Quantum Criticality in an Organic Magnet

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Exchange interactions between \( S = \frac{1}{2} \) sites in piperazinium hexachlorodicuprate produce a frustrated bilayer magnet with a singlet ground state. We have determined the field-temperature phase diagram by high field magnetization and neutron scattering experiments. There are two quantum critical points: \( H_{c1} = 7.5 \) T separates a quantum paramagnet phase from a three dimensional, antiferromagnetically-ordered state while \( H_{c2} = 37 \) T marks the onset of a fully polarized state. The ordered phase, which we describe as a magnon Bose-Einstein condensate (BEC), is embedded in a quantum critical regime with short range correlations. A low temperature anomaly in the BEC phase boundary indicates that additional low energy features of the material become important near \( H_{c1} \).

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The concept of a critical transition between different phases of matter at temperature \( T = 0 \) is central to many complex phenomena in strongly correlated systems [1]. Quantum critical points (QCPs) give rise to anomalous properties through a range of temperatures, and may be responsible for heavy fermions [2], non-fermi-liquids [3], and the anomalous normal state of doped cuprates [4]. Among the non-thermal tuning parameters accessible to the experimentalist, doping has been applied to access QCPs in heavy fermion intermetallics [5, 6] and copper oxide superconductors [7], and hydrostatic pressure has been used to expose anomalous superconducting [8] and metallic [9] phases in weak itinerant magnets. While magnetic fields generally induce conventional transitions defined by the onset of Néel order at higher field, the terms QP, LRO and FP are explained in the text. Inset: PHCC structure showing the Cu\(^{2+}\) \( S = \frac{1}{2} \) sites (solid circles) viewed along the \( b \) axis. Interacting spins are connected by lines with thickness proportional to the contribution to the \( H = 0 \) ground state energy. Red[blue] bonds are frustrated[unfrustrated] and increase[decrease] the ground state energy. Numbering corresponds to Ref. [10]. Vectors show the ordered spin structure at \( T = 1.65 \) K and \( H = 13.7 \) T.

FIG. 1: (Color online) Differential susceptibility \( \chi(H, T) \) for PHCC. Solid white line for \( H < 14.2 \) T is the the line of phase transitions defined by the onset of Néel order at higher field. The terms QP, LRO and FP are explained in the text. Inset: PHCC structure showing the Cu\(^{2+}\) \( S = \frac{1}{2} \) sites (solid circles) viewed along the \( b \) axis. Interacting spins are connected by lines with thickness proportional to the contribution to the \( H = 0 \) ground state energy. Red[blue] bonds are frustrated[unfrustrated] and increase[decrease] the ground state energy. Numbering corresponds to Ref. [10]. Vectors show the ordered spin structure at \( T = 1.65 \) K and \( H = 13.7 \) T.

phonons are important thermodynamic degrees of freedom close to the QCP.

Experiments were carried out on the quasi-2D \( S = \frac{1}{2} \) quantum AFM piperazinium hexachlorodicuprate (\([Cu_2H_2N_2]Cu_2Cl_6 \equiv \text{PHCC})\). The crystal structure is composed of Cu-Cl sheets in the \( a-c \) plane, separated by piperazinium layers [11, 12]. Magnetic properties are dominated by the Cu-Cu interactions within individual sheets shown in Fig. [11]. The magnetic connectivity is that of an oblique bilayer, with the strongest bond, \( i.e. \) the dimer, bond 1, providing interlayer coupling. Frustrated interlayer bonds 2 and 8 may also play a role in

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producing a singlet ground state with strong correlations to five near neighbors. Magnetic excitations at $H = 0$ are dominated by a dispersive triplet of magnons, also known as the triplon, with a bandwidth $W = 1.8$ meV and an energy gap $\Delta = 1$ meV. Cluster expansion analysis of the triplon are degenerate to within 0.05 meV. A room temperature graphite filter or a liquid nitrogen cooled beryllium filter was employed in the scattered beam for neutrons $H < 46$ K and 3 K, and of the $(\frac{1}{2},\frac{1}{2},0)$ Bragg peak at $H = 14.2$ T, compared to $\chi(0,H,T)$.

Magnetic susceptibility measurements were performed at the National High Magnetic Field Laboratory using a compensated-coil susceptor in pulsed fields up to $H = 50$ T for 0.46 K $\leq T \leq 30$ K. The sample was a 1.36 mg hydrogenous single crystal with $\mathbf{H} \parallel \mathbf{b}$. Elastic neutron scattering measurements were performed on the FLEX spectrometer at the Hahn-Meitner Institut (HMI). The sample was composed of two 89% deuterated single crystals with total mass 1.75 grams, coaligned within 0.5° and oriented in the $(h0l)$ scattering plane, $\mathbf{H} \parallel \mathbf{b}$. A room temperature graphite filter or a liquid nitrogen cooled beryllium filter was employed in the scattered beam for neutron energies 14.7 and 2.5 meV respectively. Beam divergence was defined by the $^{58}$Ni neutron guide before the monochromator and 60° collimators elsewhere.

Differential magnetic susceptibility data, $\chi(H,T) = dM/dH$, are shown in Fig. 4(a). At $T = 0.46$ K there is evidence for two quantum transitions from gapped phases with $\chi = 0$ for $H < H_{c1} \approx 7.5$ T and $H > H_{c2} \approx 37$ T to a magnetizable state in the intermediate field range. $\chi(H)$ at the lower transition is shown in Fig. 4(b). Integrating $\chi(H,T = 0.46$ K) yields a saturation magnetization of 1.097(3) $\mu_B$ per spin, identifying the high field phase as fully spin-polarized (FP).

In the intermediate field phase AFM Bragg peaks were found at wave vectors $\mathbf{Q} = \tau + (0.5,0,0.5)$ where $\tau$ is a reciprocal lattice vector of the chemical cell. The lower bound on the order parameter correlation length in the $\mathbf{a} - \mathbf{c}$ plane is $2.0(2) \times 10^3$ Å. Analysis of peak intensities yields the spin structure in Fig. 4 which is consistent with bond energies measured in the zero field phase in that (un)frustrated bonds correspond to (anti)parallel spins. Normalizing to incoherent scattering and assuming long range order (LRO) along $\mathbf{b}$ yields $g\mu_B(S) = 0.33(3)g\mu_B$ at $T = 1.65$ K and $H = 13.7$ T.

Figure 2 shows the order parameter onset in $H - T$-sweeps. While the onset of Bragg scattering coincides with the onset of elevated $\chi(H)$ for $T \approx 0.4$ K, Bragg peaks first appear well within the high susceptibility state for $T \approx 3$ K. A similar conclusion is reached based on the $T$-sweep at $H = 14.2$ T where the critical temperature for LRO is $T_c(14.2$ T) = 3.705(3) K compared to the $T \approx 8$ K onset of the high susceptibility state. The solid line for $H < 14.2$ T in Fig. 4 is the phase boundary inferred from neutron diffraction with further details in Fig. 2(a). For $T > 0.5$ K, the LRO phase resides well within the high susceptibility state.

At low $T$, the phase boundary to Néel order approaches the onset of the high susceptibility state, and for $T < 0.4$ K there is no intermediate phase that can be distinguished from the data. At lower $T$, field sweeps of the magnetic Bragg intensity, shown in Fig. 4(a), indicate a minimum in the phase boundary for $T \approx 0.2$ K. Plotted versus $T$ in Fig. 4(b), these data show an intensity maximum for $T \approx 0.2$ K and $7.4 < H < 7.9$ T indicating that PHCC passes into and then back out of the LRO phase in this field range.

Figures 2 and 4 show a rounded onset of magnetic scattering in PHCC. If critical fluctuations are responsible for this, the energy scale must be less than the $\approx 50 \mu$eV energy resolution. Alternatively, field inhomogeneity can smear a singular onset. The solid lines in Figs. 2 and
that if $M/M_{\text{plateau}}$ from which we obtain $v_0$. If bi-layers in PHCC were fully decoupled from each other the BEC would change into a KT vortex-unbinding transition. In 2D the crossover exponent $\phi = 1$, so in contrast to the observed phase boundary a KT phase boundary $H_{c}(T) = H_{c}(0) + CT^{\phi}$ would be linear for $T \to 0$. This is consistent with a recent comprehensive analysis of magnon condensation in 2D by Sachdev and Dunkel [27]. Hence it appears that 3D BEC rather than vortex unbinding is the appropriate description of the field induced transition to LRO in PHCC.

The experimental high $T$ limit for the critical exponent $\beta = 0.34(2)$ obtained by averaging PHCC data for $0.5 \text{ K} < T < 4 \text{ K}$ is consistent with a 3D XY model for which $\beta = 0.345$ [28]. Upon cooling through the temperature $T \approx 0.4 \text{ K}$ where $H_{c}(T)$ merges with the 2D BEC cross over inferred from magnetization data, the experimental values for $\beta$ increase. The apparent increase of the exponent $\beta$ is consistent with an expected crossover from a thermally driven transition to a quantum phase transition. Because the upper critical dimension of the

$H(a)$ were obtained by fitting the width of a rectangular field distribution as well as the critical field, $H_c(T)$, and the critical exponent, $\beta$. While a 3.6(1)% distribution width accounts for the data, it exceeds the $\approx 1\%$ width expected over the sample volume in the HMI magnet. An additional potential source of static broadening are impurities that produce effective random fields$^{20}$. An applied field drives the chemical potential for

**Systematic values for $H_c(T)$ and $\beta$ were obtained by fitting the data in Figs. 2 with the apparent field distribution width fixed at 3.6%.** The corresponding phase boundary in Fig. 3(a) affirms the existence of a wedge in $H - T$ space with neither LRO nor a spectral gap. Taylor expansion of the phase boundary about a generic point $(H_c, T_c)$ on the line of transitions, as follows $H_c(T) \approx H_c(T_c) + H_c'(T_c)(T - T_c)$, clearly shows that if $M(H, T) \propto (H - H_c(T))^\beta$ then $M(H_c, T) \propto (H_c'(T_c)(T - T_c))^\beta$. Hence the consistent values of $\beta$ extracted from $H -$ and $T -$ scans at $T \approx 3.5 \text{ K}$ instill confidence in the experiment and analysis (see Fig. 3(b)).

Recent experimental and theoretical work on interacting dimers indicates that the phase transition to long range Néel order can be described as a BEC of magnons$^{21}$. An applied field drives the chemical potential for spin polarized magnons ($S_z = 1$) to zero causing BEC at sufficiently low $T$. In 2D, BEC can only occur at $T = 0$ so we associate the sharp increase in $\chi(H)$ indicated by solid points in Figs. 2(a) and 3(a) with the corresponding finite temperature quantum critical regime. In the immediate vicinity of the LRO phase boundary the critical phase is denoted renormalized classical (RC)$^{22}$ though there are no notable distinctions between the RC and QC regimes in the present data. The the renormalized critical regime is characterized by a small population of magnons that behave as individual particles. The finite $T$ transition to Néel order may be BEC resulting from weak inter-bi-layer coupling or a 2D Kosterlitz-Thouless (KT) transition. To distinguish these scenarios we explore the corresponding theoretical phase boundaries. Following Nikuni et al. 23 and Misguich and Oshikawa 24 we treat magnons as bosons with a chemical potential $\mu = g\mu_B(H - H_c(0))$ and short range repulsion, $v_0$:

$$\mathcal{H} = \sum_k \left(\epsilon_k - \mu + v_0 n_b a_k^\dagger a_k + \frac{v_0}{V} \sum_{q,k,k'} a_q^\dagger a_k^\dagger a_{q+k} a_{q-k} a_{q-k} a_{q+k}\right).$$

$$n_c(T) = \frac{1}{V} \sum_k \frac{1}{\exp(\epsilon_k/T) - 1}$$

$$H_c(T) = H_c(0) + 2v_0n_c(T)/g\mu_B.$$  

We assume quasi-2D magnon dispersion $\epsilon_k = \epsilon_{2D}^q + 2\gamma(1 - \cos(k_y b))$ with $\epsilon_{2D}^q$ from experiments 17. When $T \ll \gamma$, only the bottom of the magnon band is thermally excited and one may replace the exact band structure with parabolic dispersion to obtain

$$n_c(T) = \zeta(3/2) \left(\frac{m_{3D} T}{2\pi h^2}\right)^{3/2},$$

where $m_{3D} = (m_a m_b m_c)^{1/3}$ is the 3D effective mass. In the limit of a very weak inter-bi-layer tunnelling there is a regime $\gamma \ll T < W$ where the in-plane dispersion can be treated as parabolic and the critical density for a quasi-2D Bose gas is obtained 26

$$n_c(T) = \frac{m_{2D} T}{2\pi h^2 b} \log \frac{2T}{\gamma}.$$
FIG. 4: (Color online) Magnetic field (a) and temperature (b) dependent scattering intensity of the $\frac{1}{2}$ spin ordered phase, showing reentrant behavior of the gapped phase near $T_c$. The solid line is the model described in text. Temperature dependence collected from individual magnetic field dependent measurements with a width of $\Delta H = 0.1$ T.

Zero-temperature BEC is $d_c = 2$, $\beta$ has a mean-field value of 1/2.

A discrepancy in the description of the phase diagram for PHCC presented so far exists for $T < 0.3$ K where the observed critical field exceeds the BEC phase boundary (Eqs. 4 and 3) with a finite $T \approx 0.2$ K minimum (Figs. 3 and 4). Various low energy aspects of PHCC may be responsible for this behavior. Owing to the low symmetry of the lattice, exchange interactions in PHCC must be anisotropic which could lead to an Ising transition at sufficiently low $T$. Alternatively nuclear spins, and phonons which are effectively decoupled from magnetism at high $T$ and normally unimportant compared to exchange interactions at low $T$ may become relevant close to the field tuned QCP. Similar low $T$ anomalies have been found in other electronic spin systems close to quantum criticality such as GGG, LiHoF$_4$, and ZnCr$_2$O$_4$. In LiHoF$_4$, the anomaly favors the spin ordered phase and is associated with hyperfine coupling to the nuclear spin system. The spin ordered phase is also favored for ZnCr$_2$O$_4$ where the anomaly is associated with magneto-elastic coupling. Low temperature spin-lattice coupling is also observed in the spin-gap systems TiCuCl$_3$ and CuHPc. For PHCC, the singlet ground state may be affected by coupling to Cu nuclear spins for $T < 0.2$ K. This could help to stabilize bond order over spin order and explain our failure to discover additional phase boundaries at low $T$. Alternatively, $H = 7.4$ T and $T = 0.2$ K may be a tetra-critical point separating the bond ordered phase, the $(0.5, 0.5)$ type spin ordered phase and a yet to be detected magneto-elastic or nuclear + electronic spin ordered phase.

The $H - T$ phase diagram for PHCC illustrates many important aspects of strongly correlated systems. There is evidence for a finite $T$ crossover to a quasi-2D RC phase with 3D BEC at lower $T$ and higher $H$. We also presented evidence for a non-monotonic phase boundary to spin order at low $T$, which indicates that exchange anisotropy, nuclear spin and/or lattice degrees of freedom can be important close to quantum criticality.

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