Identification of Nuclear Relaxation Processes in a Gapped Quantum Magnet: ^{1}H NMR in the $S = \frac{1}{2}$ Heisenberg Ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$

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The ^{1}H hyperfine shift K and NMR relaxation rate T_1^{-1} have been measured as a function of temperature in the $S = 1/2$ Heisenberg antiferromagnetic ladder compound $Cu_2(C_5H_{12}N_2)_2Cl_4$. The presence of a spin gap $\Delta \simeq J_\perp - J_\parallel$ in this strongly coupled ladder ($J_\parallel < J_\perp$) is supported by the K *and* T_1^{-1} results. By comparing T_1^{-1} at two different ^{1}H sites, we infer the evolution of the spectral functions $S_z(q, \omega_n)$ and $S_\perp(q, \omega_n)$. When the gap is significantly reduced by the magnetic field, two different channels of nuclear relaxation, specific to gapped antiferromagnets, are identified and are in agreement with theoretical predictions. [S0031-9007(97)03723-X]

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Several classes of one-dimensional Heisenberg antiferromagnets (HAF) are known to exhibit a spin gap at low temperature. For example, integer-spin chains [1] have a nonmagnetic "spin-liquid" ground state (singlet) separated from a branch of triplet excitations by an energy gap Δ. A spin-liquid ground state also exists in spin ladders, built by coupling an even number of $S = 1/2$ HAF chains with an antiferromagnetic transverse exchange $J_\perp$ [2,3]. At low energies, many physical properties are dominated by the singlet-triplet gap and do not depend on the underlying dynamical quantum processes stabilizing the ground state. For example, thermodynamic quantities (susceptibility, specific heat) are very similar in a number of gapped one-dimensional HAF.

In this Letter, the low-energy dynamical processes dominating the ^{1}H spin-lattice relaxation rate ($1/T_1$) of an organic spin ladder [$Cu_2(C_5H_{12}N_2)_2Cl_4$] are unambiguously identified by comparing the T_1 measurements at two proton sites. They coincide precisely with the processes proposed by Sagi and Affleck [4] for Haldane systems. This experimental evidence supports the idea proposed by Sachdev and co-workers [5] that spectral functions $S_{z,\perp}(q, \omega)$ are, at low energies ($\omega \ll \Delta$), common to all gapped one-dimensional HAF.

In $Cu_2(C_5H_{12}N_2)_2Cl_4$ [6], the Cu^{2+} ($S = 1/2$) ions are coupled antiferromagnetically in *well isolated* ladders [7] (see Fig. 1). The exchange parameters along the rungs ($J_\perp$) and the legs ($J_\parallel$) of the ladder are isotropic and have been accurately measured to be $J_\perp = 13.2$ K and $J_\parallel = 2.4$ K [8–10]. In many respects, this material is a model system in which theoretical predictions for Heisenberg ladders in the strong coupling limit ($J_\perp/J_\parallel \equiv 5.5 \gg 1$) can be tested.

The ^{1}H NMR measurements were carried out by pulsed spin-echo techniques on five single crystals (typically $1 \times 1 \times 0.05$ mm^3), oriented with their $\hat{b}$ axis (perpendicular to the chains axes) along the applied field $H_0 = 5.6$ T. A typical spectrum for the proton resonance shows a number of partially resolved lines [Fig. 2(a)], indicating a variety of local fields among the 24 inequivalent ^{1}H sites. In the following, we focus on the lines labeled (I) and (II), as their extreme position in the spectrum allows their study on a wide temperature (T) range [11]. With the field along $\hat{b}$, the magnetic hyperfine shift K_{bb} of the proton resonance is related to the uniform spin susceptibility $\chi_0 = \chi_i(q = 0, \omega = 0)$ at the nuclear site i, by

$$K_{bb}(T) = \frac{A_{bb}}{g_{bb}\mu_B}\,\chi_0(T) + \sigma\,, \qquad (1)$$

where A_{bb} is the hyperfine coupling constant and σ the chemical shift. The shifts of the two lines, plotted in Fig. 2(b), are opposite in sign but follow the same T dependence as χ_0, that is, a high temperature Curie-Weiss behavior followed by an exponential drop below a rounded maximum at $T_{\chi^{\max}} \simeq 8$ K, in complete agreement with previous susceptibility measurements [8,10]. Since K is proportional to the susceptibility χ_0 measured

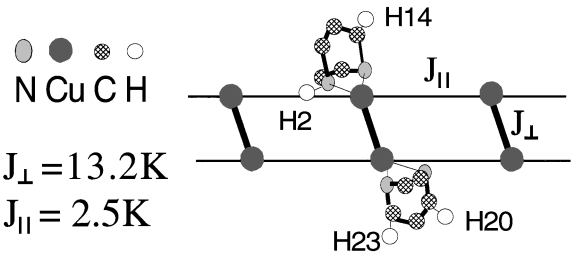

FIG. 1. Schematic structure of $Cu_2(C_5H_{12}N_2)_2Cl_4$, with the exchange parameters determined in Ref. [8]. The labeled protons contribute to the two NMR lines used in this work to probe different dynamical functions (S_z and $S_\perp$; see text).

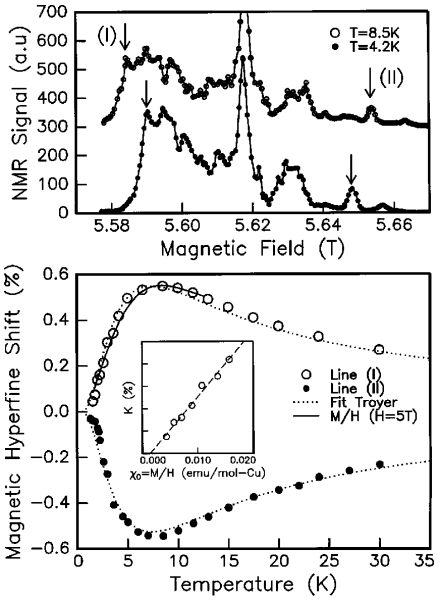

FIG. 2. (a) ^{1}H NMR spectra at fixed frequency $f_0 = 239.112$ MHz. The arrows indicate the two lines studied (their different amplitudes are due to different excitation conditions). The large central peak comes from protons in the NMR probe. (b) Magnetic hyperfine shift for the lines (I) and (II) and susceptibility at 5 T; the dashed line is a fit where the hyperfine coupling is the only adjustable parameter and temperature dependence of the susceptibility is given by Eq. (5) of Ref. [8], with $J_\perp = 13.2$ K and $J_\parallel = 2.5$ K. Inset: shift data vs susceptibility, with T as an implicit parameter.

at 5 T [inset of Fig. 2(b)], the hyperfine couplings on both sites can be estimated: $A_{bb}^{(\mathrm{I})} = +2.95 \pm 0.40$ kOe and $A_{bb}^{(\mathrm{II})} = -2.6 \pm 0.50$ kOe [12]. The largest contribution to A comes from the dipolar field on the jth nucleus created by the surrounding electronic spins, i.e., $A_j \propto -|\gamma_e|\gamma_n\hbar^2 \sum_i (1 - 3\cos^2\theta_{ij})/r_{ij}^3$, where θ_{ij} is the angle between r_{ij} and H_0. Given the atomic positions, it is straightforward to compute the dipolar field at each ^{1}H site (a reliable result is obtained by summing over 5–6 neighboring Cu spins). The total NMR spectrum is well reproduced in this way. It is therefore possible to assign the NMR lines to specific proton sites: line (II) is ascribed to protons H2 involved in the superexchange $J_\parallel$ (see Fig. 1). The line (I) is attributed to protons H20 and H23 at the outer edges of the ethyl groups. It must be stressed that the uncertainty in the site labeling could only result in adding the protons H14 and H4 to the lines (I) and (II), respectively. This essentially does not affect our analysis of the nuclear relaxation.

In a magnetic field, the triplet excitations split into three branches. In the strong coupling limit ($J_\parallel/J_\perp \ll 1$), the lowest branch is separated from the singlet ground state by an effective gap $\Delta_h = \Delta - h$, where $h = g\mu_B H_0$ is the Zeeman energy. When the temperature is small compared to Δ_h, interactions between excitations are negligible and the lowest branch dominates the temperature dependence of the susceptibility [13]

$$\chi_0 \propto \frac{1}{\sqrt{k_B T J_\parallel}} \exp\left(-\frac{\Delta_h}{k_B T}\right). \quad (2)$$

A low temperature fit of $K^{(I)}$ to Eqs. (1) and (2) gives an effective gap of $\Delta_h \simeq 3$ K in 5.6 T. This is very close to the value expected taking the zero-field gap $\Delta = 10.8$ K inferred from susceptibility and high field magnetization measurement [8] reduced by the Zeeman energy $h = 7.6$ K. Thus, the measurements of K and χ_0 are fully consistent with a spin gap $\Delta_h = (J_\perp - J_\parallel) - h$ between the singlet and triplet states of the Heisenberg ladder with strong rungs.

We now discuss the dynamical properties, as probed by the nuclear spin-lattice relaxation rate $1/T_1$. The recovery of the nuclear magnetization is always a single exponential at all temperatures. As shown in Fig. 3(a), both sites display qualitatively the same T dependence, that is, $1/T_1$ tends to be constant in the paramagnetic region, and crosses over to an activated behavior at low T. There are, however, striking differences between the two lines: (a) at high T the values of T_1 differ by 1 order of magnitude, (b) at low T the gap values differ by a factor of 2. Indeed, assuming an activated behavior $1/T_1 \propto \exp(-\Delta_{\mathrm{eff}}/k_B T)$, $\Delta_{\mathrm{eff}} \simeq 3.4 \pm 0.2$ K for the line (I), close to the value $\Delta_h = 3.0$ K deduced from the shift, but $\Delta_{\mathrm{eff}} \simeq 6.8 \pm 0.2$ K for the line (II).

In spin systems, the temporal fluctuations of the electronic spins make the nuclear polarization relax in a time T_1 related to the spectral densities $S_{z,\perp}(q,\omega)$ of the two-spin correlation functions, through [14]

$$\frac{1}{T_1} = \frac{(\gamma_n\gamma_e\hbar)^2}{2} \sum_q [F_z S_z(q,\omega_n) + F_\perp S_\perp(q,\omega_n)], \quad (3)$$

with $\omega_n \sim 0$ the nuclear Larmor frequency, and

$$S_{z,\perp}(q,\omega_n) = \int dt\, e^{i\omega_n t} \langle\{S_{z,+}(q,t) S_{z,-}(-q,0)\}\rangle. \quad (4)$$

In general, any quantitative analysis of the relaxation requires the knowledge of the hyperfine "form" factors $F(q)$ [15] in addition to a model for $S_{z,\perp}(q,\omega)$. We first discuss the structure factors $S_{z,\perp}(q,\omega)$.

Single magnon processes, which require an energy greater or equal to the gap, cannot contribute to the nuclear relaxation which involves negligible energy transfers $\hbar\omega_n \sim$ mK. Two- or three-magnon scattering processes are then required [16]. More specifically, Sagi and Affleck [4] have recently analyzed the possible nuclear relaxation processes for Haldane chains in magnetic fields. Since the low-energy excitations of $S = 1/2$ ladders and integer-spin chains are qualitatively similar [17], it is natural to consider the same processes here. Following their arguments, the nuclear spins can exchange energy through three different channels [4]:

(i) *Intrabranch* transitions involve two magnons within the same branch (i.e., with the same S_z eigenvalue).

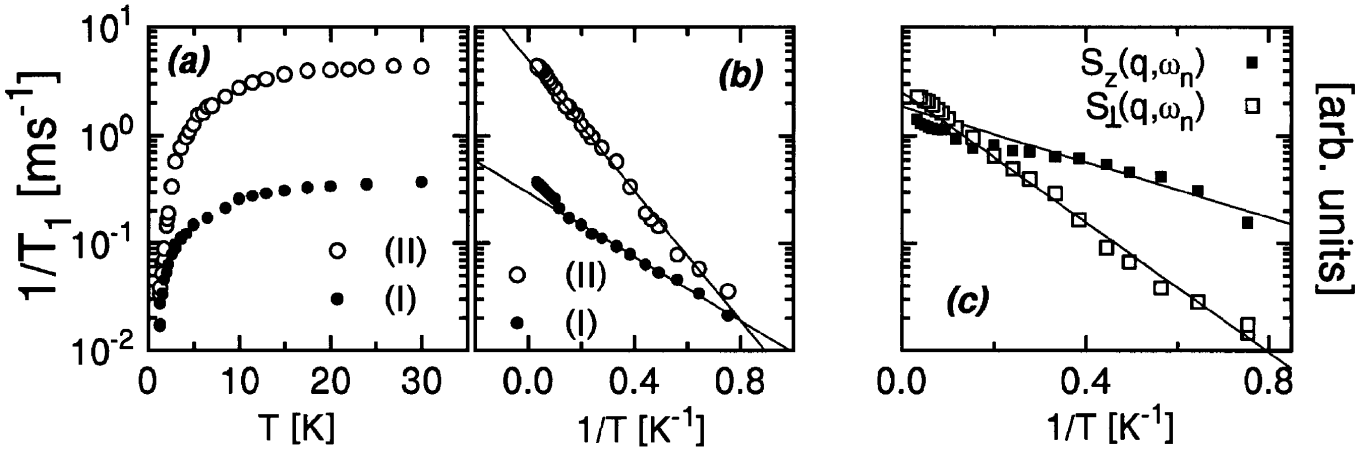

FIG. 3. ^{1}H spin-lattice relaxation rate $1/T_1$ for lines (I) and (II) as a function of T (a) and $1/T$ (b). (c) $S_z(q = 0, \omega_n)$ and $S_\perp(q = \pi, \omega_n)$ correlation functions derived from T_1 results (see text for details).

At low T, these processes have a maximum probability near the minimum at $k = \pi$ of the lowest branch of the triplet (Fig. 4), implying a momentum transfer $\Delta k = q \sim 0$ (forward scattering). For $T \ll h$, the q-integrated spectral density is expected to follow the thermal occupation of the lowest energy triplets $S_z^{\text{intra}}(\omega_n) \propto \exp[-(\Delta - h)/k_B T]$.

(ii) *Interbranch* transitions (Fig. 4), i.e., transitions from a state in a magnon branch m to a state with $m \pm 1$ ($S_\pm$ operators). Since the Zeeman splitting at 5.6 T is larger than the magnon bandwidth (~5.5 K [18]), these processes can only occur because of the finite damping of each level and are expected to be weak. Furthermore, only large momentum transfers $q \sim \pi$ (backward scattering) remain at large Zeeman splitting. One infers from [4] that $S_\perp^{\text{inter}}(\omega_n) \propto \exp(-\Delta/k_B T)$.

(iii) *Staggered* processes: when H_0 approaches the critical field $h_{c1} \approx \Delta$, one-magnon excitations ($S_\pm$ operators, $q \sim \pi$) become increasingly relevant. At finite T in the gapped phase, interactions between excitations, or equivalently finite damping, generate nonvanishing matrix elements for such transitions: this relaxation mechanism involves three-magnon (or higher order) processes, and its temperature dependence follows the square of the thermal population in the lowest triplet state, $S_\perp^{\text{stagg}}(\omega_n) \propto \exp[-2(\Delta - h)/k_B T]$.

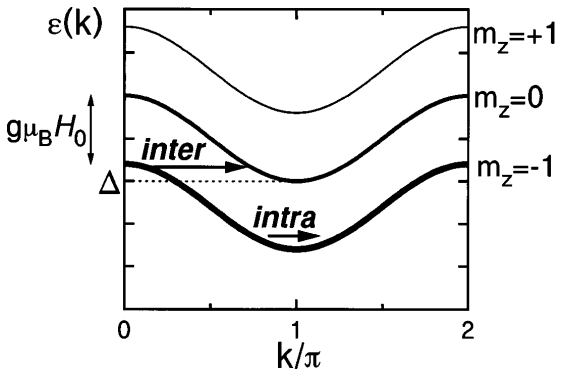

FIG. 4. Schematic picture of the two-magnon scattering processes relevant to the nuclear relaxation in a system with singlet to triplet gap, in a magnetic field H_0 [4]. In this experiment, the Zeeman splitting $g\mu_B H \sim 7.6$ K is larger than the magnon bandwidth (~5.5 K [18]).

The above discussion shows that (1) the Boltzmann factor is more favorable to intrabranch processes ($\Delta_h \simeq 3$ K); these will dominate the staggered transitions ($2\Delta_h \simeq 6$ K), while interbranch ones, if any, are essentially negligible ($\Delta \simeq 10$ K). (2) The low-T nuclear relaxation is only driven by two terms: $S_z(q \sim 0, \omega_n)$ for intrabranch transitions and $S_\perp(q \sim \pi, \omega_n)$ for staggered transitions. Accordingly, we write Eq. (3) in a simplified form,

$$1/T_1 \propto F_z(0) S_z(q = 0, \omega_n) + F_\perp(\pi) S_\perp(q = \pi, \omega_n) . \quad (5)$$

Hence, the two behaviors $1/T_1 \propto \exp(-\Delta_h/k_B T)$ for the line (I) and $1/T_1 \propto \exp(-2\Delta_h/k_B T)$ for (II) can only come from the temperature dependence of $S_z(q = 0, \omega_n) \propto \exp(-\Delta_h/k_B T)$ while $S_\perp(q = \pi, \omega_n) \propto \exp(-2\Delta_h/k_B T)$. In other words, the ratio of $F_z(0)/F_\perp(\pi)$ for lines (I) and (II) are such that, at low temperatures, only one of the exponential terms dominates the relaxation: obviously, $S_z(q = 0, \omega_n)$ component is favored for the line (I), and $S_\perp(q = \pi, \omega_n)$ one for the line (II).

This result is, to our knowledge, the first experimental identification of specific nuclear relaxation channels in a gapped antiferromagnet, a result in remarkable agreement with the work of Sagi and Affleck. Another support to this theory is that the lowest gap $\Delta_h \simeq 3$ K is also the value seen in the susceptibility. Furthermore, the observation of the staggered contribution in the gapped phase proves that interactions between fermioniclike excitations are significant in this system. This conclusion was already drawn from magnetization measurements [8].

A nice feature of this study is that the T_1 data for the two lines provide a set of two independent equations [i.e.,

Eq. (5) for each line]. Since $F_z(q)$ and $F_\perp(q)$ can be computed for each ^{1}H site, the spectral functions S_z and $S_\perp$ can, in principle, be extracted separately. Here, we found that $F_\perp(q=\pi)$ is indeed 5 times larger than $F_z(q=0)$ for the line (II), while both terms are comparable for the line (I). $S_\perp \propto \exp(-2\Delta_h/k_BT)$ is thus *overweighted* for the line (II) explaining why T_1^{II} decays with an activation energy $2\Delta_h$. On the other hand, T_1^I is predominantly sensitive to the smallest gap, Δ_h, generated by $S_z(q=0,\omega_n)$. However, one must realize that the calculation of the form factors is subject to several uncertainties: any error in atomic positions is amplified [$F(r_{ij}) \propto r_{ij}^{-6}$], the spatial extension of Cu^{2+} orbitals may play an important role [19] for the protons H2 [line (II)] which are in the superexchange pathway and closer to the Cu ion than those of line (I). Indeed, the extracted values of S_z are slightly negative suggesting that the value of $F_\perp^{II}$ has been underestimated in the calculation. In fact, the pure Heisenberg paramagnetic limit $S_z(q,\omega_n) = \frac{1}{2}S_\perp(q,\omega_n)$ should be recovered when T is large compared to $J_{\perp,\parallel}$ and h. $F_\perp^{II}$ can be rescaled to a value satisfying this limit at $T = 30$ K, where the observed value of T_1 for the line (I) is within 10% of the paramagnetic limit calculated by Moriya [14]. In any event, this rescaling does not affect the gap parameters extracted from the low-T behavior. As shown in Fig. 3(c), $S_\perp$ experiences a gap $\Delta \simeq 6.8 \pm 0.2$ K *twice* as large as in S_z (3.4 ± 0.2 K).

This analysis of the nuclear relaxation in $Cu_2(C_5H_{12}N_2)_2Cl_4$, a strongly coupled ladder, settles an ongoing controversy: the gap values derived from static (χ_0) and dynamic $S_z(q \sim 0, \omega_n)$ measurements are here *identical*, in complete agreement with the predictions of Troyer *et al.* [13] and Sagi and Affleck [4]. This strongly contrasts with the experimental observations in inorganic ladders [20,21], and in some Haldane chains [22,23]. In these materials, the different temperature dependence observed in the dynamics may be due to a second minimum in the dispersion relation. For example, it should be the case in $SrCu_2O_3$ if $J_\perp < J_\parallel$ [24,25]. Low-lying excitations near $k = 0$ such that $\Delta_{k=0} \sim \Delta_{k=\pi}$ may open up relaxation channels involving large-q interbranch transitions and would lead to a higher effective gap in T_1 measurements. Other explanations have been proposed in the limits $T \ll \Delta_h$ [26] and $J_\perp \ll J_\parallel$ [27].

In conclusion, ^{1}H NMR experiments demonstrate that the effective gap of the $S = 1/2$ HAF ladder compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ in a magnetic field h is $\Delta_h \simeq J_\perp - J_\parallel - h$. The nuclear relaxation can be quantitatively understood in the framework of the theory of Sagi and Affleck, retaining only "intrabranch" and "staggered" processes. More generally, the processes identified in this work should be generic to many gapped HAF chains in a magnetic field.

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