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

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

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The occurrence of quantum phase transitions (QPTs) 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.[1] The phase diagrams of systems from the first two classes are generally 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.[2] The spin properties of organic-based low-dimensional magnets can be fine-tuned by the chemical synthesis. This well-controlled synthesis allows the systematic investigation of the magnetic properties with well-established methods such as neutron scattering, electron spin resonance (ESR), dc/ac magnetometry, muon spin relaxation (μSR), or NMR. In low-dimensional magnets, the high sensitivity of NMR[3] to local hyperfine fields allows detailed studies of, e.g., phase transitions, the local distribution of spin moments, and low-frequency spin dynamics.

The isotropic antiferromagnetic spin-1/2 Heisenberg chain (AFHC) model is one of the main paradigms of quantum many-body physics, from both experimental and theoretical viewpoints. Its static characteristics were successfully compared with experimentally studied features of quasi-one-dimensional magnetic compounds, synthesized recently.[4] For the dynamical properties, especially in the vicinity of the quantum critical point, there is still a need for highly accurate experimental data sets for the low-frequency dynamics and their comparison to calculations.

This Rapid Communication presents a detailed comparison of field theory results with the data of recent NMR experiments,[5] probing the spin dynamics in a wide field and temperature range in one of the best realizations of the AFHC model, namely $Cu(C_4H_4N_2)(NO_3)_2$ (known as copper pyrazine dinitrate or CuPzN).[6] We find an extraordinary good agreement in the low-temperature behavior across the field-driven QPT. Our results demonstrate that the observed shift of the maximum of the field-dependent NMR relaxation rate to fields lower than the QPT is caused by the field dependence of the critical exponents of correlation functions (i.e., by essential spin-spin interactions). It cannot be explained using mean-field-like or perturbative approximations.

Owing to a relatively low value of the coupling constant $J/k_B = 10.7$ K in CuPzN, the critical field $B_s = 14.6$ T is accessible 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 interchain interactions are supposed to be small, so 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 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 Luttinger liquid (LL) regime is checked in our work. A similar approach has been used to calculate the properties of several low-dimensional systems,[2] 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[7] $T_1^{-1} = (\gamma_e^2\gamma_N^2\hbar^2/2)\int dq[F^x(q)S^{xx}(q,\omega_N)+F^z(q)S^{zz}(q,\omega_N)]$, where γ_e and γ_N are the electronic and nuclear gyromagnetic ratios, respectively; ω_N is the resonance frequency of nuclear spins; $F^{x,z}(q)$ are the hyperfine form factors of nuclear spins, parallel and perpendicular to the external dc magnetic field B; and $S^{\mu\nu}(q,\omega_N)$ $(\mu\nu = x,z)$ are the components of the tensor of the dynamical structure factor (DSF) of the AFHC, also parallel and perpendicular to B. For the transverse components, we have $S^{xx} = S^{yy}$ because of the rotational symmetry perpendicular to the field direction. Since $\omega_N \ll J\hbar,\gamma_e B$, we use the limit $\omega_N \to 0$. The asymptotic behavior of the correlation functions of the AFHC can be calculated in the framework of the conformal field theory.[8] The low-energy states approach zero ($\omega = 0$) for nonzero B at the vector $q \sim 0,\pi(1-2m)$, where m is the magnetic moment per site of the AFHC, for the

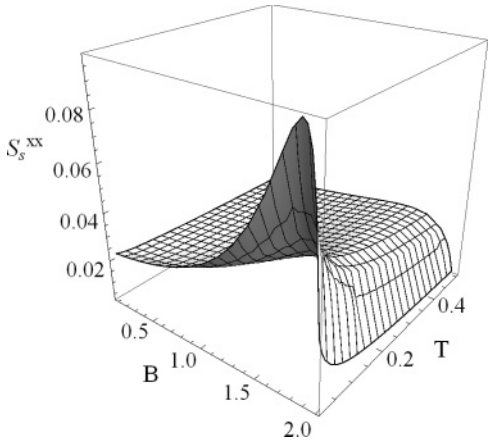

FIG. 1. The magnetic field-dependent (given in units of $J/\hbar\gamma_e$) and temperature-dependent (given in units of k_B/J) behavior of the transverse staggered component of the DSF of the AFHC model, calculated using the conformal field theory.

longitudinal component of the DSF, and at $q \sim 2\pi m, \pi$ for the transverse component.[9]

For the *transverse* component of the DSF at $q \sim \pi$ (staggered part), which yields the main contribution to the measured relaxation rate in our experiments (see below), we have

$$\frac{v S_s^{xx}}{|\cos(2\pi\gamma')|} \sim C_1 B^2 \left(\frac{\gamma'}{2}, 1-\gamma'\right) \left(\frac{2\pi\alpha k_B T}{v}\right)^{2\gamma'-1}, \quad (1)$$

where $\gamma' = 1/(4K)$; K is the critical LL exponent; v is the Fermi velocity of a spinon, the elementary excitation of the AFHC model; $B(x,y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$ is the beta function; $C_1(B)$ is the field-dependent multiplier[10]; and α is the cutoff parameter of the theory. The velocity and the LL exponent are B dependent in the AFHC model. These dependencies can be obtained from the exact Bethe ansatz solution. Recently, a simple ansatz for the field behavior of the velocity and exponent, valid in the interval $0 \leqslant B \leqslant B_s$, was proposed[11]: $v = (\pi J/2)\sqrt{[1-(B/B_s)][1-(B/B_s)+(2\hbar\gamma_e B/\pi J)]}$, $K = f/\sqrt{4f^2 - 3(\hbar\gamma_e B)^2}$, $f = \pi J[1-(B/B_s)] + \hbar\gamma_e B$. The behavior of v and K, given by those expressions, agrees with the Bethe ansatz calculations. Near the saturation point $B = B_s$, the correlation amplitude goes to zero, while at zero field the value of the correlation function in the ground state is approximately equal to 0.18.[10] Hence, we can write the multiplier as $C_1(0) = 0.18/B^2(1/4,1/2) \approx 0.0065$. The results of the calculation are presented in Fig. 1. It clearly reveals a maximum in the low-T quantum regime *below* B_s. That shift of the maximum to fields below B_s is the direct consequence of the fact that the LL exponent K is not equal to unity for fields lower than B_s. It is well known[8] that after the Jordan-Wigner transformation the Hamiltonian of the AFHC model can be written as the Hamiltonian of spinless lattice fermions. The latter consists of the quadratic part in the fermion operators (which describes noninteracting fermions), and the quartic term, which describes the interaction between fermions (namely those interactions are responsible for the existence of multispinon continua). Theoretical mean-field-like and/or perturbative methods yield a critical exponent K for the correlation functions which is independent of B (unity). Only exact (or field-theoretical) approaches describe the field dependence of that exponent.[8] In the absence of the B dependence of K (i.e., without essential LL spin-spin interactions), the transverse component of the DSF is temperature independent and reveals a divergency at $B = B_s$ (see Fig. 2; cf. Ref. 12).

For the homogenous part of the DSF at $q \sim 2\pi m$, we get

$$\frac{v S_h^{xx}}{\cos(2\pi\gamma)} \sim 2C_2 B\left(\frac{\gamma+2}{2}, -1-\gamma\right) B\left(\frac{\gamma}{2}, 1-\gamma\right) \times \left(\frac{2\pi\alpha k_B T}{v}\right)^{2\gamma+1}, \quad (2)$$

where $\gamma = K - 1 + 1/(4K)$. In the ground state, numerical calculations[10] give the value of the correlation function at zero field as ~0.03, which defines $C_2(B=0)$. At $B = 0$ the exponent for the AFHC is $K = 1/2$,[8] and, therefore, this component of the DSF, calculated in this approach, diverges at $B = m = 0$. 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 $m/\hbar\gamma_e B$. For the AFHC, the magnetic moment is proportional to the field for small values of B; hence, in that regime, the transverse magnetic susceptibility coincides with the longitudinal one. The magnetic susceptibility is related to the DSF via the fluctuation-dissipation theorem. Therefore, at low fields, $S_h^{xx} \simeq S_h^{zz}$.

For the *longitudinal* component of the DSF at $q \sim 0$ we have

$$\pi v^2 S_h^{zz} = 2K\alpha k_B T, \quad (3)$$

and for $q \sim \pi(1-2m)$ we get

$$\frac{v S_s^{zz}}{\cos(2\pi K)} \sim C_3 B^2 \left(\frac{K}{2}, 1-K\right) \left(\frac{2\pi\alpha k_B T}{v}\right)^{2K-1}. \quad (4)$$

At $m = 1/2$, this contribution has to coincide with Eq. (3), which defines $C_3(B_s)$. 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. Hence, the correct magnetic field behavior of the homogenous transverse component of the DSF has to behave as the homogeneous longitudinal component for small values of the field and must 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 $2\pi m = \pi$.

It is worth mentioning that 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.[8] Those corrections can be taken into account (see, e.g., Ref. 13), which yields the additional multiplier $\sqrt{\ln(24.27J/\alpha k_B T)}/(2\pi)^{3/2}$ to the right-hand-side of Eqs. (1)–(4).

Recently, it was pointed out[14] that the low-energy dynamics of quantum chains is determined not only by the Fermi points but also by high-energy states of the system; i.e., the nonlinearity of the dispersion relations was taken into account. Generalizing the approach of Ref. 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

states. In the conformal field theory, we replace $\Delta M \to (\Delta M - n_{\rm imp})$, $\Delta D \to (\Delta D - d_{\rm imp})$, where ΔM and ΔD are integers, determining the finite-size spectra of the chain,[8] and $n_{\rm imp} = \pm(\sqrt{K} - 1)$ and $d_{\rm imp} = -(1/2\sqrt{K})n_{\rm imp}$ are the parameters of high-energy states of the AFHC model. Thus, in Eq. (1) we have to replace $\gamma' \to (1/2) - (\sqrt{K}/2) + (K/4)$ for a high-energy hole, and $\gamma' \to (1/2) + (1/K) - (1/2\sqrt{K}) + (K/4) - (\sqrt{K}/2)$ for a high-energy excitation. In Eq. (2) we need to replace the exponent $\gamma \to (9K/16) - (1/2) - (3\sqrt{K}/4)$ for a high-energy hole, and $\gamma \to (1/K) + K - (1/2) + (\sqrt{K}/2) - (1/2\sqrt{K})$ for a high-energy excitation. The behavior of the longitudinal homogeneous component of the DSF, Eq. (3), is, obviously, not renormalized. In Eq. (4) we have 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 $K \to (1/2) - (1/2\sqrt{K}) + (1/4K) + (K/4) - (\sqrt{K}/2)$ for a high-energy excitation. The T and B dependencies of the components of the DSF, obtained within that conjecture, do not agree with our experimentally observed data. It can be explained as follows. A small interval of quasimomenta of spinons near $\omega = 0$ mostly contributes to T_1^{-1}. In that interval, one expects the "traditional" LL exponent near the Fermi point, and renormalized exponents close to the edges of the interval, with a smooth crossover. The calculation of that crossover is a subtle point, not yet performed. Our NMR experiments suggest that the main contribution to T_1^{-1} 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}. To ensure well-defined comparability with the theory for S^{xx}, the hyperfine form factor F^z, which scales the contribution of S^{zz} to T_1^{-1}, was minimized. This was done via an orientation-dependent study of the NMR frequency shift and T_1^{-1}, determining the angle $\angle(B,b) = 50^\circ$ in the b-c plane.[5] In this orientation the critical field is $B_s = (2J/\hbar\gamma_e) = 14.6$ T, adjusted according to the anisotropic g factor from recently published ESR results.[15] In this case we have

$$T_1^{-1} = F_s^{'x}(q)S_s^{xx} + F_h^{'x}(q)S_h^{xx}, \qquad (5)$$

leaving only the two form factors and the cutoff α as free parameters to fit our calculations to the experimental data.[16] The results of this fit procedure are shown in Figs. 2 and 3. The B dependence of T_1^{-1}, shown in Fig. 2, is reproduced by considering only S_s^{xx}. 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 $F_s^{'x}(q)$ and α, obtained from the fit of the field dependence, were kept constant for the scaling of S_s^{xx} 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. (1). Again, the critical regime, i.e., $T_1^{-1}(T)$ at 12.8 T and 13.8 T, is fully described by $F_s^{'x}(q)S_s^{xx}$. Note that one expects the accuracy of the 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 $T \sim 2J/k_B$ (cf. inset of Fig. 3). In this field regime, S_s^{xx} is almost T independent and S_h^{xx}, linear in T, becomes relevant. To avoid the unphysical divergence of S_h^{xx} at very low fields, in the fit of $1/T_1$ at 2 T and 6 T according to Eq. (5) for $T < J/\hbar\gamma_e$, we used, as discussed above, S_h^{zz}

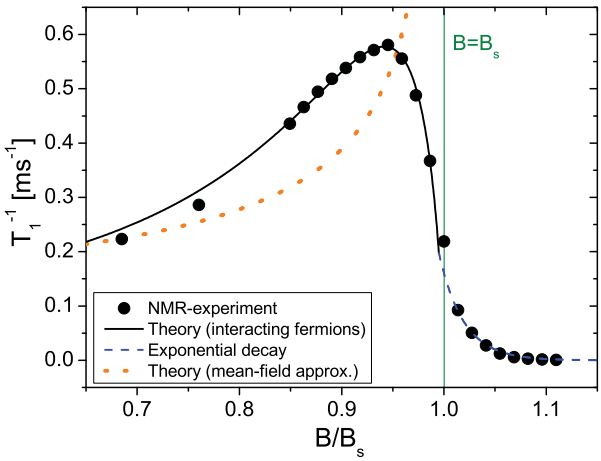

FIG. 2. (Color online) B dependence of T_1^{-1} at $k_BT/J = 0.15$ (error bars are within symbol size). The effective field theory results for the AFHC model are given by the solid (black) line for fields up to B_s. Above B_s, an exponential function was fitted to the data [dashed (blue) line]. The relaxation rates resulting from the model with fermion-fermion interactions taken in the mean-field approximation, given by the dotted (orange) line, diverge at $B = B_s$ at all T.

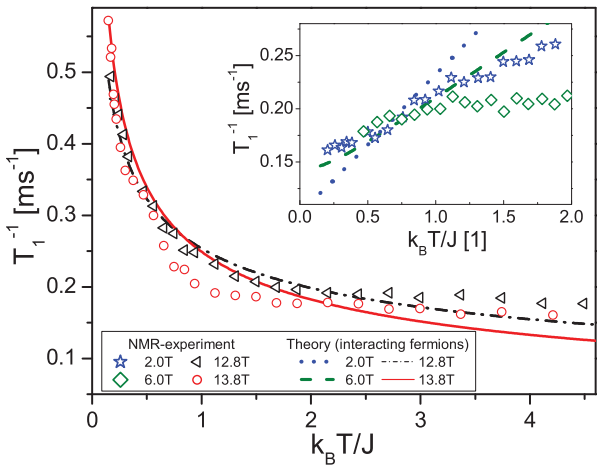

FIG. 3. (Color online) Comparison of temperature-dependent experimental (symbols) and theoretical (lines) T_1^{-1} rates at different external fields. At low fields (see inset), an additional contribution from the homogeneous DSF is included in the theoretical rates (see text).

instead of S_h^{xx} at 2 T. Thus, we find a very satisfying agreement at low temperatures and fields.

In summary, based on the conformal field theory, we presented a comprehensive calculation of both the transverse and the longitudinal low-frequency DSF of the AFHC model in the LL regime. The comparison to NMR results on the AFHC system CuPzN was performed for a large temperature interval $0.19 < (k_B T)/J < 4.5$ and for fields up to $B \sim 2.2J/\hbar\gamma_e$. Our results manifest that the observed shift of the maximum of $T_1^{-1}(B)$ to fields lower than the critical field B_s is caused by the field dependence of the LL exponent, i.e., by substantial spin-spin interactions. It cannot be explained using mean-field-like or perturbative approximations. We stress that CuPzN is so far the only compound with an experimentally fully accessible magnetic behavior, for which this good agreement has been found.

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[16] The field-dependent multipliers $C_{1,2,3}(B)$ cannot be defined within the conformal field theory. They were determined only numerically at $T = 0$ for finite spin chains.[10] Therefore, in our calculations we used them as constants. This can also explain the limited agreement between the experiment and the field theory at lower values of B.