Spin and Hole Dynamics in Carrier-Doped Quantum Haldane Chain

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\textbf{Abstract.} Quantum spins in one-dimensional (1D) chains exhibit characteristic features such as the Haldane gap ($S = 1$) and the spin-Peierls state ($S = 1/2$). Multiple degrees of freedom associated with quantum spins have recently become a focus of attention. We present here the spin dynamics in lightly hole-doped Nd$_{2-x}$Ca$_x$BaNiO$_5$ ($x = 0.1$), a 1D Haldane system, using pulsed neutron inelastic scattering. The entire dispersion of the 1D Haldane chain was clearly observed with a $\sim$14 meV spin gap (Haldane gap) at the magnetic zone center. Below the gap, much spectral weight was observed, indicating an in-gap state possibly originating from the doped holes in Haldane chains.

1. Introduction

In a low-dimensional system, the quantum nature of spins appears in macroscopic phenomena. A Haldane gap is one such \textit{unconventional} property of one-dimensional (1D) integer spin systems in which a spin gap exists between the ground state and the first excited state [1, 2]. Inorganic nickelate Y$_2$BaNiO$_5$ was found to be a good candidate for a Haldane system with a spin gap of 10 meV at the magnetic zone center (MWC) [3]-[6]. In contrast, R$_2$BaNiO$_5$ (where R is a magnetic rare earth) is known as a classical antiferromagnet showing threedimensional (3D) long-range magnetic ordering at low temperature [7]. However, the saturation moment of the sublattice magnetization of the Ni$^{2+}$ spins is somewhat suppressed, indicating a remaining quantum spin fluctuation. Indeed, inelastic neutron scattering experiments revealed the existence of a spin gap at the MZC even in R$_2$BaNiO$_5$ with magnetic rare earth ions [8]-[11]. In R$_2$BaNiO$_5$ (R = Nd, Pr), the observed excitation energy is quite similar to the Haldane gap in Y$_2$BaNiO$_5$ and shows a structure factor reflecting a 1D Ni chain correlation. In addition, the magnetization and gap properties have been investigated by synthesizing a solid solution of Y$^{3+}$ and Nd$^{3+}$, namely, (Y$_{1-x}$Nd$_x$)$_2$BaNiO$_5$, to ascertain how the magnetic system (R = Nd) and the nonmagnetic system (R = Y) are connected within the context of the Haldane system [10, 11]. Surprisingly, for all values of $x$ at various ordered temperatures, the gap properties can be scaled by the temperature. Above the Néel temperature $T_N$ for each value of $x$, spin gap excitations at around $\Delta \approx 10$ meV are clearly observed. Once the temperature drops below...
T_N, however, the gap energy abruptly increases with decreasing temperature. Moreover, the gap intensity starts decreasing below T_N. All these experimental results indicate that the new Haldane system Nd_2BaNiO_5 can be interpreted as a “pure 1D Haldane chain” only above T_N without any magnetic perturbation from magnetic rare earth ions. Near T_N, Nd^{3+} sublattices begin ordering and applying an internal effective field to the Ni^{2+} sublattice (1D chains). Thus, in this temperature region, the Ni chain can be explained well as a “Haldane chain in a staggered field” [12]. A theoretical evaluation of this scenario also supports the temperature dependence of the observed gap energy [13, 14]. Thus, Nd_2BaNiO_5 is found to not be a simple Haldane system.

Another topic of interest regarding transition metal chain oxides is carrier doping, 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_2BaNiO_5 is a charge-transfer insulator [15, 16], and some quantity of hole carriers is successfully introduced primarily on oxygen sites by replacing part of the off-chain R^{3+} with Ca^{2+} [4]. The spin dynamics of hole-doped Ni 1D chains have also been addressed 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_2BaNiO_5 measured by means of a pulsed neutron scattering technique to survey the entire area of the Brillouin zone in momentum and energy space.

2. Experimental procedure
The carrier content can be controlled by replacing a portion of the Nd^{3+} ions with Ca^{2+}. Lightly doped (x = 0.1) Nd_{2−x}Ca_xBaNiO_5 was chosen for the neutron experiments. T_N is evaluated as 30 K. Two cylindrical single crystals were assembled with a total mass of 13 g in an aluminum can. Inelastic neutron scattering experiments were conducted at the High-Resolution Chopper spectrometer (HRC) installed at the Materials and Life Science Experimental Facility in J-PARC [22, 23]. The HRC is a direct geometry time-of-flight neutron spectrometer. The measurement temperatures were 4, 20, 30, 40, and 150 K, which are above and below T_N. An incident neutron energy E_i of 102.0 meV was chosen to measure a wide Q–ω space. A Fermi chopper [23] was used to monochromatize the incoming neutron energy; its rotational frequency of 200 Hz yielded an energy resolution of dE/E_i ∼ 6%.

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, ω) at T = 4.0 K (well below T_N = 30 K) and T = 40 K (above T_N). Both spectra are normalized by the measurement time (proton current measured just before the neutron target). Intense crystal electric field (CEF) excitations of Nd^{3+} ions lie at E = 24 and 38 meV. The site symmetry of Nd^{3+} in Nd_2BaNiO_5 is sufficiently low to split the tenfold degenerate J = 9/2 multiplet into five Kramers doublets. In addition to the CEF excitations, excellent dispersion relations for the Ni 1D chain are observed at both temperatures for the entire first and second Brillouin zones. The minima of the dispersion observed at the MZC, H = 0.5, 1.5, and even 2.5, occur where the magnetic scattering intensity becomes weak because of the magnetic form factor, and phonon scattering is dominant in this high-Q region. On the other hand, at H = 1.0 and 2.0, the weight of the magnon dispersion is known to be zero at the zone boundary. At low temperature [Fig. 1 (a)], the magnon bandwidth reaches 60 meV, with a somewhat large gap energy of Δ ~ 20 meV compared to the bare (unperturbed) 1D Haldane gap [5]. In addition, a flat band lying at E = 65 meV and corresponding to a phonon or magnon optical branch was observed. At T = 40 K, the Haldane gap is lowered, and
Figure 1. Observed dispersion relation of $x = 0.1$ at (a) $T = 4.0$ K ($<T_N$) and (b) $T = 40$ K ($>T_N$). Flat bands at $E = 24$ and $38$ meV are contributions from crystal field excitation of Nd$^{3+}$ ions. Oscillating signals showing minima at magnetic zone center ($H = 0.5$ and 1.5) are from 1D chain. The spectral weight is slightly shifted with respect to the MZC. The boundary energy is almost the same at both temperatures.

To survey the spectra near the gap, constant-$Q$ cuts are shown in Fig. 2 for both temperatures. Because the transfer energy in Figs. 1 and 2 is strongly related to the wave vector parallel to the incoming neutron beam $k_i$ (crystallographic $c$ axis in our experiment), the 1D spectra are also a function of $L$. However, in the 1D system, only the chain direction can be varied, and the wave numbers in the other direction are totally unchanged. Thus, we can safely accumulate the spectra with a finite index $L$. The spectra at $T = 40$ K, where the 1D Ni chain can be bare without any magnetic perturbation, shows the original gap value of $\sim 14$ meV. In contrast, the gap peak merged into the CEF peaks at 24 meV, which shows a much narrower profile. Although the energy resolution is not sufficient to show the detailed structure below the Haldane gap, considerable weight was observed, indicating a hole dynamical structure as an in-gap state. By analogy with the slightly doped ($x = 0.035$) compound [24], the weight at the MZC ($H = 0.5$) appeared as a result of hole doping. We now plan to perform further experiments at a high energy resolution to observe the dynamical structure below the gap.

Thus, the entire dynamical set of properties of a hole-doped 1D Ni chain was successfully measured by pulsed neutron inelastic scattering. At $T_N$, the dynamical structure changes dramatically, presenting new features—a local excitation at $E \sim 10$ meV and doped hole dynamics below the gap energy—in addition to a view of the entire 1D chain dispersion.

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Figure 2. Energy spectra at $Q = (0.5, 0, L)$. Open symbol is the measurement at $T = 4$ K, which is well below $T_N$. Solid symbol is at $T = 40$ K (above $T_N$). The gap value was evaluated at $\Delta=14$ meV from 1D profiles.

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