NMR evidence for a ”generalized spin-Peierls transition” in the high magnetic field phase of the spin-ladder \(\text{Cu}_2(\text{C}_5\text{N}_2\text{H}_{12})_2\text{Cl}_4\)

H. Mayaffre\(^1\), M. Horvatić\(^2\), C. Berthier\(^{1,2}\), M.-H. Julien\(^1\), P. Ségransan\(^1\), L. Lévy\(^2,3\), and O. Piovesana\(^4\)

\(^1\)Laboratoire de Spectrométrie Physique, Université J. Fourier, BP87, F-38402 St. Martin d’Hères, France
\(^2\)Grenoble High Magnetic Field Laboratory, CNRS and MPI-FKF, BP 166, F-38042 Grenoble Cedex 09, France
\(^3\)Institut Universitaire de France, Université J. Fourier, BP41, F-38402 St. Martin d’Hères, France
\(^4\)Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy

(December 17, 2021)

The magnetic field-induced 3D ordered phase of the two-leg spin-ladder \(\text{Cu}_2(\text{C}_5\text{N}_2\text{H}_{12})_2\text{Cl}_4\) 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 \(H_{c2} = 13 T\) 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, involving a displacement of the protons along the longitudinal exchange \((J_\parallel)\) path.

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 \(\Delta\) from the first excited states which are triplet \((S = 1)\). 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.

The fascinating properties of spin-liquids can also be revealed through the effect of a magnetic field \(H\). This can be described in four steps: (1) For \(H \neq 0\), the gap is reduced as \(\Delta(H) = \Delta - g\mu_B H\). (2) At the so-called quantum critical point \(H = H_{c1} = \Delta/g\mu_B H\), the spin-gap vanishes. At \(T = 0\), this defines a (quantum) phase transition between gapped singlet and gapless magnetic phases. (3) For \(H > H_{c1}\), the gapless spin system still exhibits 1D behavior at finite temperature, but as \(T\) is reduced the magnetic correlation length and the spin-spin correlation functions now diverge (Luttinger liquid behaviour). This behaviour can be observed up to a saturation field \(H_{c2}\) where all spins are polarized by \(H\). (4) For \(H_{c1} < H < H_{c2}\), the transverse coupling \(J_\perp\) between ladders should drive the system towards a 3D magnetic ordering at low \(T\). The nature of the 3D phase, in the vicinity of the two quantum critical points, is expected to be highly unconventional.

Points (1-3) were previously observed in NMR studies \(^2\) in the low values of the AF exchange coupling (between spins 1/2 on Cu\(^{2+}\) ions) along the legs \((J_\perp \simeq 3 K)\) and along the rungs \((J_\parallel \simeq 13 K)\), lead to experimentally accessible values of \(H_{c1} (\simeq 7.5 T)\) and \(H_{c2} (\simeq 13.5 T)\). As to point (4), specific heat measurements \(^3\) in the field range 7-12 T have indeed revealed a phase transition towards a 3D ordered phase for \(T < 1 K\). However, no microscopic experimental insight has been reported so far, although this phase currently generates a large interest.\(^3\)

In this Letter, we present a \(^1\)H NMR study of \(\text{Cu}_2(\text{C}_5\text{N}_2\text{H}_{12})_2\text{Cl}_4\) in the field range 7.5-14 T, including the \(T\)-dependence (in the range 70 mK-1.2 K) of the lineshape 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 along the legs of the ladder. This is argued to demonstrate the magneto-elastic nature of the transition, which is in some way analogous to the incommensurate magnetic phase of spin-Peierls systems.

Experiments have been performed on a single crystal placed inside the mixing chamber of a \(^3\)He-\(^4\)He dilution refrigerator, the \(b\)-axis of the crystal being parallel to \(H\). In this orientation, the number of inequivalent \(^1\)H sites in the crystal is reduced to 24. All sites experience different hyperfine fields through their dipolar coupling to the electronic spins localized at the Cu sites \(^4\). 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. \(^4\) is shown the low frequency part of such spectra recorded at 70 mK at various values of \(H\). One clearly observes a splitting of all lines starting at \(H = 7.55 T\) and increasing for higher \(H\) values. This is the signature of an ordered magnetic phase. Following the evolution of the spectrum with \(H\) for different \(T\) values allows an accurate determination of the transition.
line $T_c(H)$. As shown in Fig. 3, $T_c$ rapidly increases as a function of $H - H_{c1}$ and then saturates around 900 mK for $H \geq 9$ T. In this range, the transition was determined at fixed value of $H$ and decreasing $T$. Again, we observe a line splitting (Fig. 1), which quickly increases below $T_c$ and then saturates at lower $T$, as expected for an order parameter. The resulting experimental phase diagram is shown in Fig. 2.

There are a few theoretical calculations of the line $T_c(H)$: Close to $H_{c1}$, Giamarchi and Tsvelik predict a variation as $(H - H_{c1})^{2/3}$, resulting from the condensation of dilute hard core bosons [16]. Wessel and Haas rather propose an $(H - H_{c1})^{3/2}$ variation [12]. As shown in the inset to Fig. 2, $T_c$ can be well-fitted to $\propto (H - H_{c1})^{2/3}$, with $H_{c1} = 7.52$ T. Note that the prediction of a first order transition with a jump of magnetization for values of $H$ close to $H_{c1}$ is not observed in our data even very close to $H_{c1}$. In all cases, each line splits at $T_c$, keeping the same center of gravity, thus indicating that the magnetization is continuous with $T$ or $H$, in agreement with earlier thermodynamic measurements [12].

A careful examination of the whole $^1$H spectrum (Fig. 3) 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. These two lines are assigned to the protons H(2) and H(4) [2], which are along the exchange path $J_2$ corresponding to the atom sequence Cu-N-H-Cu-I-Cl-Cu (see inset to Fig. 3). Since the shift of a proton $^1$H(i) is given by $\delta h(i) = A(i)\chi_{Cu}$, in which $A(i)$ is its hyperfine field and $\chi_{Cu}$ 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. This is thus 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 change is indeed observed in $T_1$ data, measured between 1.2 K and 70 mK and reported in Fig. 4. There are three striking features in these data: i) the huge decrease of $1/T_1$ up to 5 orders of magnitude at $H = 8.0$ T and 10.85 T. This decrease can be fitted by a power law $(1/T_1 \propto T^{-5})$ [16]. ii) the increase of $1/T_1$, attributed to the divergence of the spin correlation functions, 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 lineshape).

We now discuss the possible nature of this 3D ordered ground state. 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 [17]. In this representation, $H$ acts as the chemical potential $\mu$, and for $H = H_{c1}$, $\mu$ lies exactly at the bottom of the band. Increasing $H$ further fills the band in. Since the value of the Fermi-wave vec-
tor $k_F$ is set by the field, $k_F$ is incommensurate (IC) with the underlying lattice, except at half filling. Due to 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 [17].

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 $H_{\text{eff}}$ 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 $J_\perp$, leading to some kind of AF order when $J_\perp k_B T$ or a spin-Peierls (SP) transition in presence of magneto-elastic coupling [19]. 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 arise, in this case, from to the 3D nature of the elastic modes.

The case of a transverse magnetic coupling for an assembly of ladders has been treated by Giamarchi and Tsvelik [10]. In their 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 magneto-elastic scenario has been treated by Nagaosa and Murakami [11], who considered a modulation of the exchange along the rungs $J_\perp$ and by Caleczuk et al. [8] who found that a modulation of $J_\parallel$ better explains specific heat data [18]. 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 $H_c$ [19]. 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$_5$N$_2$H$_{12}$)Cl$_4$). 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.

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 line I-III in our spectra, we cannot distinguish whether each line transforms this way or simply splits.

At variance with the lineshape, the $T$-dependence of $1/T_1$ is expected to depend strongly on the nature of the ground state. A purely magnetic ground state [7,14] 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 $\sim 1.3$ K, is indeed related to the Luttinger liquid behavior of the gapless 1D system, as explained in [8]. This increase cannot be attributed to critical fluctuations linked to the transition, since it starts too far above $T_c$ [8] and furthermore we now find that it even stops above $T_c$. This is particularly obvious for the data at 7.65 T (right

---

**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 $T \approx 1.5$ K. This can only be explained 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 [1]. Right panel: data at $H = 7.65$ T measured on line I.
crease is noticeably slower. However, for this field value, while it was measured on the line II for to the elastic degrees of freedom. Hence, there is no di-

suppressed even above the 3D ordering by the coupling to the IC nature of the ground state, the relaxation rate 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 ob-

served here. As shown in Fig. 4, a faster decrease is observed for $H = 10.85$ T, which corresponds approximately to $H_{\text{eff}} = (H_{\text{c1}} + H_{\text{c2}})/2$ where commensurability occurs. For $H = 7.65$ T, a field close to $H_{\text{c1}}$, the decrease is noticeably slower. However, for this field value, $1/T_1$ was measured on the line I (protons H(2) and H(4)), while it was measured on the line II for $H = 8.0$ T and 10.85 T (see inset to Fig. 3). As discussed in Ref. [3], the corresponding sites 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 $H_{\text{c1}}$.

In summary, for approximately the same $T$-range where $1/T_1$ decreases, we observe displacements of protons located in the hydrogen bonding along the exchange path $J_{\|}$. 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 be-

tween the ladders [10], and strongly support a ”general-

ized spin-Peierls” scenario. We also found that the field dependence of $T_c$ is consistent with the predictions of a Bose condensation type of transition ($T_c \propto (H - H_{\text{c1}})^{2/3}$).

It must be stressed that NMR spectra only tell us about the time-averaged displacements of these protons. Would the displacements of protons H(2) and H(4) be purely static, only the value of $J_1$ would change (and thus that of $H_{\text{c1}} \propto J_{\perp} - J_{\|}$). 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 excita-

cations and leading to a dynamic modulation of $J_1$.

This magneto-elastic 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 freeze-

ing of this collective mode would finally lead to a static IC modulation of the position of the protons along the legs of the ladder.

We note that preliminary data show that anomalous

shifts, related to proton movements, are still observed very close to $H_{\text{c1}}$, where $T_c \to 0$. This can be explained by the fact that, already at $H = H_{\text{c1}}$, the system has in-

terest in suppressing the quantum magnetic fluctuations through the magneto-elastic coupling. However, an ordering cannot be achieved at finite temperature since there is no finite magnetization along the individual ladders.

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

[1] For a review, see E. Dagotto and T. M. Rice, Science 271, 618 (1996) and E. Dagotto, Rep. progr. Phys. 62, 1525 (1999).
[2] G. Chaboussant et al., Phys. Rev. Lett. 79, 925 (1997).
[3] G. Chaboussant et al., Phys. Rev. Lett. 80, 2713 (1998).
[4] G. Chaboussant et al., Eur. Phys. J. B 6 167 (1998).
[5] B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, Inorg. Chem. 29, 1172 (1990).
[6] G. Chaboussant et al., Phys. Rev. B 55 3046 (1997).
[7] P.R. Hammar, D.H. Reich, C. Broholm and F. Trouw, Phys. Rev. B 57 7846 (1998).
[8] R. Calemczuk et al., Eur. Phys. J. B 7 171 (1999).
[9] M. Hagiwara et al., [cond-mat/9912383].
[10] T. Giamarchi and A. Tsvelik, Phys. Rev. B 59 11398 (1999).
[11] N. Nagaosa and S. Murakami, J. Phys. Soc. Jpn. 67, 1876 (1998).
[12] F. Mila, Eur. Phys. J. B 6, 201 (1999).
[13] S. Wessel and S. Haas, [cond-mat/9910259].
[14] For those protons which are the closest to the Cu atoms, some supertransferred hyperfine interaction is very likely too.
[15] 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.
[16] Although $1/T_1$ decreases by five order of magnitude, this occurs over only one decade in $T$ so that an activated behaviour below 250 mK cannot be fully excluded (inset to Fig. 4).
[17] R. Chitra and T. Giamarchi, Phys. Rev. B 55, 5816 (1997).
[18] Considering the structure of the ladder, it is much easier to modify the exchange along the hydrogen bond, than to modulate the Cu-Cu bridges.
[19] J.W. Bray, L.V. Interrante, I.S. Jacobs, J.C. Bonner, in Extended Linear Chain Compounds, ed. J.S. Miller, (Plenum Press, New York, 1982) p. 253.
[20] R. Blinc, Phys. Rep. 79, 331 (1981).
[21] Y. Fagot-Revurat et al., Phys. Rev. B 55, 1261 (1998).
[22] At $H = H_{\text{c1}}$, the divergence of the spin-spin correlation functions is seen through $1/T_1 \propto T^{-0.5}$. [3].