NMR Evidence for a "Generalized Spin-Peierls Transition" in the High-Magnetic-Field Phase of the Spin Ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$

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(Received 7 March 2000)

The magnetic-field-induced 3D ordered phase of the two-leg spin ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$ has been probed through measurements of ^{1}H NMR spectra and $1/T_1$ in the temperature range 70 mK–1.2 K. The second order transition line $T_c(H)$ has been determined between $H_{c1} = 7.52$ T and $H_{c2} = 13.5$ T and varies as $(H - H_{c1})^{2/3}$ close to H_{c1}. From the observation of anomalous shifts and a crossover in $1/T_1$ above T_c, the mechanism of the 3D transition is argued to be magnetoelastic as in spin-Peierls chains, here involving a displacement of the protons along the longitudinal exchange ($J_\parallel$) path.

PACS numbers: 75.10.Jm, 75.40.Cx, 76.60.–k

Two-leg $S = 1/2$ ladders are 1D objects formed by two antiferromagnetically (AF) coupled Heisenberg spin chains. In zero external magnetic field, their ground state is a collective singlet state ($S = 0$), separated by a gap Δ from the first excited states which are triplets ($S = 1$) [1]. As a consequence, the spin-spin correlations remain of short range even when $T \to 0$, in spite of the strong interactions. There is currently considerable interest in these systems, often named *spin liquids,* since the short range singlet correlations of the ground state are believed to lead to superconducting correlations when mobile charges are added [1].

The fascinating properties of spin liquids can also be revealed through the effect of a magnetic field H. For $H \neq 0$, the gap is reduced as $\Delta(H) = \Delta - g\mu_B H$. At the so-called quantum critical point $H = H_{c1} = \Delta/g\mu_B$, the spin gap vanishes. At $T = 0$, this defines, *in a purely 1D scheme,* a (quantum) phase transition between gapped singlet and gapless magnetic phases. For $H > H_{c1}$, the magnetic correlation length and the spin-spin correlation functions of this gapless 1D spin system now diverge (Luttinger liquid behavior) as T is reduced towards zero. This behavior persists up to a saturation field H_{c2} where all spins are polarized by H. As a consequence of these divergences, any transverse coupling J_t between ladders should drive the system in the field range $H_{c1} < H < H_{c2}$ towards a 3D magnetic long range order at low T. The nature of this 3D phase, which is possibly gapped, is expected to be highly unconventional, in particular, in the vicinity of the two quantum critical points.

The 1D features of the above phase diagram were previously observed in NMR studies [2–4] of the spin ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$ [5] in which the low values of the AF exchange coupling (between spins 1/2 on Cu^{2+} ions) along the legs ($J_\parallel \simeq 3$ K) and along the rungs ($J_\perp \simeq 13$ K) lead to experimentally accessible values of $H_{c1} \simeq 7.5$ T and $H_{c2} \simeq 13.5$ T [6]. As to the possibility of 3D ordering, specific heat measurements [7–9] in the field range 7–12 T have indeed revealed a phase transition for $T < 1$ K. However, no microscopic experimental insight has been reported so far, although this phase currently generates a large interest [4,7–13].

In this Letter, we present a ^{1}H NMR study of $Cu_2(C_5H_{12}N_2)_2Cl_4$ in the field range 7.5–14 T, including the T dependence (in the range 70 mK–1.2 K) of the line shape and of the nuclear spin-lattice relaxation rate $1/T_1$. From the splitting of NMR lines, we define the transition line $T_c(H)$ below which 3D ordering occurs. In addition, we observe through $1/T_1$ a drastic change in the low-energy spin excitations below $\simeq$1.3 K, which is above T_c. This behavior is correlated with anomalous shift of some ^{1}H lines, which we attribute to the displacement of protons involved in the exchange path $J_\parallel$. This is argued to demonstrate the magnetoelastic nature of the transition, which is in some way analogous to the incommensurate magnetic phase of spin-Peierls systems, in agreement with the proposal of [8].

Experiments have been performed on a single crystal ($0.1 \times 0.3 \times 0.4$ mm^3) placed inside the mixing chamber of a ^{3}He-^{4}He dilution refrigerator, the b axis of the crystal being approximately parallel to H. In this ideal orientation, the number of inequivalent ^{1}H sites in the crystal is reduced from 48 to 24. All sites experience different hyperfine fields through their dipolar coupling to the electronic spins localized at the Cu sites [14]. For large polarization of the electronic moments, these couplings lead to ^{1}H spectra extending over several MHz, which have been recorded at fixed field by sweeping the frequency. In Fig. 1 is shown the evolution of the low frequency part of these spectra recorded at fixed $T = 70$ mK at various values of H (upper panel) and at fixed $H = 7.65$ T at various values of T. In both cases, a clear modification of the spectra can be observed ($H > 7.55$ T, $T = 70$ mK, and $T < 350$ mK, $H = 7.65$ T), which in first approximation can be described as a splitting of all individual lines observed in the normal phase [15]. In addition, a new feature

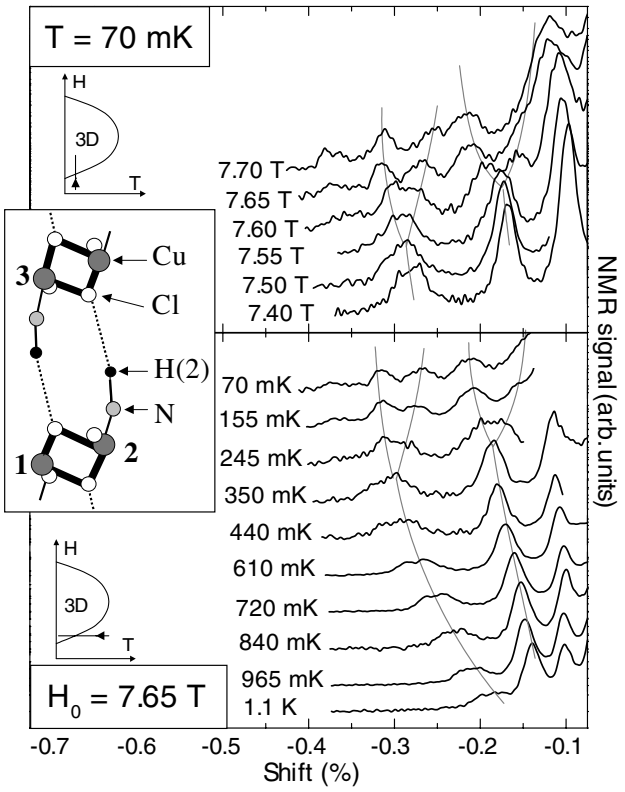

FIG. 1. Upper panel: low frequency side of ^{1}H spectra recorded at fixed values of H at $T = 70$ mK. The onset of the transition at $H = 7.55$ T is revealed by the splitting of the lines. Lower panel: low frequency side of ^{1}H spectrum at various T for $H = 7.65$ T; the transition occurs between 350 and 245 mK.

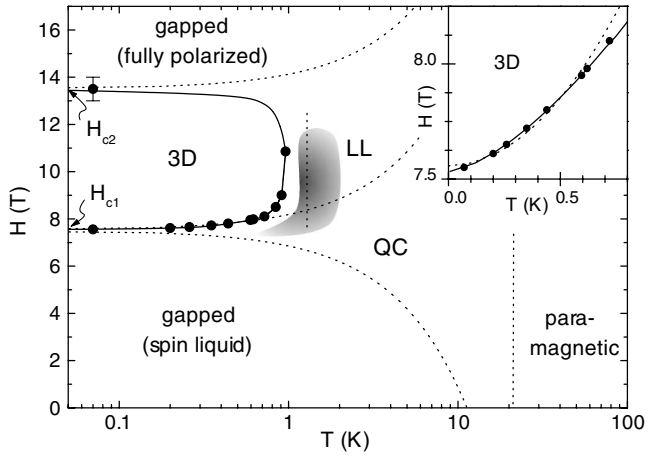

FIG. 2. Phase diagram in the H-T plane as determined from NMR experiments (this work and [4]). The dotted lines separate different regimes [QC stands for quantum critical and LL for Luttinger liquid (see [4])]. The shaded area corresponds to the T range in which proton motion is observed (see text). The inset shows the variation of $T_c(H)$ in the vicinity of H_{c1}. The solid line is a fit to $\propto (H - H_{c1})^{2/3}$ and the dotted one to $\propto (H - H_{c1})^{1/2}$.

appears on the left on the spectrum, indicating that the modification of the line shape is more subtle than a simple splitting. This change in the line shape, which is observed on the whole spectrum, is the signature of an ordered magnetic phase and allows an accurate determination of the transition line $T_c(H)$. The resulting experimental phase diagram is shown in Fig. 2. T_c rapidly increases as a function of $H - H_{c1}$ and then saturates around 900 mK for $H \geq 9$ T.

A careful examination of the whole ^{1}H spectrum *above* T_c reveals that the T dependence of the shifts of the two lines at the left side of the spectrum does not scale with that of other ^{1}H lines at low T (Fig. 3). However this scaling holds for the temperature range 2–30 K, for any field between H_{c1} and H_{c2}, and their line shapes modify at the same time as all the others when entering the 3D ordered phase. This clearly rules out the possibility that they could be assigned to a spurious phase. These two lines are indeed assigned to the protons H(2) and H(4) [2], which are along the exchange path $J_\parallel$ corresponding to the atom sequence Cu-N-H$\cdots$Cl-Cu (see inset of Fig. 1). Since the shift of a proton ^{1}H(i) is given by $\delta h(i) = A(i)\chi_{\mathrm{Cu}}$, in which $A(i)$ is its hyperfine field and χ_{Cu} the spin susceptibility per Cu atom, the absence of scaling can only be explained if $A(2)$ and $A(4)$ become T dependent. This, in turn, can only occur if the distances H(2)-Cu and H(4)-Cu change [16]. This is clear evidence that some kind of lattice instability occurs prior to the magnetic ordering.

Since these protons are along the exchange path corresponding to $J_\parallel$, any modification of the hydrogen bond should clearly change the magnetic excitation spectrum of the system, which can be probed by the nuclear spin-lattice relaxation rate $(1/T_1)$.

Such a change is indeed observed in T_1 data, measured between 1.2 and 70 mK and reported in Fig. 4. For $H = 7.65$ T, $1/T_1$ was measured on line I, and on line II

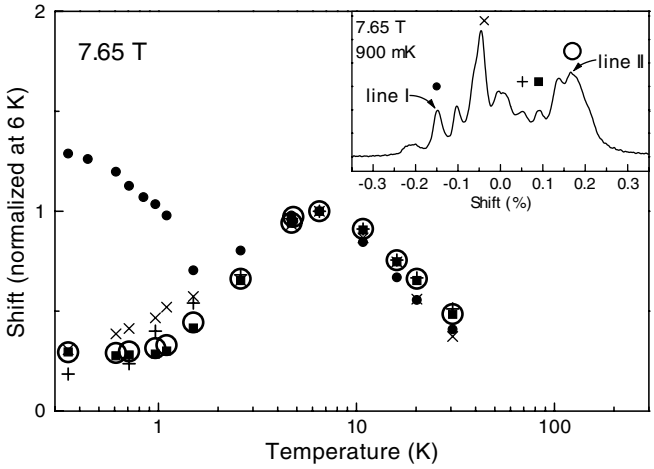

FIG. 3. T dependence of the shift $K(T)$ of various proton lines (the full spectrum is shown in the inset), normalized at 6 K. $K(T)$ scales to the uniform spin susceptibility for all lines, except for those corresponding to protons H(2) and H(4) which strongly deviate below $T \simeq 1.5$ K. This can be explained only if the position of these protons, hence their hyperfine field, varies in this T range.

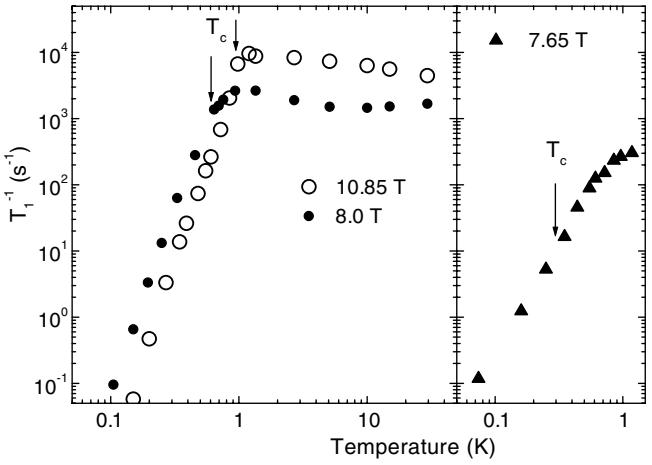

FIG. 4. T dependence of proton $1/T_1$ at different values of H. Left panel: data at $H = 8.0$ T and 10.85 T, measured on line II (see inset to Fig. 3). Data above 1.1 K are taken from [3]. Right panel: data at $H = 7.65$ T measured on line I.

for $H = 8.0$ and 10.85 T (see inset of Fig. 3) [17]. The recovery of the magnetization was fitted to a stretched exponential form $e^{-(t/T_1)^{\alpha}}$ where $\alpha = 0.92$ is independent of H and T. There are three striking features in these data: (i) the huge decrease of $1/T_1$ up to 5 orders of magnitude at $H = 8.0$ and 10.85 T. This decrease can be fitted by a power law ($1/T_1 \propto T^{-5}$) [18]. (ii) The increase of $1/T_1$, attributed to the divergence of the spin correlation functions [3], stops around 1.3 K for all field values between H_{c1} and H_{c2}. (iii) $1/T_1$ starts decreasing *before* the onset of the 3D transition (as detected by the modification of the line shape). For $H = 7.65$ T, a field close to H_{c1}, the decrease is noticeably slower. However, as discussed in [2], the sites corresponding to lines I and II have different form factors, and do not probe the same linear combination of the transverse and longitudinal spin-spin correlation functions. So, we cannot really attribute the weaker T dependence of $1/T_1$ at 7.65 T to the proximity to H_{c1}.

In order to understand the possible nature of this 3D ordered ground state, it is first necessary to recall the main properties of the 1D regime. From a theoretical point of view, the spin-ladder Hamiltonian can be transformed into an interacting spinless fermion model through the canonical Jordan-Wigner transformation [19]. In this representation, H acts as the chemical potential μ, and for $H = H_{c1}$, μ lies exactly at the bottom of the band. Increasing H further fills the band in. Since the value of the Fermi wave vector k_F is set by the field, k_F is *incommensurate* (IC) with the underlying lattice, except at half filling. Because of the divergence of the spin susceptibility at $2k_F$, the on-site magnetization of the ordered phase is also expected to be incommensurate. Between H_{c1} and H_{c2}, and at sufficiently low T, the low-energy properties of the system are those of a Luttinger liquid [19].

In the same field range, the spin-ladder Hamiltonian can also be approximately mapped onto that of an XXZ $S = 1/2$ chain [4,12]. In this latter representation, an effective spin 1/2 is introduced, whose eigenstates correspond to the singlet and the lowest state of the triplet on a rung, and the effective field $H_{\rm eff}$ is equal to $H - (H_{c1} + H_{c2})/2$. In the following discussion, we shall use either the spinless fermion or the XXZ language.

It is well known that there are two possibilities to achieve 3D ordering at finite T for quantum spin chains: a transverse magnetic coupling J_t, leading to some kind of AF order when $J_t \xi_{\parallel}^2 \simeq k_B T$ or a spin-Peierls (SP) transition in presence of magnetoelastic coupling [20]. In the latter case, a modulation of the lattice occurs, which is stabilized by the energy gain due to the opening of a gap in the magnetic excitation spectrum. The 3D character of the transition arises, in this case, from the 3D nature of the elastic modes.

The case of a transverse magnetic coupling for an assembly of ladders has been treated in Ref. [10]. In this model, the 3D ordering corresponds to a freezing of the XY degrees of freedom of the triplet states, and below T_c, the local magnetization $M_z(R)$ is incommensurate along the direction of the ladders. A magnetoelastic scenario has been considered in Ref. [11], with a modulation of the exchange along the rungs $J_{\perp}$. On the other hand, a modulation of $J_{\parallel}$ was found to better explain specific heat data [8,21]. As in the purely magnetic scenario, the local magnetization $M_z(R)$ is IC along the ladder direction, and the 3D ordered phase is in some sense similar to the IC magnetic phase observed in spin-Peierls systems above their threshold field H_c [20,22].

We now compare our data to the predictions of these different models. All of them predict an IC modulation of $M_z(R)$, giving rise to an infinite number of inequivalent sites. This should transform each NMR line into a double horned line shape [23] or more complicated structures [24]. Because of the high density of ^{1}H lines in our spectra, we cannot distinguish whether each line transforms this way or simply splits.

There are a few theoretical calculations of the line $T_c(H)$. Close to H_{c1}, Giamarchi and Tsvelik predict a variation as $(H - H_{c1})^{2/3}$. Wessel and Haas rather propose an $(H - H_{c1})^{1/2}$ variation [13]. As shown in the inset of Fig. 2, T_c can be better fitted to $\propto (H - H_{c1})^{2/3}$, with $H_{c1} = 7.52$ T than to $\propto (H - H_{c1})^{1/2}$.

At variance with the line shape, the T dependence of $1/T_1$ is expected to depend strongly on the nature of the ground state. A purely magnetic ground state [7,10] implies a divergence of $1/T_1$ at the transition, which is not observed experimentally.

The increase of $1/T_1$ upon cooling, seen on Fig. 4 above $\simeq$1.3 K, is indeed related to the Luttinger liquid behavior of the gapless 1D system, as explained in [3]. This increase cannot be attributed to critical fluctuations linked to the transition, since it starts too far above T_c [3] and furthermore we now find that it even stops above T_c. This is particularly obvious for the data at 7.65 T (right panel of Fig. 4).

In contrast, in a spin-Peierls-like transition, the low-energy spectral weight of AF fluctuations starts being suppressed even above the 3D ordering by the coupling to the elastic degrees of freedom. Hence, there is no divergence, but a rapid decrease of $1/T_1$ due to the opening of a gap. This was experimentally observed at the transition from the uniform phase and the IC high field phase in the spin-Peierls compound $CuGeO_3$ [25]. Because of the IC nature of the ground state, the relaxation rate well below T_c should be dominated by the phasons, which are the standard Goldstone modes of IC phases, so that the decrease of $1/T_1$ is not necessarily thermally activated. This could be the origin of the apparent power law observed here. As shown in Fig. 4, a faster decrease is observed for $H = 10.85$ T, which corresponds approximately to $H_{\text{eff}} = (H_{c1} + H_{c2})/2$ where commensurability occurs.

It must be stressed that NMR spectra tell us only about the *time-averaged* displacements of protons H(2) and H(4). Would these displacements be purely static, only the value of $J_\parallel$ would change (and thus that of $H_{c1} \propto J_\perp - J_\parallel$). The dynamics, evidenced by the divergence of $1/T_1$ in the 1D regime, would not be affected. To alter the magnetic excitation spectrum, a dynamical modulation of the position of these protons must be present. In other words, they have to participate to some phonon mode coupled to the magnetic excitations and leading to a dynamic modulation of $J_\parallel$. This magnetoelastic coupling appears prior to the "spin-Peierls transition" at $T_c(H)$ and it readily explains the change in the T dependence of $1/T_1$ above T_c. The freezing of this collective mode would finally lead to a static IC modulation of the position of the protons along the legs of the ladder.

In summary, we have investigated the 3D ordered phase induced by the magnetic field in the spin ladder $Cu_2(C_5H_{12}N_2)_2Cl_4$, and found evidence for precursor effects of the 3D transition through a crossover in ^{1}H $1/T_1$ and displacements of protons located in the exchange path $J_\parallel$. These three features, namely, (i) absence of $1/T_1$ divergence at T_c, (ii) decrease of $1/T_1$ above T_c, and (iii) evidence for proton displacements in the same T range, rule out any model involving solely a magnetic coupling between the ladders [7,10], and strongly support a "generalized spin-Peierls" scenario [8].

We thank T. Giamarchi for discussions and P. Van der Linden for technical help.

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[14] For those protons which are the closest to the Cu atoms, a supertransferred hyperfine interaction is very likely too.
[15] Note that the line at the left of the spectra shown in Fig. 1 looks already slightly splitted in the normal phase. This splitting, which is T independent likely corresponds to a slight deviation from the orientation $H \parallel b$, which doubles from 24 to 48 the number of inequivalent sites, and is clearly distinct from the "splitting" occurring in the 3D ordered phase, which is strongly T dependent.
[16] The dipolar coupling with electronic spins varies as r^{-3}. A supertransferred hyperfine field, through the path Cu-N-H, should vary exponentially with the N-H distance.
[17] To select the lines for $1/T_1$ measurements, the duration of the $\pi/2$ (π) pulses were adjusted to 4 μs (8 μs), respectively.
[18] Although $1/T_1$ decreases by 5 orders of magnitude, this occurs over only one decade in T so that an activated behavior below 250 mK cannot be fully excluded.
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[21] Considering the structure of the ladder, it is much easier to modify the exchange along the hydrogen bond than to modulate the Cu-Cl-Cu bridges.
[22] There is, however, a noticeable difference: in regular SP compounds, there is a commensurate (dimerized) phase, which is a collective singlet for $0 < H < H_c$. In the spin-ladder system, the commensurability occurs for $H = (H_{c1} + H_{c2})/2$ (i.e., $H_{\text{eff}} \simeq 0$). Any extension of the commensurability around this H value would correspond to a plateau in the magnetization [which is not observed in $Cu_2(C_5H_{12}N_2)_2Cl_4$]. Along the same line, the parts of the phase diagram close to H_{c1} or H_{c2} in the ladder case correspond to a field range close to the saturation of the magnetization in the case of a regular SP system.
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