Nuclear Magnetic Resonance Study of the $S = 1/2$ Heisenberg Ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$: Quantum Phase Transition and Critical Dynamics

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We present an extensive NMR study of the spin-1/2 antiferromagnetic Heisenberg ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$ in a magnetic field range 4.5–16.7 T. By measuring the proton NMR relaxation rate $1/T_1$ and varying the magnetic field around the critical field $H_{c1} = \Delta/g\mu_B \approx 7.5$ T, we have studied the transition from a gapped spin liquid ground state to a gapless magnetic regime which can be described as a Luttinger liquid. We identify an intermediate regime $T \geq |H - H_{c1}|$, where the spin dynamics is (possibly) only controlled by the $T = 0$ critical point H_{c1}. [S0031-9007(98)05638-5]

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One of the most fascinating effects in quantum magnetism is perhaps the possibility to realize a $T = 0$ phase transition [1] from a "quantum disordered" (gapped spin liquid) ground state to a Luttinger liquid state in one dimension (1D) [2] or to a Néel ordered state in two dimensions (2D) [3,4]. There are well known examples of gapped spin liquids in 1D: for integer-spin Heisenberg antiferromagnetic (HAF) chains [5,6] or spin-1/2 HAF even-leg ladders [7], quantum fluctuations induce a spin gap Δ between a singlet ($S = 0$) ground state and triplet ($S = 1$) excited states. An external magnetic field lifts the triplet degeneracy and induces a second order $T = 0$ phase transition at a critical field $H_{c1} \equiv \Delta$ when the lowest branch of the triplet crosses the ground state. At this critical field, dynamical properties are defined by universal exponents [8–10]. Above H_{c1}, the ground state is magnetic with an algebraic decay of the correlation functions. Close to H_{c1}, the low frequency ($\omega < T$) spin dynamics should be governed in a universal way by the $T = 0$ critical point H_{c1}. In the vicinity of this point, divergent quantum correlations are cutoff by thermal fluctuations at a length ξ_T which becomes the only relevant length scale. This is the *quantum critical* regime (QCR) where the temperature is the only relevant energy scale over the large intermediate region $J > T > |H - H_{c1}|$ [4]. The true challenge to experiments is to observe in a single system all the sequences of the $T \to 0$ regimes as well as the finite temperature critical regime.

In a gapped HAF, such quantum phase transition can be experimentally studied only if the gap Δ is comparable to accessible magnetic fields. The situation is hopeless in the $S = 1/2$ spin ladder compound $SrCu_2O_3$ ($\Delta \geq 400$ K) [11]. On the other hand, it is now well established that the organometallic compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ [12] is a unique representative of HAF $S = 1/2$ ladders with small exchange constants ($J_\perp \approx 13.2$ K, $J_\parallel \approx 2.5$ K) and a spin gap ($\Delta_{k=\pi} \simeq J_\perp - J_\parallel = 10.5 \pm 0.3$ K) [13–16] which makes the entire phase diagram experimentally accessible.

This Letter describes a proton (^{1}H) NMR study of $Cu_2(C_5H_{12}N_2)_2Cl_4$ in magnetic fields ranging from 4.5 to 16.7 T. The complete phase diagram (including the various temperature crossovers) has been observed experimentally. We unambiguously identify three different regimes when $T \to 0$: (1) A *gapped phase* for $H < H_{c1} \approx 7.5$ T, defined by a spin liquid ground state, where the energy gap, deduced from nuclear spin-lattice relaxation time (T_1) measurements, is linearly reduced by the magnetic field; (2) a *magnetic phase* with a gapless ground state for $H_{c1} < H < H_{c2} \approx 13.2$ T, characterized by a power-law divergence of $1/T_1$ consistent with an interpretation based on fermions in one dimension; and (3) a *fully polarized gapped phase* above H_{c2}. At intermediate temperatures, we analyze the crossovers between these regimes and give for the first time convincing evidences that a quantum critical regime is observed when $\Delta > T > |H - H_{c1}|$.

Proton NMR experiments have been performed with the magnetic field direction along the $\vec{b}$ axis (perpendicular to the [101] ladder direction) of small single crystals (typically 100–200 μg each). We used conventional pulse spin-echo sequences and frequency-shifted (summed Fourier transform) processing [17]. In a first run ($H < 8.7$ T), a set of five crystals with their $\vec{b}$ axis oriented has been used; for larger fields, *one* single crystal was used. While spectra displayed minor variations, the absolute values of T_1 were found reproducible between these two runs. A typical proton NMR spectra is displayed in Fig. 1. Note that the large magnetization at 16.7 T allows one to resolve all 24 proton sites. However, since the total width of the spectra follows the magnetization M, this discrimination becomes increasingly difficult as $M \to 0$. The arrow in Fig. 1 indicates the

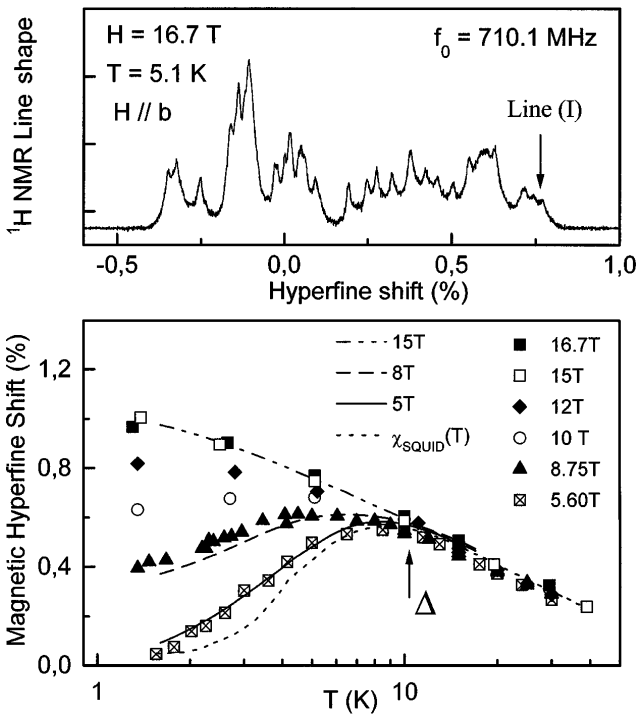

FIG. 1. Top panel: ^{1}H NMR spectrum at $f_0 = 710.1$ MHz and $T = 5.1$ K. All measurements reported here were made on the line marked by an arrow. Bottom panel: Magnetic hyperfine shift K_I as a function of H and T. Bold and dotted lines represent macroscopic susceptibility data obtained by AC-SQUID magnetometer ($h = 0.1$ T) and torsional oscillator magnetometer, respectively [18]. The normalization factor gives a hyperfine coupling $A_I \approx 2.9$ kOe.

line (I) where the hyperfine shift K and T_1 have been measured (see Ref. [19] for a discussion of the proton sites assignment).

The temperature dependence of the magnetic hyperfine shift $K \sim \langle S_i^z \rangle / H$ at various magnetic fields is shown in Fig. 1. The uniform static ($q = 0, \omega = 0$) susceptibility $\chi_0 = M/H$ at different fields is also displayed on the same scale using the relation $K = (A_I/g_b\mu_B)\chi_0$ with the hyperfine coupling $A_I \approx 2.9$ kOe and the g factor $g_b = 2.03$ [14]. For $H < H_{c1}$, both K and χ_0 drop exponentially due to the effective gap $\Delta_h = \Delta - g\mu_B H$ between the singlet and the lowest triplet state.

As the critical field H_{c1} is crossed, *both* K and χ_0 show a clear persistent downturn at low temperatures due to residual short range antiferromagnetic correlations in the intermediate phase. When $T \to 0$, K and χ_0 go to a finite value, which rises continuously as the field is increased from H_{c1} to H_{c2}, following the increase of ground state magnetization. Above H_{c2} where $M_{(T=0)}$ is saturated [14], M/H should decrease as $1/H$ ($H > H_{c2}, T \to 0$). This is already visible at $T \approx 1.4$ K, where K at 16.7 T is smaller than at 15 T. The maximum value of K, extrapolated to $T = 0$ corresponds to $\langle S^z \rangle = \frac{1}{2}$. Above $T \approx J_\perp$, we recover a Curie-like tail for all fields, which defines the "classical" (decorrelated) regime.

We now discuss the spin-lattice relaxation rate $1/T_1$ which is expressed in terms of the magnetic structure factors [20]

$$\frac{1}{T_1} = \frac{(\gamma_n \gamma_e \hbar)^2}{2} \sum_{q,\alpha} F_\alpha(q) S_\alpha(q, \omega_n),$$
$$S_\alpha(q, \omega_n) = \int \exp(i\omega_n t)\, dt\, \langle S_\alpha(q,t) S_\alpha(-q,0) \rangle, \quad (1)$$

where $F_\alpha(q)$ are hyperfine form factors of dipolar origin [21] and $\alpha = z, \pm$ represents the longitudinal and transverse components, respectively.

At low fields and low temperatures, $T \ll H_{c1} - H$ (*singlet gapped phase*), $1/T_1$ falls off exponentially with a characteristic energy gap $\Delta_h = \Delta - g\mu_B H$ [see Fig. 2(a)]. This effective gap is represented in the lower graph of Fig. 2(a). This result can easily be understood: for line (I), it has been shown in a previous study [19] that two-magnon processes (near $k = \pi, q \simeq 0$) in the "intrabranch" channel [22] dominate the nuclear relaxation. It follows that $1/T_1$, in this gapped phase, is driven by longitudinal correlations $S_{zz}(q \simeq 0, \omega_n) \sim \exp(-\frac{\Delta_h}{T})$. As we approach the critical field, $T \approx H_{c1} - H$, the analysis breaks down since competing mechanisms like "staggered" direct, $q = \pi$, processes take over and dominate the relaxation [22]. At higher temperatures, $T \geq \Delta$, $1/T_1$ is constant, as expected in the classical limit [20].

In the *magnetic phase* ($H_{c1} < H < H_{c2}$) [14], $1/T_1$ turns upward at low temperature in striking contrast with its behavior in the gapped phase [see top parts of Figs. 2(a) and 2(b)]. Very close to H_{c1}, a divergence is readily visible below 2–3 K. As the magnetic field is increased just above H_{c1} ($7.5 < H < 9$ T), the divergence becomes more pronounced and develops at temperatures below 5 K. At higher fields, the divergent behavior is replaced by a smooth increase as the temperature is lowered below 10 K and progressively vanishes as we approach the upper critical field H_{c2}.

To conclude the $T = 0$ limit, we discuss the "high field phase" which appears above $H_{c2} = J_\perp + 2J_\parallel$ [14]. It is apparent [bottom of Fig. 2(b)] that the relaxation rate *decays exponentially* at low temperatures with an activation energy $\Delta^{\text{up}} = g\mu_B(H - H_{c2})$. Since the $T = 0$ magnetization is saturated above H_{c2}, the spin system is fully polarized [14] and all dimers are in the triplet state $|\uparrow\uparrow\rangle$. Δ^{up} can therefore be interpreted as the energy gap between the "fully polarized" ground state $|\text{FGS}\rangle = \Pi_i |\uparrow\uparrow\rangle_i$ and the lowest excited states generated by a single spin flip. The balance between the energy gain $J_\perp + 2J_\parallel$ when the antiferromagnetic couplings are satisfied and the Zeeman term $g\mu_B H$ determines the value $g\mu_B(H - H_{c2})$ for the energy gap.

At this stage, we propose the experimental phase diagram schematically shown in Fig. 3. The $T = 0$ phases discussed above are as follows: (1) The gapped

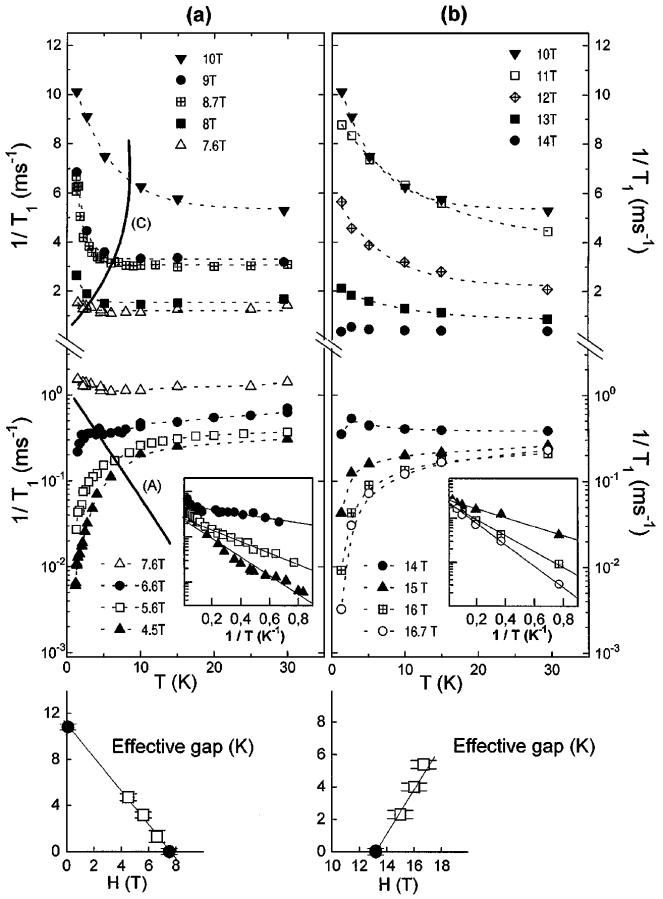

FIG. 2. Panel (a): Temperature dependence of $1/T_1$ through the critical field H_{c1}. The lower part covers the singlet gapped phase ($H < H_{c1}$), while the upper part is in the magnetic phase above H_{c1}. The dashed lines are guides to the eyes. Lines in the inset are low-T fits to the field dependent energy gap $\Delta_h = \Delta - g\mu_B H$ with $g_b = 2.03$. Experimental values of Δ_h are shown in the lower graph (□) together with those obtained from $\chi(T)$ and $M(H)$ (•) [14]. Lines labeled (A) and (C) correspond to the crossover lines of Fig. 3. Panel (b): Temperature dependence of $1/T_1$ through the critical field H_{c2}. The upper part is in the magnetic phase as H_{c2} is approached while the lower part is in the "fully polarized" gapped phase ($H > H_{c2}$). Lines in the inset are low-T fits with an energy gap $\Delta^{\text{up}} = g\mu_B(H - H_{c2})$ and $g_b = 2.03$. Experimental values of Δ^{up} are shown in the lower graph (□) together with H_{c2} (•) [14].

spin liquid phase; (2) a magnetic phase to be characterized (see below); and (3) the gapped polarized phase.

At finite temperatures, these phases are separated by crossover lines: (A) and (B) in Fig. 3 correspond, respectively, to the onset of the gapped spin liquid regime and of the gapped polarized regime, both characterized by an exponential decay of $1/T_1$. Line (C) sets the upper boundary of the "magnetic phase," where a divergent behavior of $1/T_1$ [$\sim T^{-\alpha}$] is observed. At higher temperatures ($T \geq \Delta$), we have the classical regime defined by $1/T_1 \approx cst$ [20] and a Curie-like behavior of $K \sim 1/T$ at all magnetic fields (see Fig. 1). What can be said about the large intermediate region between these crossover

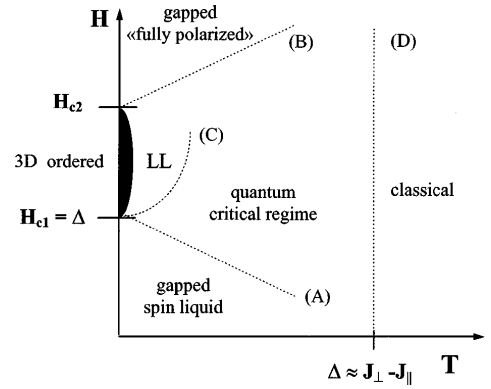

FIG. 3. H-T phase diagram which can be tentatively drawn from the present experiment. Dashed lines represent crossovers between the different regimes discussed in the text: line (D) is the QCR-classical crossover, and lines (A) and (B) correspond to $T \approx H_{c1} - H$ and $T \approx H_{c2} - H$, respectively. Line (C) is the QCR to Luttinger liquid (LL) regime crossover. The black region corresponds to the 3D ordered phase with $T_N(\text{max}) \approx 0.8$ K [23].

lines? On one hand, $1/T_1$ is found to be nearly T independent in the range $6.6 < H < 9$ T, above a characteristic temperature "T_0" $\sim |H - H_{c1}|$ (see Fig. 2). On the other hand, K shows a clear field dependence below $T < \Delta$. This is no longer a classical regime: we propose that this region corresponds to a QCR where $1/T_1$ is predicted to be almost temperature independent [4] while, at the same time, static properties depart from the classical picture.

In the final part of this Letter, we discuss the nature of the magnetic phase, particularly the origin of the low temperature divergence of $1/T_1$ between H_{c1} and H_{c2}.

Since a 3D field-induced ordering above H_{c1} has been observed in specific heat measurements below $T_N(H) \leq 0.8$ K [23], we first consider critical fluctuations as a possible origin for the observed divergence. In this scenario, one expects a divergence of $1/T_1$ *in a range* $\delta T \approx T_N$ above T_N [24] with a generic behavior $T_1^{-1} \sim (T - T_N)^{-\nu}$ ($0.5 < \nu < 1$). *The exponent* ν *must be independent of the magnetic field*. We cannot fit our data taking into account the known field dependence of $T_N(H)$ [23] without releasing this constraint. Moreover, $1/T_1$ starts to diverge at $T \approx 5$ K, which is at least $\delta T \approx 5 - 6T_N$ above T_N. From these arguments, it is clear that the onset of a 3D ordering cannot explain alone the behavior of $1/T_1$ in this temperature range ($T \geq 1.3$ K). Hence, 1D quantum fluctuations have to be invoked to explain our results [25].

We then propose an analysis in terms of fermions in one dimension (i.e., a Luttinger liquid [2]) in the regime $T \ll H - H_{c1}$. The spin-ladder Hamiltonian can be converted into a 1D interacting spinless fermions model using a Jordan-Wigner transformation [6,10,26]. The spectrum consists of two bands with energies $\hbar\omega_k = \pm(\Delta + \frac{c^2}{2\Delta}k^2)$. In this mapping, the magnetic field H

plays the role of the chemical potential $\mu = g\mu_B(H - H_{c1})$ of the fermions (at $H = 0$, μ lies in the middle of the spectrum). Above H_{c1} ($\mu > 0$), the density of fermions n increases with μ as $n \propto M \sim \sqrt{\mu}$ [9,27]. Since there is no gap, direct nuclear relaxation processes are allowed, and one expects an enhancement of the relaxation by an amount related to the magnetization ($M \propto n$) of the electronic system. Within this picture, the staggered part $S_\perp(q \approx \pi, \omega_n)$ leads to $1/T_1 \sim T^{-\alpha}$ ($\alpha = 0.5$) when $H \to H_{c1}^+$ [6,22]. At higher fields, n increases and interactions give rise to nonuniversal behaviors of the spin correlations, i.e., dependent of the microscopic details. For instance, Ref. [10] predicts that α stays close to 0.5 above H_{c1} for a ladder in contrast with other $S = 1/2$ gapped systems.

This picture agrees with our results, at least below 9 T, and becomes poorer above due, possibly, to large interactions between excitations [14,19]. The data in Fig. 2 show that the divergent term (controlled by the exponent α), increases from H_{c1} and is maximum around $H \approx 8.5-9$ T. When $H \to H_{c2}$, the divergence weakens and the exponent α cannot be reliably estimated. An important point is that the exponent α is related to the exponent $\eta(= 1 - \alpha)$ controlling the decay of the spatial correlation, $\langle S_0 S_r \rangle \sim (-1)^r |r|^{-\eta}$. Our data are roughly consistent with exact diagonalization calculations of $\langle S_0 S_r \rangle$ for Haldane chains in the gapless phase [28]: both η and α are close to 0.5 at H_{c1} and H_{c2}. In between, η should have a minimum value $\eta \approx 0.3$ [28], meaning a maximum of α. To summarize, we have shown that the field dependent $1/T_1$ divergence is a 1D effect and not an onset of the 3D ordering which occurs at lower temperature. Even though the exponent α cannot be estimated precisely, a value of $\alpha = 0.5$ at H_{c1} is consistent with our data.

In conclusion, the magnetic field-temperature phase diagram of the spin-1/2 HAF ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$ has been *completely* explored by probing the low frequency spin dynamics. Three $T \to 0$ regimes are identified: (1) A gapped spin liquid phase for $H < H_{c1}$; (2) a Luttinger liquid phase, well defined for $H_{c1} \leq H$, characterized by a field-dependent correlation exponent α; and (3) a fully polarized gapped phase $H > H_{c2}$. We emphasize that the exponent α derived from our data is in qualitative agreement with a Luttinger liquid picture very close to H_{c1}^+. Nevertheless, further studies of the field dependence of the exponent α are needed. Finally, various temperature crossovers are observed and closely resemble theoretical predictions for a "quantum critical" regime in a range $\Delta > T > |H - H_{c1}|$.

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