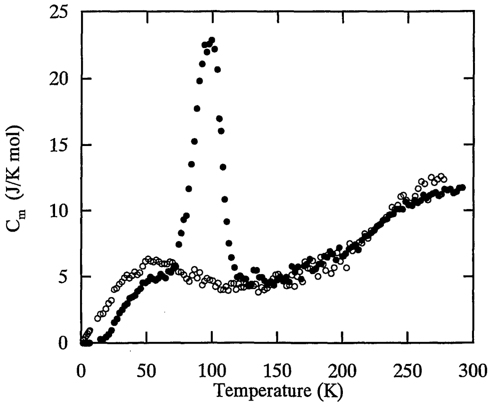

Fig. 2. The magnetic specific heat of $Y_{1-x}Sc_xMn_2$. $x=0.0$ (closed circle), $x=0.03$ (open circle).

The magnetic entropy is calculated by,

$$S_m = \int_0^T \frac{C_m}{T} \, dT.$$

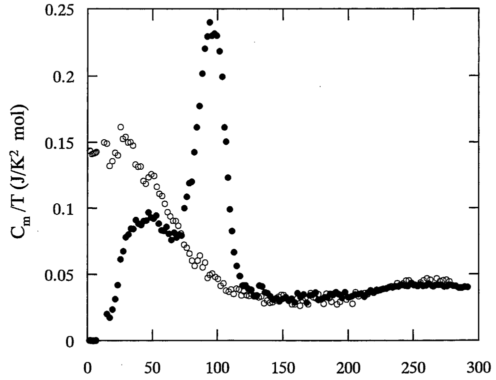

Fig. 3. The temperature dependence of C_m/T for $Y_{1-x}Sc_xMn_2$. $x=0.0$ (closed circle), $x=0.03$ (open circle).

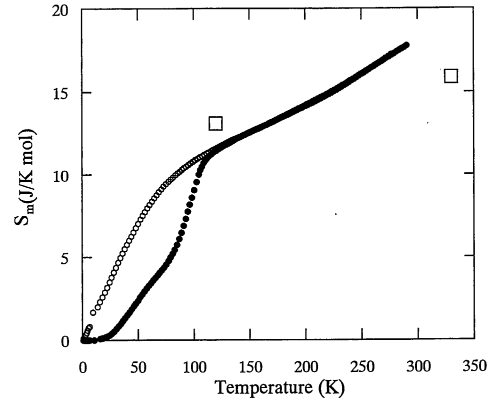

Fig. 4. The temperature dependence of the magnetic entropy for $Y_{1-x}Sc_xMn_2$. $x=0.0$ (close circle), $x=0.03$ (open circle). Open squares are estimated from neutron scattering data for $Y_{1-x}Sc_xMn_2$ at 120 and 330 K.

The S_m vs. temperature curves of YMn_2 and $Y_{0.97}Sc_{0.03}Mn_2$ are represented in Fig. 4. The magnetic entropy of YMn_2 gradually increases, followed by an abrupt rise in the temperature range of 80 K and 120 K, which is due to the magnetic transition. Above T_N, the magnetic entropy increases with increasing temperature. This is reasonably ascribed to the thermal excitation of spin fluctuations. On the other hand, $Y_{0.97}Sc_{0.03}Mn_2$ shows a rapid increase in S_m below 100 K in spite of the absence of the magnetic order. Above 120 K, S_m of $Y_{0.97}Sc_{0.03}Mn_2$ coincides with that of YMn_2. These results indicate that the paramagnetic state of two compounds is equivalent from the thermodynamical point of view, which means the same amplitude of spin fluctuations for both compounds. Therefore, the entropy change due to the antiferromagnetic transition, which was observed in YMn_2, has to be released in low temperatures below 100 K in $Y_{0.97}Sc_{0.03}Mn_2$, as the increase of entropy due to the thermal excitation of spin fluctuations, resulting in the enhancement of γ value, as predicted in a previous paper.[18)]

The present results have revealed the remarkable growth of spin fluctuations in $Y_{0.97}Sc_{0.03}Mn_2$ below 100 K. Above 100 K, it increases nearly linearly with increasing temperature as well as that of YMn_2. Previously, we have estimated the amplitude of spin fluctuations of $Y_{0.97}Sc_{0.03}Mn_2$ by neutron scattering measurements.[15)] According to those results, the total amplitude of spin fluctuations is less sensitive to the temperature, while that of thermal spin fluctuations, which can be estimated from energy gain scattering, increases with increasing temperature. The estimated values of the paramagnetic Mn moment, m_{Mn}, are 0, 1.2 and 1.6 μ_B at $T=8$, 120 and 330 K, respectively. These results suggest that the increase in m_{Mn} is remarkable at low temperatures. In this context, the present results are consistent with the neutron scattering data. The observed S_m value is considerably large, being 17 J/K mol at 300 K, and it still increases with increasing temperature. At the high temperature limit, where spin fluctuations are completely saturated, the magnetic entropy should approach to $S_m=2R\ln(2S+1)=23.1$ J/K mol, for $S=3/2$ which corresponds to about 3 μ_B of the antiferromagnetic state. A factor 2 is the number of Mn atoms per formula unit. This entropy would be released at around 700 K, where the static susceptibility of YMn_2 forms a maximum. Therefore, it is understandable that S_m continues to increase in the temperature range that we studied. If we extend the same formula, $S_m=2R\ln(2S+1)$ for unsaturated spin fluctuations with $2S=m_{Mn}$, we obtain $S_m=13.1$ and 15.9 J/K mol at 120 K and 330 K, respectively. As shown in Fig. 4 by open squares, these values approximately agree with the present results. Although such a picture is too simplified, it is rather interesting that the entropy of the itinerant antiferromagnetic system can be represented by the formula for the local moment systems. In order to confirm this point, further experimental efforts, especially the collection of the neutron scattering data for giant spin fluctuations are strongly desired.

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