

^{89}Y NMR Imaging of the Staggered Magnetization in the Doped Haldane Chain $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$

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We present a *static*, model-independent, experimental determination of the spin-spin correlation length ξ in a quantum spin system. This is achieved in the doped Haldane (i.e., $S = 1$ Heisenberg antiferromagnetic) chain $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$ by ^{89}Y NMR imaging of the staggered magnetization induced around the Mg impurities (i.e., chain boundaries) by a magnetic field. The magnitude of this magnetization is found to decay exponentially, with ξ equal to the theoretical prediction for an infinite $S = 1$ chain and the staggered magnetic moment at the edge site showing the Curie behavior of an effective $S = 1/2$ spin.

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One dimensional (1D) quantum antiferromagnetic (AF) spin systems such as spin ladders, spin-Peierls systems, and spin chains have recently attracted an increasing interest, partly as a possible way to approach from a lower dimension the physics of the copper-oxide high T_c superconductors. In all of these systems, the spin-spin correlation function is a quantity of fundamental importance, which can be experimentally probed as a function of wave vector and energy by inelastic neutron scattering, or by studying the *static* response of the system to the perturbation created by impurities, through NMR imaging of local spin polarization. In recent examples of this latter technique applied to high T_c superconductors [1], spin-ladder systems [2], or $S = 1/2$ chains [3], the broadening of the NMR lines (or the modification of the line shape) due to impurities has always been interpreted within a specific model in order to obtain information on the correlation length ξ , making conclusions manifestly *model dependent*. In this Letter we present an NMR study of a doped Haldane (i.e., $S = 1$ Heisenberg AF spin) chain, in which individual spin sites near impurities are resolved as satellite peaks in the NMR spectra. In this way the real-space dependence of the spin polarization is followed site by site, providing a complete and model independent picture of the impurity screening, and giving thus a direct access to ξ . Such a study should be compared to the observation of satellite lines revealing screening of normal [4] or Kondo [5] impurities in a metal, but it applies here to a low-dimensional quantum antiferromagnet, i.e., to a class of systems in which screening of nonmagnetic impurities has generated recently a large body of theoretical works [6].

The main characteristic of integer spin chains is the existence of a gap between the lowest energy levels, predicted by Haldane [7] and experimentally observed in several compounds [8–13]. If such a system is doped

by nonmagnetic impurities, an ideal infinite chain is "cut" to an ensemble of open segments of length L , in which the lowest lying eigenstates are a singlet $|0\rangle$ and a triplet $|1, S_z^z\rangle$, with an energy separation exponentially decreasing with L [14]. The Haldane gap [7], defined for $L \rightarrow \infty$, is the one above the resulting fourfold quasidegenerate ground state. In the state $|1, 1\rangle$ it has been shown by numerical calculations [15–18] that the expectation value of the local spin operator $\langle S_i^z \rangle$ decreases exponentially [19] from the boundary with staggered phase. In particular, for a pure Heisenberg model, one has an effective spin-1/2 at the edge of the chain ($\langle S_i^z \rangle \approx 1/2$) and a characteristic decay length $\xi \approx 6$ [15], a value very close to the zero-temperature correlation length (ξ_∞) of an infinite chain. Thus, it has been argued that the zero-temperature local magnetization (corresponding for long chains to $\langle S_i^z \rangle$ in the state $|1, 1\rangle$) reflects indeed the decay of the correlation function in the Haldane phase.

$S = 1/2$ boundary spins have been experimentally observed in low-temperature ESR spectra of pure and doped $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2(\text{ClO}_4)$ [20,21] and Y_2BaNiO_5 [22]. Also specific heat measurements [23] can be explained in terms of $S = 1/2$ excitations [24]. On the other hand, no direct experimental determination of the site dependence of the local magnetization has been reported until now. Moreover, the temperature dependence of the expectation value of edge spins and the relationship between the decay of the staggered magnetization and the infinite chain correlation function have not been established yet at temperatures where the excited states are populated.

The compound Y_2BaNiO_5 , due to the low inter-chain/intrachain coupling ratio ($|J'/J| \leq 5 \times 10^{-4}$, with $J = 285$ K) and the small single-ion anisotropy [11], is a prototype one-dimensional $S = 1$ Heisenberg AF. Moreover, a controlled substitution of

$\text{Ni}^{2+}(S=1)$ by $\text{Mg}^{2+}(S=0)$ offers the possibility to obtain open chains of average length $\langle L \rangle \cong 1/x$. In $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$, Ni^{2+} local magnetization generates a site dependent hyperfine field at ^{89}Y nuclei inducing a multippeak structure in ^{89}Y NMR spectra. These spectra are sort of a map of $\langle S_i^z \rangle$, inaccessible by any other technique because a nonhomogeneous, variable-amplitude response to the external field is involved.

^{89}Y NMR measurements have been carried out on $x = 0.05$ and $x = 0.10$ powder samples of $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$, at the NMR facility of the Grenoble High Magnetic Field Laboratory. The ^{89}Y NMR spin-echo spectra have been obtained at fixed frequency by sweeping the magnetic field H_0 . Figure 1 shows representative spectra for the $x = 0.05$ sample. Several peaks can be observed, their shift from the central line increasing with decreasing temperature. These peaks p_I are labeled by an index I according to a decreasing magnitude of their shift $\Delta(p_I) = H_0(p_I) - H_0(p_c)$ with respect to the central line p_c . This labeling provides direct assignment of peaks to the position i along the chain, as explained in detail below. The magnitude of the edge-peak shift $|\Delta(p_{I=1})|$ is reported in Fig. 2 as a function of T . A comparison of spectra for two samples with different average chain lengths shows that for $T \approx J$ the peak positions are independent on $\langle L \rangle$ (see the inset of Fig. 2). Figure 3a shows the position dependence of $|\Delta(p_I)|$ at different temperatures. It is found that it decreases exponentially

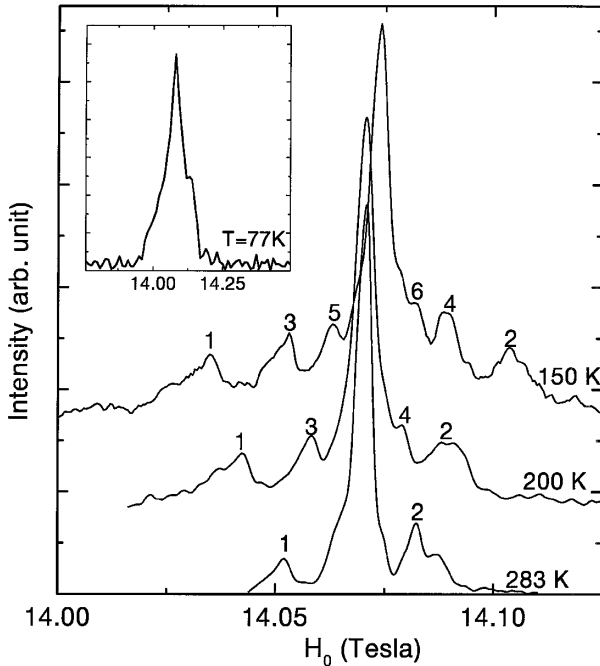


FIG. 1. ^{89}Y NMR spectra in $\text{Y}_2\text{BaNi}_{0.95}\text{Mg}_{0.05}\text{O}_5$ recorded at fixed frequency $\nu_{\text{RF}} = 29.4$ MHz by sweeping magnetic field. Resolved satellite peaks are labeled with the index I , following the decreasing magnitude of their shift (measured from the central line). In the inset, all of the peaks are shown to be smeared in a single wide line when the temperature is lowered.

with I at all temperatures above ~ 100 K. Below 100 K the peaks are smeared into a single broad line (inset of Fig. 1), preventing us from extending the analysis to a lower temperature.

The intensity of the NMR spectrum is proportional to the number of ^{89}Y nuclei which, for the irradiation frequency ν_{RF} , obey the resonance condition

$$\nu_{\text{RF}} = \frac{\gamma}{2\pi} (H_0 + h_j^z) = \frac{\gamma}{2\pi} \left[H_0 + \left(\sum_{l,k} \hat{A}_{lkj} \langle \tilde{S}_{lk} \rangle \right)^z \right], \quad (1)$$

where $(\gamma/2\pi) = 2.0859$ MHz/T is the ^{89}Y gyromagnetic ratio, h_j^z is the z component of the hyperfine field at the j th nucleus and $\hat{A}_{lkj}$ is the Ni^{2+} - ^{89}Y hyperfine coupling tensor. In Eq. (1), k is a chain index and l is an in-chain site index. A given ^{89}Y has two Ni^{2+} nearest neighbors (nn) belonging to the same chain and two next nearest neighbors (nnn) on adjacent chains (see Fig. 4 in Ref. [25]). On the basis of the NMR results in pure Y_2BaNiO_5 , one can assume that only nnn sites contribute to h_j^z :

$$\begin{aligned} A_{lkj}^{\alpha\beta} &= A = 13 \text{ kG} & \text{if } \alpha = \beta \text{ and } (j)-(l,k) \text{ are nnn,} \\ A_{lkj}^{\alpha\beta} &= 0 & \text{if } \alpha \neq \beta \text{ or } (j)-(l,k) \text{ are not nnn.} \end{aligned} \quad (2)$$

In the following, we summarize the main reasons supporting this assumption [26]. The NMR powder spectra [13] having a shift much larger than the line broadening indicate that the hyperfine coupling is essentially scalar and,

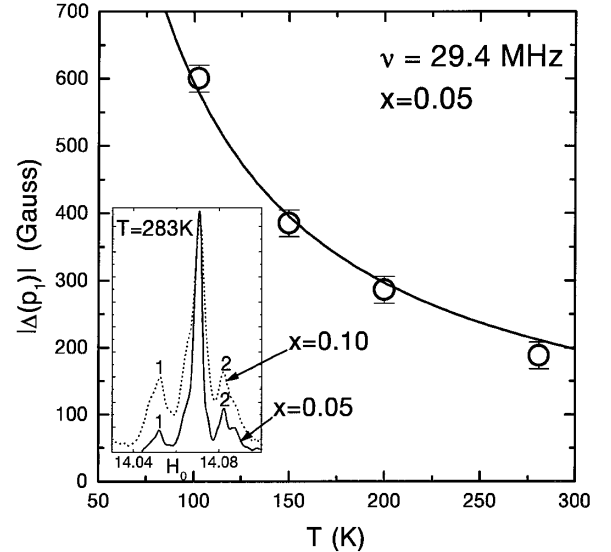


FIG. 2. Temperature dependence of the shift of the p_1 peak in ^{89}Y NMR spectra (measured from the central line, see Fig. 1). The solid line is a Curie function for $S = 1/2$ spins [Eq. (3) in the text]. Inset shows the doping dependence of the room temperature spectra of $\text{Y}_2\text{BaNi}_{1-x}\text{Mg}_x\text{O}_5$ demonstrating that peak positions do not depend on the chain length.

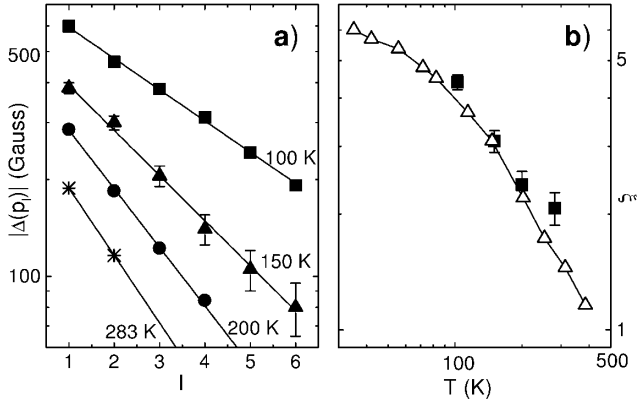


FIG. 3. (a) Site dependence of the magnitude of shift of p_I peaks in $\text{Y}_2\text{BaNi}_{0.95}\text{Mg}_{0.05}\text{O}_5$ taken at $\nu_{\text{RF}} = 29.4$ MHz. Solid lines are fits [Eq. (4) in the text], defining a decay length $\xi(T)$ of the boundary magnetization. (b) Comparison of an experimental $\xi(T)$ value (full squares) and the infinite chain correlation length $\xi_\infty(T)$ (up triangles) as calculated in Ref. [27].

hence, due to a transferred hyperfine interaction. Since the mechanism of transferred hyperfine interaction requires extension of the $\text{Ni}^{2+} - 3d$ orbitals at the Y site, only nn and nnn Ni^{2+} can couple to ^{89}Y . On the other hand, as already noticed [12], the lattice position of the ^{89}Y is strongly unfavorable for transferred interaction from nn Ni^{2+} , and the coupling can be assumed essentially limited to two equivalent contributions from nnn ions only. Since for an infinite chain in a uniform magnetic field the magnetization is uniform, $\langle S_{ik}^z \rangle = \langle \tilde{S}^z \rangle$, from the standard plot of the shift of the NMR line as a function of the spin susceptibility one derives $\sum_{l,k} A_{lki} = 2A = 26$ kG. Furthermore, small inter-chain coupling J' allows us to consider the nnn ions (which belong to different chains) contributing to h_i^z as completely uncorrelated. Thus, Eqs. (1) and (2) link the position of the maxima in the NMR spectra to the different values of the local magnetization along one chain. In particular, the high temperature spectra shown in Fig. 1 correspond to a large number of Ni^{2+} spins having the same expectation value $\langle S_i^z \rangle = \langle S_c^z \rangle$ corresponding to central peak p_c , and to a certain number of sites for which $\langle S_i^z \rangle \neq \langle S_c^z \rangle$, yielding the peaks p_I . According to $T = 0$ numerical results [15–18], one expects the induced magnetization $\langle S_i^z \rangle - \langle S_c^z \rangle$ to be maximal near Mg impurities, (i.e., at the chain ends at positions $i = 1$ and L), with its absolute value decreasing away from the perturbation. As the shift of the line $\Delta(p_I)$ with respect to the central peak is proportional to induced magnetization, we assign the peaks p_I of the spectra to the positions $i = I$ and $(L - I + 1)$ along the chain following the decreasing magnitude of $\Delta(p_I)$. This attribution is readily confirmed by regular alternation of the sign of $\Delta(p_I)$ as a function of I , corresponding to the staggered nature of induced magnetization, and reflecting the AF character of the exchange coupling.

As shown in Fig. 2 (solid line) the temperature evolution of $\Delta(p_I)$ is very well accounted for by a hyperfine

field of the form

$$|[\Delta(p_I)](T)| = A \frac{g\mu_B S(S+1)}{3k_B T} H_0, \quad (3)$$

with $S = 1/2$, $g = 2$, and $H_0 = 14$ T. This means that, for $\Delta_H \lesssim T \lesssim J$ (where $\Delta_H \approx 100$ K is the Haldane gap for pure Y_2BaNiO_5), the nonuniform magnetization associated to the extreme sites of the chain is close to the one corresponding to “free” $S = 1/2$ spins. Since no doping (i.e., $\langle L \rangle$) dependence of $\Delta(p_I)$ has been found at room temperature (inset of Fig. 2), this conclusion is independent on the chain length at least for $\langle L \rangle \gtrsim 10$ and $T \approx J$. One could observe that a $S = 1/2$ Curie-like behavior can be obtained as a thermal expectation value of the edge spins on the lowest energy states (singlet and triplet) of the *finite* chain, provided they are separated by an energy gap $\Delta E \ll g\mu_B H_0$. According to Monte Carlo calculations [15], ΔE is indeed considerably smaller than the Zeeman energy in a field of 14 T ($\approx 0.08J$) for $L \approx 20$ (i.e., $x = 0.05$), while $\Delta E \approx g\mu_B H_0$ for $L \approx 10$ (i.e., $x = 0.10$). However, one has to notice that for $T > \Delta_H$ a precise calculation of the thermodynamic properties of the system has to take into consideration also the excited states, as is evident from the analysis of the spin-spin correlation reported below.

The dependence $\Delta(p_I)$ on I can be fitted to an exponential decay:

$$|[\Delta(p_I)](T)| = |[\Delta(p_1)](T)| e^{-(I-1)/\xi(T)} \quad (4)$$

(solid lines in Fig. 3a), and the characteristic decay length $\xi(T)$ of the magnetization can be extracted. As shown in Fig. 3b, $\xi(T)$ obtained in this way is very close to the values of the *infinite* chain correlation length ξ_∞ calculated by Kim *et al.* [27]. This remarkable conclusion indicates that the picture of boundary defects, which reflects the bulk correlation of an infinite chain, holds not only in the Haldane phase ($T \ll \Delta_H$) [18], but in general for $T < J$. A possible way to interpret this result can be based on a heuristic extension from zero to finite temperature of the model proposed in Ref. [17]. There the expectation values of S_i^z in the state $|1, 1\rangle$ are shown to decay exponentially over a length $\xi = \xi_\infty(T = 0)$, due to the interaction of the fields describing the translational invariant chain in the free boson model, with the effective fields originating from two end of chain $S = 1/2$ spins. The experimental findings reported in Fig. 3 are then immediately recovered if one assumes that these edge “extra” spins are practically Curie-like (as indicated by the behavior of p_1 in Fig. 2), and substitutes $\xi_\infty(T = 0)$ by $\xi_\infty(T)$ and the expectation values of S_i^z in $|1, 1\rangle$ by the thermal average.

At low temperature the progressive increase of the width $d(p_I)$ of the NMR peaks (see Fig. 1) prevents a meaningful analysis of the boundary magnetization along the lines used for $T \gtrsim 100$ K. However, the characteristic shape of the NMR spectra [26] clearly indicates the

persistence of field-induced staggered magnetization. The origin of the broadening is likely related to the anisotropy terms in the magnetic Hamiltonian [11], which in powder samples causes a distribution of $\langle S_i^z \rangle$. This observation is corroborated by the fact that the ratio between the easy-axis anisotropy $D = 8$ K and the Zeeman energy is of the same order of magnitude as $d(p_I)/\Delta(p_I)$. In order to extend the data to lower temperature, it is thus necessary to work on single crystals. However, an additional source of broadening is a distribution of chain lengths around the average value $\langle L \rangle$, which is expected to be important at $T \lesssim 100$ K. Indeed, at low temperature ξ is increasing, and for short chains with $L/2 \lesssim \xi$ the magnetization is becoming L dependent. In principle, these effects can be resolved by decreasing the dopant concentration x ; however, this will proportionally decrease the size of our satellite peaks, i.e., the “resolution” of NMR spectrum.

In summary, through ^{89}Y NMR in Mg doped Y_2BaNiO_5 , we have been able to image the local magnetization induced by “free” boundaries in a $S = 1$ Heisenberg AF spin chain, in the temperature range $\Delta_H \lesssim T \lesssim J$. By mapping the lattice positions onto the different peaks in the NMR spectra, we have shown that the characteristic decay length $\xi(T)$ of the boundary magnetization is equal to the theoretical prediction for the correlation length of the Haldane chain. The nonuniform magnetization of the edge spin in a finite chain follows a $S = 1/2$ Curie-like behavior. These results provide direct experimental confirmation that the NMR of doped quantum AF spin systems is the right technique to access the spin-spin correlation function. Improving the choice of experimental system (e.g., by using single crystals) and using an appropriate nucleus for NMR imaging, this technique should provide more reference data for comparison to the theory.

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