End-Chain Spin Effects in Haldane Gap Materials

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This paper overviews the behavior of the end-chain spins of linear chain systems possessing a Haldane gap. The physical properties of the end-chain spins are described by reviewing the results obtained primarily with materials known as NENP, Ni(C₂H₅N₂)₂NO₂(ClO₄), and NINAZ, Ni(C₄H₁₀N₂)₂N₄(ClO₄).

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INTRODUCTION

Since the birth of quantum mechanics, low dimensional magnetic systems have been the subject of numerous theoretical and experimental investigations [1–3]. In 1983, Haldane [4] suggested that a one-dimensional Heisenberg antiferromagnet with integer spin possessed an energy gap between the nonmagnetic ground state and the first excited one. In addition, this Haldane gap was not present in noninteger spin systems. Haldane’s humdinger prediction renewed interest in the field where most of the theoretical and experimental investigations [1–3]. In 1983, Haldane [4] suggested that a one-dimensional Heisenberg antiferromagnet with integer spin possessed an energy gap between the nonmagnetic ground state and the first excited one. In addition, this Haldane gap was not present in noninteger spin systems. Haldane’s humdinger prediction renewed interest in the field where most of the results may be explained by a spin Hamiltonian written as

\[ H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + D \sum_i (S_i^z)^2 + E \sum_i [(S_i^x)^2 - (S_i^y)^2] \]

\[ -\mu_B \vec{H} \cdot \sum_i \vec{g}_i \cdot \vec{S}_i + J' \sum_j \vec{S}_j \cdot \vec{S}_{j+1}, \]

(1)

where \( J \) is the nearest-neighbor spin intrachain interaction, \( D \) is the single-ion anisotropy, \( E \) is the orthorhombic anisotropy, \( H \) is the externally applied magnetic field, and \( J' \) is the nearest-neighbor spin interchain interaction.

The purpose of this paper is not to provide a detailed review of theoretical and experimental work that lead to the identification of the Haldane phase. Rather, this paper overviews the behavior of the end-chain spins of linear chain systems possessing a Haldane gap. Due to space limitations, this discussion cannot be comprehensive and will focus on aspects of our experimental work, since a few general reviews have been published [5–10]. Finally, this paper will be organized in a quasi-chronological manner, so the reader may receive a sense of how the subject has evolved.

![FIG. 1. A VBS model schematic representation of an S = 1 chain.](image)

PREDICTION AND OBSERVATION OF END-CHAIN SPINS IN NENP

The valence bond solid (VBS) model, introduced by Affleck, Kennedy, Lieb, and Tasaki [11], provides a physically intuitive picture of integer spin antiferromagnetic chains. For example as illustrated in Fig. 1, an \( S = 1 \) site has two \( S = \frac{1}{2} \) entities, as represented by two points enclosed in a circle, that are coupled to neighboring sites by valence bonds represented by a solid line. When compared to the resonating valence bonds [12] of an \( S = \frac{1}{2} \) chain, no degeneracy is available in forming the \( S = 1 \) chain, so the singlet ground state is a solid. Naturally at the ends of the chains, \( S = \frac{1}{2} \) spins are predicted by the model.

Initial evidence of the presence of the end-chain spins was an enhanced impurity tail in the magnetic susceptibility of NENP, Ni(C₂H₅N₂)₂NO₂(ClO₄) [13,14], doped with Cu²⁺ magnetic impurities [15]. Later, using X-band ESR on a similar sample, Hagiwara et al. [16] observed hyperfine interactions that could be attributed to the interactions between \( S = \frac{1}{2} \) variables and the Cu²⁺ \( S = \frac{1}{2} \) impurities. Furthermore, the temperature dependence of the main ESR peak, i.e. the peak attributed to the end-chains spins, was fit with an empirical formula whose form was later confirmed by Mitra, Halperin, and Affleck [17]. In order to break the chains while avoiding magnetic impurities, Glarum et al. [18] studied samples of NENP doped with Cd, Zn, and Hg. These workers observed various asymmetric ESR peaks, depending upon the orientation of the magnetic field with respect to the crystal axes. Recently, Ajiro et al. [19] have reported a more extensive study of this doped system, and the asymmetries of the ESR signals were attributed to the staggered magnetization present in the sample.

In our first experimental study [19] of Haldane materials, we used single crystals of NENP and measured the magnetic susceptibility from 300 K down to below 300 \( \mu \)K. Fig. 2. Our initial goal was to test the prediction [20] that the \( J'/J \) value of NENP (\( J'/J \approx 10^{-4} \)) was smaller than a critical value, so...
the material would remain disordered down to $T = 0$. Our work revealed the presence of end-chain spins below 100 mK, and the corresponding signal established a roadblock for searching for long-range magnetic order. Nevertheless, circumstantial evidence of some type of ordering is provided by a hysteresis in the signal while cooling-warming near 4 mK, Fig. 2. In an attempt to shift this transition to a higher temperature, a system with a larger $J$ value was needed, and NINAZ, Ni(C$_5$H$_{10}$N$_2$)$_2$N$_3$(ClO$_4$) $^{[22]}$ with $J \approx 125$ K $^{[23]}$, was chosen.

It is important to stress that although subsequent experiments $^{[24]}$ $^{[25]}$ $^{[26]}$ have been interpreted in terms of $S = \frac{1}{2}$ end-chains, these studies have not conclusively eliminated the $S = 1$ end-chain spin description asserted by Ramirez et al. $^{[24]}$. The reason for this ambiguity is that the ESR work was restricted to low frequencies where $S = 1$ end-chain spins could not be measured, if they were present. Furthermore, the temperature dependence of the central peak of the ESR signal in doped samples of NENP $^{[13]}$ $^{[16]}$ and of TMNIN $^{[30]}$ $^{[33]}$, which is (CH$_3$)$_4$N[Ni(NO$_2$)$_3$] $^{[34]}$, have been described by the model of Mitra, Halperin and Affleck $^{[16]}$. However, since the lineshapes are severely distorted in doped samples, the linewidths, and therefore the interactions between the end-chain spins on the same chain, could not be observed. Although nonmagnetic dopants are used to increase the end-chain spin concentration, doped samples have their limitations. For example in NENP doped beyond $\sim 0.5\%$, the dopant no longer breaks chains by direct substitution $^{[32]}$. Even in a material with a nonmagnetic isomorph $^{[29]}$, doping beyond a certain level is nonlinear with respect to the number of observed end-chain spins. Furthermore, it is important to stress that dopants cause changes in the magnetic environment and may shift, split, and/or broaden the ESR spectra. The material known as NINAZ allows us to avoid the doping difficulties and is well-suited to study the $S = \frac{1}{2}$ versus $S = 1$ issue. In addition, the magnetic properties of NINAZ may be related to the interactions between the end-chain spins on the shortest chains and between the magnetic excitations on the chains and the end-chain spins.

Finally, it is noteworthy that end-chain spin effects are not restricted to $S = 1$ systems. The VBS model $^{[11]}$ may be generalized, and $S = 1$ end-chain spins are expected for $S = 2$ Haldane gap materials $^{[35]}$ $^{[37]}$. Experimental evidence of these $S = 1$ end-chain spins has been obtained in the $S = 2$ linear-chain materials of MnCl$_3$(bipy) $^{[35]}$ and CsCrCl$_3$ doped with Mg $^{[38]}$.

**END-CHAIN SPINS IN NINAZ**

The material NINAZ circumvents difficulties associated with doping because it shatters while passing through a structural transition at $\sim 255$ K, thereby producing end-chain spins without doping $^{[1]}$ $^{[22]}$ $^{[34]}$. Since the nascent crystals shattered upon cooling but remained oriented, these specimens are referred to as polycrystalline samples. To increase the number of end-chain spins, two grinding techniques were used. Initial grindings used a pestle and mortar to produce a sample referred to as powder. Subsequent grindings, using a standard ball mill, yielded a sample referred to as ultrafine powder.

![Graph of χ(T) for NENP](image)
Electron spin resonance at 9, 94, and 190 GHz, and magnetization studies on all of the samples confirmed that the end-chain spins are \( S = 1/2 \) and show no evidence for \( S = 1 \) end-chains \[22\]. More specifically, the magnetization data as a function of magnetic field up to 5 T while at a temperature of 2 K may be fit using the sum of two Brillouin functions, one for \( S = 1/2 \) and the other for \( S = 1 \). The fits of the data demonstrate that the end-chain spins are predominately \( S = 1/2 \) and that only trace amounts of \( S = 1 \), consistent with the presence of some uncoupled Ni\(^{2+} \), exist in any of the samples. Furthermore, the high frequency ESR studies did not reveal the presence of any \( S = 1 \) or higher spin contributions. Consequently, we conclude that all the end-chain spins are \( S = 1/2 \).

For our 9.25 GHz ESR work, the measured derivative spectra of all the samples were integrated at a variety of temperatures \[22\]. The data were fit with the expressions generated by Mitra, Halperin, and Affleck \[16\] and yield values for two parameters, namely the average chain length \( (L_0) \) and the minimum chain length \( (L_{\text{min}}) \). The values of \( L_0 \) for the different samples are in reasonable agreement with the ones independently obtained from fits of the ESR and magnetization data. For the analysis of the ESR data, \( L_{\text{min}} = 60 \pm 20 \) sites was used.

Typical 9.25 GHz ESR lines acquired at 4 K are shown in Fig. 3, where the full width half maxima (FWHM) for each sample is approximately 8 mT \[22\]. For the purpose of comparison, the ESR spectrum for a 0.5% Hg doped polycrystalline specimen is shown as an inset to Fig. 3. These results indicate that the signals are dependent on orientation and demonstrate why linewidth measurements of doped materials have not been reported in detail (i.e. doping broadens the main line and adds extrinsic ones). The temperature dependencies of the linewidths are shown as another inset to Fig. 3. For \( T \leq 7 \) K, the FWHM is temperature independent, and this limit is governed by the interactions between the \( S = 1/2 \) end-chains on the shortest chains. Following the model of Mitra, Halperin, and Affleck \[16\], this interaction may be roughly estimated as

\[
e = \Delta \exp(-L_{\text{min}}/\xi),
\]

where \( \Delta \approx 42 \) K \[23\] is the Haldane gap and \( \xi \approx 6 \) \[24\] is the correlation length. When \( L_{\text{min}} = 50 \), then the resultant energy is \( \epsilon \approx 10 \) mK \( \approx 8 \) mT. Although we cannot completely eliminate the possibility that the temperature independent FWHM value is a consequence of dipole-dipole broadening, the estimates for \( L_{\text{min}} \) are consistent with fits of the temperature dependence of the main peak and with numerical work \[23\] \[26\].

When magnetic excitations are present on the chains, there are two mechanisms \[16\] by which these bosons may influence the linewidth. Firstly, bosons changing energy levels (via interactions with the end-chain spins) could affect the linewidth, where this change in energy is quantized in units of

\[
\delta E \approx \frac{(h \pi c)^2}{2 \Delta T^2},
\]

where \( c = 2.55 \times 10^4 \) m/s \[24\] is the speed of the spin wave and \( L \) is the length of the chain. Using the independently measured \[22\] values of \( c \) and \( \Delta \) and taking \( L = L_0 \), \( \delta E \approx 5 \) mT for the powder and \( \approx 12 \) mT for the ultrafine powder. These values of \( \delta E \) are about the size of the FWHM, and consequently, these interactions contribute to the linewidth once a chain acquires a boson. The temperature dependence of the linewidth near the central peak has been derived by Mitra, Halperin, and Affleck \[16\], so the FWHM may be modeled by

\[
\text{FWHM} = \epsilon + \Lambda T \exp(-\Delta/k_B T),
\]

where \( \Lambda \) is a parameter which is beyond the scope of the present model \[16\]. The temperature dependence of the FWHM is reasonably reproduced when \( \epsilon = 8 \) mT and \( \Lambda = 35 \) mT/K, as shown in Fig. 3a. In other words, the major contribution to the FWHM, at \( T \leq 7 \) K, comes from the end-chain spins on the shortest chains interacting with each other and, at \( T \geq 7 \) K, arises from the interactions between the magnetic excitations on the chains and the end-chain spins. Finally, the other possible broadening mechanism arises from a small change in the energy of a boson that experiences a phase shift when interacting with an end-chain spin. This effect is significantly weaker than the exchange of energy \( \delta E \) and, consequently, is not detectable in our measurements.
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