Pressure-Induced Unconventional Quantum Phase Transition with Fractionalization in the Coupled Ladder Antiferromagnet C$_9$H$_{18}$N$_2$CuBr$_4$

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We present a comprehensive study of the effect of hydrostatic pressure on the magnetic structure and spin dynamics in the spin-1/2 coupled ladder compound C$_9$H$_{18}$N$_2$CuBr$_4$. The applied pressure is demonstrated as a parameter to effectively tune the exchange interactions in the spin Hamiltonian without inducing a structural transition. The single-crystal heat capacity and neutron diffraction measurements reveal that the Néel ordered state breaks down at and above a critical pressure $P_c \sim 1.0$ GPa through a continuous quantum phase transition. The thorough analysis of the critical exponents indicates that such transition with a large anomalous exponent $\eta$ into a quantum-disordered state cannot be described by the classic Landau’s paradigm. Using inelastic neutron scattering and quantum Monte Carlo methods, the high-pressure regime is proposed as a Z$_2$ quantum spin liquid phase in terms of characteristic fully gapped vison-like and fractionalized excitations in distinct scattering channels.

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Landau’s symmetry-breaking theory [1, 2] has been the cornerstone of understanding phases of matter in condensed matter physics. Despite its remarkable success, various phenomena, including the fractional quantum Hall effect [3, 4] and topologically ordered quantum matter [5, 6] have shown the limitations of this paradigm. Furthermore, continuous zero-temperature quantum phase transitions (QPTs), which exhibit emergent gauge fields and fractionalized (deconfined) degrees of freedom, also extend beyond this conventional framework. In recent years, several model systems, proposed to exhibit deconfined quantum criticality, have been exhaustively studied by analytical [7, 8] and numerical [9–12] methods. However, to the best of our knowledge, thus far there has still been no experimental realization of such unconventional QPT with fractionalization.

The $S=1/2$ magnetic insulator C$_9$H$_{18}$N$_2$CuBr$_4$ (DLCB for short) has been synthesized recently [13]. Based on the crystal structure in Fig. 1a, it is composed of coupled two-leg spin ladders with the chain direction extending along the $b$-axis. The inter-ladder coupling in DLCB is sufficiently strong to drive the system to an antiferromagnetically ordered phase below 2.0 K [14]. The staggered moments point alternately along an easy axis ($\equiv \hat{z}$), the $c^*$-axis in the reciprocal space with an ordered moment size of 0.39(5) $\mu_B$, just 40% of the saturated moment size due to strong quantum fluctuations.

The magnetic excitations of DLCB at ambient pressure can be described quantitatively [15] by the Hamiltonian of a two-dimensional model for the magnetic interactions:

$$H = \sum_{\gamma,\langle i,j \rangle} J_\gamma \left[ S_i^\gamma S_j^\gamma + \lambda \left( S_i^x S_j^x + S_i^y S_j^y \right) \right],$$

where the subscript $\gamma$ reads either ‘rung’, ‘leg’, or ‘int’–for $J_\gamma$ being the rung, leg, or interladder exchange constant—and $i$ and $j$ are the nearest-neighbor lattice sites. The parameter $\lambda$ specifies an interaction anisotropy [16], with $\lambda=0$ and 1 being the limiting cases of Ising and Heisenberg interactions, respectively. Owing to an Ising-type anisotropy, the polarized neutron study [17] confirms that the gapped triplet ($S=1$ and $S_z=0, \pm 1$) excitation energy splits into a gapped doublet ($S=1$ and $S_z=\pm 1$) as the transverse mode (TM) and a gapped “singlet” ($S=1$ and $S_z=0$) as the longitudinal or amplitude mode (LM) [18].
reflecting spin fluctuations perpendicular and parallel to the easy axis, respectively. Importantly, analysis of the spin Hamiltonian suggests that DLCB is close to the quantum critical point (QCP) at ambient pressure and zero field [14, 13, 17, 19] thus its magnetic properties could be extraordinarily responsive to an external stimulus such as hydrostatic pressure.

In this Letter, we present the compelling AC heat capacity and neutron scattering results in DLCB with hydrostatic pressure applied up to 1.7 GPa, which directly detect the magnetic order and dynamic structure factor (DSF) thus allowing us to address the nature of the static and dynamic spin-spin correlations under pressure. Figure 2(a-b) shows the order parameter of DLCB using the single-crystal neutron diffraction method. Figure 2(a-b) shows the order parameter of DLCB using the single-crystal neutron diffraction method. In order to gain more insight into the nature of this pressure-induced disordered phase, inelastic neutron scattering has been used to probe the evolution of the dynamic spin-spin correlation function of DLCB as a function of pressure. Figures 3(a) and (b) show the background-subtracted energy scans at the same AFM wavevector for various pressures. The spectral line-shapes for $P < P_c$ (or $P > P_c$) are spin-gapped and were modelled by superposition of two (or single) double-Lorentzian damped harmonic-oscillator (DHO) models convolved with the instrumental resolution function. At ambient pressure, the best fit yields the gap energies of TM and LM as $\Delta_{TM}=0.32(3)$ meV and $\Delta_{LM}=0.58(4)$ meV, respectively. Their values are consistent with the previous report [17]. We find that the peak profiles of both TM and LM for $P \leq 0.82$ GPa are limited by the instrumental resolution. Notably, TM becomes broad at 0.95 GPa with an intrinsic full width at half maximum (FWHM)=0.15(4) meV. Figure 3(b) summarizes the pressure dependence of the extracted excitation energies $\Delta_{TM}$ and $\Delta_{LM}$ across the phase transition. The slightly growing gap energy of $\Delta_{TM}$ can delay the thermal depletion of the magnetic order to higher $T_N$. $\Delta_{LM}$ becomes softened with a decrease of the ordered moment and the best fit to $\Delta_{LM} \propto (P_c - P)^\nu$ gives the correlation-length exponent $\nu=0.32(4)$ that is much smaller than $\nu \simeq 0.63$ for the 3D Ising universality class as expected for the coupled XXZ ladders [22]. Notably, recent QMC work finds a similarly small value of $\nu \simeq 0.45$ at the deconfined QCP in the $S=1/2$ square-lattice $J$-$Q$ model [26, 27]. At 1.06 GPa, slightly above $P_c$, LM has a very small gap which cannot be distinguished by the limited instrumental resolution while $\Delta_{TM}$ moves further to 0.44(3) meV. Based on the spin Hamiltonian at ambient pressure in Eq. (1), the ground state in the quantum disordered phase is expected to be a trivial dimer-
FIG. 1: (a) Crystal structure of deuterated C$_9$H$_{18}$N$_2$CuBr$_4$ projected along the crystallographic c-axis to show the stacking of discrete DMA$^+$ (C$_2$D$_4$N) and 35DMP$^+$ (C$_7$D$_{10}$N) cations.Outlined is a nuclear unit cell. (b) Phase diagram of DLCB as a function of pressure and temperature, including the pressure dependence of anisotropic energy gaps. Circle and diamond points are the energy gaps of the TM and LM, respectively. The red and black solid lines are guides to the eye. The blue line was obtained from a fit of $\Delta_LM(P) \propto (P_c - P)^\nu$ with $P_c$ fixed at 1.03 GPa and the fitted exponent $\nu = 0.32(4)$. The olive short-dashed line is obtained from $T_N(P) \propto 1/\ln(P_c - P)^{-1}$. (c) The AC heat capacity $C_P$ of DLCB as a function of temperature at ambient pressure, 0.48, 0.8, 1.0, 1.28 and 1.72 GPa. For clarity, the data are shifted upwards. The transition temperature is indicated by an arrow.

ized quantum paramagnet, where spins are paired into singlet bonds arranged in a regular pattern. Such a phase has sharp excitations. Surprisingly, the spectral line shape of the TM signal becomes significantly broader than the instrumental resolution and the best fit to the same double-Lorentzian DHO model gives an intrinsic linewidth FWHM=0.42(5) meV. Such spectral broadening persists at least up to 1.3 GPa beyond the QCP, where FWHM becomes 0.34(5) meV.

To allow a quantitative comparison to the theoretical characterization of spin dynamics, we examine the DSF using large scale QMC calculations of the same spin Hamiltonian. The Hamiltonian parameters at ambient conditions were obtained to best match the experimentally observed magnetic dispersions as $J_{\text{leg}}=0.62$ meV, $J_{\text{rung}}=0.66$ meV, $J_{\text{int}}=0.20$ meV and $\lambda=0.87$ [15]. We establish that the applied pressure is effectively tuning the exchange coupling ratio $\alpha$ between the inter-ladder and intra-ladder couplings and assume no impact on the interaction anisotropy $\lambda$ and the ratio between $J_{\text{rung}}$ and $J_{\text{leg}}$ (see the Supplementary Material [22] for further details). At the critical point or 1.3 GPa, $\alpha$ is reduced to 0.14 or 0.05 from 0.32 at ambient pressure and the parameter set ($J_{\text{leg}}=0.91$ meV, $J_{\text{rung}}=0.97$ meV and $J_{\text{int}}=0.13$ meV) or ($J_{\text{leg}}=1.03$ meV, $J_{\text{rung}}=1.1$ meV and $J_{\text{int}}=0.05$ meV) [28] gives the best agreement with the experimental value of $\Delta_{\text{TM}}$. The calculated spectral lineshape profiles as indicated by the orange lines in Fig. 3(a) are visibly limited by the instrumental resolution. Moreover, Fig. 4 shows the comparison over the entire Brillouin zone between the experimental excitation spectra at 1.06 and 1.3 GPa and DSF calculated by QMC and convolved with the instrumental resolution function. Clearly, the experimental data cannot be reproduced by QMC calculations for the Hamiltonian in Eq. (1).

So what is the probable origin of the continuum-like broad excitation of DLCB? We have carried out single-crystal neutron diffraction experiments under pressure by measuring more than 300 nuclear Bragg peaks and the fitting outcome as listed in Tabs. S2-S5 of the Supplementary Material [22] does not reveal any evidence of chemical disorder under pressure except a small H/D isotope effect on site occupancy. The latter has no influence on the magnetism of non-hydrogen-bonded systems such
as DLCB. Consequently, it can be ruled out that the observed broadening is due to disorder. The other possible broadening effect, attributed to spontaneous quasiparticle decays [29, 30], is also discussed in the Supplementary Material [22] and can be excluded mainly due to violation of the kinematic conditions [31]. Moreover, at the critical pressure, the critical exponent $\eta$ which describes the decay of the correlation function is related to other critical exponents by the scaling law [23]: $\eta = 2\beta/\nu - (d + z - 2)$, where $d$ is the number of spatial dimensions and $z$ is the dynamic critical exponent. Assuming $d = 2$ based on the strong two-dimensional character of the magnetism in DLCB, and $z = 1$ at the pressure-induced quantum phase transition [23], we obtain $\eta = 3.0(5)$ from $\beta = 0.65(5)$ and $\nu = 0.32(4)$ as already stated above. This is in marked contrast to the value $\eta = 0.036$ in the conventional 3D Ising transition [22]. With fractionalization, the Landau order parameter becomes a composite operator of partons, which leads to a large $\eta$ [12]. The large $\eta$ can explain the broad spectral linewidth near the transition in DLCB and further suggests that emergence of the gapped phase with fractionalized excitations through this pressure-induced phase transition cannot be described by Landau’s paradigm.

Consequently, we propose that the quantum disordered phase with $P > P_c$ is a gapped quantum spin liquid (QSL) state with fractionalized degrees of freedom. In order to stabilize such a QSL state in DLCB, a mechanism that is not included in the original Hamiltonian is required. Indeed, for unfrustrated interactions, an ordinary quantum phase transition to a trivial quantum paramagnet emerges [23]. The possibility of diagonal frustrating couplings in the ladders can be eliminated due to their unfavorable superexchange paths in DLCB. On general grounds, higher order four-spin interactions such as those around plaquettes are also expected to be negligible for molecular ladder systems. One may also consider further anisotropic exchange terms, the Dzyaloshinskii-Moriya (DM) interactions. In DLCB, DM interactions are forbidden along the rungs of the ladders and between the ladders by the inversion symmetry, but are allowed along the ladder legs. DM anisotropy has been investigated by ESR measurements in other metal-organic ladder compounds including (C$_7$H$_{12}$N)$_2$CuBr$_4$ (BPCB) [32] and (C$_7$H$_{10}$N)$_2$CuBr$_4$ (DIMPY) [32, 33], and was found to be about 5% of the dominant exchange interactions. In general, DM interactions prefer non-collinear magnetic structures, and in DLCB the effects of the DM interactions on the collinear ordered state within the Néel phase should thus be very weak. Indeed, the field dependence of the anisotropic energy gaps at ambient pressure [17]
FIG. 4: Comparison between the experimental data and QMC calculations. False-color maps of the excitation spectra as a function of energy and wavevector transfer along two high-symmetry directions (H,H,-0.5) and (0.5,0.5,-L) in the reciprocal space, respectively. Experimental data were collected at MACS at $T=1.5$ K and (a) $P=1.06$ GPa and (c) $P=1.3$ GPa. Data for H less than 0.4 r.l.u. are not shown due to a contamination by the direct neutron beam. (b) and (d) are dynamic structure factors of the TM calculated by QMC using the parameter sets at the critical point and 1.3 GPa, respectively, as described in the text. Simulations were convolved with the instrumental resolution function where the neutron polarization factor and the magnetic form factor for Cu$^{2+}$ were included.

(c) High-resolution inelastic neutron scattering measurements at CNCS at $T=0.25$ K and $P=1.3$ GPa. The excitation spectra at $T=15$ K are shown in Fig. S4(c) of the Supplementary Material [22]. No smoothing or symmetrization was applied to all experimental data.

agrees well with the Zeeman spectral splitting, which suggests that $S^z$ is a good quantum number. It is possible, that the effects of the DM interactions become enhanced within the QSL phase. Although we note that a recent study finds that QSL phases can be stable at weak DM interactions [35], further theoretical work is needed to establish the proper lattice Hamiltonian for the entire phase diagram.

One simple example of gapped QSL with fractionalization is the $Z_2$ spin liquid, which has been shown to exist in quantum dimer model on the triangular lattice [36] and also XXZ spin model on the Kagomé lattice [37]. Such a $Z_2$ QSL state exhibits non-trivial topological order, which is characterized by, e.g., the topological degeneracy of the ground states. It furthermore exhibits two primary types of excitations: spinons that carry a $Z_2$ gauge charge and visons that carry $Z_2$ gauge flux [38, 39]. These excitations are bosonic, with a semi-ionic mutual statistics. In the easy-axis limit, the visons transform as $S^z=0$ (singlet) excitations under the U(1) symmetry about the easy-axis [37], i.e., they reside within the LM channel for DLCB. High-resolution inelastic neutron scattering was used in order to nail down the possible vison excitations deep in the QSL phase. The excitation spectra at $P=1.3$ GPa in Fig. 4(c) clearly show two well-separated gapped modes including one broad continuum-like and another almost dispersionless excitation. At the AFM wavevector, cf. Fig. 4(b), we clearly identify two distinct excitations: (i) a broad peak at about 0.56(4) meV with a FWHM of 0.36(4) meV, which we identify as arising from fractionalized excitations as spinons, and (ii) an additional, resolution-limited excitation at 0.25(3) meV, identified as the vison excitation.

In summary, we have performed neutron scattering experiments under pressure on DLCB at low temperature and continuously tuned the ground state of the compound $C_9H_{18}N_2CuBr_4$ from the AFM Néel state, through an unconventional QPT with a large anomalous exponent $\eta$, to an exotic quantum disordered state. By contrasting with QMC calculations for the conventional spin model for DLCB, the unique ability of neutron scattering to probe spin pair correlation functions allows one to experimentally identify fully gapped vison-like and fractionalized excitations consistent with a possible $Z_2$ QSL state. Our study offers a much-needed experimental platform to search for QSL physics along with the associated quantum criticality within a single compound.

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[1] L. D. Landau, Phys. Z. Sowjetunion 11, 26 (1937).
In order to minimize the number of fitting parameters to be determined from the experimental dispersion data, we assume that $\lambda$ is the same for all $J$’s. Note that this assumption is made to prevent overparameterization and would not affect the main conclusion of this work.

In a broad maximum at $T \approx 1$ K in the AC heat capacity is observed above $P_c$. It is attributed to a Schottky anomaly, which is not indicative of a phase transition but indicative of a gapped ground state with short-range spin correlations.

See Supplemental Material for details on experimental methods, data analysis, quantum Monte Carlo calculations, the unusual phase boundary near the transition, spontaneous quasiparticle decays and crystal structure and magnetic interactions under pressure.