Field-Induced Quantum Criticality and Universal Temperature Dependence of the Magnetization of a Spin-1/2 Heisenberg Chain


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High-precision dc magnetization measurements have been made on Cu(C4H4N2)(NO3)2 in magnetic fields up to 14.7 T, slightly above the saturation field Hs = 13.97 T, in the temperature range from 0.08 to 15 K. The magnetization curve and differential susceptibility at the lowest temperature show excellent agreement with exact theoretical results for the spin-1/2 Heisenberg antiferromagnet in one dimension. A broad peak is observed in magnetization measured as a function of temperature, signaling a crossover to a low-temperature Tomonaga-Luttinger-liquid regime. With an increasing field, the peak moves gradually to lower temperatures, compressing the regime, and, at Hc, the magnetization exhibits a strong upturn. This quantum critical behavior of the magnetization and that of the specific heat withstand quantitative tests against theory, demonstrating that the material is a practically perfect one-dimensional spin-1/2 Heisenberg antiferromagnet.

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Quantum spin systems in one dimension have been the subject of intensive experimental and theoretical studies because of their intriguing properties arising from strong quantum fluctuations [1]. Among them, one of the simplest is the spin-1/2 one-dimensional (1D) Heisenberg antiferromagnet (HAF), whose ground state is a quantum critical state called a Tomonaga-Luttinger liquid (TLL) [2]. Two hallmarks of this unique state are gapless elementary excitations, which are interacting spin-1/2 quasiparticles carrying spin 1/2 [4,5]; the ground states in the regions H ≥ Hs and H ≤ Hc can be considered vacuums, in which excitations are, respectively, Sc = 1 and Sc = 1 magnons [6].

In the dilute limit, these 1D magnons can be exactly mapped onto free fermions [7,8]. As a result, the number of magnons, Nm, near the QCPs is given by

\[ \frac{N_m}{L} = \int_0^\infty d\epsilon \left( \frac{f(\epsilon - \mu)}{\epsilon} \right) \sim \sqrt{\frac{2mk_BT}{\pi \hbar}} \int_0^\infty dx \frac{dx}{e^{\epsilon - \mu/k_BT} + 1} \quad (2) \]

where L is the number of spins, \( f(\epsilon - \mu) \) the Fermi distribution function, and D(\epsilon) the density of states of the free fermions, whose dispersion at the band edge is quadratic, \( \epsilon = \hbar^2k^2/2m \). Here, m is the effective mass, and the chemical potential \( \mu \) is \( g\mu_B(H_s - H) \) or \( g\mu_B(H - H_c) \) [6,9]. Magnetization per spin, M/L, is \( (M_s - N_m)/L \) and \( N_m/L \) near \( H_s \) and \( H_c \), respectively, where \( M_s \) is the saturation magnetization.

According to Eq. (2), the magnetization at a given \( \mu \) has an extremum at [6]

\[ k_BT_{ex} = 0.76238\mu, \quad (3) \]

where \( N_m \) becomes minimum. This universal relation, confirmed in the spin-ladder system (Cu2HgN)2CuBr2 (DIMPY) near \( H_c = 3 \) T [10], marks the boundary at
specific-heat measurements, on Cu dc magnetization measurements, supplemented by some detail. For this purpose, we have performed high-precision 10 pound with a relatively small intrachain coupling of specific heat and magnetization down to 0.05 K, well anomaly indicative of the ordering has been found in 0.046 K. Consistent with such a small which is less than 3
magnetic ordering at 4.2 K
relaxation experiment has detected three-dimensional (3D)

agreement with Eqs.(2) and (3) and with QTM results. Preliminary results have been reported in Ref.[21].

In CuPzN, chains of $S=1/2$ Cu $^{2+}$ run along the crystallographic a axis [18,22]. A zero-field muon-spin-relaxation experiment has detected three-dimensional (3D) magnetic ordering at $T_N=0.107$ K [23]. From this, the interchain coupling constant $J'$ has been estimated to be 0.046 K. Consistent with such a small $J'$ relative to $J$, no anomaly indicative of the ordering has been found in specific heat and magnetization down to 0.05 K, well below $T_N$ [24].

Our dc magnetization measurements were performed on a 3.59 mg sample of CuPzN, using a force magnetometer [25]. A $^3$He-$^4$He dilution refrigerator and a sorption-type $^3$He refrigerator were used in the temperature ranges 0.08 K $\leq T \leq 2$ K and 0.3 K $\leq T \leq 15$ K, respectively. Static magnetic fields up to 14.7 T were applied along the b axis, perpendicular to the spin-chain direction. Precise calibration of the magnetization was made by comparing the $M(H)$ data at 4.2 K with those obtained by a superconducting-quantum-interference-device magnetometer. In addition, specific-heat measurements were performed on a 1.10 mg sample at 14 T with a relaxation technique. The samples for both measurements were single crystals grown by slow evaporation of a mixture of deuterated pyrazine with a heavy-water solution of copper nitrate [22].

Figure 1(a) shows the magnetization $M$ and the magnetic susceptibility $dM/dH$ of CuPzN at 0.08 K as a function of the magnetic field up to 14.7 T. Figure 1(b) is an enlarged view of Fig. 1(a) near the saturation field $H_s$, along with the well-known exact Bethe-ansatz curve at $T=0$ [26] recomputed for the present purpose. The best fit of the curve to the data gives $J=10.8(1)$ K and $g=2.30(1)$, which agree well with previously reported values [18,27], and $H_s$ is found to be 13.97(6) T. The fit is excellent up to 13.9 T, but the data very near $H_s$ do not exhibit a square-root singularity, $M_s-M \propto (H_s-H)^{1/2}$, predicted by theory [28,29]. Accordingly, $dM/dH$ has a prominent peak at 13.95 T but does not diverge. However, fitting the expression $1-M/M_s=D(1-H/H_s)^{1/6}$ to the data between 13.6 T and 13.9 T yields $D=1.24(8)$, $H_s=13.98(1)$ T, and $\delta=1.98(8)$, with $D$ and $\delta$ agreeing with the predicted values $4/\pi \approx 1.273$ [29] and 2, respectively. Moreover, our exact curve for $T=0.08$ K, calculated by the QTM method and shown in Figs. 1(a) and 1(b), is in close

FIG. 1 (color online). (a) Field dependence of the magnetization $M$ (solid circles) and the differential susceptibility $dM/dH$ (solid squares) at 0.08 K, along with the result of exact QTM calculations for the 1D spin-1/2 HAF at 0.08 K (open symbols). (b) Enlarged plot near $H_s=13.97$ T. The dashed line is a Bethe-ansatz result for $T=0$. In both panels, thin solid lines are guides to the eye.
agreement with the data even near $H_s$. These observations strongly suggest that the rounding of $M$ and the corresponding nondivergence of $dM/dH$ at $H_s$ are not caused by the interchain coupling $J'$, but by thermal fluctuations in the vicinity of the QCP [30].

The temperature at which the $M(H)$ curve was measured, 0.08 K, is definitely below the zero-field $T_N$ of 0.107 K. Therefore, the boundary of the 3D ordered phase will cross this temperature at some field below $H_s$. Nonetheless, the $M(H)$ curve exhibits no anomaly that indicates such a transition, in accordance with the previous experiment on a powder sample [24]. Taken together, these results suggest that the 3D ordering has a negligible effect on the thermodynamic properties of CuPzN.

The temperature dependence of the magnetization is shown in Fig. 2 for several magnetic fields. The magnetization has been divided by the field to compare data taken at different fields. In the limit of $H \to 0$, $M/H$ is expected to reach a maximum at $T_p \sim 0.64 J$ [29,31]. This relation, combined with the experimental value of $T_p = 6.89$ K at 1 T, yields $J = 10.8$ K, in perfect agreement with the value determined from the $M(H)$ data. With the increasing field, $T_p$ gradually decreases, and, at 13.9 T, the magnetization peak eventually vanishes into a temperature region well below 0.08 K [see Fig. 2(b)]. At 14 T, the data show a strong upturn as $T \to 0$, indicative of quantum criticality. At fields above $H_s$, where the ground state is a gapped, field-induced ferromagnetic state, the magnetization levels off at low temperatures as seen in the 14.5 T data. These features have been expected by numerical calculations for spin-1/2 1D HAFs [34].

Figure 3(a) shows the variation of $(M_s - M)/H$ with temperatures for several fields very near $H_s$ in a log-log plot. At 14 T, a field that is indistinguishable from $H_s$, within experimental uncertainty, $(M_s - M)/H$ is approximately proportional to $\sqrt{T}$ down to the lowest temperature investigated; the best fit of the expression $(M_s - M)/H \propto T^{\beta}$ to the data below 1 K yields $\beta = 0.48(1) \approx 1/2$. This power-law behavior can be explained by Eq. (2), in which the integral becomes a constant at $H = H_s$, where $\mu = 0$ yielding

$$M_s - M = 0.24132 \mu_B \sqrt{k_BT}/J$$

per Cu$^{2+}$, because $m = \hbar^2/J$. As shown in Fig. 3(b), the equation $M_s - M = B \sqrt{k_BT}/J$ can be fitted very well to the 14 T data over the entire temperature range of the measurements, up to 15 K, by choosing $M_s$ and $B$ as separate fitting parameters, while $J$ is set at 10.8 K obtained from the $M(H)$ data. The fit gives $M_s = 1.14 \mu_B$ per Cu$^{2+}$, in excellent agreement with 1.15 $\mu_B$ obtained from the $M(H)$ data (see Fig. 1), and $B = 0.230(1) \mu_B$ in good agreement with the exact prefactor in Eq. (4). Moreover, as is also shown in the figure, the data are in nearly perfect agreement with our QTM calculation at $H_s$, using the $J$ and $g$ obtained from the $M(H)$ data.

At this field, specific heat divided by temperature, shown in the inset to Fig. 3(b), also exhibits characteristic power-law behavior. The best fit of the relation $C/T \propto T^{-\alpha}$ to the data below 2 K yields $\alpha = 0.49(1) \approx 1/2$. This power-law dependence arises directly from the density of states in one

![FIG. 2](color online). (a) Temperature dependence of $M/H$ at various fields. The black arrows indicate the peak position $T_p$. (b) Low-temperature part ($T \leq 1.5$ K) of the $M/H$ plot for magnetic fields slightly below (open symbols) and slightly above (solid symbols) $H_s$. Thin lines are guides to the eye.
dimension, \( D(e) \propto 1/\sqrt{c} \): since \( C/T \) is approximately proportional to \( D(k_B T) \) when \( \mu = 0 \), it follows that it is proportional to \( 1/\sqrt{T} \) [34]. To be precise,

\[
C/T = 0.22894k_B^{3/2}/\sqrt{JT} \tag{5}
\]

per \( \text{Cu}^{2+} \). Fitting the expression \( C/T = A/\sqrt{JT} \) to the data below 2 K—where \( A \) is the only fitting parameter, with \( J \) the one obtained from the \( M(H) \) data—yields \( A = 0.215(1)k_B^{3/2} \) in good agreement with the exact prefactor in Eq. (5). As is also shown in the figure, the data are in excellent agreement with our QTM calculation using the \( J \) obtained from the \( M(H) \) data.

At fields slightly away from \( H_s \), the \((M_s - M)/H \) vs \( T \) plots in Fig. 3(a) deviate from the \( \sqrt{T} \) behavior at low temperatures but retain it above 1 K. This trend can also be explained by Eq. (2). Since \( H \) and \( T \) appear in the integrand of Eq. (2) only as the combination \( \mu/k_B T \), Eq. (4) holds for \( k_BT \gg g\mu_B(H_s - H) \) as long as the dispersion is quadratic. It should be emphasized, however, that the \( \sqrt{T} \) behavior persists down to \( T = 0 \) only at \( H_s \).

A brief remark on the power-law exponents is in order. Obviously, the combination \( \alpha + \beta(1 + \delta) = 1.92(4) \) of the exponents \( \alpha = 0.49(1) \), \( \beta = 0.48(1) \), and \( \delta = 1.98(8) \) from our experiment is very close to the universal scaling value 2. In fact, \( \alpha = 1/2 \) can be obtained simply from the scaling relation \( \alpha = 2 - (d + \delta)/z \), where the dynamical exponent \( z \) is 2 for free fermions and the spatial dimension \( d \) is 1. Similarly, \( \beta = 1/2 \) and \( \delta = 2 \) can be derived by employing a scaling argument [9].

Finally, the magnetic phase diagram of CuPzN is presented in Fig. 4 on the basis of \( d(M/H)/dT \), with \( T_p \) from Fig. 2 superposed to indicate the crossover to the TLL phase. Note that Eq. (3) gives a parameter-free expression for \( T_p \),

\[
T_p = 0.76238\frac{g\mu_B}{k_B}(H_s - H). \tag{6}
\]

This universal relation, shown as a dotted line with the \( g \) and \( H_s \) obtained from the \( M(H) \) data, with no fitting parameter, agrees excellently with the data near \( H_s \). The linear dependence, distinct from the power-law dependence for a Bose-Einstein condensation (BEC) of magnons [35], indicates that the 3D magnetic ordering of CuPzN due to \( J' \) is irrelevant in the temperature range of the present work, at least near \( H_s \). This is further supported by the 1D exponents for the specific heat and magnetization, \( \alpha = 0.49(1) \sim 1/2 \) and \( \beta = 0.48(1) \sim 1/2 \), which are in marked contrast to \( \alpha = -1/2 \) and \( \beta = 3/2 \) found in the magnon BEC in NiCl2-4SC(NH2)2 [36]. As the magnetic field further decreases, \( T_p \) deviates downward from the straight line, owing to repulsion between magnons [6].

In summary, we have examined in detail a crossover of CuPzN from a thermally disordered high-temperature phase to the Tomonaga-Luttinger-liquid phase, and the critical behavior of the magnetization and specific heat near the saturation field \( H_s \). The crossover temperature \( T_p \)—the temperature of the broad magnetization peak—starts off at a low field with the theoretical value that has been well known for 50 years [29] for the one-dimensional spin-1/2 Heisenberg model, decreases with increasing field, and smoothly connects near \( H_s \) to the universal, linear line for free fermions. At \( H_s \), the magnetization and specific heat are in excellent agreement with universal power laws for free fermions and with exact results calculated with the QTM method. The magnetization curve at 0.08 K is also in excellent quantitative agreement with an exact Bethe-ansatz result up to 99% of \( H_s \). The deviation very near \( H_s \) is fully accounted for by QTM calculations at this temperature. These findings demonstrate that CuPzN is a practically perfect one-dimensional spin-1/2 Heisenberg antiferromagnet.

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[30] This conclusion may be surprising, since one expects that the interchain coupling $J'$ would raise the saturation field $H_s$ by about $4J'(g_{\mu B}) = 0.12$ T and cause $M$ to become round over a field interval, of a comparable size, below the raised $H_s$ — a rounding in addition to that due to thermal fluctuations. However, according to first-principles calculations of exchange interactions in CuPzN [37], $J'$ is antiferromagnetic between chains that lie on the crystallographic {011} planes, whereas it is ferromagnetic between chains on the ab plane. The antiferromagnetic $J'$ couples a larger number of neighboring spins, but it is geometrically frustrated. We, therefore, attribute the seemingly surprising absence of evidence, in our data, for additional rounding caused by $J'$ to the competition between the antiferromagnetic and ferromagnetic $J'$, a competition which leads to a much smaller shift of $H_s$ and, with it, much less rounding than expected.
[31] At $H = 0$, the magnetic susceptibility is expected to also exhibit a logarithmic singularity at zero temperature [32]. Such a singularity will require temperatures lower than about 0.0005$J$ to observe [33]. For CuPzN, this temperature is about 5 mK, an order of magnitude lower than the lowest temperature of the experiment.