Thermodynamics of a frustrated quantum magnet on a square lattice

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We report the magnetic and calorimetric measurements in single crystal samples of the square lattice \( J_1 - J_2 \) quantum antiferromagnet \( \text{BaCdVO(PO}_4\text{)}_2 \). An investigation of the scaling of magnetization reveals a “dimensionality reduction” indicative of a strong degree of geometric frustration. Below a characteristic temperature of \( T^* \approx 150 \text{ mK} \) we observe the emergence of a new strongly fluctuating quantum phase close to full magnetic saturation. It is separated from the magnetically ordered state by 1-st and 2-nd order phase transitions, depending on the orientation of the applied magnetic field. We suggest that the new phase may indeed be the theoretically predicted spin nematic state.

The quest for the so-called spin nematic state started more than three decades ago, but continues to this day [10]. This exotic magnetic order spontaneously breaks rotational symmetry, while keeping time reversal symmetry intact. It can be understood as a quantum condensate of bound magnon pairs [2–4]. The key characteristics of any potential host system are competing ferro- (FM) and antiferromagnetic (AF) interactions and extreme quantum fluctuations. The baseline model is the \( S = 1/2 \) square lattice Heisenberg Hamiltonian with FM nearest-neighbor exchange \( J_1 \) and AF next nearest neighbor coupling \( J_2 \) [3, 7–10] sketched in Fig. 1(a) alongside its phase diagram. The classical critical point at \( J_1 / J_2 = -1/2 \) separates FM and columnar-AF states, but becomes destabilized by quantum fluctuations. This gives rise to a spin nematic phase in its immediate vicinity [3, 9]. Even outside this narrow parameter range, spin nematicity can be induced by an external magnetic field close to saturation [3, 11].

Despite the vast body of theoretical work, experimentally the spin nematic state on a frustrated square lattice remains elusive. One obvious problem is that the tensorial order parameter is invisible to most conventional magnetism probes. What is an even bigger obstacle, is that potential model compounds are few and hard to synthesize. The most promising known candidate is \( \text{BaCdVO(PO}_4\text{)}_2 \) [12, 13]. The applicability of the \( J_1 - J_2 \) model to this compound has been validated by DFT calculations [14]. The material features strong geometric frustration \((J_1 / J_2 \approx -0.9)\) and easily accessible energy scales (saturation field about 4 T, AF order below \( T_N = 1.05 \text{ K} \)). The high temperature thermodynamics is consistently described by \( J_1 = -3.6 \text{ K} \) and \( J_2 = 3.2 \text{ K} \) [12]. For lack of other candidates, \( \text{BaCdVO(PO}_4\text{)}_2 \) has been a subject of intense theoretical studies, including specific predictions for inelastic neutron scattering [15] and nuclear magnetic resonance [16]. Disappointingly, a lack of single crystals has severely impeded experimental studies. To date, no empirical evidence of a spin nematic phase or any related unconventional magnetism has been reported.

In the present Letter we describe the unusual magnetic and thermodynamic properties of single crystal samples of \( \text{BaCdVO(PO}_4\text{)}_2 \). We map out the anisotropic magnetic phase diagram and study the “dimensionality reduction” and peculiar scaling of magnetization near the field-induced quantum phase transition. In what may be the first sign of spin-nematicity, we report evidence of

![FIG. 1.](image-url)
a novel low-temperature field-induced strongly fluctuating quantum phase just below saturation. In an axially symmetric geometry the new phase emerges in a 1-st order transition, and is preceded by substantial precursor fluctuations in the magnetically ordered state.

High quality green transparent single crystals of BaCdVO(PO$_4$)$_2$ were grown using the self-flux Bridgman method. The crystal structure (orthorhombic $P_{baa}$, $a = 8.84$, $b = 8.92$, $c = 19.37$ Å) was validated using single crystal X-ray diffraction on a Bruker APEX-II instrument, and found to be totally consistent with that reported previously [18]. New insights were obtained already in straightforward magnetization studies. Magnetic susceptibility [19], measured on a 16 mg crystal in fields applied along each of the three crystallographic axes reveals the special role of the $H||a$ orientation. Above $T_N$ the susceptibilities [Fig. 1(b)] are identical up to the corresponding $g$-factor values. The latter were determined to be $g_{a,b,c} = [1.95(1), 1.97(1), 1.92(1)]$ [17], consistent with powder EPR estimates [20]. In contrast, at low temperatures $\chi_b(T)$ and $\chi_c(T)$ remain more or less constant below $T_N$, while $\chi_a(T)$ shows a rapid decrease upon cooling. This suggests a collinear magnetic structure with spins along the $a$ axis. This interpretation is backed by isothermal magnetization $M(H)$ scans at $T = 0.55$ K [Fig. 1(c)]. For the $H || a$ case (and only for that geometry) there is a pronounced magnetization jump around $H_{SF} \simeq 0.5$ T. This behavior is characteristic of a spin-flop transition driven by the weak Ising-like anisotropy, $a$ being the magnetic easy axis. Thus, using a simple Heisenberg model to describe the system can only be done with caution. Below we shall refer to experiments with $H || a$ as the axial geometry, and to those with a field in perpendicular directions as transverse.

The most striking feature of the measured magnetization curves is there extreme convex shape close to the saturation. It serves as a reliable indicator of the significant magnetic frustration, indirectly confirming the nearly-critical positioning of BaCdVO(PO$_4$)$_2$ on the $H-T$ phase diagram. To see this, we note that the measured convex magnetization curve is reminiscent of the cusp singularity occurring at saturation in the AF spin chains [21, 22]. This feature is endemic to one dimension (1D), but appears in our essentially 2-dimensional material thanks to “dimensional reduction” [23, 24]. Due to frustration, the otherwise 2D spin wave minima become flattened along one of the momentum directions as $H_c$ is approached. This renders the low-energy spectrum as being effectively 1D [24].

To make this argument for BaCdVO(PO$_4$)$_2$ quantitative, we studied the $H-T$ scaling of magnetization near saturation in the axial geometry. $M(H,T)$ data measured vs. applied field at different temperatures are shown in Fig. 2(a). Quantum criticality implies the following general scaling relation:

$$1 - M(H,T)/M_{sat} = T^m \mathcal{M}\left(\frac{g\mu_B(H - H_c)}{T^{1/\varphi}}\right). \quad (1)$$

All measurements are thus expected to collapse onto a single scaling curve if rescaled with appropriate exponents. In order to determine the latter, for the data in Fig. 2(a) we defined an empirical goodness-of-overlap $\chi^2$ following [17, 25]. Using $H_c = 3.95(2)$ T obtained in calorimetric measurements as described below, we plot $\chi^2$ as a function of $m$ and $1/\varphi$ in the inset in Fig. 2(b). The best overlap is found for $m = 0.8(1)$ and $1/\varphi = 1.6(3)$, and results in a spectacular data collapse shown in Fig. 2(b) (main panel). The measured finite-$T$ exponents are quite distinct from those in the pure one-dimensional case, where $m = 1/2$ and $\varphi = 1$ [21, 26]. Nonetheless, the observed exponent describing the magnetization cusp in the $T \rightarrow 0$ limit $M_{sat} - M(H) \propto (H_c - H)^{m\varphi}$ is the same, namely $m\varphi = 0.5 \pm 0.15$, and agrees well with this prediction made for the perfectly frustrated square lattice [24].

Further unusual behavior was revealed by specific heat measurements. These were carried out on a standard Quantum Design relaxation calorimetry option and the $^3$He-$^4$He Dilution Refrigerator inset for PPMS. Two measuring geometries $H || a$ and $H || b$ were realized by mounting a 2.3 mg flat single crystal sample on a small silver foil angle with Apiezon N grease. In both orientations, cooling in zero applied magnetic field the $C_p(T)/T$ curve displayed in Fig. 3(a) shows a pronounced lambda anomaly at $T_N = 1.05$ K, followed by a power law decrease, consistent with the previously reported powder data [12].

Tracking the phase transition to reconstruct the $H - T$ phase diagram is often easier in constant-$H$ scans, shown in Figs. 3(f)-(j). However, these data reveal a striking difference between axial and transverse geometries. The

![Figure 2](image-url)
FIG. 3. Low temperature specific heat in BaCdVO(PO$_4$)$_2$ for axial and transverse geometries of the magnetic field. (a-e) $C_p(H,T)/T$ as the function of $T$ for different magnetic fields. Dashed lines show the power laws that can be identified in the data. (f-j) $C_p(H,T)$ at fixed temperature as the function of $H$. Arrows indicate excess specific heat appearing at low temperatures above the field-induced phase transition.

FIG. 4. Magnetocaloric effect in BaCdVO(PO$_4$)$_2$ at low temperatures in the axial field geometry. The $T(H)$ dependencies taken at different temperatures with the field sweeping rate of ±5 Oe/sec.

FIG. 5. Magnetic phase diagram for $H \parallel a, b$. The background shows the false color map of $C_p(T,H)/T$, thin and thick black solid lines represent the phase transitions (of second or first order correspondingly) and grey dashed lines mark crossovers. Points are the ordered phase boundary data obtained from $C_p$ anomalies. The phases are: PM — paramagnetic, FP — fully polarized, AF — antiferromagnetic, SF — antiferromagnetic after the spin flop, QC — quantum critical regime, LT — unconventional low temperature regime. Crossover lines marking the QC regime follow $T \propto |H - H_c|^\varphi$ with the same crossover exponent $\varphi$ found from scaling Eq. (1).

First key result of our calorimetry studies is that in the axial case, the field-induced transition becomes discontinuous at low temperatures. Above $T^* \simeq 0.15$ K both geometries yield a sharp $C_p(H)$ peak, marking a second-order transition [Figs. 3(f)-3(h)] at a critical field $H_c$. In the vicinity of $H_c$ and at all field above it the data for the two geometries are virtually indistinguishable. In contrast, below $T^*$ the character of the anomaly in the axial geometry changes. As shown in Figs. 3(i),3(j) it rapidly evolves from a peak to a step-like feature, similar to the step found at the spin flop (a textbook example of discontinuous transition in a magnet).

The discontinuous character of the low-temperature field-induced transition in the axial case is also confirmed by measurements of the magnetocaloric effect. Utilizing the same setup as for the relaxation calorimetry, we directly read the sample temperature during slow magnetic field sweeps, while keeping the heat bath temperature constant. In this so-called equilibrium regime the excess thermal power created due to the sample’s entropy change is balanced by the temperature gradient between the sample and the bath across the weak heat link. The evolution of the resulting sample’s $T(H)$ curves for up and down magnetic field sweeps is shown in Fig. 4. The first order spin flop transition manifests itself as a highly asymmetric peak-like feature at all the temperatures. This is a direct consequence of the entropy discontinuity. In contrast, at elevated temperatures the
magnetocaloric anomaly at $H_c$ is very symmetric, as it should be for a continuous transition \cite{20,30}. However, below around $T^*$ this anomaly rapidly becomes rather asymmetric as well, confirming the change of the transition type.

The second and perhaps most important finding of our calorimetry experiments is that there is an additional anomalous contribution to specific heat at the lowest temperatures above $H_c$ in both geometries. It can be seen in both constant-$T$ \cite{Fig. 3(j)] and constant-$H$ scans [Fig. 3(c)]. At 100 mK it persists as a plateau all the way up to $H_c^* \approx 5.2$ T, but vanishes at higher fields [Fig. 3(c)]. We conclude that in BaCdVO(PO$_4$)$_2$ at the lowest temperatures $H_c$ does not correspond to the full saturation. Indeed, the latter would open a Zeeman gap in the spectrum and suppress any magnetic specific heat. Instead, $H_c$ indicates the appearance of a new quantum phase with substantial low-energy fluctuations. As shown above, in the axial geometry it is entered from the spin-flop AF phase through a discontinuous transition. Incidentally, this is exactly the type of behavior expected for the spin-nematic phase predicted to emerge just below full saturation \cite{10}.

In the transverse geometry, the spin nematic phase can not exist in a field due to a lack of axial symmetry \cite{31}. While strong spin fluctuations may persist in this case as well, as they do in BaCdVO(PO$_4$)$_2$, there will be no nematic order. This may explain why the transition at $H_c$ remains continuous in this setting.

There are indications that spin fluctuations associated with the new low-temperature high-field phases are present already in the ordered states. There too we find anomalous contributions to specific heat below the crossover temperature $T^* \approx 0.15$ K [Figs. 3(a)-3(c)]. They roughly follow $C_p(T) \propto T^{-1.5}$ and are particularly strong in the axial geometry in the spin flop state.

In the above discussion we don’t make any mention of a possible nuclear contribution to specific heat. As detailed in the supplement, we can convincingly show that the observed features are totally inconsistent with the specific heat of free spins corresponding to the nuclei in the system. In short, the latter is expected to increase with field as $C_{p}^{\text{Nuc}} \propto (H/T)^2$ \cite{17,32}, while the observed anomalous contribution actually vanishes above $H_c^*$. Nonetheless, since nuclear spin $I = 7/2$ is also carried by the magnetic $S = 1/2$ $^{51}$V$^{4+}$ ions, some complex behavior induced by hyperfine coupling close to the quantum critical point can not be fully ruled out. There are some experimental \cite{33} and theoretical \cite{34} studies of hyperfine coupled settings, but not for the strongly frustrated 2D case.

Our results for BaCdVO(PO$_4$)$_2$ are summarized in the $H-T$ phase diagram in Fig. 3. We distinguish conventional paramagnetic (PM), field polarized (FP) and antiferromagnetic states (AF and its post-spin-flop version SF). At intermediate temperatures a quantum critical regime (QC) is observed above $H_c$. The new low-temperature field-induced phases, which in the axial case we suggest may be a spin nematic state, are labeled as LT. While they are separated from the ordered states by obvious phase transitions, their finite-$T$ boundaries can not be clearly identified in our calorimetry data.

The high hopes for finding unconventional magnetism in BaCdVO(PO$_4$)$_2$ appear to be well justified. Future work aimed at understanding its origins will have to specifically focus on the lowest temperatures.

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