Spin Fluctuations in $(Y_{0.97}Sc_{0.03})Mn_2$: A Geometrically Frustrated, Nearly Antiferromagnetic, Itinerant Electron System

R. Ballou*
Laboratoire de Magnétisme Louis Néel–CNRS, BP 166, 38042 Grenoble Cedex 9, France

E. Lelièvre-Berna
Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

B. Fåk
Commissariat à l'Energie de Physique Theorique, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS/MDN, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
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Inelastic neutron-scattering experiments have been performed on a single crystal of $(Y_{0.97}Sc_{0.03})Mn_2$. The spin fluctuation spectrum is broad in energy and strongly correlated in wave vector, with maximum intensity at the Brillouin zone boundary. There is no magnetic scattering for Brillouin zones centered at the origin and at certain reciprocal lattice points, suggesting the existence of short-lived 4-site collective spin singlets. The unusual features of the dynamical susceptibility discovered in this experiment result from geometrical frustration and give new insight into the heavy-fermion-like behavior of the compound.

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Geometrical frustration of antiferromagnetic interactions in a crystal is inherent to exchange loops involving odd numbers of spins, and leads to degenerate manifolds of spin configurations differing from each other by local spin transformations. A basic outcome is that short-wavelength spin fluctuations are enhanced and the formation of local spin singlets is favored, which may induce novel magnetic phases. Quantum spin liquid states [1] are thus expected in localized spin systems, and it has been suggested that non-Néel magnetic order may exist in itinerant electron systems [2]. So far, however, the effects of geometrical frustration have not been considered extensively in itinerant magnets, and in particular not close to a magnetic-nonmagnetic instability. Experimentally, this has become possible since the discovery of Mn itinerant magnetism in the RMn_2 intermetallic compounds, where R stands for Y, Sc, Th, or a lanthanide element [3]. A mixed phase, where magnetic and nonmagnetic Mn atoms coexist, was discovered in some compounds of the series [4] and interpreted in terms of a frustration-induced vanishing of moments [5]. Unusual behaviors are also observed in the paramagnetic phase, in particular, in YMn_2 [3]. In this Letter, we report on new experimental findings about the Mn spin fluctuation spectrum in this phase.

YMn_2 crystallizes in the cubic C15 Laves phase structure (space group $Fd\bar{3}m$), where the Mn atoms form a lattice of corner sharing tetrahedra: a three-dimensional analog of the kagomé net, which is at the origin of the geometrical frustration of the antiferromagnetically coupled nearest-neighbor Mn spins. Complex magnetic order sets in through a first-order transition at a Néel temperature T_N of about 100 K. It may be described as a double-Q structure, with propagation vectors (1 0 0) and (0 1 0), in which the sum of the spins on each Mn tetrahedron cancel [6]. Additional long-wavelength distorted helical components were revealed by high resolution neutron diffraction measurements [7]. The magnetic order is suppressed by applying a rather weak hydrostatic pressure (of the order of 0.1 GPa), or by substituting a small amount of Sc for Y that creates a chemical pressure. At low temperature, the compound then shows a behavior typical of heavy-fermion systems with a linear contribution γT to the specific heat and a quadratic contribution AT^2 to the electric resistivity, both strongly enhanced ($\gamma \approx 160$ mJ K^{-2} mol^{-1} [8,9] and $A/\gamma^2 \approx 10^{-5}$ $\mu\Omega$ cm(K mol/mJ)^2 [10]) to values quite unexpected for nearly antiferromagnetic metals [11]. A large magnetic contribution to the thermal expansion was reported and attributed to thermally excited spin fluctuations [12]. The latter have been directly observed in neutron-scattering experiments on powder samples, using polarized neutrons to separate the magnetic scattering from the scattering of nuclear origin (phonons) [13–15] or by time-of-flight technique for unpolarized neutrons, where the Q dependence of the scattering was used to separate magnetic from nuclear contributions [16,17]. In all these measurements a thermal increase of the mean square local amplitude of the spin fluctuations has been reported.

When no magnetic order sets in, the spin fluctuations are observed down to the lowest temperature, which has led to the speculation that the ground state could be a quantum spin liquid stabilized through the geometrical frustration [18]. According to this interpretation, the thermal excitation of low energy spin fluctuations from this singlet ground state should lead to a fast increase of the magnetic entropy and of the electron collision rates, in agreement with the heavy-fermion-like behavior observed

in the specific-heat and resistivity measurements. In order to further the understanding of the role of the spin fluctuations, we have performed neutron-scattering measurements on single crystals starting with $(Y_{0.97}Sc_{0.03})Mn_2$, which remains paramagnetic down to the lowest temperatures.

The single crystals were grown under argon atmosphere by the Czochralski method, using a high-frequency induction technique with a water-cooled copper crucible. The obtained ingots were analyzed by x rays and scanning electron microscopy to check for phase purity and homogeneity, and to isolate single grains. A single crystal of $(Y_{0.97}Sc_{0.03})Mn_2$ about 0.6 g was selected. A small sample was extracted for low-temperature specific heat measurements. We found for the coefficient γ of the linear contribution a value of about 200 $mJ\,K^{-2}\,mol^{-1}$ [19], which is considerably higher than reported previously [8,9].

Neutron inelastic scattering measurements were performed on the 1 T thermal-beam triple-axis spectrometer at the Orphée reactor of the Laboratoire Léon Brillouin. Most measurements were performed with a vertically focusing PG(002) monochromator and a horizontally focusing PG(002) analyzer with a fixed final energy E_f of 34.8 meV, giving an energy resolution of $\Delta E = 3.5$ meV. A PG filter in the scattered beam was used to suppress higher-order contamination. Other configurations were also used for complementary measurements, e.g., $E_f = 14.7$ meV with $\Delta E = 0.9$ meV, as well as measurements using full polarization analysis [20]. The sample was mounted in a closed-loop helium refrigerator, with either the [110] and [001] or the [100] and [010] axes in the horizontal scattering plane. The measurements presented here were performed at a temperature of 10 K, but measurements at higher temperatures have also been done [20].

In order to locate the magnetic signal in reciprocal space, we performed a wide rocking scan of the $(Y_{0.97}Sc_{0.03})Mn_2$ single crystal, mounted with the [110] and [001] axes in the horizontal scattering plane, for a spectrometer setting of $Q = 1.5$ Å^{-1} and $\hbar\omega = 10$ meV, where a maximum in the magnetic scattering has been found in powder samples [13–17]. A broad maximum was observed at a wave vector $\mathbf{Q}_0 \approx (1.25\ 1.25\ 0)$ (in reciprocal lattice units). The energy response of the magnetic scattering at $\mathbf{Q}_0$ is shown in Fig. 1, where the data have been corrected for nuclear scattering (phonons and incoherent elastic scattering) and background. The phonon contribution was obtained from an energy scan at $\mathbf{Q}_0 + (4\ 4\ 0)$, where the phonon structure factor is the same as at $\mathbf{Q}_0$, except for a factor Q^2, and where the magnetic scattering is negligible due to the rapidly decreasing Mn^{2+} magnetic form factor [21]. The validity of this phonon subtraction procedure was confirmed by measurements using full polarization analysis [20]. The energy response of the magnetic scattering can be approximated by a quasielastic Lorentzian $S(\mathbf{Q},\omega) \propto \omega/(\omega^2 + \Gamma_{\mathbf{Q}}^2)$ of

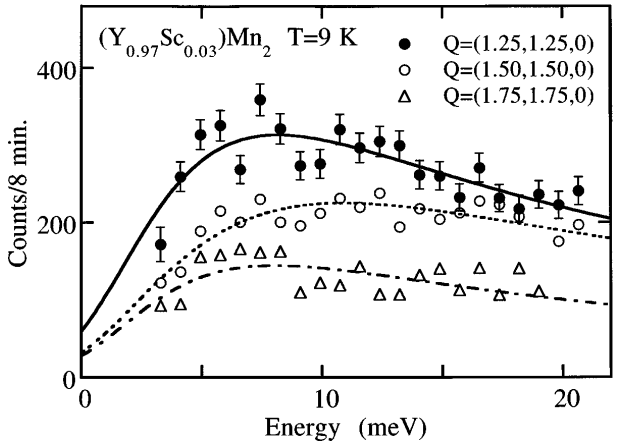

FIG. 1. Energy response of the magnetic scattering at different wave vectors $\mathbf{Q}$ for $E_f = 34.8$ meV. The lines are quasielastic Lorentzian fits.

width (HWHM) $\Gamma_{\mathbf{Q}} = 8-10$ meV at $T = 10$ K. Measurements at other wave vectors and symmetry directions show that there is no significant dispersion of the magnetic scattering with $\mathbf{Q}$ in the 1–20 meV energy range.

Figure 2 shows a Q scan in the [110] direction at an energy transfer of 10 meV. The two peaks are located at two identical points in the same Brillouin zone, but at opposite sides of the reciprocal lattice vector (2 2 0). Their intensity scales with the square of the magnetic form factor, giving further strong evidence that the signal at $\mathbf{Q}_0$ is of magnetic origin. Similar scans performed at both smaller and larger energy transfers (between 5 and 15 meV) show the same structure, after correction for phonons. These scans are well described by two Lorentzians (after correction for the magnetic

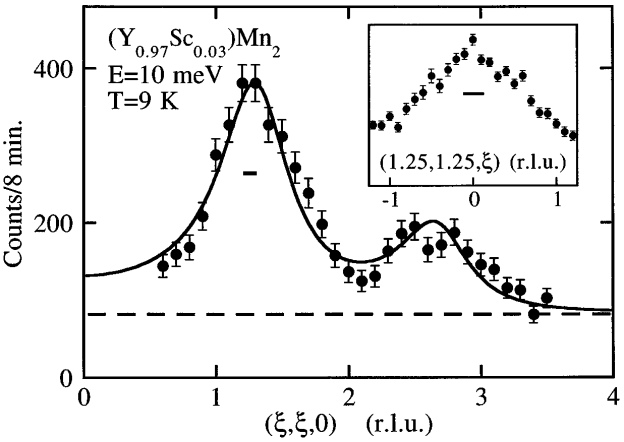

FIG. 2. Q scan in the [110] direction at an energy transfer of 10 meV. The line is a fit with two Lorentzian functions of the same width, multiplied by the square of the magnetic form factor. The inset shows a scan in the [001] direction at the maximum of the magnetic signal. In both plots, the horizontal bar shows the projection of the resolution ellipsoid in the scan direction.

form factor) of the same width located at $(2 \pm \xi\ 2 \pm \xi\ 0)$, with $\xi = 0.70(3)$. The intrinsic width (HWHM) of these Lorentzians is $\kappa = 0.30$ reciprocal lattice unit (0.35 Å^{-1}), which is much larger than the instrumental resolution (see Fig. 2). Thus, the correlation length is $\kappa^{-1} = 2.8(2)$ Å, which corresponds to the distance between two neighboring Mn atoms (2.72 Å).

Since the magnetic signal observed in energy scans for several **Q**'s was always rather flat, the magnetic correlations were studied by performing Q scans, $(\xi\ \xi\ l)$ and $(h\ h\ \xi)$ on a rectangular grid, at an energy transfer of 10 meV, with scans separated by Δh or Δl of about 0.3 Å^{-1} and with a step size $\Delta\xi$ of about 0.1 Å^{-1}. These steps are close to the **Q** resolution, which is approximately 0.22 (0.09) Å^{-1} in directions perpendicular (parallel) to the scattering wave vector **Q**. Figure 3 shows the image reconstructed from these data. A flat background, determined from measurements at negative energy transfer and by rotating the analyzer by 6°, was subtracted from the raw data and a smoothing [22] was performed. For the low temperatures and small **Q**'s for which the data were measured, the contamination from phonons is negligible. This is rather clear from Fig. 2, and has been confirmed by complementary measurements of the phonon dispersion and structure factors at higher temperatures and larger **Q**'s. We are thus convinced that Fig. 3 shows predominantly the magnetic signal of $(Y_{0.97}Sc_{0.03})Mn_2$ in the [110]-[001] scattering plane. Several interesting features emerge immediately.

First, the maximum of the magnetic signal occurs at wave vectors $\mathbf{Q} = \mathbf{K} \pm \mathbf{q}$, where **K** is a reciprocal lattice vector and $\mathbf{q} \approx (3/4\ 3/4\ 0)$. This is in contrast to the low temperature ordered magnetic phase of YMn_2 [7], where the magnetic Bragg peaks are observed for **q**'s belonging to the star of (0 0 1). Consequently, the short-time spin dephasing between neighboring Mn tetrahedra is different in the two phases. A subsequent inelastic neutron-scattering experiment, performed in the high temperature paramagnetic phase of a single crystal of YMn_2, demonstrated this conclusion to be independent of the substitution of Sc for Y. This is not inconsistent with a first-order transition, all the more as a large volume discontinuity ($\Delta V/V \approx 4.7\%$), driven by a substantial jump of the Mn spin amplitude upon ordering, is observed at T_N. Therefore the magnetoelastic interactions should certainly play a relevant role in inducing the magnetic transition and selecting a different magnetic state.

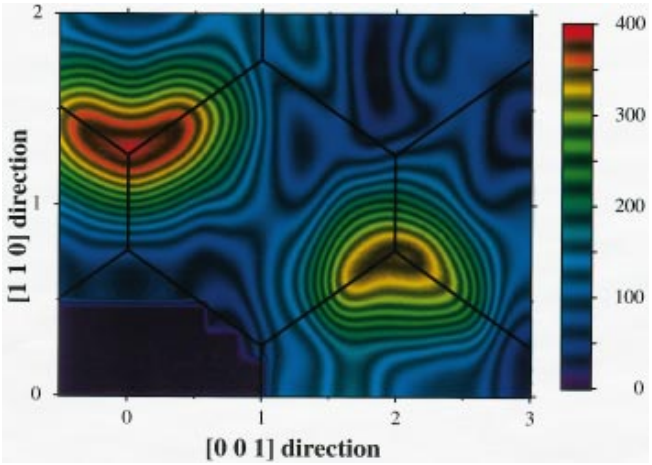

FIG. 3 (color). Wave vector dependence of the spin fluctuation amplitude in the [110]-[001] scattering plane, measured at 10 K for an energy transfer of 10 meV. The black lines represent the intersections of the Brillouin zones with the scattering plane. Color bar units are in counts per 8 min. The uniform area around the origin was not accessed experimentally.

Second, we observe that the signal is extended along the directions of the Brillouin zone boundary. This is illustrated in Fig. 2: The magnetic signal is broader in the [001] than in the [110] direction. As mentioned above, the inverse correlation length in the [110] direction is $\kappa = 0.35$ Å^{-1}, while it is $\kappa = 0.58$ Å^{-1} in the [001] direction, corresponding to a real space distance much smaller than the interatomic distance. The magnetic scattering in the plane containing the [100] and [010] axes is extended in the same way, with nearly the same maximum intensity on practically the whole Brillouin zone boundary around lattice points of type $\mathbf{K} = (2\ 2\ 0)$. The signal is always comparably narrower in directions perpendicular to the Brillouin zone boundary [20]. We believe that this quite unusual **Q** dependence of the magnetic scattering (and therefore of the susceptibility) is due to the existence of a degeneracy of states associated with the geometrical frustration, as in localized spin systems [23], and that it prevents any second-order Néel transition. It has been invoked to be the origin of the large linear contribution to the specific heat [24]. A physical analogy with $4f$ and $5f$ heavy-fermion materials would relate to the fact that Kondo fluctuations are localized in real space, which also leads to a flat dynamical susceptibility in Q space.

A last important feature of the map shown in Fig. 3 is that the magnetic signal is observed in the Brillouin zone around only certain reciprocal lattice points. It reflects the fact that there are four Mn atoms in the elementary unit cell, and hence the magnetic scattering has a structure factor, similar to that for phonons. This provides additional information on the spin correlations within the Mn tetrahedra: The absence of any magnetic signal in the Brillouin zone around the origin (0 0 0) and reciprocal lattice vectors of type (0 0 4), (2 2 2), ..., implies that the self-time correlation of the sum of the spins within each tetrahedron is zero. This suggests the formation of strong 4-site collective spin singlets. As given from the energy width of the magnetic scattering, the lifetime of these spin singlets is short, of the order of 7×10^{-14} s. Hence, for short times, the nearest neighbor spins within each tetrahedron are strongly correlated and form singlets, while for longer times the spins are uncorrelated. Although the exchange energy gives rise to

normally only one energy scale, the existence of these singlets transposes to strong intratetrahedral and weak intertetrahedral spin-spin correlations induced by pure geometrical effects and allows further analogy with $4f$ and $5f$ heavy-fermion materials where two energy scales coexist: the Kondo temperature and the RKKY exchange interactions.

In conclusion, we have performed inelastic neutron-scattering measurements on a single crystal of $(Y_{0.97}Sc_{0.03})Mn_2$ that have brought into light new features concerning the spin fluctuations, which, to our knowledge, are observed for the first time. The dynamical susceptibility is strongly extended with respect to the wave vector in directions parallel to the Brillouin zone boundary, and sharp in perpendicular directions, indicating an underlying degeneracy of magnetic states. It cancels around certain reciprocal lattice points, suggesting that spins are correlated so as to form short-lived 4-site collective spin singlets. Both peculiarities of the spin fluctuations are inherent to the geometrical frustration of antiferromagnetic interactions. They provide new insights into the heavy-fermion behavior of the compound, which remains puzzling within the present theoretical understanding of itinerant magnetism. The energy response of the magnetic signal is broad and somewhat unusual since no significant dispersion can be measured, a result which calls for theoretical explanation as well. There is no indication of a gap (expected for a quantum spin liquid ground state) in the magnetic excitation spectrum, although the best energy resolution of the present experiment cannot exclude the existence of a gap smaller than 1 meV.

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*Electronic address: ballou@labs.polycnrs-gre.fr

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