Quantum criticality in the spin-1/2 Heisenberg chain system copper pyrazine dinitrate

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INTRODUCTION

A quantum phase transition arises when the ground state of a quantum system changes as a function of an external parameter such as pressure or magnetic field. The quantum fluctuations associated with this instability often give rise to exotic behavior that is in stark contrast to the conventional properties of materials (1). They are suggested to be at the origin of the anomalous characteristics of a series of correlated electron systems like high-£Tcu cuprates, Fe-based superconductors, or heavy-fermion compounds (2–6). However, these systems are so complex that the underlying quantum phase transitions are often hard to identify. In this context, exactly solvable models provide an important guidance for the analysis of enigmatic quantum phase transitions in more complex systems.

Such solvable model systems can be realized by low-dimensional quantum magnets when the exchange interactions J between localized spins are effectively restricted to one or two dimensions. A particularly important model is the spin-1/2 XXZ chain

\[ \mathcal{H} = \sum_i \left[ J \left( S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z \right) + g \mu_B H S_i^z \right] \tag{1} \]

Here, $S_i^x$ is the spin-1/2 operator on site $i$, $g$ is the electronic g factor, $\mu_B$ is the Bohr magneton, $\Delta$ describes an anisotropy of the exchange coupling $J$, and a quantum phase transition can be induced by the magnetic field $H$. For $\Delta \gg 1$ or $\ll 1$, the model described by Eq. 1 covers Ising or XY spin chains, respectively, and in both cases, a transverse magnetic field, that is, $H \perp \hat{z}$, induces the Ising quantum phase transition, which is the most prominent textbook example of quantum criticality (7). Experimental realizations are, for example, the materials LiHoF$_4$ (8), CoNb$_2$O$_6$ (9) with Ising-type anisotropy, and Cs$_2$CoCl$_4$ (10, 11) with XY-type anisotropy.

A quantum phase transition belonging to a different universality class arises in spin-1/2 chains with isotropic Heisenberg exchange ($\Delta = 1$). This model represents one of the most fundamental strongly correlated quantum systems, and the exact solution of its ground state was pioneered by Bethe in 1931 (12). Much later (13, 14), this was extended to finite-temperature calculations of the free energy $F_{1D}(T, H)$ and then further improved (15), which now allows for a precise quantitative prediction of all thermodynamic properties. Up to a critical field $g \mu_B H_c = 2J$, the ground state constitutes a gapless Tomonaga-Luttinger spin liquid, whereas at $H \geq H_c$ an excitation gap opens and the magnetization is fully saturated. Close to this quantum critical field $H_c$, the free energy per spin obeys the asymptotic expansion

\[ F_{1D}(T, H) = \frac{J}{4} \left( \frac{g \mu_B H}{k_B T} \right)^2 + \frac{1}{\sqrt{J}} f_0 \left( \frac{g \mu_B H}{k_B T} \right) + \ldots \tag{2} \]

with the scaling functions $f_0(x) = -\frac{1}{\sqrt{\pi}} \int_0^\infty dy \log(1 + e^{-y^2-x})$ and $f_1(x) = -\frac{1}{2} f_0(x)f_0'(x)$ (see the Supplementary Materials). The first term in Eq. 2 is the ground-state energy of the field-polarized state that linearly decreases with increasing magnetic field. The second term defines the asymptotic scaling behavior close to quantum criticality. It arises from the thermal population of noninteracting spinon excitations, which are single spin-flip excitations of the polarized ground state that obey Fermi statistics. Their dispersion can be approximated by $\varepsilon_k = \frac{4J}{\pi} - \mu$ with mass $m = h^2/(a^2)$, chemical potential $\mu = 2J - g \mu_B H$, and lattice constant $a$. The free energy of these free spinons can be expressed in terms of the function $f_0$ after substituting $y = \lambda T k$ in the momentum integral with the thermal wavelength $\lambda_T = h/\sqrt{2mk_B T}$. The resulting linear scaling $T \sim |H - H_c|^{\nu_c}$ implies that $\nu_c = 0$ with the correlation-length exponent $\nu = 1/2$ and the dynamical exponent $z = 2$. The third term in Eq. 2 is attributed to the interaction between spinons and describes the leading correction to scaling.

An almost ideal material to study this quantum phase transition is copper pyrazine dinitrate (CuPzN$_2$). It comprises spin-1/2 chains of Cu$^{2+}$ ions along the a axis, which interact via the...
pyrazine rings (C₄H₄N₂) (see inset of Fig. 1), with an antiferromagnetic exchange J/k₀ = 10.6 K (16, 17). The electronic g factor is weakly anisotropic (18), with gₘ = 2.27 for H // b, resulting in a critical field H_c ≈ 13.9 T that is accessible by laboratory magnets. Typical signatures of quantum criticality have been reported for CuPzN (19) based on measurements of magnetization (20–22), nuclear magnetic relaxation (23), thermal expansion (24), and magnetic heat transport (25). Deviations from the Heisenberg spin chain model, Eq. 1 with Δ = 1, may result from interchain couplings or anisotropies due to staggered g tensor components, and both perturbations are present in CuPzN. However, the spin chain’s symmetry remains preserved for H // b (26), and the interchain couplings are so weak that long-range antiferromagnetic order only develops below T_N ≈ 107 mK (27) in zero magnetic field. Close to the critical field, no indication of this could be detected even down to 80 mK (20). Here, we compare a comprehensive set of thermodynamic data of CuPzN to the analytic Bethe-Ansatz solutions of the Heisenberg chain model.

RESULTS

Figure 2 gives an overview of the experimental data. The a axis thermal expansion α = (∂L_a/∂T)/L_a and magnetoostricition λ = (∂μ_a/∂(μ_aH))/L_a in part presented already in a preliminary report (24), are displayed as open symbols in Fig. 2 (A and B, respectively). Below 10 K, α is almost entirely of magnetic origin; phonons hardly contribute anymore, as is illustrated in the inset. In zero field, the magnetic contribution results in a broad maximum around 5 K, which shifts to lower temperature with increasing field. A characteristic sign change of α is observed close to H_c, reflecting entropy accumulation close to the quantum phase transition (28). Close to the critical field, the magnetostriiction λ exhibits a strong anomaly that sharpens with decreasing temperature. The magnetic contributions of the Heisenberg chain (1) to α and λ result from a pressure-dependent β(T) (for uniaxial p∥ a) and are given by α_{1D} = 1/ν_{p a} β_{p a} and λ_{1D} = 1/ν_{p a} β_{p a} μ_a(T), respectively. Here, Vₕ = 202 Å³ is the volume per spin in CuPzN and β_{2D} = β_{p a} μ_a(T). The resulting fits based on F_{1D}(T, H) of the Bethe-Ansatz solution are shown by the solid lines in Fig. 2 (A and B). For α(T, H) = α_{1D}(T, H) + α_{phon}(T), a field-independent phononic background based on the Debye model (see inset) has been included. Both α(T, H) and λ(T, H) are well reproduced, apart from some minor deviations of the low-field α(T) around 5 K, which may, in part, arise from an improper description of α_{phon}(T). The quantum critical signatures around H_c are perfectly reproduced, although there is essentially only one adjustable parameter d H/∂T} = 0.25 K GPa⁻¹ because J/k₀ = 10.6 K and gₘ = 2.27 are known from previous studies (16, 18). Note that this pressure dependence is more than one order of magnitude smaller than the corresponding values of the spin-Peierls system CuGeO₃ (29). This suggests that the magnetoelastic contribution in CuPzN is small enough that the magnetic order at 107 mK preempts a spin-Peierls transition, which is an inherent instability of half-integer spin chains toward a combined lattice and spin dimerization (30, 31).

The magnetization of CuPzN is compared to the Bethe-Ansatz solutions in Fig. 2C. At 0.3 K, the magnetic moment per spin m has a relatively sharp kink close to μ_m,H_c ≈ 13.9 T and reaches saturation above about 15 T, which causes an asymmetric peak in the differential susceptibility χ = dm/dH shown in the upper inset. With increasing temperature, the critical signatures broaden systematically, and the data are well described by the Heisenberg model (solid lines), although the agreement at lowest temperature is not as good as that of λ. The lower inset shows that the model also reproduces χ(T, μ_m,H = 1 T) up to high temperature.

The molar specific heat C as a function of temperature and field is displayed in Fig. 2 (D and E, respectively). At zero field, C(T) strongly resembles the thermal expansion. This is rooted in the single energy scale J of the Heisenberg model (1) and implies a Grüneisen scaling (C/ν_m)_{H=0} = c_{GR} · ν_m H/H, with the molar volume V_m = N_a Vₕ. The low-temperature C(H) is characterized by a slightly asymmetric double-peak structure centered at H_c that broadens with increasing temperature. Such a double peak is generic for metamagnetic quantum criticality (32). The positive curvature d²C/dH² at H_c is linked via a Maxwell relation to the curvature of the susceptibility d²χ/dT² that is positive because of the diverging χ(T → 0, H = H_c).

The behavior of C(T, H) is dominated by the magnetic contribution of the Heisenberg chains, but for its quantitative description, we also have to consider contributions from phonons and from nuclear spins. Although the phonons start to contribute above about 5 K, the nuclear contribution is relevant at lowest temperatures and high fields only, as is shown exemplarily for T = 0.3 K by the dotted line in Fig. 2E. The calculated total specific heat is then given by the solid lines, which perfectly reproduce the experimental data up to 1 K, whereas some systematic deviations on the order of 10% are found around 2.5 K, whose origin remains unclear (see the Supplementary Materials). Finally, in Fig. 2F, we present the isothermal magnetocaloric effect, that is, the field derivative of the molar entropy ∂S/∂H. Similar to α, this quantity shows a characteristic sign change approaching a divergence on decreasing temperature, which directly reflects the entropy accumulation close to H_c. Again, the experimental data are fully reproduced by the Bethe-Ansatz solution of Eq. 1 (solid lines in Fig. 2F). Note that there is also a contribution from the nuclear spin entropy, shown by the dotted line, but it is so small that it can be safely neglected.

DISCUSSION

Now, we turn to a discussion of the field-induced quantum criticality and compare the data with the scaling predictions of Eq. 2. For this,
we confine ourselves to data obtained below 2 K in the field range $\mu_B H_c \pm 4$ T. To extract the bare magnetic properties of the Heisenberg spin chains, phononic and/or nuclear background contributions are subtracted. From the full fits of Fig. 2, however, it is inferred that $C_{nuc}$ causes the only relevant correction in this low-temperature range. According to Eq. 2, susceptibility $\chi_{ID}$, specific heat coefficient $C_{ID}/T$, thermal expansion $\alpha_{ID}$, and magnetostriiction $\lambda_{ID}$ are all predicted to diverge as $1/\sqrt{T}$ at the critical field. After multiplying by $\sqrt{T}$, these quantities are described by universal scaling functions asymptotically close to the quantum critical point when plotted versus the scaling variable $g_B \mu_B \mu_0 (H - H_c)/(k_B T)$. These scaling functions are directly related to $f_0$ of Eq. 2 and are shown as solid black lines in Fig. 3 (A to D). We find a very good scaling collapse for $C_{ID}$ and $\alpha_{ID}$, but substantial deviations are observed for $\chi_{ID}$ and are even more pronounced for $\lambda_{ID}$. These deviations arise from corrections to scaling that, depending on their relative magnitude, can spoil a full scaling collapse in an extended parameter range. This is confirmed by the blue and red dashed lines that display the Bethe-Ansatz solutions for temperatures 0.25 and 2 K, respectively. As discussed in the Supplementary Materials, these corrections to scaling are only negligible in the limit $\sqrt{k_B T}/J \ll 1$, whereas $\sqrt{k_B T}/J = 15\%$ is still sizeable even at $T = 0.25$ K. The good scaling collapse observed for $C_{ID}$ and $\alpha_{ID}$ is attributed to numerical factors that are small, although formally of order one.

A quantity of particular interest close to field-induced quantum criticality is the adiabatic magnetoecaloric effect defined by the magnetic field–dependent Grüneisen parameter $\Gamma_H = - (\partial S_nuc/\partial H)/C$ that quantifies the ability of the system to adiabatically change the temperature upon a field change. General scaling considerations predict that $\Gamma_H$
diverges with characteristic exponents close to quantum criticality, which allows one to identify and classify the quantum critical point \((28,33)\). Figure 3E shows that with decreasing temperature, the obtained \(\Gamma_{\text{H,1D}}(T, H)\) of CuPzN approaches a sign-change singularity at \(H_c\), in agreement with the expected asymptotic quantum critical behavior

\[
\Gamma_{\text{H,1D}} = \frac{1}{H - H_c} \Phi \left( \frac{g \mu_B \mu_0 (H - H_c)}{k_B T} \right)
\]  

(3)

The scaling function is related to \(f_0\) of Eq. 2 via \(\Phi(x) = 2x(-f_0(x) + 2x f_0'(x))/[3f_0(x) - 4x(f_0(x) - x f_0'(x))]\). The critical \(\Gamma_{\text{H,1D}}(T, H)\) is plotted as solid lines in Fig. 3E and perfectly reproduces the experimental \(\Gamma_{\text{H,1D}}(T, H)\). The asymptotics for \(x \rightarrow \pm \infty\) result in characteristic zero-temperature divergencies \(\Gamma_{\text{H,1D}}(H - H_c)^{-1}\), with the universal prefactors \(\Phi(x \rightarrow \pm \infty) = 1 \pm 1/2 (33)\), respectively, as shown by the dashed lines. The data at 0.4 K are already close to this universal behavior but only for \(H < H_c\). Close to the critical field, \(\Phi(x) \sim C x\) with \(C \approx 0.527\) that results in the divergence \(\mu_B^{-1} \Gamma_{\text{H,1D}}(T, H_c) = k/T\), with \(k = C \mu_B \mu_0 / (k_B T) \approx 0.804 K/T\), which perfectly agrees with the data (see inset of Fig. 3E).

Closely related to \(\Gamma_{\text{H}}\) is the pressure-dependent Grüneisen parameter \(\Gamma_p = V_m \partial \alpha / \partial p\) \((28,33)\). The most singular contribution to \(\alpha_{1D}\) arises from the pressure-dependent \(H_c(p)\) so that, asymptotically, \(\alpha_{1D} V_m = - \partial S_{1D} / \partial p = (\partial S_{1D} / \partial H)(\partial H_c / \partial \tilde{p})\). This yields the proportionality

\[
\Gamma_{p,1D} = -\frac{\partial H_c}{\partial \tilde{p}} \Gamma_{\text{H,1D}} = -\frac{2}{g \mu_B \mu_0} \frac{\partial f}{\partial \tilde{p}} \Gamma_{\text{H,1D}}
\]  

(4)

close to quantum criticality. The experimentally obtained \(\Gamma_{p,1D} = V_m \partial \alpha_{1D} / \partial p\) is displayed in Fig. 3F and already indicates that, apart from the opposite signs, the field and temperature dependences of \(\Gamma_{p,1D}\) and \(\Gamma_{\text{H,1D}}\) are identical. This is quantitatively confirmed in Fig. 3 (G and H), showing that both \(\Gamma_{\text{H,1D}}(H - H_c)\) and \(-\Gamma_{p,1D}(H - H_c)/ \partial \tilde{p}\) perfectly collapse on the very same scaling function \(\Phi(x)\) from Eq. 3.

In summary, the low-temperature thermodynamics of CuPzN is excellently described by the Heisenberg spin-1/2 chain model after taking into account small phononic and/or nuclear background contributions. We have demonstrated the emergence of universal scaling behavior close to its field-induced quantum critical point. Comparison between experiment and the exact Bethe-Ansatz solution has elucidated the importance of corrections to scaling, which varies from

Fig. 3. Quantum critical scaling of thermodynamic quantities close to the critical field \(H_c\). Noncritical background contributions due to phonons and/or nuclear spins have been subtracted. Multiplication by \(\sqrt{T}\) and plotting versus the scaling parameter \(g \mu_B \mu_0 (H - H_c)/(k_B T)\) cause a collapse of (A) \(C_{1D}/T\), (B) \(\alpha_{1D}\), (C) \(\chi_{1D}\), and (D) \(\lambda_{1D}\) toward critical scaling functions (solid black lines), which are derived from \(f(x)\) of Eq. 2; symbol colors indicate different temperatures from 0.3 (blue) to 2.0 K (red). The corresponding Bethe-Ansatz results calculated for \(T = 2 K\) are shown as red dashed lines in (A) to (D) and, in addition, for \(T = 0.25 K\) as blue dashed lines in (C) and (D). The importance of corrections to scaling increases from (A) to (D), spoiling a complete scaling collapse. (E) The experimentally obtained magnetic field–dependent Grüneisen parameter \(\Gamma_{\text{H,1D}}\) (symbols) is perfectly described by its critical behavior (solid lines) given by Eq. 3. The dashed lines show the universal divergences of Eq. 3 in the zero-temperature limit, and the inset compares the corresponding \(k/T\) divergence at \(H = H_c\) with the experimental data (symbols). (F) The pressure-dependent Grüneisen parameter \(\Gamma_{p,1D}\) is, according to Eq. 4, proportional to \(\Gamma_{\text{H,1D}}\), and consequently, both Grüneisen parameters collapse on the very same scaling function \(\Phi(x)\) of Eq. 3, as shown in (G) and (H).
quantity to quantity and might spoil a scaling collapse over an extended parameter regime. This unprecedented quantitative understanding establishes CuPzN as an instructive reference material for the emergence of quantum criticality.

MATERIALS AND METHODS
Sample preparation and measurements
Single crystals of CuPzN were grown from an aqueous solution of pyrazine and Cu nitrate via slow evaporation. Typical crystals have a length along the a axis of about 10 mm. Perpendicular to the a axis, the crystals are usually smaller than 1 mm, with b being the shortest axis. Crystals of CuPzN are orthorhombic (Pnma), with the lattice constants a = 6.712 Å, b = 5.142 Å, and c = 11.73 Å (34). Magnetic fields were applied along the crystallographic b axis. Measurements of the thermal expansion and the magnetostriction were performed using a home-built capacitance dilatometer in a transverse configuration, that is, measuring the length change along the chain direction a, with the magnetic field applied along b. The uniaxial thermal expansion coefficient α and the magnetostriction coefficient λ of the a axis were obtained from the data by numerical differentiation, \( \xi = \frac{1}{\lambda} \int \frac{\partial H(x)}{\partial T} \). The specific heat was measured using a home-built calorimeter based on the relaxation time method. The addenda were obtained in a separate run and subtracted from the obtained total specific heat. The magnetization was measured with a capacitative Faraday magnetometer that was previously calibrated in magnetic fields and matched to the data taken at temperatures larger than 2 K, with the vibrating sample magnetometer (VSM) option of a commercial physical property measurement system (PPMS) (Quantum Design). The magnetocaloric effect was measured in a continuous way, as described in the Supplementary Materials.

Theoretical modeling
For the calculation of the thermodynamical potential of the spin-1/2 Heisenberg chain, we used the method described by Klümper (15). This requires the numerical solution of a set of just two nonlinear integral equations (NLIEs) for auxiliary functions. There are equivalent but numerically differently conditioned formulations of these NLIEs. Here, we used the formulation of Klümper and Scheeren (35).

The free energy per site for temperature \( T \) and magnetic field \( H \) is obtained as a contour integral

\[
\mathcal{F}_{1D}(T, H) = \frac{J - 2gH_BH}{4} - \frac{k_B T}{2\pi} \int_{C} \log(1 + a(y)) dy
\]

Here, \( C \) is a narrow closed contour around the entire real axis involving an auxiliary function \( a(x) \). This function satisfies the NLIE

\[
\log a(x) = \frac{J}{2k_B T x} + \frac{gH_B H}{k_B T} - \frac{1}{\pi} \int_{C} \log(1 + a(y)) \frac{dy}{(x-y)^2 + 1}
\]

In this formulation, the invariance of the free energy under a sign change of the magnetic field \( H \rightarrow -H \) is not manifest but, of course, true. The NLIE can be solved iteratively with fast convergence for positive values of \( H \). In numerical calculations, the integral over a function \( g(x) \) along the contour \( C \) was replaced by integrals over two functions \( g(x + i/2) \) and \( g(x - i/2) \) along the real axis. In this manner, the single-contour NLIE is equivalent to two coupled NLIEs. Convolutions were treated by fast Fourier algorithms.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/12/eaao3773/DC1

REFERENCES AND NOTES


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**Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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