Unconventional spin fluctuations in the hexagonal antiferromagnet YMnO$_3$

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We used inelastic neutron scattering to show that well below its Néel temperature, $T_N$, the two-dimensional (2D) $XY$ nearly triangular antiferromagnet YMnO$_3$ has a prominent central peak associated with 2D antiferromagnetic fluctuations with a characteristic lifetime of 0.55(5) ps, coexisting with the conventional long-lived spin waves. Existence of the two time scales suggests competition between the Néel phase favored by weak interplane interactions, and the Kosterlitz-Thouless phase intrinsic to the 2D $XY$ spin system.

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I. INTRODUCTION

Geometrical frustration and low dimensionality are the two key concepts in the statistical physics that provide unusual spin dynamics as well as phase transitions.$^{1-3}$ The simplest realization of the two concepts is two-dimensional triangular lattice antiferromagnets (2DTLAFMs). A particular interest is placed on the $XY$ spin system (2DXYTLAFM), where its ground-state manifold has the continuous degeneracy associated with U(1) global spin rotations, as well as the discrete Ising-like degeneracy due to $Z_2$ chirality configurations.$^4$ Because of the U(1) symmetry, the well-known Kosterlitz-Thouless (KT) phase involving vortex binding$^5$ is expected at low temperatures. Experimentally, little evidence can be found in the literature due to the lack of good model systems.$^6$

Rare-earth manganites RMnO$_3$ ($R$ = Y, Lu, and Sc) are ferroelectric compounds with considerably high ferroelectric Curie temperature above 1000 K.$^7$ Below the ferroelectric transition, these compounds crystallize in a hexagonal structure with the space group $P6_3cm$. The Mn$^{3+}$ ($S=2$) ions are at the 6c(x,0,0) positions [x = 0.323(1) for $R$ = Y (Ref. 7)], forming nearly triangular networks in $z$ = 0 and 1/2 layers. These layers stack in the ABAB sequence along the $z$ axis (see Fig. 1).$^7-9$ with a wide separation introduced by intervening $R$ and O ions. This wide separation suggests predominant two-dimensional (2D) character in the $ab$ plane, and thus the RMnO$_3$ compounds can be good candidates for the 2DTLAFMs. Their bulk susceptibility data show that despite strong antiferromagnetic interactions the magnetic ions order long range at much lower temperatures $T_N$ than the magnetic energy scale inferred by the Curie-Weiss (CW) temperatures $\Theta_{\text{CW}}$ (for instance, $\Theta_{\text{CW}} = -705$ K and $T_N = 70$ K for YMnO$_3$).$^7-9$ Previous powder neutron-diffraction studies showed that the spins at the lowest temperature formed the so-called 120° structure in the $ab$ plane coinciding with the ground state for 2DTLAFMs, and the frozen moments, $\langle M \rangle$, were reduced from the expected value for the fully polarized Mn$^{3+}$ [e.g., $\langle M \rangle = 2.90(2) \mu_B < gS \mu_B$ for YMnO$_3$ ($S = 2$)].$^7,8,10$ The reduction in $T_N$ and $\langle M \rangle$ is a signature of strong spin fluctuations due to geometrical frustration and/or low dimensionality in the systems. The low $T_N$, compared to the ferroelectric transition temperature, also infers weak coupling between the magnetism and ferroelectricity. In the powder neutron-diffraction pattern, a broad peak was additionally observed at finite $Q$ around $T_N$, indicative of strong short-range spin correlations.$^7,10$ However, due to intrinsic limitations of the powder-diffraction technique, further experimental studies, especially inelastic single-crystal neutron-scattering measurements, are necessary to understand the nature of the spin excitations.

In this paper, we report inelastic neutron-scattering measurements on powder and single-crystal samples of the hexagonal rare-earth manganite YMnO$_3$. We have found that YMnO$_3$ is a good model system for the 2DXYTLAFM with weak trimerization. Our most important finding is that in the Néel phase there are fast 2D spin fluctuations with a characteristic time scale of 0.55(5) ps in addition to the conventional long-lived spin-wave (SW) excitations. The inverse of dynamic correlation length associated with the fast 2D spin fluctuations has similar $T$ dependence as that expected for the KT phase in a 2D $XY$ spin system, suggesting that the spin fluctuations are reminiscence of the KT phase. The coexistence of the long-lived magnons and the fast 2D spin fluctuation.

FIG. 1. Schematic drawing of Mn positions and spin ordering in YMnO$_3$. Filled (open) circles represent Mn positions in the $z$ = 0 ($z$ = 1/2) plane, whereas the dotted parallelogram shows the magnetic unit cell that is identical to the chemical unit cell. Lattice constants are $a = 6.140 \text{ Å}$ and $c = 11.393 \text{ Å}$. The lattice is weakly trimerized with the intratrimer and intertrimer Mn-Mn distances of 3.42 Å and 3.62 Å, respectively (Refs. 7 and 9) which is exaggerated in the drawing.
horizontal collimations were 40°, was used to get rid of higher-order contamination. The holo-
temperatures. The powder-averaged scattering intensity is re-
spectrometer and single-crystal experiments at the cold neutron triple-axis
II. EXPERIMENT
A 50-g powder sample and a 2-g (φ5 mm×22 mm) single
crystal of YMnO$_3$ were used in our neutron-scattering mea-
surements. Methods of sample preparation were reported
elsewhere.$^9$ Neutron-scattering measurements were per-
formed at the National Institute of Standards and Technology
(NIST) Center for Neutron Research. Powder experiments
were performed at the Disk Chopper time-of-flight Spec-
trometer (DCS) using an incident energy of $E_i = 15.46$ meV
and single-crystal experiments at the cold neutron triple-axis
spectrometer BT9. At SPINS, pyrolytic graphite (PG) 002
reflections were used for monochromator and analyzer, and a
cooled Be filter was placed after the sample to eliminate
higher-order contamination. We used horizontal collimations
of 80°–80° and a final energy $E_f = 5$ meV for most scans,
while $E_f = 2.6$ meV and 80°–40° were used when better en-
ergy resolution was needed. At BT9, the PG monochromator
and analyzer were used with $E_f = 14.7$ meV, and a PG filter
was used to get rid of higher-order contamination. The hori-
zontal collimations were 40°–40°–40°–80°.

III. RESULTS AND DISCUSSION
Figure 2 provides an overview of the inelastic neutron-
scattering intensity $I(Q, \omega)$ for the powder sample at three
temperatures. The powder-averaged scattering intensity is re-
lated to the dynamic spin-correlation function $S^{ab}(\vec{Q}, \omega)$
as
\[
I(Q, \omega) = \int \frac{d\Omega}{4\pi} \left| \frac{g}{2} F(Q) \right|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \vec{Q}_\alpha \vec{Q}_\beta) S^{\alpha\beta}(\vec{Q}, \omega),
\]
where $F(Q)$ is the magnetic form factor for Mn$^{3+}$. For $T
>T_N$, there is a cooperative paramagnetic continuum cen-
tered at $Q = 1.2 \text{ Å}^{-1}$ due to fluctuations of small AFM
clusters, as is commonly found in geometrically frustrated
AFMs.$^{12}$ By integrating $I(Q, \omega)$ over $\omega$ and $Q$, we obtained
the sum rule of $S(5+1) = 5.2(5)$ at 80 K, which is close to
the expected value for dynamic Mn$^{3+}$ ($S = 2$) ions. This
and the $Q$ dependence$^{13}$ tell us that the scattering is magnetic.
For $T < T_N$, as the magnetic long-range order develops,
spectral weight at low energies gradually shifts to higher
energies. At $T = 4$ K there is strong scattering above $\omega \sim 5$
meV and weak scattering below.

Next, to obtain $\vec{Q}$-directional dependence of the magnetic
excitations, we have performed single-crystal inelastic-
scattering experiments. Figure 3 shows the representative
contant-$\vec{Q}$ scans at the antiferromagnetic zone center Γ,
namely, $\vec{Q} = (1,0,0)$ and equivalent positions. For $T > T_N$
the cooperative paramagnetic continuum appears as a quasi-
elastic peak centered at $\omega = 0$ meV. For $T < T_N$, the quasi-
elastic peak intensity decreases and two prominent magnon
peaks develop at nonzero energies. The energy values of the
magnon peaks increase as $T$ decreases, becoming $\omega = 2.3$
and 5.3 meV at 7 K. A constant $\vec{Q} = (1,0,1)$ scan with a
better energy resolution revealed an additional mode at $\omega
= 0.22$ meV [Fig. 3(e)].

FIG. 3. (a)–(d) Constant $\vec{Q} = (1,0,0)$ scans at four different temperatures. (e) Constant-$\vec{Q}$ scans at $\vec{Q} = (1,0,2)$ and $\vec{Q} = (1,0,1)$ at $T = 7$ K. The scan at $\vec{Q} = (1,0,1)$ was taken under the higher
energy-resolution configuration with $E_f = 2.6$ meV, and its unit is
arbitrary. Solid lines are fits to Eq. (2), whereas dashed lines repre-
sent the quasielastic part (see the text).

FIG. 2. (Color online) Contour maps of the powder-averaged
neutron-scattering intensity versus magnitude of wave-vector trans-
ferring the phase transition at $T_N = 70$ K.

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neutron-scattering intensity versus magnitude of wave-vector trans-
ferring the phase transition at $T_N = 70$ K.
We analyzed the observed spectra using the following scattering function with Lorentzians for the quasielastic (qel) and magnon peaks:

\[
\tilde{T}(\vec{Q}, \hbar \omega) \propto \hbar \omega [1 + n(\hbar \omega)] \left[ I_{\text{qel}} \frac{\Gamma_{\text{qel}}}{\Gamma_{\text{qel}} + \hbar \omega^2} + \sum_k I_{\text{sw}}^k \frac{\Gamma_{\text{sw}}}{\Gamma_{\text{sw}} + (\hbar \omega - \hbar \omega_k)^2} \right],
\]

where \([1 + n(\hbar \omega)] = [1 - \exp(-\hbar \omega/k_B T)]^{-1}\). This function was convoluted with the instrumental resolution function to fit the observed spectra.

Let us first discuss the magnon dispersion relations at \(T = 7 \text{ K} < T_N\). Figure 4 shows the dispersion relations along a few high-symmetry directions, obtained from several constant-\(\vec{Q}\) and constant-\(\hbar \omega\) scans. To explain the observed dispersion relations, we introduce the following model spin Hamiltonian:

\[
\mathcal{H} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D_{1} \sum_i (\mathbf{S}_i^z)^2 - D_{2} \sum_i (\mathbf{S}_i^z \cdot \mathbf{n}_i)^2,
\]

which consists of two in-plane \((J_1, J_2)\) and two interplane \((J'_1, J'_2)\) interactions, and the easy-plane \((D_1)\) and in-plane easy-axis \((D_2)\) anisotropies (see Fig. 1 for the definition of the interactions). The anisotropy \(D_2\), parallel to the spin directions \(\mathbf{n}_i = (\mathbf{S}_i^z)/|\mathbf{S}_i^z|\), is necessary to reproduce the small (0.22 meV) gap at the antiferromagnetic zone center, and is presumably due to the local structural distortion around \(\text{Mn}^{3+}\). The conditions \(J'_1 > 0\) and \(J'_2 > J'_1\) are necessary for the particular interplane stacking in \(\text{YMnO}_3\), given as the \(\Gamma_1\) spin structure in Ref. 8, to be the ground state.

The model Hamiltonian is linearized using the Holstein-Primakoff approximation, and numerically diagonalized to obtain one-magnon dispersion relations using the standard equation-of-motion technique. Analytic expressions for the gap energies at the \(\Gamma\) point were also derived assuming sufficiently small \(D_2, J'_1, \) and \(J'_2\):

\[
\hbar \omega_1 = 2S \sqrt{-D_2 \lambda_1},
\]

\[
\hbar \omega_2 = 2S \sqrt{-D_2 \lambda_1 - 2(J'_1 - J'_2) \lambda_1},
\]

\[
\hbar \omega_3 = S \sqrt{2(D_1 \lambda_2 - D_2 \lambda_3 - 2D_1 J'_1)},
\]

\[
\hbar \omega_4 = S \sqrt{2[D_1 \lambda_2 - D_2 \lambda_3 - D_1 (J'_1 - 2J'_2) - 2(J'_1 - J'_2) \lambda_1]},
\]

from low to high energies, where \(\lambda_1 = D_1 + (3/2)J_1 + 3J_2, \lambda_2 = (3/2)J_1 + 3J_2, \) and \(\lambda_3 = 2D_1 + (3/2)J_1 - J_2\).

fitting the calculations to the data, we obtained \(J_1 = -3.4(2)\) meV, \(J_2 = -2.02(7)\) meV, \(J'_1 - J'_2 = 0.014(2)\) meV, \(D_1 = -0.28(1)\) meV, and \(D_2 = 0.0007(6)\) meV. Solid lines in Fig. 4 represent the calculated dispersion relations with \(J'_2 = 0\). The good agreement confirms the validity of the model Hamiltonian.

In the above paragraph, we could only determine the difference \(J'_1 - J'_2\) for interplane interactions. From the analytic expressions of Eq. (4), we see that \(h \omega_3\) and \(h \omega_4\) must be accurately determined in order to obtain \(J'_1\) and \(J'_2\) separately. However, this was impossible since they appear as one peak at \(\hbar \omega = 5.3\) meV in Fig. 3(d) or 3(e) due to the insufficient energy resolution at high energies. Since the splitting between \(h \omega_3\) and \(h \omega_4\) becomes sensitive to \(J'_1\) (or \(J'_2\)) at \(\vec{Q} = (1.05, 0, 0)\), we performed a constant-\(\vec{Q}\) scan at this \(\vec{Q}\) and found an almost resolution-limited peak at \(\hbar \omega = 5.4\) meV. This requires the splitting to be less than the energy resolution \(\Delta E = 0.5\) meV, and consequently an upper limit of 0.08 meV is obtained for \(J'_1\) and \(J'_2\). Hence, the interplane interactions are at most 2.4% of the in-plane interaction \(J_1\), confirming the good two dimensionality. One may note that \(J_1\) is 3.4 meV, which makes \(\text{YMnO}_3\) rather closer to the ideal THAFM than a system of weakly coupled trimers.

Our \(J_1 = -3.4\) meV is one order-of-magnitude smaller than \(J\) deduced in a recent Raman-scattering study by Taka-hashi et al.\(^{15}\) They obtained \(J \sim 140\) cm\(^{-1}\) \((\sim 17\) meV\) by assigning a broad peak appearing at 1800 cm\(^{-1}\) \((\sim 220\) meV\) to two-magnon scattering. However, our results clearly show that the peak cannot be due to the two-magnon process because the bandwidth of the one-magnon branch is only about 16 meV. Their broad peak at 220 meV must be vibrational or electronic in origin rather than magnetic. There very recently also appeared a comment questioning the two-magnon origin of the broad Raman-scattering peak.\(^{16}\)

Now let us turn to the low-energy quasielastic continuum observed below \(T_N\), clearly seen in Figs. 3(b) and 3(c). For \(T = 7 \text{ K} < T_N\), Fig. 3(e) shows a \(\hbar \omega_1 = 0.55\) meV mode at \(\vec{Q} = (1.0, l)\) with \(l \neq 0\) which is due to in-plane transverse spin fluctuations. The in-plane transverse fluctuations cannot, however, appear at \(\vec{Q} = (1.0, 0)\) because the polarization factor in Eq. (1) vanishes for the ordered spin structure in \(\text{YMnO}_3\). Note that such a mode is not present in Fig. 3(d). Therefore we rule out the in-plane transverse spin fluctuations as the origin of the quasielastic continuum existing in the Néel phase. In order to understand the continuum, we performed constant \(h \omega = 1\) meV around \((1.0, 0)\) at several temperatures and along different \(\vec{Q}\) directions. Shown in
YMnO$_3$ is known to show formation of crystallographic phase.

Below $T_N$, the energy width of the domains is irrelevant for the coexisting two phases. However, the domains are magnetically nontriangular, and is related to the vortex dynamics intrinsic to the KT phase.

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LAFMs; earlier studies are mostly on three-dimensional systems, such as the nonoxide $ABX_3$ magnets, which apparently lack the two dimensionality.


13 We rule out the phonon as the origin because intensity does not follow the $Q^2$ behavior.


