# Ni-chain gap excitations in $(Nd_xY_{1-x})_2BaNiO_5$: One-dimensional to three-dimensional crossover

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Linear-chain mixed-spin antiferromagnets $(Nd_xY_{1-x})_2BaNiO_5$ were investigated by powder inelastic neutron scattering for $x=0.25$, 0.5, and $x=0.75$. Long-range magnetic ordering was observed in all samples. The temperature dependence of the Ni-chain spin-gap modes was measured and compared to previous results for the $x=0$ and $x=1$ materials. In the magnetically disordered phase the spin dynamics was shown to have a composition-independent character. The results suggest that one-dimensional gap excitations seen in the paramagnetic and Néel phases of $Nd_2BaNiO_5$ are inherently related to Haldane spin excitations in the quantum-disordered system $Y_2BaNiO_5$. [S0163-1829(97)10617-8]

## I. INTRODUCTION

For a $S=1$ one-dimensional (1D) Heisenberg antiferromagnet (HAF) a singlet ground state and finite energy gap in the spin-excitation spectrum were predicted nearly two decades ago by Haldane.[1,2] Since then the interest in the Haldane-gap problem has not shown any signs of decline. The theoretical, numerical, and experimental work of many authors led to a pretty good understanding of the ground state and $T=0$ excitations in quasi-1D integer-spin HAF systems. A comprehensive list of references may be found in several recent publications, as for example, in Refs. 3–7. Much attention was given to the study of crossover from 1D (singlet ground state and Haldane-gap modes) to 3D (Néel ground state and conventional spin-wave modes) behavior. From this point of view, $CsNiCl_3$ (Refs. 8–10) and isostructural compounds such as $RbNiCl_3$,[11] were studied with greatest scrutiny.

Another family of quasi-1D $S=1$ antiferromagnets that seem to be promising model systems for the study of the 1D to 3D crossover is that of linear-chain nickelates with the general formula $L_2BaNiO_5$, where $L$ is one of the rare-earth elements or Y (see reference list in Ref. 12). $Y_2BaNiO_5$ was probably the first metal oxide material, for which a singlet ground state and spin gap were observed and interpreted within the framework of the Haldane conjecture.[13–17,6] All the $L\neq Y$ species feature magnetic rare-earth ions positioned in between the Ni chains. The coupling of these moments to the Ni subsystem results in 3D Néel ordering with transition temperatures ranging between 24 and 80 K.[12,18–21] Recent inelastic neutron scattering studies of $Pr_2BaNiO_5$ (Refs. 22,23) and $Nd_2BaNiO_5$ (Refs. 24) have shown that 1D gap excitations associated with the Ni chains exist in these materials as well, both above and below the Néel temperature, and are strikingly similar to Haldane-gap modes in $Y_2BaNiO_5$

One unique advantage of linear-chain nickelates compared to most other quasi-1D $S=1$ systems is that they open new opportunities for investigating the interplay between 3D and 1D behavior. Substituting part of the rare-earth ions by nonmagnetic $Y^{3+}$ should allow us to observe, step by step, how the 3D to 1D crossover occurs. As a realization of this approach, we present herein our inelastic neutron-scattering results on $(Nd_xY_{1-x})_2BaNiO_5$ for $x=$ 0.25, 0.5, and 0.75. We compare the new data to those previously obtained for $Y_2BaNiO_5$ $(x=0)$ and $Nd_2BaNiO_5$ $(x=1)$.

## II. EXPERIMENTAL PROCEDURES

$(Nd_xY_{1-x})_2BaNiO_5$ samples were prepared by solid-state reaction method. Three samples, roughly 15 mg each, were fabricated with $x=0.25$, 0.5, and 0.75. The samples were characterized by conventional x-ray powder diffraction. In each case the diffraction pattern was found to be that of a single-phase compound and totally consistent with a $Y_2BaNiO_5$-type orthorhombic structure (space group $Immm$) with no ordering of Y and Nd on the $L$ sites. The refined lattice parameters for our samples are listed in Table I along with those found in literature for $Y_2BaNiO_5$ and $Nd_2BaNiO_5$.

Neutron-scattering experiments were performed on the H8, H4M, and H7 triple-axis spectrometer installed at High Flux Beam Reactor at Brookhaven National Laboratory. For

TABLE I. Lattice parameters and Néel temperatures in $(Nd_xY_{1-x})_2BaNiO_5$.

| Nd content $x$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $T_N$ (K) |
|---|---|---|---|---|
| 0 [a] | 3.76 | 5.76 | 11.33 | |
| 0.25 | 3.780 | 5.810 | 11.412 | 19(1) |
| 0.5 | 3.794 | 5.844 | 11.484 | 29.5(0.5) |
| 0.75 | 3.832 | 5.926 | 11.652 | 39(0.5) |
| 1.0 [b] | 3.832 | 5.910 | 11.652 | 48 |

[a]Sakaguchi *et al.* (Ref. 17).
[b]Zheludev *et al.* (Ref. 19)

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all three $(Nd_xY_{1-x})_2BaNiO_5$ samples we tried to reproduce the same experimental conditions of previous measurements on $Nd_2BaNiO_5$.[24] Neutron beams of fixed final energies $E_f=14.7$ meV or $E_f=30.5$ meV were used with a pyrolitic graphite (PG) filter positioned after the sample. PG (002) reflections were employed in both monochromator and analyzer. At all times the collimation setup was $40'-40'-40'-80'$. The sample temperature was controlled in the range 3.5–300 K with the precision of at least 0.5 K by standard or two-stage closed-cycle refrigerators.

## III. RESULTS

### A. Magnetic phase transition and spin structure

In all three $(Nd_xY_{1-x})_2BaNiO_5$ samples a magnetic phase transition was observed at finite temperatures by means of neutron powder diffraction. The measurements were performed in the triple-axis mode to improve the signal-to-noise ratio in our data. The low-temperature phase in all three compounds is characterized by magnetic Bragg reflections of the type $(m+1/2,\ k,\ n+1/2)$ with $m$, $k$, $n$: integer, $m+n+k$: even. The Néel temperatures were determined by measuring the $T$ dependence of the (0.5, 1, −0.5) magnetic peak and are listed in Table I along with that for $Nd_2BaNiO_5$ ($x=1$).[19] The Néel temperature $T_N$ is plotted against Nd concentration $x$ in Fig. 1(a) (solid circles).

We were not able to collect sufficient magnetic diffraction data to do a complete refinement of the spin structure in our samples. Nevertheless, having assumed that in all the compounds studied the magnetic order is the same as in $Nd_2BaNiO_5$,[19,21] we could separately determine the magnetizations of Ni and Nd sublattices. This was achieved by analyzing the intensities of only three magnetic reflections, (0.5, 1, −0.5), (0.5, 1, 1.5), and (0.5, 0, 2.5), that were measured at several temperatures in each sample and normalized by the intensities of nuclear Bragg peaks. The (0.5, 1, 1.5) and (0.5, 0, 2.5) peaks overlap and were therefore treated as a single reflection. In the analysis we have utilized the $Ni^{2+}$ and $Nd^{3+}$ magnetic form factors from Ref. 25. For the $x=0.5$ and $x=0.75$ samples the results are visualized in Fig. 1(b). In the $x=0.25$ sample the magnetic peaks were too weak to be quantitatively analyzed. The observed Nd-sublattice magnetization is well described by the mean-field model developed in Ref. 21 for $Nd^{3+}$ in $Nd_2BaNiO_5$ and is rather universal for all the compositions studied [Fig. 1(b), solid lines]. In contrast, the approach to saturation for the $Ni^{2+}$ moments becomes visibly more gradual as the Nd concentration is reduced. Open symbols in Fig. 1(a) show the concentration dependence of the extrapolated ($T=0$) saturation moments for Ni and Nd in $(Nd_xY_{1-x})_2BaNiO_5$.

### B. Magnetic gap excitations

For $(Nd_xY_{1-x})_2BaNiO_5$ we performed essentially the same type of inelastic measurements as were previously done for $Nd_2BaNiO_5$.[24] The powder-averaged cross section $S_{pow}(Q,\omega)$ for gap excitations with a Haldane-like 1D dynamic structure factor was derived in Ref. 24 and herein we adopt the notation introduced in that paper. Conveniently, $S_{pow}(Q,\omega)$ can be written as a product of $Q$- and $\omega$-dependent parts: $S_{pow}(Q,\omega)\approx S_{pow}(Q)F(\omega)$. $S_{pow}(Q)$ has

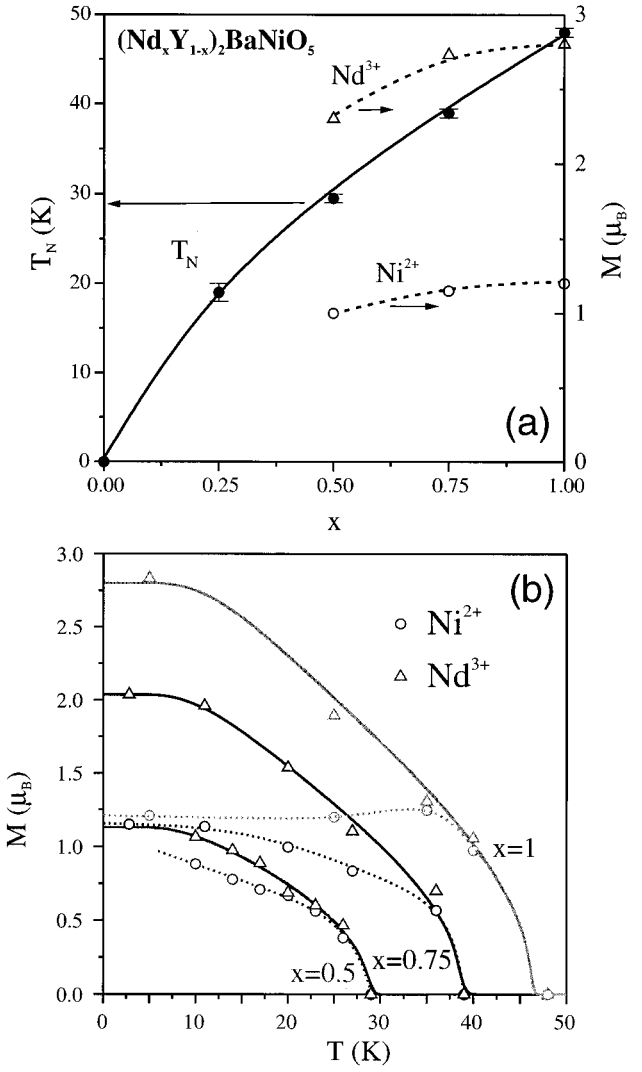


FIG. 1. (a) Néel temperature versus Nd concentration $x$ as measured in $(Nd_xY_{1-x})_2BaNiO_5$ (solid circles). Estimated saturation moments for the $Ni^{2+}$ (open circles) and $Nd^{3+}$ (open triangles) ions. The lines are guides to the eye. (b) Temperature dependence of magnetic moments on $Ni^{2+}$ (open circles) and $Nd^{3+}$ (open triangles) in $(Nd_xY_{1-x})_2BaNiO_5$. For the Nd moment the solid lines represent fits resulting from a mean-field treatment as described in Ref. 21. In the case of Ni the dashed lines are guides for the eye. The data for $Nd_2BaNiO_5$ are taken from Ref. 19.

the characteristic saw-tooth shape with maxima around $Q_m=\{[(2n+1)/2]a^*\}$,[14,24] and can be written as

$$S_{pow}(Q)\approx\frac{f(Q)}{Q}\sum_{m:|Q_m|\le Q}[1+(Q_m/Q)^2]. \tag{1}$$

Here $f(Q)$ is the magnetic form factor for $Ni^{2+}$. The peak shapes in constant-$Q$ inelastic scans are given by[24]

$$F(\omega)\propto\frac{1}{\sqrt{(\hbar\omega)^2-\Delta^2}}. \tag{2}$$

Both above and below the Néel temperatures constant-$Q$ scans at $Q=0.65a^*$ reveal the presence of a gap excitation around 10 meV in all three $(Nd_xY_{1-x})_2BaNiO_5$ compounds

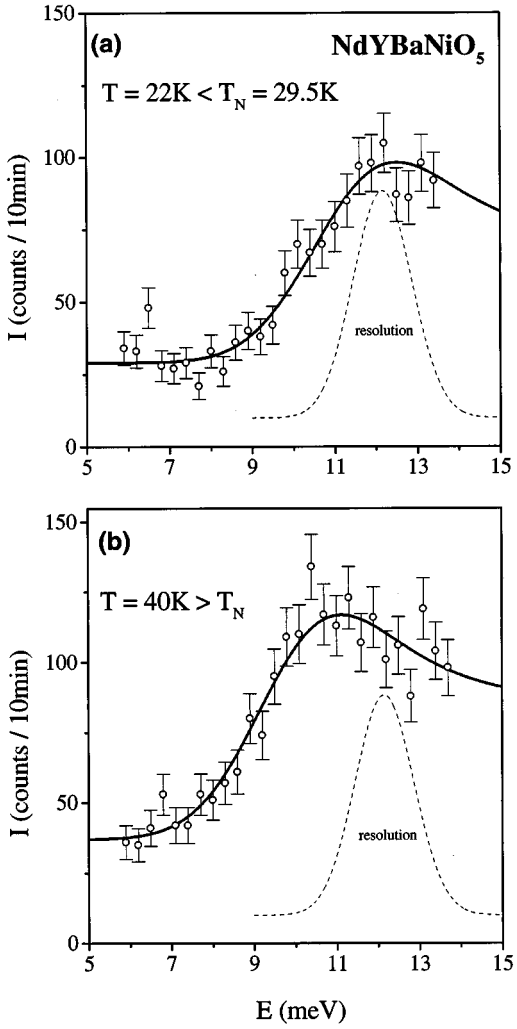


FIG. 2. Typical inelastic constant-$Q$ scans measured in $(Nd_{0.5}Y_{0.5})_2BaNiO_5$ above and below the Néel temperature $T_N = 29.5$ K. The solid lines represent fits described in the text.

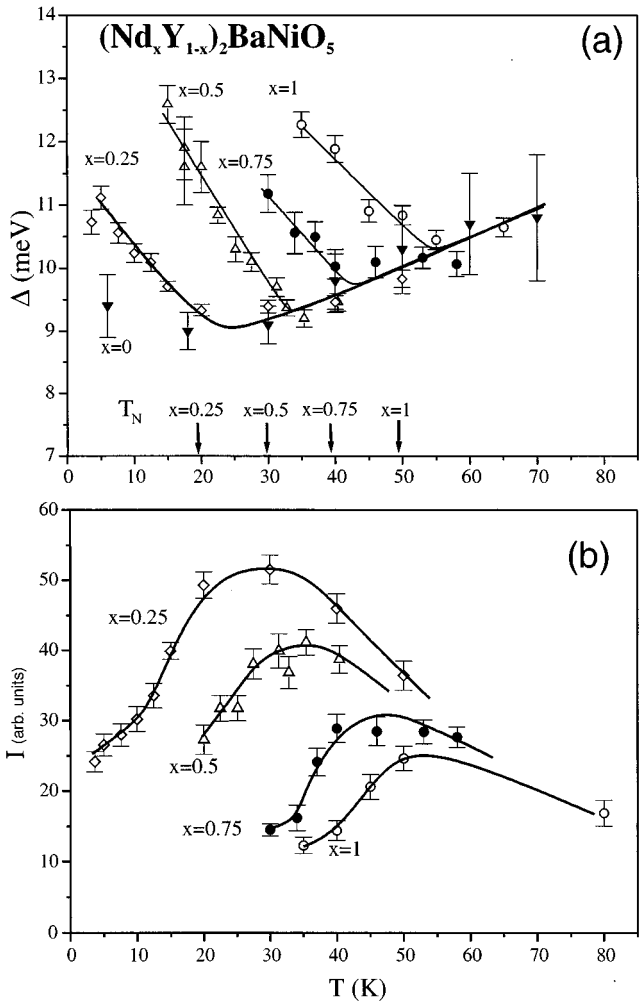


FIG. 3. (a) Temperature dependence of the spin gap in $(Nd_xY_{1-x})_2BaNiO_5$. The data for $x=0$ and $x=1$ are from Refs. 17 and 24, respectively. (b) Temperature dependence of the energy-integrated intensity in the gap modes in $(Nd_xY_{1-x})_2BaNiO_5$. The $x=1$ data are from Ref. 26.

studied. Some typical raw data for the $x=0.5$ sample are shown in Fig. 2. As in the case of $Nd_2BaNiO_5$,[24] an intense inelastic peak at $\hbar\omega \approx 16$ meV associated with a crystal-field transition in Nd and kinematic constraints forced us to limit the inelastic scans to 14 meV energy transfer. The data were analyzed using the form (2), convoluted with a Gaussian energy-resolution function. Refining the gap value, intensity and intrinsic energy width $\Gamma$ of the inelastic feature produces reasonably good fits (Fig. 2, solid lines). The gap energy for $(Nd_xY_{1-x})_2BaNiO_5$ ($x=0.25$, 0.5 and $x=0.75$) is plotted against temperature in Fig. 3(a). The same figure shows the data for $x=0$ (Ref. 17) and $x=1$.[24] At all compositions the gap energy decreases linearly on cooling from $T=70$ K and starts to increase, also in a linear fashion, below $T_N$.

Figure 3(b) shows the temperature dependence of the energy-integrated intensity of the 10 meV peak as deduced from the least-squares analysis described above. In this figure we also show some unpublished $Nd_2BaNiO_5$ data.[26] Unfortunately, no relevant data on $Y_2BaNiO_5$ is currently available. Between samples of different composition the inelastic intensities were scaled by the intensities of (0,1,1) powder lines measured with the same setup as used for inelastic experiments. In $(Nd_xY_{1-x})_2BaNiO_5$ ($x \neq 0$) a decrease of inelastic intensity is observed on cooling through $T_N$, that is, at the same temperature the gap energy starts to increase.

To verify the 1D nature of the 10 meV gap modes constant-$E$ scans were performed for $(Nd_{0.5}Y_{0.5})_2BaNiO_5$ at $T=20$ K and $T=32$ K (above and below $T_N=29.5$) for energy transfers of 12 and 10 meV, respectively. The results are shown in Fig. 4. The solid line represents a fit to our data with the expression for $S_{pow}(Q)$ derived in Ref. 24 for excitations polarized perpendicular to the chain direction and convoluted with the longitudinal $Q$ resolution of the spectrometer. An excellent fit is obtained by refining only the overall scaling factor and background level (solid lines in Fig. 4).

## IV. DISCUSSION

The most important result of this work is that at $T > T_N$ the Ni-chain spin gap $\Delta$ is *composition-independent* [Fig. 3(a)]. In $Y_2BaNiO_5$ (Ref. 17) $\Delta$ increases slowly with $T$ as

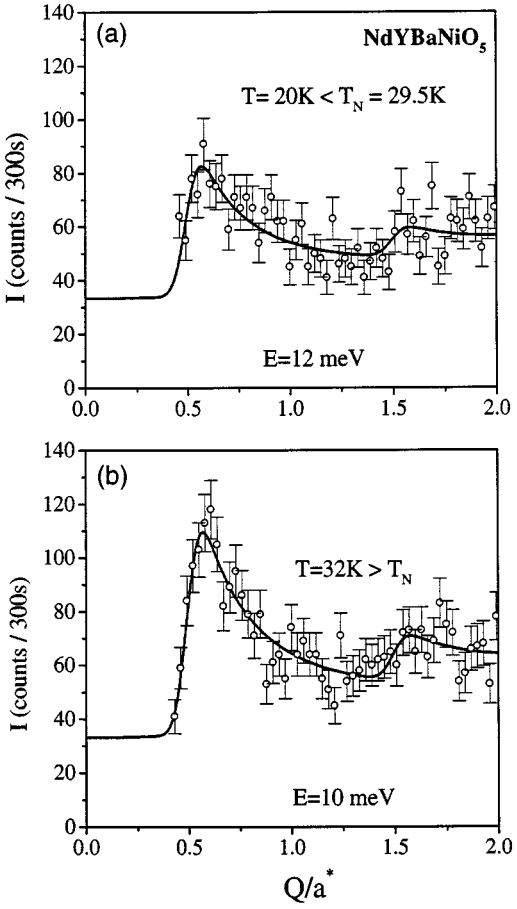


FIG. 4. Typical constant-$E$ scans measured in $(Nd_{0.5}Y_{0.5})_2BaNiO_5$ above and below the Néel temperature $T_N = 29.5$ K. The solid lines are fits to the data as described in the text.

in other Haldane-gap systems.[27,7] The increase is substantially smaller than predicted by the nonlinear $\sigma$ model.[28] In the paramagnetic phase of all $(Nd_xY_{1-x})_2BaNiO_5$ species studied $\Delta$ increases gradually with $T$ as well. As $x$ and, accordingly, the Néel temperature decrease, the gap in $(Nd_xY_{1-x})_2BaNiO_5$ coincides with that in the pure Y nickelate in an increasingly broad temperature range. It appears that in the disordered phase there is virtually no difference between $L_2BaNiO_5$ systems that do or do not have a magnetically ordered phase at low temperatures. This in turn may suggest that gap modes in Nd-containing nickelates are of the same nature as those in $Y_2BaNiO_5$, i.e., are Haldane-gap excitations. We do note however, that even for the latter system there still is some ongoing controversy on whether the magnetic excitations are to be associated with a Haldane ground state and the integrity of the spins involved.[29]

The experimental difficulties that limit our inelastic measurements to 14-meV energy transfers[24] have previously prevented the study of Ni-chain gap excitations in $Nd_2BaNiO_5$ for $T \lesssim 0.7T_N$. For all compositions studied in this work though, the minimum gap energy (at $T \approx T_N$) is smaller than in the $x=1$ compound. We were, therefore, able to observe the gap excitations in a much broader temperature interval, as for example in $(Nd_{0.25}Y_{0.75})_2BaNiO_5$ where the gap was seen even at $T \approx 0.2T_N$. In all cases the gap increases *linearly* with decreasing $T$ in the ordered phase. Linear behavior is what one expects from most general physical considerations. Indeed, $\Delta$ must be a function of the magnetic order parameter alone, i. e., the only relevant thermodynamic characteristic of the system in the ordered phase at thermal equilibrium. The first symmetry-permitted term in the power-series expansion of $\Delta$ is proportional to the square of the order parameter. The temperature dependence of the latter has been measured in $Nd_2BaNiO_5$ with very high accuracy using resonant magnetic x-ray diffraction,[21] and shown to scale as $(T_N - T)^{0.5}$ near the transition point. This immediately tells us that the change in the gap energy must be linear with $(T - T_N)$. The nontrivial experimental result is that the gap shows this linear behavior in a very wide temperature range. Only for $(Nd_{0.25}Y_{0.75})_2BaNiO_5$ a hint of saturation in $\Delta(T)$ at $T \to 0$ is observed [Fig. 3(a)].

The temperature dependence of the energy-integrated intensity of the gap excitations shows some composition-independent trends as well [Fig. 3(b)]. In all samples at $T > T_N$ this intensity decreases with increasing $T$ and appears to follow a master curve. As previously observed in $Pr_2BaNiO_5$, on cooling through the Néel point the intensity goes down to roughly half its maximum value. For most samples the progressive increase in the gap energy prevents us from performing the measurements at $T \to 0$. However, in the case of $(Nd_{0.25}Y_{0.75})_2BaNiO_5$ it is clear that the intensity extrapolates to a finite value at low temperature. Although in Ref. 22 we have proposed a handwaving explanation for the decrease of the spectral weight of the gap modes in the ordered phase, we are still lacking a quantitative quantum-mechanical theory for the effect.

## V. CONCLUSION

The temperature-dependent behavior of the 1D gap excitations in $(Nd_xY_{1-x})_2BaNiO_5$ was studied by inelastic neutron-scattering experiments. The spin gap in the magnetically disordered phase was shown to be independent of Nd concentration $x$. A linear increase of the gap was observed on cooling through the Néel temperature. The results suggest that Ni-chain spin dynamics in these species is very similar to that in the Haldane-gap compound $Y_2BaNiO_5$. A consistent finite-$T$ theory for gap excitations in those $L_2BaNiO_5$ systems that undergo long-range magnetic ordering is yet to be developed.

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