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Spin-Liquid to Spin-Glass Transition in $Y(Sc)(Mn_{1-x}Al_x)_2$: Polarized Neutron Scattering Study

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The scattering of polarized neutrons has been measured in order to study the spin dynamics in $Y_{0.97}Sc_{0.03}Mn_2$ and $Y_{0.97}Sc_{0.03}(Mn_{0.9}Al_{0.1})_2$. A large magnetic scattering peak observed at around $Q = 1.6\,\text{Å}^{-1}$ indicates the existence of strong antiferromagnetic spin fluctuations. The energy and Q spectra obtained at 290 K exhibit nearly the same profiles for both samples, while those obtained at low temperatures are quite different; for $Y(Sc)Mn_2$ the intensity and the energy width decrease only slightly with decreasing temperature and the intrinsic width remains finite ($2\Gamma = 20 \pm 5$ meV) at the lowest temperature (10 K), whereas for $Y(Sc)(Mn_{0.9}Al_{0.1})_2$, the intensity increases rapidly due to narrowing of the energy spectrum to the resolution limit ($2\Gamma_{\text{res}} = 5.8$ meV) at 10 K, and instead, diffuse scattering was clearly observed at positions corresponding to the magnetic Bragg peaks of YMn_2, implying a slowing down of spin fluctuations and the presence of short range magnetic order at the low temperature. These results are discussed in terms of a spin-liquid to spin-glass transition caused by Al substitution.

KEYWORDS: YMn_2, neutron scattering, spin fluctuations, spin liquid, spin glass

The Laves phase intermetallic compound YMn_2 is an antiferromagnet with a long-range helically modulated structure.[1)] The Néel temperature is about 100 K and the ordered moment is $2.7\mu_B$. The antiferromagnetism is easily suppressed by applying pressure[2)] or substituting a small amount of a third element, which results in compressive chemical pressure, such as Sc.[3)] $Y_{0.97}Sc_{0.03}Mn_2$ is paramagnetic down to the lowest temperature. The absence of static Mn moments was confirmed by NMR down to 70 mK.[4)] Paramagnetic $Y(Sc)Mn_2$ exhibits striking characteristics. The low-temperature specific heat coefficient γ is very large compared to those of other 3d metals, being 150 mJ/K^{2}mol, which is about 15 times larger than expected from the bare density of states.[5)] It is likely that this enhancement of the γ-value is due to strong spin fluctuations in this system. In fact, by measuring neutron scattering, we have observed giant spin fluctuations with strong antiferromagnetic correlations even at 8 K.[6)] Noting that the Mn sublattice in the C15 structure is equivalent to the B site in the cubic spinel lattice and forms a fully frustrated system, we have speculated that the frustration of antiferromagnetic interactions suppresses the formation of long range magnetic order and that the ground state of $Y(Sc)Mn_2$ is a spin-liquid state.[7)] If this is the case, it is expected that the substitution of nonmagnetic atoms for Mn should give rise to a transition from a spin liquid to a spin glass as predicted by Villain.[8)] By measuring the susceptibility, the specific heat and the electrical resistivity, we have shown that the substitution of Al for Mn does result in spin-glass-like behaviors in $Y(Sc)(Mn_{1-x}Al_x)_2$ compounds with $x \geq 0.05$.[7)] In this letter, we report the results of polarized neutron scattering measurements for $Y_{0.97}Sc_{0.03}(Mn_{1-x}Al_x)_2$ (abbreviated as $Y(Sc)(Mn_{1-x}Al_x)_2$ in this letter) and the dramatic change in spin dynamics due to Al substitution, supports the above point of view.

Polycrystalline samples of $Y_{0.97}Sc_{0.03}Mn_2$ and $Y_{0.97}Sc_{0.03}(Mn_{0.9}Al_{0.1})_2$ with masses of about 60 g were prepared by argon arc-melting followed by annealing at 800°C for seven days. In order to determine the magnetic scattering caused by spin fluctuations in the paramagnetic state unambiguously, polarized neutron scattering experiments were performed using the triple axis spectrometer, PONTA-5G, installed at JRR-3M. Magnetized Heusler alloy crystals were used in both the monochromator and the analyzer. Both constant energy (E) and constant wave vector (Q) scans were carried out at 10, 120 and 290 K. The fixed incident neutron energy was 80 meV for $Y(Sc)Mn_2$ and 35 meV for $Y(Sc)(Mn_{0.9}Al_{0.1})_2$. The energy resolutions of the spectrometer, $2\Gamma_{\text{res}}$, were 19.3 and 5.8 meV for the former and latter configurations, respectively, with a collimation sequence of (40′-80′-80′-80′). In order to calibrate the intensities and to measure the intrinsic polarization of the instrument, the elastic scattering of the (111) nuclear Bragg peak was monitored under the various conditions used in the experiments. To obtain pure magnetic signals the difference between the spectra for spin flip scattering in the $\mathbf{H} /\!/ \mathbf{Q}$ and $\mathbf{H} \perp \mathbf{Q}$ configurations is determined, where $\mathbf{H}$ is the guide field applied at the sample position and $\mathbf{Q}$ is the scattering vector. Other details of the experiments have been described previously.[11)] In addition to the paramagnetic scattering with polariza-

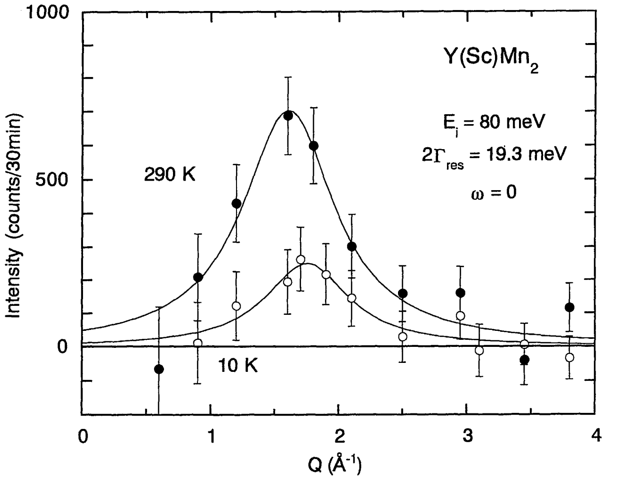

Fig. 1. Magnetic neutron scattering rate of Y(Sc)Mn_2 as a function of wave vector Q measured at zero energy transfer ($\omega = 0$) with an energy resolution of $2\Gamma_{\text{res}} = 19.3$ meV at 10 K (○) and 290 K (●). Solid curves are guides for the eyes.

tion analysis, elastic neutron diffraction measurements without polarization analysis were carried out for the Y(Sc)$(Mn_{0.9}Al_{0.1})_2$ sample to determine the static spin arrangements in the ground state.

Figure 1 shows the results of polarized quasi-elastic Q-scans with an energy window of $2\Gamma_{\text{res}} = 19.3$ meV for Y(Sc)Mn_2 obtained at 10 and 290 K. A large scattering amplitude was observed centered around $Q = 1.6\,\text{Å}^{-1}$. The corresponding wavelength is approximately equal to twice the mean interatomic distance, indicating antiferromagnetic correlations of spin fluctuations. The amplitude decreases with decreasing temperature. Scattering was still observed even at 10 K, suggesting the existence of strong zero-point spin fluctuations. These results are consistent with those of previous neutron scattering experiments for the same sample obtained using a high-energy neutron source and a wide-energy-window spectrometer.[6]

Figure 2 shows the results of E-scans of Y(Sc)Mn_2 measured at $Q = 1.6\,\text{Å}^{-1}$, which corresponds to the peak position of the quasi-elastic Q-scan. We analyzed the data by assuming a Gaussian resolution function $R(\omega)$ and a Lorentzian quasi-elastic scattering function $S(Q, \omega)$. The spectra were fitted using the equation

$$I(\omega) = C \int R(\omega - \omega')S(Q, \omega)\mathrm{d}\omega', \tag{1}$$

where

$$R(\omega) = \frac{1}{\Gamma_{\text{res}}}\sqrt{\frac{\ln 2}{\pi}} \exp\left(-\ln 2 \frac{\omega^2}{\Gamma_{\text{res}}^2}\right), \tag{2}$$

$$S(Q, \omega) = A(Q)\frac{1}{1 - \exp(-\hbar\omega/k_{\text{B}}T)}\frac{\omega\Gamma}{\Gamma^2 + \omega^2}. \tag{3}$$

By choosing appropriate values for $CA(Q)$ and Γ, which are shown in Table I, we obtained fairly good fits as shown in Fig. 2, where the dashed line indicates the deconvoluted spectrum, that is, $S(Q, \omega)$. At 10 K, scattering was observed only on the neutron energy-loss side ($\omega > 0$) of the spectrum, implying the absence of thermally excited spin fluctuations. The full width at half-maximum of Lorentzian, 2Γ, is 20 ± 5 meV, indicating that the characteristic frequency of zero-point fluctuations is $\Gamma/\hbar = 4.8 \times 10^{12}$ Hz. At higher temperatures, the amplitude of the scattering peak increases on both the neutron energy-loss ($\omega > 0$) and energy-gain ($\omega < 0$) sides, indicating an increase of thermally excited spin fluctuations. The width 2Γ also increases with increasing temperature. These observations support the view that the magnetic state of paramagnetic Y(Sc)Mn_2 can be regarded as a spin liquid. Recently, Ballou *et al.* performed inelastic neutron scattering experiments using a single crystal of Y(Sc)Mn_2.[9] They found that the magnetic scattering due to spin fluctuations is localized at particular positions on the reciprocal lattice and suggested that the existence of 4-site collective spin singlets is characteristic of a spin liquid in the C15 structure.

The results for Y(Sc)$(Mn_{0.9}Al_{0.1})_2$ are different. Figure 3(a) shows the neutron diffraction patterns obtained

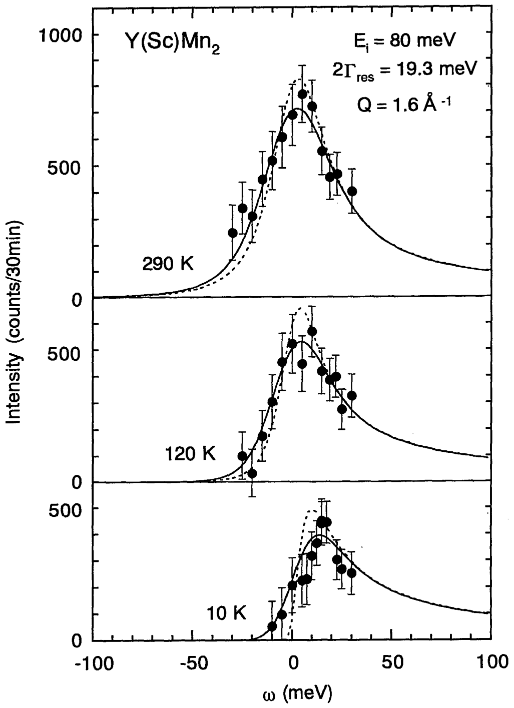

Fig. 2. Magnetic neutron scattering rate of Y(Sc)Mn_2 as a function of energy transfer measured for a momentum transfer of $Q = 1.6\,\text{Å}^{-1}$ at 10, 120 and 290 K. The energy resolution $2\Gamma_{\text{res}}$ is 19.3 meV. Solid curves indicate the spectra calculated using eq. (1) with the parameters given in Table I. Dashed curves indicate the deconvoluted spectra, i.e., $S(Q, \omega)$.

Table I. Parameters used for the fitting of the energy spectra measured at $Q = 1.6\,\text{Å}^{-1}$ (Figs. 3 and 5) to eq. (1).

	T (K)	$CA(Q)$ (Arbitrary units)	2Γ (meV)	$2\Gamma_{\text{res}}$ (meV)
Y(Sc)Mn_2	10	1000 ± 50	20 ± 5	19.3
	120	700 ± 50	25 ± 5	
	290	550 ± 50	30 ± 5	
Y(Sc) $(Mn_{0.9}Al_{0.1})_2$	10	> 4000	< 0.3	5.8
	120	250 ± 20	8 ± 2	
	290	120 ± 10	20 ± 5	

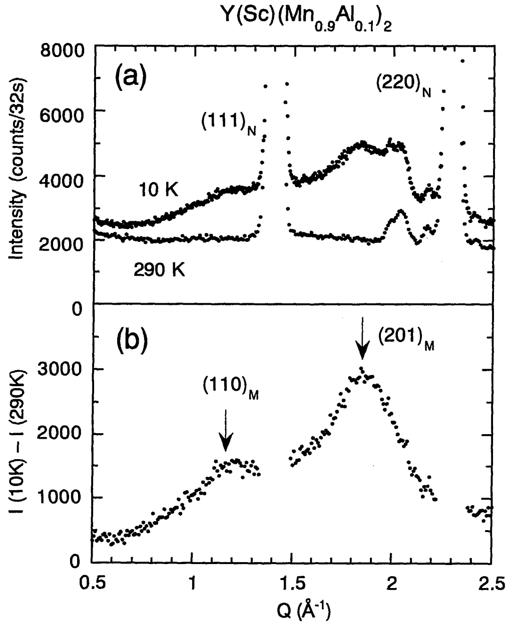

Fig. 3. (a) Neutron diffraction patterns for $Y(Sc)(Mn_{0.9}Al_{0.1})_2$ obtained near the (111) and (220) nuclear peaks at 10 and 290 K. (b) Difference between the intensities at 10 and 290 K, which is the magnetic diffuse scattering. Arrows indicate the positions of magnetic Bragg peaks observed for YMn_2 in the antiferromagnetic state. The profile suggests the existence of short-range magnetic ordering in the YMn_2-type antiferromagnetic structure.

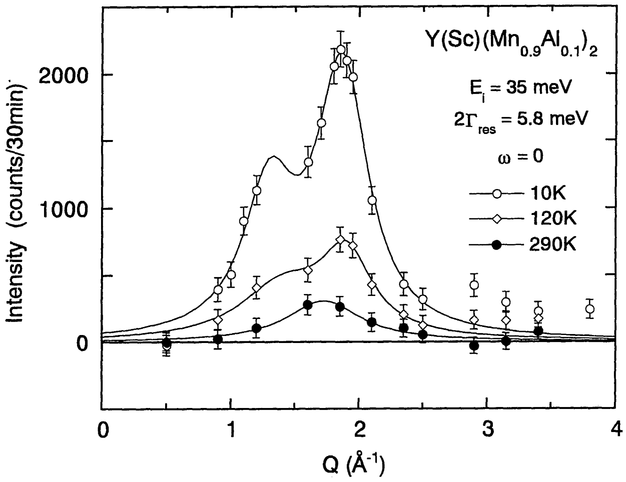

Fig. 4. Magnetic neutron scattering rate of $Y(Sc)(Mn_{0.9}Al_{0.1})_2$ as a function of wave vector Q measured at zero energy transfer ($\omega = 0$) with an energy resolution of $2\Gamma_{\text{res}} = 5.8$ meV at 10 K (●), 120 K (◇) and 290 K (○). Solid curves are guides for the eyes.

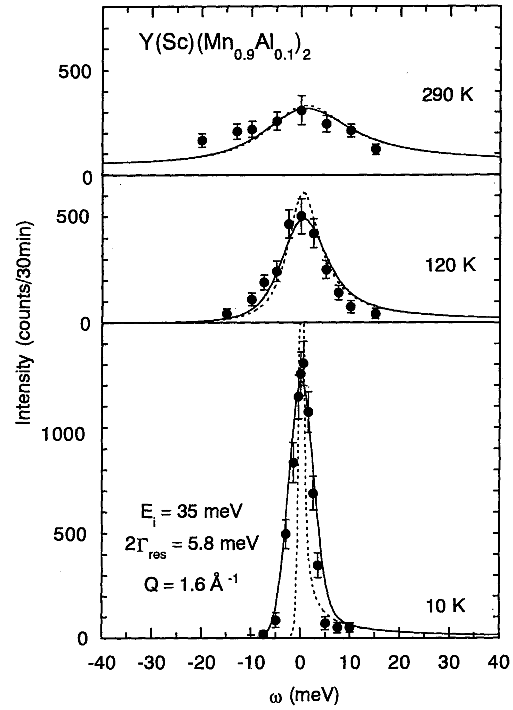

Fig. 5. Magnetic neutron scattering rate of $Y(Sc)(Mn_{0.9}Al_{0.1})_2$ as a function of energy transfer measured for a momentum transfer of $Q = 1.6\,\text{Å}^{-1}$ at 10, 120 and 290 K. The energy resolution $2\Gamma_{\text{res}}$ is 5.8 meV. Solid curves indicate the spectra calculated using eq. (1) and the parameters given in Table I. Dashed curves indicate the deconvoluted spectra, i.e., $S(Q, \omega)$.

at 10 and 290 K measured in the elastic condition without polarization analysis. The difference between the intensities at 10 K and 290 K is shown in Fig. 3(b). Strong diffuse scattering is observed with peaks at around $Q = 1.2$ and $1.8\,\text{Å}^{-1}$, which correspond to the (110) and (201) magnetic Bragg peaks for antiferromagnetic YMn_2, respectively, indicating the existence of short-range antiferromagnetic order. We conclude that the ground state of the Al-substituted compound is a concentrated spin glass, which maintains the spin structure of YMn_2 over a short range.

Figure 4 shows the results of polarized quasi-elastic Q-scans with an energy window of 5.8 meV for $Y(Sc)(Mn_{0.9}Al_{0.1})_2$ obtained at 10, 120 and 290 K. The spectrum obtained at 290 K is similar to that for $Y(Sc)Mn_2$, with a broad peak at around $Q = 1.6\,\text{Å}^{-1}$, although the intensity is much smaller due to the narrower energy window. In contrast to the results for $Y(Sc)Mn_2$, the scattering amplitude increases with decreasing temperature. At 10 K, a double peak structure similar to that of the elastic neutron diffraction pattern was observed.

Figure 5 shows the energy spectra for $Y(Sc)(Mn_{0.9}Al_{0.1})_2$ measured at $Q = 1.6\,\text{Å}^{-1}$. The profile of the spectrum obtained at 290 K is again similar to that for $Y(Sc)Mn_2$. The width of the spectrum was estimated to be $2\Gamma = 20 \pm 5$ meV, which is smaller than that for $Y(Sc)Mn_2$. With decreasing temperature, 2Γ decreases rapidly and approaches the energy resolution limit of the spectrometer at 10 K. This result shows that the spin fluctuations in the Al-substituted compound are strongly suppressed at low temperatures, as expected for the spin-glass freezing at low temperatures. The rapid increase of the scattering amplitude with decreasing temperature in the quasi-elastic Q-scan spectra can be simply explained in terms of narrowing of the energy spectra. When quasi-elastic Q-scan measurements are carried out with a wider energy window ($2\Gamma_{\text{res}} = 19.3$ meV), the scattering intensity at 290 K becomes comparable to that at 10 K, although the double peak structure was not observed at 290 K as was already seen in Fig. 4. The absence of the double peak structure at high temperatures is reasonable because rapid fluctuations mask the short-range space correlation observed in the spin-glass state.

It is of interest to know the local amplitude of spin fluctuations, $\langle S_L^2 \rangle$. In order to estimate $\langle S_L^2 \rangle$ correctly, a full range of data for $S(Q, \omega)$ with respect to Q and ω spaces is necessary, which was not obtained in the present study. Values of $2\sqrt{\langle S_L^2 \rangle}$ for Y(Sc)Mn$_2$ were estimated in a previous study using a high-energy neutron source and a spectrometer with an energy window wide enough to include most of the high frequency fluctuations. Values of $1.8\mu_B$ per Mn atom at 330 K and $1.3\mu_B$ at 8 K were obtained.$^{6)}$ The value of $2\sqrt{\langle S_L^2 \rangle}$ for Y(Mn$_{0.9}$Al$_{0.1}$)$_2$ was estimated using the same method as $2.5\mu_B$.$^{10)}$ Since the effect of Sc substitution is not expected to be significant for this Al composition because the lattice expansion due to Al substitution more than compensates for the compression due to Sc, the magnitudes of $\langle S_L^2 \rangle$ for Y(Sc)(Mn$_{0.9}$Al$_{0.1}$)$_2$ should be similar to those for Y(Mn$_{0.9}$Al$_{0.1}$)$_2$. Furthermore Motoya *et al.* reported that $\langle S_L^2 \rangle$ for Y(Mn$_{0.9}$Al$_{0.1}$)$_2$ is almost independent of temperature in the temperature range of 5-766 K.$^{11)}$

Combining this information regarding $\langle S_L^2 \rangle$ and the present polarized neutron scattering results we can interpret the spin dynamics in the present system as follows. At 290 K, Y(Sc)Mn$_2$ and Y(Sc)(Mn$_{0.9}$Al$_{0.1}$)$_2$ exhibit almost the same behavior, that is, Mn local moments of around $2\mu_B$ fluctuate with an average frequency of 5 THz, maintaining antiferromagnetic correlation. In this sense, they are in a spin-liquid state. With decreasing temperature, on the other hand, the spin dynamics of these two compounds are very different. For Y(Sc)Mn$_2$, the amplitude and frequency of the fluctuations decrease only moderately and the characteristic frequency remains finite at the lowest temperature, implying that the ground state of this compound is a quantum spin-liquid state in the sense that the characteristic energy of the spin fluctuations is much larger than the thermal energy but much lower than the typical Fermi energy for a normal Pauli paramagnet. For Y(Sc)(Mn$_{0.9}$Al$_{0.1}$)$_2$, the frequency of antiferromagnetic fluctuations decreases markedly with decreasing temperature and Mn local moments freeze to form a spin-glass state, with short-range antiferromagnetic order. Such a drastic effect resulting from the substitution of Al for Mn on the spin dynamics can be understood to result from the effects of impurities on a frustrated system, as discussed in a previous paper.$^{7)}$ The present results provide evidence for a spin-liquid to spin-glass transition resulting from partial lifting of spin configurational degeneracies in a fully frustrated system due to impurity effects.

Similar behavior has been observed in β-Mn and β-Mn$_{0.9}$Al$_{0.1}$.$^{12)}$ The Q-dependence of the cross section of magnetic scattering for Y(Sc)Mn$_2$ and β-Mn measured at 290 K under the same condition are shown in Fig. 6. The energy spectra and the effect of the substitution of Al for Mn on the spin dynamics are similar to those for Y(Sc)Mn$_2$, implying that the absence of spin order in β-Mn may be due to a frustration effect.

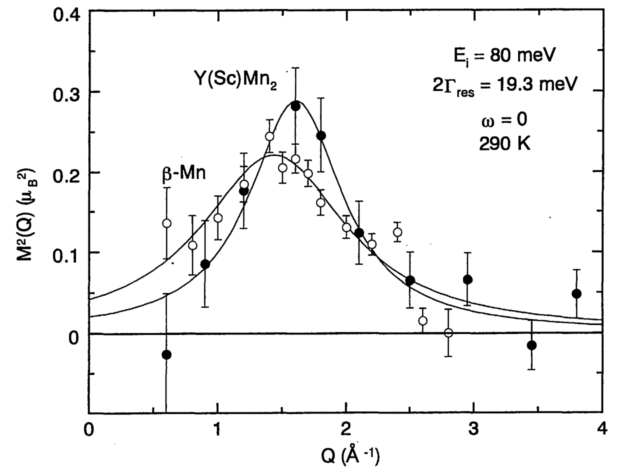

Fig. 6. Magnetic neutron scattering cross sections for Y(Sc)Mn$_2$ (●) and β-Mn (○) at 290 K as a function of wave vector Q measured in the quasi-elastic mode ($\omega = 0$) with the same energy resolution, $2\Gamma_{\rm res} = 19.3$ meV. The ordinate represents the equivalent squared Bohr magneton number of the scattering amplitude, which was estimated by comparison with the magnitude of the (111) nuclear Bragg peak. Solid curves are guides for the eyes.

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