Dynamics of a Heisenberg spin chain in the quantum critical regime: NMR experiment versus effective field theory

H. Kühne,1 A.A. Zvyagin,1,2 M. Günther,1 A.P. Reyes,3
P.L. Kuhns,1 M.M. Turnbull,4 C.P. Landee,4 and H.-H. Klauss1

1Institut für Festkörperphysik, TU Dresden, 01069 Dresden, Germany
2Institute for Low Temperature Physics and Engineering of the NAS of Ukraine, Kharkov, 61103, Ukraine
3National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA
4Carlson School of Chemistry and Department of Physics, Clark University, Worcester, Massachusetts 01610, USA

(Titled: July 26, 2010)

A comprehensive comparison between the magnetic field- and temperature-dependent low frequency spin dynamics in the antiferromagnetic spin-1/2 Heisenberg chain (AFHC) system copper pyrazine dinitrate, probed via the 13C-nuclear magnetic resonance (NMR) relaxation rate $T_1^{-1}$, and the field theoretical approach in the Luttinger liquid (LL) regime has been performed. We have found a very good agreement between the experiment and theory in the investigated temperature and field range. Our results demonstrate how strongly the quantum critical point affects the spin dynamics of Heisenberg spin chain compounds.

PACS numbers: 75.10.Pq, 71.10.Pm, 76.60.-k

The occurrence of quantum phase transitions (QPT) in systems of correlated electrons is a very important topic in current solid-state physics. These transitions are present in, e.g., high-$T_c$ superconductors, heavy-fermion metals, or magnetic insulators. The phase diagrams of systems from the first two classes are in general complex due to several interaction mechanisms. In contrast, the purely magnetic interactions in magnetic insulators, in particular for one-dimensional spin systems, give the rare occasion to perform exact calculations of their characteristics and to compare them with experimental data sets of well characterized sample systems. The spin properties of organic-based low-dimensional magnets can be fine-tuned by chemical synthesis/ization methods. This well controlled synthesis allows the systematic investigation of the magnetic properties with well established methods such as neutron scattering, ESR, dc/ac magnetometry, µSR or NMR. In low-dimensional magnets the high sensitivity of NMR to local hyperfine fields allows to perform detailed studies of, e.g., phase transitions, or the local distribution of spin moments.

The isotropic AFHC model is one of the main paradigms of quantum many-body physics both from the experimental and theoretical viewpoint. Its static characteristics were successfully compared with experimentally studied features of quasi-one-dimensional magnetic compounds, synthesized recently. For dynamical properties, especially in the vicinity of the quantum critical point, there is still an insufficiency of experimental data sets for the low frequency part and their comparison to calculations.

In this Letter we present a detailed comparison of field theory results with the data of recent NMR experiments probing the spin dynamics in a wide field- and temperature range in one of the best realizations of the AFHC model, namely Cu(C$_4$H$_6$N$_2$)(NO$_3$)$_2$ (also known as copper pyrazine dinitrate or CuPzN). We find an extraordinary good agreement in the low temperature behavior across the field driven QPT.

Due to a relatively low value of the coupling constant $J/k_B=10.7$ K in CuPzN, the critical field value $B_c = 14.6$ T is well reachable by standard laboratory equipment. Therefore, one can examine the spin dynamics in the region of fields and temperatures, where spin-spin correlations manifest themselves in the most prominent way, and compare with the results of various theoretical methods. The inter-chain interactions are supposed to be small, so that the magnetic ordering ($T_c \sim 107$ mK) did not affect the AFHC behavior down to the lowest $T$ studied in the NMR-experiment. Whereas these data were compared with numerical Quantum Monte Carlo (QMC) simulations, their agreement with results of a field theory approach (which serves as a very good description namely at low $T$, where QMC simulations often produce larger errors) for the LL regime is checked in our work. A similar approach has been used to calculate the properties of several low-dimensional systems, but so far no comparison with NMR-data of a direct realization of the AFHC has been done, especially in the vicinity of the QPT.

The NMR relaxation rate $T_1^{-1}$ can be presented as $T_1^{-1} = \langle \gamma_e^2 \gamma_N^2 \hbar^2/2 \rangle \int dq [F^z(q)S^{zz}(q,\omega_N) + F^{xx}(q)S^{xx}(q,\omega_N)]$, where $\gamma_e$ and $\gamma_N$ are the electronic and nuclear gyromagnetic ratios, respectively, $\omega_N$ is the resonance frequency of nuclear spins, and $F^{xx}(q)$ are the hyperfine form-factors of nuclear spins, parallel and perpendicular to the external dc magnetic field $B$, $S^{\mu\nu}(q,\omega_N)$ are the components of the tensor of the dynamical structure factor (DSF) of the AFHC, also parallel and perpendicular to $B$. For the transverse com-
ponents we have $S^{xx} = S^{yy}$, because of the rotational symmetry perpendicular to the field direction. Since $\omega_N \ll J/\hbar \gamma_c B$, we use the limit $\omega_N \to 0$. The ground state behavior of the DSF of the AFHC in the external magnetic field has been studied in [3], where it was supposed that continua of low-energy gapless excitations of the AFHC (known as spinons) yield the main contribution to the DSF. That conjecture, supported by numerical calculations for small-size spin chains [3], was later confirmed by the exact calculation, which used Bethe ansatz equations in the ground state of the AFHC [3]: About 75% of the DSF of the AFHC is determined by the two-spinon continuum. At $B = 0$ the DSF is isotropic, and at $\omega \to 0$ two points, $q = 0$ and $q = \pi$, contribute mostly to the relaxation rate. $B \neq 0$ introduces anisotropy in the components of the DSF of the AFHC. For $B \neq 0$ the main contribution to the components of the DSF of the spin chain is determined by the lower and upper boundaries of the two-spinon continua [3]. The nonzero field causes the shift of the most important contribution for $S^{zz}(q, \omega = 0)$ from $q = \pi$ to $q = \pi(1 - 2m)$, where $m$ is the magnetic moment per site of the AFHC, while the point $q = 0$ remains important. For $S^{zz}(q, \omega = 0)$ the point $q = \pi$ remains relevant, while instead of $q = 0$ the main contribution comes from $q = 2\pi m$.

The asymptotic behavior of the correlation functions of the AFHC can be calculated in the framework of the conformal field theory [10]. The low-energy states approach zero ($\omega = 0$) at the vector $q \sim P_F$, where $P_F$ is the Fermi momentum. For the longitudinal component of the DSF at $q \sim P_F = 0$ we have

$$\pi v^2 S^{zz}_h = 2K \alpha k_B T,$$

where $K$ is the LL exponent, $v$ is the Fermi velocity of a spinon, and $\alpha$ is the cut-off parameter of the theory. For $q \sim P_F = \pi(1 - 2m)$ we get

$$\frac{vS^{zz}_x}{\cos(2\pi K)} \sim C_1 B^2 \left( \frac{K}{2}, -1 - K \right) \left( \frac{2\pi k_B T}{v} \right)^{2K-1},$$

(2)

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$ is the beta function, and $C_1$ is the field-dependent multiplier [11]. At $m = 1/2$ this contribution has to coincide with Eq. (1), which defines $C_1(B_\alpha)$. The calculated longitudinal components of the DSF manifest weak dependencies on $T$ and $B$, except in the vicinity of the QPT (at which $v \to 0$), where they show a strong growth linear in $T$.

For the transverse component of the DSF at $q \sim P_F = \pi$, we have

$$\frac{vS^{xx}_s}{\cos(2\pi \gamma')} \sim C_2 B^2 \left( \frac{\gamma'}{2}, -1 - \gamma' \right) \left( \frac{2\pi k_B T}{v} \right)^{2\gamma'-1},$$

(3)

where $\gamma' = 1/(4K)$. Near the saturation point $B = B_s$ the correlation amplitude goes to zero, while the value of the correlation function at zero field in the ground state is approximately equal to 0.18 [11]. Hence, we can write the multiplier as $C_2 = 0.18/B^2(1/4, 1/2) \approx 0.0065$. This component yields the main contribution to the measured relaxation rate, see below, and the results of its calculation are presented in Fig. 1. For $q \sim P_F = 2\pi m$ we get

$$\frac{vS^{xx}_s}{\cos(2\pi \gamma)} \sim 2C_3 B \left( \frac{\gamma + 2}{2}, -1 - \gamma \right) B \left( \frac{\gamma}{2}, 1 - \gamma \right) \left( \frac{2\pi \alpha k_B T}{v} \right)^{2\gamma+1},$$

(4)

where $\gamma = K - 1 + 1/(4K)$. In the ground state numerical calculations [11] give the value of the correlation function at zero field $\sim 0.03$, which defines $C_3(B = 0)$. At $B = 0$ the exponent for the AFHC is $K = 1/2$, [10] and, therefore, this component of the DSF, calculated in this approach, diverges at $B = m = P_F = 0$. However, that divergency is well-known to be nonphysical. It is easy to calculate the transverse homogeneous magnetic susceptibility for the Heisenberg spin system at $q = 0$; it is equal to $m/\hbar \gamma_c B$. For the AFHC the magnetic moment is proportional to the field for small values of $B$, hence, in that region the transverse magnetic susceptibility coincides with the longitudinal one. The magnetic susceptibility is related to the DSF via the fluctuation-dissipation theorem. The correct magnetic field behavior of this transverse component of the DSF has to behave as the homogeneous longitudinal component for small values of the field, and decay to zero at $B \to B_s$, i.e. to coincide with the staggered transverse component there, because at $B = B_s$ we have $m = 1/2$, and $P_F = 2\pi m = \pi$.

The velocity and the LL exponent of spinons are $B$-dependent. These dependencies can be obtained from the exact Bethe ansatz solution. Recently, a simple ansatz for
the magnetic field behavior of the velocity $v$ and exponent $K$, valid in the interval $0 \leq B \leq B_s$, was proposed [12]:

$$v = (\pi J/2)\sqrt{\left[1 - (B/B_s)\right][1 - (B/B_s) + (2\hbar\gamma_e B/\pi J)]},$$

$$K = f\sqrt{4f^2 - 3(\hbar\gamma_e B)^2},$$

where $f = \pi J[1 - (B/B_s)] + \hbar\gamma_e B$. The behavior of $v$ and $K$, given by those expressions, agrees with the Bethe ansatz calculations. Finally, marginal operators (from the renormalization group viewpoint) introduce logarithmic corrections to the asymptotic behavior of correlation functions of the AFHC in the conformal limit at low $T$.

Those corrections can be taken into account, see, e.g., [13], which yields the additional multiplier $\sqrt{-\ln(24.27 J/\alpha k_B T)/(2\pi)^{3/2}}$ to the right hand sides of Eqs. (1)-(4).

During the last years a new approach for the calculation of the critical exponents was developed [14]. It was pointed out that the low-energy dynamics of quantum chains is determined not only by Fermi points, but also by high-energy states of the system, i.e. the non-linearity of the dispersion relations was taken into account. Contributions from those high-energy states were approximated as an interaction of the LL with an effective impurity, which parameters are determined by quasi-momenta of excitations. The theory, which determines the renormalization of exponents of quantum chains in the presence of impurities, was presented in [10]. Generalizing the approach of [14], we conjecture that the $B$- and $T$-behavior of the DSF is determined by Eqs. (1)-(4) with exponents, renormalized due to high-energy excitations. In the conformal field theory we replace $\Delta M \rightarrow (\Delta M - n_{imp})$, $\Delta D \rightarrow (\Delta D - d_{imp})$, where $\Delta M$ and $\Delta D$ are integers, determining the finite-size spectra of the chain, and $n_{imp}$ and $d_{imp}$ are the parameters of that effective impurity. The latter are defined as [14] $n_{imp} = \pm(\sqrt{K} - 1)$, and $d_{imp} = -(1/2\sqrt{K})n_{imp}$. The plus sign corresponds to the negative “valence” of the impurity, i.e. to the hole in the Fermi sea, and the minus sign corresponds to the positive “valence”, i.e. to the excitation above the Fermi sea. The behavior of the longitudinal homogeneous component of the DSF, Eq. (1), is, obviously, not renormalized. For the longitudinally staggered-like component of the DSF, in Eq. (2) we need to replace the exponent $K$ to $(1/2) - (1/2\sqrt{K}) + (1/4K) + (9K/16) - (3\sqrt{K}/4)$ for a high-energy hole, and $K \rightarrow (1/2) - (1/2\sqrt{K}) + (1/4K) + (K/4) - (\sqrt{K}/2)$ for a high-energy excitation. In Eq. (3) for the transverse staggered component of the DSF, we need to replace $\gamma \rightarrow (1/2) - (\sqrt{K}/2) + (K/4)$ for a high-energy hole, and $\gamma \rightarrow (1/2) + (1/K) - (1/2\sqrt{K}) + (K/4) - (\sqrt{K}/2)$ for a high-energy excitation. Finally, for the transverse “homogeneous” component, in Eq. (4) we need to replace the exponent $\gamma \rightarrow (9K/16) - (1/2) - (3\sqrt{K}/4)$ for a high-energy hole, and $\gamma \rightarrow (1/K) + K - (1/2) + (\sqrt{K}/2) - (1/2\sqrt{K})$ for a high-energy excitation. However, the $T$-and $B$-dependencies of the components of the DSF, obtained within our conjecture (taking into account the high-energy excitation/hole of the AFHC), do not agree with the experimentally observed data. This can be explained as follows. For the calculation of the NMR relaxation rate one performs the integration with respect to quasi-momenta, where only a small interval near $\omega = 0$ contributes mostly. The behavior of exponents in those intervals is not homogeneous: One expects the “traditional” LL exponent near the Fermi point and renormalized exponents close to the edges of the interval, with a smooth crossover between the exponents. The calculation of that crossover is a subtle point, not yet performed analytically. Thus, NMR experiments suggest, that in the interval of integration the main contribution comes from the region, where the “traditional” exponent is applicable.

The NMR measurements were performed in two different standard NMR setups, each with a superconducting magnet, a $^4$He temperature insert and a commercial/homebuild spectrometer. An inversion-recovery pulse sequence was used to measure the $^{13}$C-nuclear relaxation rate $T_1^{-1}$. In order to ensure a well defined comparability with theory, the hyperfine form-factor $F^S$, which relates $T_1^{-1}$ to $S^{zz}$, was minimized. This was done by an orientation-dependent study of the NMR frequency shift and $T_1^{-1}$, determining the angle of $\angle(B,b) = 50^\circ$ in the $b-c$ plane [3]. In this orientation the critical field is $B_s = (2J/\hbar\gamma_e) = 14.6$ T, which is a slight adjustment to the previous value, considering the anisotropic $g$-factor from recently published ESR-results [15]. In this case we have $T_1^{-1} = F^x_N(q)S^{zz}_N + F^y_N(q)S^{xx}_N$, which leaves only two form factors and the cut-off $\alpha$ as free parameters to fit our calculations to the experimental data. The results of this fit procedure are shown in Figs. 2 and 3. As for
the $B$-dependence shown in Fig. 2 the main contribution to the $T_1^{-1}$ rate comes from $S^{xx}_{s}$. For fields larger than $B_s$, a spin excitation gap opens linear with $B - B_s$, leading to an exponential decay of the relaxation rate. We find an excellent agreement between our calculations and the NMR experiment for the whole region of fields, in particular near the QPT.

The temperature dependence of $T_1^{-1}$ at different fields is shown in Fig. 3. The values of $F_{s}^{xx}(q)$ and $\alpha$ obtained from the fit of the field dependence were used for the scaling of $S^{xx}_{s}$ at all $B$ and $T$. At $B$ close to $B_s$, the experimental and theoretical NMR-relaxation rates show a diverging behavior as $T \to 0$. This singularity occurs when $B$, acting as the chemical potential for spinons, crosses the boundary of the dispersion relation (at this QPT $v$ goes to zero), cf. Eq. 2. Again, the critical regime, i.e. $T_1^{-1}(T)$ at 12.8T and 13.8T, can be fully described by $F_{s}^{xx}(q)S^{xx}_{s}$. Fitting the experimental rates with a power-law decay for $T < 2J/h\gamma_c$, in the region $0.7J \leq T \leq 2J$ we find the exponents to be slightly smaller than the theoretically calculated values, cf. Fig. 3. Notice that one expects the accuracy of field-theoretical calculations to significantly decrease for $T > J/k_B$. The agreement with experiment is, nevertheless, surprisingly good for the whole region of temperatures measured, with $T_1^{-1}$ becoming almost $T$-independent at high temperatures. At low fields, the experimental rates show an approximately linear $T$-dependence up to $T \sim 2J/k_B$. This behavior is not reflected by $F_{s}^{xx}(q)S^{xx}_{s}$. As described above, for low fields $S^{xx}_{s}$ has to be equivalent to $S^{zz}_{s}$. The fit of $F_{s}^{xx}(q)S^{xx}_{s} + F_{s}^{z}(q)S^{zz}_{s}$ for $T < 2J/h\gamma_c$, with $F_{s}^{zz}$ as a free parameter gives much better agreement with the experimental data in this low-T region. The ratio of $F_{s}^{xx}(q)$ at 2T and 6T is $\sim 5/2$, explainable by the shifting of the Fermi point in $q$ as a function of $B$ and the asymmetric position of the $^{13}$C probe between two magnetic $\text{Cu}^{2+}$ ions.

To summarize, based on the conformal field theory, we presented a comprehensive calculation of both the transverse and the longitudinal DSF of the AFHC model in the LL regime. Considering the hyperfine coupling as a free parameter, the comparison to NMR results on the AFHC system CuPzN was performed for temperatures $0.19 < (k_BT)/J < 4.5$ and fields up to $B \sim 2.2J/h\gamma_c$. The spin dynamics close to the quantum critical point can be extraordinary well described by the staggered part of the transverse DSF. At low fields contributions from the homogeneous part of the DSF have to be taken into account. We thank T. Giamarchi for suggesting us to perform this study, I.I. Glazman for the discussions on the range of applicability of exponents, and W. Brenig for the discussion on the QMC. This work was supported by the DFG through Grant No. KL1086/8-1 of FOR 912. AAZ acknowledges the financial support by the DFG via the Mercator program.

\begin{thebibliography}{10}
\bibitem{[1]} S. Sachdev, \textit{Quantum Phase Transitions} (Cambridge University Press, Cambridge 1999); Nature Physics Focus, \textbf{4}, 157 (2008).
\bibitem{[2]} M. Klanišek \textit{et al.}, Phys. Rev. Lett. \textbf{101}, 137207 (2008); B. Lake \textit{et al.}, Nature Materials \textbf{4}, 329 (2005).
\bibitem{[3]} F. Borsa, and M. Mali, Phys. Rev. B \textbf{9}, 2215 (1974); M. Takigawa \textit{et al.}, Phys. Rev. Lett. \textbf{76}, 4612 (1996); A.U.B. Wolter \textit{et al.}, \textit{ibid.} \textbf{94}, 057204 (2005).
\bibitem{[4]} \textit{Quantum Magnetism}, ed. by U. Schollwöck, J. Richter, D.J.J. Farnell, and R.F. Bishop, (Springer, Berlin-Heidelberg 2004).
\bibitem{[5]} H. Kühne \textit{et al.}, Phys. Rev. B \textbf{80}, 045110 (2009); H. Kühne \textit{et al.}, Physica Status Solidi \textbf{B 247}, 671 (2010).
\bibitem{[6]} T. Lancaster \textit{et al.}, Phys. Rev. B \textbf{73}, 020410(R) (2006); P.R. Hammar \textit{et al.}, \textit{ibid} \textbf{59}, 1008 (1999); M.B. Stone \textit{et al.}, Phys. Rev. Lett. 91, 037205 (2003).
\bibitem{[7]} T. Moriya, Prog. Theor. Phys. \textbf{16}, 23 (1956).
\bibitem{[8]} G. Müller \textit{et al.}, Phys. Rev. B \textbf{24}, 1429 (1981).
\bibitem{[9]} J.-S. Caux, and J.-M. Maillet, Phys. Rev. Lett. \textbf{95}, 077201 (2005).
\bibitem{[10]} See, e.g., A.A. Zvyagin, \textit{Finite Size Effects in Correlated Electron Models: Exact Results} (Imperial College Press, London, 2005).
\bibitem{[11]} S. Lukyanov and A. Zamolodchikov, Nucl. Phys. B \textbf{493}, 571 (1997); S. Lukyanov, Phys. Rev. B \textbf{59}, 11163 (1999);
\end{thebibliography}
V. Barzykin, *ibid.* **63**, 140412(R) (2001); T. Hikihara and A. Furusaki, *ibid.* **69**, 064427 (2004).

[12] A.A. Zvyagin, Phys. Rev. B **81**, 224407 (2010).

[13] M. Bocquet *et al.*, Phys. Rev. B **64**, 094425 (2001).

[14] M. Pustilnik *et al.*, Phys. Rev. Lett. **96**, 196405 (2006); R.G. Pereira *et al.*, *ibid.* **96**, 257202 (2006); M. Khodas *et al.*, *ibid.* **99**, 110405 (2007); R.G. Pereira, S.R. White, and I. Affleck, *ibid.* **100**, 027206 (2008); A. Imambekov, and L.I. Glazman, Science **323**, 228 (2009); A. Imambekov, and L.I. Glazman, Phys. Rev. Lett. **102**, 126405 (2009); T.L. Schmidt, A. Imambekov, and L.I. Glazman, *ibid.* **104**, 116403 (2010).

[15] A.A. Validov *et al.*, J.Phys.: Conf. Series **200**, 022070 (2010).