Dynamical Properties of Spins and Holes in Carrier Doped Quantum Haldane Chain

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Abstract. Quantum spins in one-dimensional (1D) chains exhibit characteristic features such as the Haldane gap (S=1) and the spin-Peierls state (S=1/2). Recently multi degrees of freedom in cooperation with quantum spins are focused. We present here spin dynamics in the lightly hole doped Nd$_{2-x}$Ca$_x$BaNiO$_5$ ($x=0.035$), 1D Haldane system by means of pulsed neutron inelastic scattering method. One-magnon band with a spin gap (Haldane gap) was visible with the decrease of the zone boundary energy to 60 meV. In contrast, the spin gap slightly increases. Dynamical structures inside spin gap upon carrier doping showing incommensurate structure centered at the magnetic zone center was newly observed which is possibly originating from the doped holes in Haldane chains.

1. Introduction

Despite the three decades that have passed since Haldane’s prediction on a one-dimensional (1D) Heisenberg chain with integer spin, much attentions are still paid on its research [1, 2]. Inorganic nickelate Y$_2$BaNiO$_5$ was found to be a good candidate of Haldane system with a spin gap of 10 meV at the magnetic zone center (MZC) [3]-[6]. In contrast, R$_2$BaNiO$_5$ (where R is a magnetic rare earth) has been known as a classical antiferromagnet (AF) showing three-dimensional (3D) long range magnetic ordering at low temperature [7]. However, the saturation moment of the sublattice magnetization of Ni$^{2+}$ spins is rather suppressed indicating a remaining quantum spin fluctuation. Indeed, inelastic neutron scattering experiments revealed the existence of spin gap at the MZC even in the R$_2$BaNiO$_5$ with magnetic rare earth ions [8]-[11].

Another interest in transition metal chain oxides is the doping of carriers, which yields phenomena ranging from strongly renormalized Fermi liquid behavior to high-temperature superconductivity. In view of the enhanced quantum fluctuations in 1D systems, doping of transition metal chains could well lead to equally surprising discoveries. R$_2$BaNiO$_5$ is a charge transfer insulator [15, 16] and some amount of hole carriers are successfully introduced primarily on oxygen sites by replacing a part of the off-chain R$^{3+}$ by Ca$^{2+}$ [4]. The spin dynamics of hole doped Ni 1D chains have also been addressed by using a theoretical approach [17]-[19] and through neutron experiments [20, 21]. In this article, we present the spin and hole dynamics of
hole doped Nd$_2$BaNiO$_5$ measured by means of a pulsed neutron scattering technique to survey
the entire area in momentum and energy space of the Brillouin zone.

2. Experimental procedure
The carrier content can be controlled by substituting a portion of the Nd$^{3+}$ ions by Ca$^{2+}$. Slightly
doped $x=0.035$ in the chemical formula Nd$_{2-x}$Ca$_x$BaNiO$_5$ was chosen for neutron experiments.
$T_N$ is evaluated at 38 K. The measurement temperatures were 5 K (7.8 K for $E_i=102.4$ meV),
50 K and 150 K. Inelastic neutron scattering experiments were carried out on the High-Resolution
Chopper spectrometer (HRC) installed at Materials and Life Science Experimental Facility in
J-PARC [22, 23]. Two sets of incident neutron energies $E_i=102.4$ and 30.6 meV were selected
to measure the wide $Q$- $\omega$ space and the detailed structure around the MZC, respectively. The
energy resolution of our experimental condition is $\frac{dE}{E_i} \sim 7\%$ ($dE \sim 7$ meV for $E_i=102.4$ meV and
$dE \sim 2$ meV for $E_i=30.6$ meV).

3. Results and discussion
In the neutron scattering experiment, the $[H \ 0 \ L]$ zone was into the horizontal scattering
plane, where $H$ corresponds to the chain direction (crystallographic $a$-axis). Figure 1 shows
the obtained dynamical structures $S(Q, \omega)$ at $T=7.8$ K (well below $T_N=38$ K) and $T=50$ K
(above $T_N$) are shown. Both spectra are normalized by the measurement time (proton current
measured just before the neutron target) and also normalized by the Bose population factor
as temperature correction. Intense crystal field excitations of Nd$^{3+}$ ions lie at $E=24$ meV
and 38 meV. The site symmetry of Nd$^{3+}$ in Nd$_2$BaNiO$_5$ is sufficiently low to split the tenfold
degenerate $J=9/2$ multiplet into five Kramers doublets. The stripes in 2D maps appearing as
moire patterns viewed particularly at low-$Q$ region are spurious and result from data-binning
processes. We are currently working on resolving this problem.

![Figure 1](image-url)

Figure 1. Observed dispersion relation of $x=0.035$ sample at (a) $T=7.8$ K $< T_N$, and (b) $T=50$ K $> T_N$. 
Excellent dispersion relations for the Ni 1D chain are observed at both temperatures. The minima of the dispersion observed at the MZC, $H=0.5$, 1.5 and even 2.5, occur where magnetic scattering intensity gets weak because of the magnetic form factor and phonon scattering is dominant in this high-$Q$ region. At low temperature, the magnon band width (energy at the zone boundary) reaches at 60 meV with a somewhat large gap energy of $\Delta \sim 20$ meV. Also, a flat band lying at $E=65$ meV corresponding to a phonon or magnon optical branch was observed. At $T=50$ K, the gap is closed and the spectral weight at the zone boundary is slightly shifted with respect to the MZC. The boundary energy is almost similar both temperatures.

To survey in the vicinity of the gap, low incident energy experiments were performed [24]. Figure 2 shows a $Q$-$\omega$ map measured at three temperatures. At $T=50$ K, in addition to the Haldane gap at $\Delta=10$ meV, a weak excitation at the MZC ($H=0.5$) was appeared as a result of hole doping. Since the hole content is low, the structure below the gap still follows the commensurate respecting to 1D $H$ direction. At well above $T_N$, $T=150$ K, the $S(Q, \omega)$ observed at $T=50$ K seems to be identical except for its intensity, the change of which can be interpreted by thermal smearing. However, marked changes are taking place at $T=5$ K. The 1D chain dispersion with the Haldane gap almost completely disappears around the MZC. Still weak signals at around 10 meV and below 10 meV remain. Also, a flat localized excitation newly appears at 4 meV. In this mixed-spin system, the Haldane gap is known to rapidly increase in energy under the effective staggered magnetic field [13, 14]. The 3D magnetic correlation of Ni$^{2+}$ ions via rare earth (Nd$^{3+}$) ions is well developed at low temperature. Therefore, the gap is effectively diminishing. Note that the intense CEF excitations are located above 20 meV. The somewhat broad feature at around 10 meV corresponds to the structure newly found by Sasaki and co-workers [21]. It shows localized but broad in $Q$-$\omega$ space centered at the MZC. The origin of this excitation is unclear at present and further experiments are necessary. The weak feature below 10 meV vertically spreading at the MZC ($H=0.5$) can be interpreted as a dynamical properties of doped holes. Holes are not well conductive in this system but still dynamically moved in the 1D chains. At high hole content, an incommensurate structure along the $Q$ direction is observed [20, 21]. The incommensurability, however, does not drop to zero even at $x=0$. The

![Figure 2](image-url)

**Figure 2.** Low energy region with $E_i=30$ meV. All the temperature scans are normalized by the proton current. Also, the temperature factor is corrected to compare each spectrum directly.
neutron inelastic scattering. At $T_N$, the dynamical structure drastically changes presenting new features of a local excitation at $E \sim 10$ meV, doped hole dynamics below the gap energy, and 4 meV flat excitation well below $T_N$ in addition to the whole picture of the 1D chain dispersion. We plan to further experiments with various hole content and temperature dependence in order to identify all the properties found.

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References

[1] Haldane F D M 1983 Phys. Lett. 93 464
[2] Haldane F D M 1983 Phys. Rev. Lett. 50 1153
[3] Darriet J and Regnault L P 1993 Solid State Commun. 86 409
[4] DiTusa J F, Cheong S W, Park J H, Aeppli G, Broholm C and Chen C T 1994 Phys. Rev. Lett. 73 1857
[5] Yokoo T, Sakaguchi T, Kakurai K and Akimitsu J 1995 J. Phys. Soc. Jpn. 64 3651
[6] Sakaguchi T, Kakurai K, Yokoo T and Akimitsu J 1996 J. Phys. Soc. Jpn. 65 3025
[7] Sachan V, Buttrey D J, Tranquada J M and Shirane G 1994 Phys. Rev. B 49 9658
[8] Zheludev A, Tranquada J M, Vogt T and Buttrey D J 1996 Phys. Rev. B 54 7210
[9] Zheludev A, Tranquada J M, Vogt T and Buttrey D J 1996 Phys. Rev. B 54 6437
[10] Yokoo T, Zheludev A, Nakamura M and Akimitsu J 1997 Phys. Rev. B 55 11516
[11] Yokoo T, Raymond S, Zheludev A, Maslov S, Ressouche E, Zaliznyak I, Erwin R, Nakamura M and Akimitsu J 1998 Phys. Rev. B 58 14424
[12] Raymond S, Yokoo T, Zheludev A, Nagler S E, Wildes A and Akimitsu J 1999 Phys. Rev. Lett. 82 2382
[13] Maslov S and Zheludev A 1998 Phys. Rev. B 57 68
[14] Maslov S and Zheludev A 1998 Phys. Rev. Lett. 80 5786
[15] Mattheiss L F 1993 Phys. Rev. B 48 4532
[16] Eisaki H and Uchida S 1995 J. Phys. Chem. Solids 56 1811
[17] Dagotto E, Riera J, Sandvik A and Moreo A 1996 Phys. Rev. Lett. 76 1731
[18] Batista C D, Alienia A A and Eroles J 1998 cond-mat/9810387
[19] Peng K and Shiba H 1995 Phys. Rev. B 52 R715
[20] Xu G, Aeppli G, Bishen M E, Broholm C, DiTusa J F, Frost C D, Ito T, Oka K, Paul R L, Takagi H and Treacy M M J 2000 Science 289 419
[21] Sasaki T, Yokoo T, Katano S and Akimitsu J 2005 J. Phys. Soc. Jpn. 74 267
[22] Itoh S, Yokoo T, Sato S, Yano S, Kawana D, Suzuki J and Sato T J 2011 Nucl. Instrum. Methods A 631 90
[23] Itoh S, Ueno K and Yokoo T 2012 Nucl. Instrum. Methods A 661 58
[24] By using the neutron energy coming through the Fermi chopper with different rotational phasing $2\pi n$ (where $n$ is an integer), inelastic spectra can be measured simultaneously in a multi-incident energy measurement known as a repetition rate multiplication (RRM) method.