Polarized-neutron study of longitudinal Haldane-gap excitations in Nd$_2$BaNiO$_5$.

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Polarized and unpolarized inelastic neutron scattering is used to study Haldane-gap excitations in the mixed-spin linear-chain antiferromagnet Nd$_2$BaNiO$_5$. The longitudinal mode, polarized along the direction of ordered moments, is observed for the first time. The model of isolated Haldane chains in a static staggered exchange field, that is known to work very well for static properties and transverse spin excitations in R$_2$BaNiO$_5$ compounds, fails to explain new results for the longitudinal spin gap.

75.30.Ds, 75.50.Ee, 75.40.Gb

The novel quantum-disordered ground state and the famous Haldane gap in the magnetic excitation spectrum $\Delta_{H}$ have kept integer-spin one-dimensional (1-D) Heisenberg antiferromagnets (AF) at the center of attention of condensed matter physicists for almost 2 decades. Among the more recent developments are studies of such systems in external magnetic fields (comprehensive bibliography can be found in Refs. [2-3]). As the uniform magnetic field $H$ is increased, the Haldane triplet splits linearly with $H$, one of the three excitations decreases in energy and eventually softens at some critical field $H_c$. The result is a transition to a radically new phase with long-range magnetic order (see for example Refs. [4-5]). The effect of strong a staggered field $H_{\pi}$, to which the Haldane chain is most susceptible, is expected to be no less dramatic. According to recent theoretical results [6] and numerical simulations [7], all three Haldane gap energies increase quadratically with $H_{\pi}$. The degeneracy of the Haldane triplet is removed: for the excitation polarized along the direction of induced moments (longitudinal mode) the gap increases three times more rapidly than for the two transverse modes. The longitudinal mode is of particular interest, as it is a purely quantum feature, totally absent in the classical spin wave theory that predicts a pair of transverse order-parameter excitations (magnons).

The discovery of coexistence of Haldane gap excitations and magnetic long-range order in R$_2$BaNiO$_5$ (R=magnetic rare earth) compounds [10,11] presented a unique opportunity to investigate experimentally the effect of a strong staggered field on Haldane spin chain. In R$_2$BaNiO$_5$ the initially quantum-disordered AF $S=1$ Ni$^{2+}$-chains become subject to an effective staggered exchange field produced by the $R$-sublattice, when the latter orders magnetically at low temperatures. The magnitude of this field can be tuned by varying the temperature and thereby the ordered moment on the $R^{3+}$ sites. A wealth of neutron scattering data for a number of R$_2$BaNiO$_5$ compounds, particularly Pr$_2$BaNiO$_5$ [10] and (Nd$_x$Y$_{1-x}$)$_2$BaNiO$_5$ [11,12], have been accumulated to date. The quadratic increase in the gap energy in the magnetically ordered state has been clearly observed [10,12], and the measured temperature dependencies of sublattice magnetizations [13] was shown to be quantitatively consistent with predictions for isolated Haldane chains in a staggered field [13]. Surprisingly, the splitting of the Haldane triplet could never be found. In fact, no clear evidence for the very existence of the longitudinal mode in R$_2$BaNiO$_5$ has been obtained: all the measured staggered field dependencies of the Haldane gap energies are in quantitative agreement with calculations for transverse excitations in isolated chains [6,7,8,4]. The present paper is aimed at resolving this mystery. We report the first direct experimental observations of the longitudinal mode in a R$_2$BaNiO$_5$ compound using spin-polarized inelastic neutron scattering. In the ordered phase we find that the theory of an isolated chain in a static staggered field, that seems to apply well to transverse Haldane excitations in R$_2$BaNiO$_5$, does not work for the longitudinal mode.

The material of choice for our studies was Nd$_2$BaNiO$_5$, one of the few “2115” nickelates for which high-quality single crystals can be prepared. The orthorhombic crystal structure of R$_2$BaNiO$_5$ compounds is discussed in great detail elsewhere [13] and we only note here that the $S=1$ Ni$^{2+}$-chains run along the $a$ axis of the crystal (Ni-Ni spacing $a = 3.85$ Å), with the $R^{3+}$ sites positioned in between these chains. The Néel temperature for Nd$_2$BaNiO$_5$ is $T_N = 48$ K. Long range magnetic ordering gives rise to magnetic Bragg reflections of the type $(2m\pi, k, \frac{2n\pi}{c})$, with $m$, $k$ and $n$ integer [13,14]. The Ni$^{2+}$ moments are confined in the $(a, c)$ crystallographic plane and are aligned roughly along the $c$ axis [14].

In previous studies the attempts to determine the polarization of the Ni-chain spin excitations in R$_2$BaNiO$_5$ were performed using unpolarized neutrons. In this type of experiment, for scattering vectors almost along the chain direction (crystallographic $a$-axis) one only sees only the fluctuation of spin components along the $b$- and
c-axes of the crystal, thanks to the intrinsic polarization dependence of the neutron scattering cross section. When the scattering vector is almost perpendicular to the chain axis and almost parallel to c, for example, only the \(a\)- and \(b\)- spin components contribute to scattering. In principle, comparing the intensities measured at several wave vectors can yield a complete analysis of the mode polarization. In practice however, such measurements on \(\text{Nd}_2\text{BaNiO}_5\) were inconclusive. The main difficulty is that a number of intrinsic effects, particularly neutron absorption in the sample and focusing, are very difficult to account for with sufficient accuracy when comparing measurements for a large irregularly shaped sample and substantially different scattering vectors.

Even if a polarization analysis could not be properly performed in the above-mentioned experiment, a splitting of the triplet, if present at all, should have been seen. Our first guess was that the mode splitting was obscured by the relatively low energy resolution (2.6 meV FWHM resolution at 15 meV energy transfer) of previous experiments. As a first step in clarifying the behavior of the longitudinal mode we therefore performed additional unpolarized measurements at the High Flux Isotope Reactor at Oak Ridge using a high-resolution setup that employed a Be(002) monochromator, a PG(002) analyzer and 60° - 40° - 40° - 240° collimations to yield a 1.6 meV FWHM resolution an 15 meV energy transfer (fixed final energy 14.7 meV). In these studies we used the same large sample as in Ref. \[\text{[13]}\]. A typical inelastic constant-
\(Q\) scan through the Haldane gap excitations at the 1-D AF zone-center \(Q = (1.5, 0, 0)\) is shown in Fig. \[\text{1}\] and corresponds to \(T = 38\) K. The background was measured and subtracted as in Ref. \[\text{[13]}\]. From the prediction for an isolated chain \[\text{[8]}\], we expect the longitudinal mode to show up at \(\approx 19\) meV energy transfer at this temperature, where no additional feature is observed. In fact, none of our inelastic scans performed in the temperature range 30–55 K revealed any splitting of the triplet, in agreement with low-resolution studies \[\text{[13]}\].

So, where is the longitudinal Ni-chain mode? To finally answer this question we made use of a totally different technique to measure the polarization of the magnetic gap excitations in \(\text{Nd}_2\text{BaNiO}_5\). Employing a polarized neutron 3-axis setup \[\text{[20]}\] we performed all the measurements at a single position in reciprocal space to avoid any complications of absorption or focusing. Magnon polarization was determined by comparing the inelastic intensity measured with different combinations of incident and final neutron polarizations. The experiment was carried out at the IN-20 polarized neutron spectrometer at the Institut Laue-Langevin in Grenoble. The sample that was previously used in unpolarized experiments was mounted on the spectrometer with the c-axis vertical. A combination of Heussler-alloy monochromator and analyzer and two Mezei-type flipper allowed us to polarize and analyze the incident and outgoing beams parallel or antiparallel to the vertical axis at will. The measured flipping ratio for each flipper was approximately 21. In this geometry in the non-spin-flip (NSF) channel one sees only the fluctuation of spin components along the vertical c-axis, i.e., only longitudinal spin fluctuations. In contrast, in a spin-flip (SF) configuration only the \(a\)- and \(b\)-axis (transverse) spin components are seen. The experiment was done using 14.7 meV fixed-final energy neutrons with a PG filter positioned after the sample. All constant-Q scans were collected at \(Q = (1.5, 0.5, 0)\) that corresponds to a wave vector transfer \(q_0 = 3\pi\) along the Ni-chain axis. For the particular scattering geometry in the SF channel 21% and 79% of the intensity is due to \(a\)- and \(b\)-axis spin components, correspondingly. The background was measured at \(Q = (1.4, 0.5, 0)\) \[\text{[13]}\]. As the background predominantly comes from crystal-field excitations associated with \(\text{Nd}^{3+}\) \[\text{[11]}\] and thus has a large magnetic (polarization-dependent) contribution, it was separately measured in the NSF and SF configurations.

The main difficulty in a polarized neutron experiment is the long counting times that result from the typically low flux of spin-polarized neutrons. To use the available beam time with greatest efficiency, we concentrated on the temperature range 35–55 K where all the action is expected to take place. Indeed, at the high-temperature end \(T > T_N = 48\) K the system is in the paramagnetic phase. At \(T = 35\) K, on the other hand, the \(\text{Ni}^{2+}\) moments have already achieved as much as 75% of their saturation value (\(\approx 1.1\) \(\mu_B\)) \[\text{[5,13]}\]. The bulk of our polarized-neutron inelastic data (background subtracted) is shown in Fig. \[\text{2}\]. At \(T = 55\) K > \(T_N\) in both SF and NSF channels, at the 1-D AF zone-center \(Q = (1.5, 0.5, 0)\), we clearly see two well-defined inelastic peaks of almost equal intensity, centered at 11 and 12 meV, respectively \[\text{[Fig. \text{2}(a)]}\]. As the temperature is decreased through \(T_N\), both peaks move to higher energies \[\text{[Fig. \text{2}(b-d)]}\]. The peak observed in the NFS configuration (longitudinal mode), if anything, moves to higher energies \textit{slower} than the SF peak (transverse modes). The intensity in the transverse modes appears to be practically temperature-independent.

To make the above discussion more quantitative we analyzed our inelastic scans with the following one-dimensional cross-section that is routinely employed do model the dynamic structure factor of Haldane excitations:

\[
(h\omega)^2 = c_s^2 q_0^2 + \Delta^2 \quad \text{(1)}
\]

\[
S(q_0, \omega) = \frac{A e^\Delta}{\Gamma \Delta} \left( 1 + \frac{c_s (q_0 - \pi/a)}{\Delta} \right)^2 \left( \frac{\omega - \omega_0}{\Gamma} \right)^2 \quad \text{(2)}
\]

Here \(c_s = 210\) meV·Å is the spin wave velocity measured with great accuracy using unpolarized neutrons \[\text{[21]}\], \(\Delta\) is the Haldane gap energy, \(a\) is the chain lattice constant,
and $\Gamma$ is the intrinsic energy width of the excitation. The prefactor $A$ is proportional to the energy-integrated intensity of the excitation. The dynamic structure factor $S(Q)$ was numerically convoluted with the spectrometer resolution function. For $\Gamma$ we used the same values as in Ref. [13], derived from previous $\Gamma(T)$ measurements on $Y_2\text{BaNiO}_5$. The parameters $\Delta$ and $A$ were then refined to best-fit each scan. The resulting curves fall on the data points rather well and are shown in solid lines in Fig. 3. In Fig. 3 (large open and solid circles) we plot the temperature dependence of the gap energy and integrated intensity that characterize the longitudinal and transverse excitations in $\text{Nd}_2\text{BaNiO}_5$.

It is important to make sure that our new findings are consistent with unpolarized neutron scattering results. The temperature dependence of the gap energy measured previously at $Q = (1.5, 0, 0)$ with unpolarized neutrons (Ref. [13]) is plotted in small triangular symbols in Fig. 3(a). For the intensity of the excitations we have to compare the average measured intensity of the longitudinal and transverse excitations in our experiments [dashed line in Fig. 3(b)] to the intensity measured without polarization analysis [Fig. 3(b), small solid triangles]. Finally, using the parameter values obtained through fitting Eq. 2 to the polarized neutron scans we can simulate unpolarized scans (an example is shown solid line in Fig. 3). We see that within the statistical scattering in the data points our new results agree very well with all existing unpolarized data.

The most important result of the present study is the unambiguous evidence for the existence of longitudinal mode and its survival at least in an appreciable temperature range in the magnetically ordered state. Now there remains little doubt that the Ni-chain excitations in $\text{Nd}_2\text{BaNiO}_5$ are indeed a Haldane triplet. In fact, at $T > T_N$, the intensity of the longitudinal and transverse modes are practically equal, as in the case of an isolated Haldane spin chain. As far as the Ni-chain spin dynamics is concerned, in the paramagnetic phase there seems to be little difference between $\text{Nd}_2\text{BaNiO}_5$ and the reference Haldane system $\text{Y}_2\text{BaNiO}_5$, as previously suggested by the measured temperature dependence in mixed ($\text{Nd}_{x}\text{Y}_{1-x})_2\text{BaNiO}_5$ compounds [12]. For example, just as in $\text{Y}_2\text{BaNiO}_5$ [23], our values for the $c$- and $b$-axis gaps in $\text{Nd}_2\text{BaNiO}_5$ are different by roughly 1 meV. This initial splitting of the triplet is believed to be a result of the weak single-ion anisotropy on the Ni$^{2+}$ sites.

Another important finding is that the intensity of transverse excitations in $\text{Nd}_2\text{BaNiO}_5$ is not affected by magnetic ordering. The previously observed decrease of intensity of the Haldane excitations in $\text{R}_2\text{BaNiO}_5$ below $T_N$ is thus entirely due to a suppression of the longitudinal mode. This interpretation was first presented as a conjecture in one of the first papers dealing with the Ni-chain excitations in a $\text{R}_2\text{BaNiO}_5$ system, without any supporting data available at the time [11]. An overall decrease of inelastic intensity is of course to be expected: in the ordered state a substantial amount of the spectral weight associated with Ni$^{2+}$ moments becomes transferred from dynamic to static spin correlations, i.e., into the magnetic Bragg reflections.

A totally new and yet unexplained result of our polarized neutron studies is the relatively slow increase of the longitudinal gap seen upon cooling through the ordering temperature. Indeed, for an isolated chain in a static staggered field the longitudinal gap $\Delta_L$ is expected to increase with decreasing $T$ three times as fast as $\Delta_L$, as shown in a dashed line in Fig. 3(a). This discrepancy with the static field model means that one can not consider the Ni and Nd magnetic degrees of freedom to be totally independent, at least for longitudinal fluctuation. The longitudinal mode apparently involves both the Ni and Nd moments, and may also be coupled with higher-energy crystal-field levels of the rare earths. A further investigation of this problem is required. In particularly, a more detailed RPA analysis of the interactions between the Ni- and rare earth subsystems would be very useful.

In summary, we have for the first time observed the longitudinal Ni-chain excitation in a $\text{R}_2\text{BaNiO}_5$ system. We have shown that the “Haldane chain in a staggered field model” may be a good starting point, but fails to account for all the details of the spin excitation spectrum in these remarkable mixed-spin quantum magnets.

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FIG. 1. A typical inelastic scan measured in Nd$_2$BaNiO$_5$ with unpolarized neutrons. The background has been subtracted from the data. The shaded Gaussian represents the experimental energy resolution. The solid line is a simulation based on Eq. 2 and parameters determined in a polarized-neutron experiment. The arrow shows the position of a second inelastic peak predicted by the static-staggered-field model.

FIG. 2. Temperature evolution of constant-Q scans measured in Nd$_2$BaNiO$_5$ using unpolarized neutrons. Open and solid circles correspond to spin-flip and non-spin-flip scattering. The solid lines are fits to the data with based on Eq. 3.

FIG. 3. (a) Measured temperature dependence of the energy gap in the longitudinal (open circles) and transverse (solid circles) Ni-chain excitations in Nd$_2$BaNiO$_5$. The solid lines are guides for the eye. The dashed line is the theoretical prediction for the longitudinal mode in the static staggered field model [8,13]. Small triangles show the data previously obtained with unpolarized neutrons [11,8,13]. (b) Measured temperature dependence of the energy-integrated intensity of the longitudinal (open circles) and transverse (solid circles) Ni-chain modes in Nd$_2$BaNiO$_5$. The lines are guides for the eye. Small triangles are as in (a).
Fig. 1

Nd$_2$BaNiO$_5$, $T=38K$, $Q=(1.5,0,0)$

60'-Be(002)-40'-40'-PG(002)-240'

Intensity (arb. u.)

$E$ (meV)
Fig. 2

Nd$_2$BaNiO$_5$
$Q=(1.5 0.5 0)$
$T=55$ K

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E (meV)

Intensity (renormalized to counts / 13 min)

T=45 K

T=40 K

T=35 K

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Fig. 2
Fig. 3

Integrated intensity (arb. u.) vs. T (K)

(a) Longitudinal and transverse components of the measured and expected properties of Nd$_2$BaNiO$_5$.

(b) Integrated intensity for longitudinal and transverse components vs. temperature.

$T_N$ denotes the transition temperature.