Interplay of frustration and magnetic field in the two-dimensional quantum antiferromagnet Cu(tn)Cl₂

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(1) INTRODUCTION

Two-dimensional quantum antiferromagnets have attracted a significant amount of theoretical and experimental attention due to the unconventional magnetic properties resulting from the interplay between quantum fluctuations and geometrical frustration.1–3 One example is the $S = 1/2$ spatially anisotropic triangular antiferromagnet, which can be treated as a square lattice with the nearest-neighbor (nn) interaction $J$ and frustrating next-nearest-neighbor (nnn) interaction $J'$, Fig. 1. Between the limiting values of $J'/J = 0$ (ideal square lattice) and $J'/J > 1$ (spin chain), several phases exist for varying ratios of $J'/J$,4–8 while the presence of an applied magnetic field provides an additional constraint. Considerable theoretical interest in the spin liquid phase ($J'/J > 1$) in a magnetic field9–11 was triggered by experimental studies of Cs₂CuCl₄, a spatially anisotropic triangular magnet with $J'/J ≈ 3$.12–14

Recently, Cu(tn)Cl₂ has been identified as a potential model system for the realization of the spatially anisotropic triangular lattice from the collinear Néel phase ($J'/J < 0.6$).15 For Cu(tn)Cl₂ studied in $B = 0$, no evidence for long-range magnetic order was observed down to 60 mK, and the data suggested intralayer inter-

FIG. 1: Realization of Heisenberg model of a spatially anisotropic triangular lattice within a single bc layer in Cu(tn)Cl₂. The layers are stacked along the a direction. The full circles denote Cu²⁺ ions.
The motivation of the present work was to explore the response of Cu(tn)Cl$_2$ in $B \neq 0$, especially at low temperatures, $T \ll J/k_B$. For this purpose, experimental specific heat and ac susceptibility studies were performed over a wide range of temperatures (40 mK $\leq T \leq$ 10 K) and magnetic fields (0 $\leq B \leq$ 14 T). The low value of the intralayer exchange coupling affords easy access to the magnetic phases below and above the saturation field. On the basis of the magnetic field induced features observed in the specific heat and ac susceptibility, a magnetic phase diagram is constructed and analyzed within a model of a field induced Berezinski-Kosterlitz-Thouless (BKT) phase transition theoretically predicted for the pure 2D square lattice with zero nnn coupling.\textsuperscript{16} It is noteworthy that the long-range orderings in some quasi-2D, square lattice systems, namely Sr$_2$CuO$_2$Cl$_2$ and several Cu(pyrazine)$_2$-based materials (pyz = pyrazine), have been placed close to the BKT transition.\textsuperscript{17–19}

Our presentation begins with a discussion of the sample and experimental details, which are followed by a description of our experimental results. Next, an analysis and a discussion of the results are given before the salient points are assembled into the magnetic phase diagram. The paper concludes with a summary and some comments about possible future directions.

II. SAMPLE AND EXPERIMENTAL DETAILS

The crystal structure of Cu(tn)Cl$_2$ (tn = C$_3$H$_{10}$N$_2$), established at 150 K, is orthorhombic (space group Pna$_2_1$) with the lattice parameters $a = 17.956$ Å, $b = 6.859$ Å, and $c = 5.710$ Å.\textsuperscript{15} The structure consists of covalently bonded ladders running along the c-axis, while the adjacent ladders in the bc-plane are linked through intermolecular N–H···Cl hydrogen bonds formed by all four H atoms of the amino groups. In the a direction, the layers are connected by weak C–H···Cl type interactions. The strongly elongated octahedra coordinating the Cu(II) ions stabilize the $d_{z^2}$ electronic ground state. Consequently, the propagation of exchange pathways between Cu(II) ions leads to the formation of a spatially anisotropic triangular lattice in the bc-plane (Fig. 1).

The synthesis of all Cu(tn)Cl$_2$ samples followed the established procedure,\textsuperscript{15} which produces polycrystals that are powdered and pressed into pellets (nominally 3 mg to 10 mg) for the specific heat studies or placed into appropriate specimen holders for the magnetic susceptibility investigations. A sample with a mass of 26 mg was used in the ac magnetic measurements.

Using several experimental probes and instruments, the specific heat measurements were performed over the temperature range from 100 mK to 10 K and in magnetic fields up to 14 T. More specifically, the studies in the millikelvin temperature region and in magnetic fields up to 2.5 T were performed using a relaxation calorimeter mounted on a dilution refrigerator. A commercial (Quantum Design PPMS) device was used for the specific heat studies over the temperature range from 1.8 K to 10 K and in fields up to 9 T, while the low temperature studies down to 0.35 K and in fields up to 14 T utilized another commercial instrument equipped with a $^3$He insert. In each instance, the contribution of the background addenda was determined in separate runs. Finally, the separate study of the specific heat of a diamagnetic isomorph, Zn(tn)Cl$_2$, allowed the phonon contribution to be determined.

The magnetic susceptibility studies were performed with ac (232 Hz) mutual inductance coils mounted on a dilution refrigerator equipped with a 10 T magnet. With the sample immersed in pure $^3$He that provided intimate thermal contact with the mixing chamber, the in-phase and out-of-phase signals of the susceptibility were recorded by a two channel lock-in amplifier. Typically the data were obtained by isothermal field sweeps at a rate of 50 mT/min, and the data were independent of the direction of the field sweep.

III. EXPERIMENTAL RESULTS

A. Specific heat in $B \neq 0$

Evidence of the presence of 2D magnetic correlations was initially observed as a round maximum in the temperature dependence of the total specific heat, $C_{\text{TOT}}(T)$, near 2 K in $B = 0$,\textsuperscript{15} and our present work found this feature to evolve with magnetic fields up to 9 T, Fig. 2. In fact, the influence of the magnetic field can be separated into two regimes. For $B < 4$ T, the height of the specific heat maximum, $C_{\text{max}}$, decreases with increasing field.

![FIG. 2: Temperature dependence of the total specific heat, $C_{\text{TOT}}$, of Cu(tn)Cl$_2$ in various magnetic fields. Solid lines represent data for $B = 0$, 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 3.5 and 4 T, while the dashed lines correspond to $B = 5$, 6, 7, 8 and 9 T. The dot-dashed line represents the specific heat of the diamagnetic isomorph Zn(tn)Cl$_2$.](image-url)
while its temperature, $T_{\text{max}}$, remains nearly unchanged, whereas for $B > 4$ T, $C_{\text{max}}$ increases with increasing field and $T_{\text{max}}$ shifts towards higher temperatures. The phonon contribution to the specific heat can be approximated by the specific heat of the diamagnetic isomorph Zn(tn)Cl$_2$, Fig. 2. These high temperature measurements were extended to lower temperatures in $B \leq 2.5$ T, and the results of the total specific heat are shown in Fig. 3. These studies revealed the presence of an anomaly appearing at about 0.8 K when $B \neq 0$, and this feature develops with increasing magnetic field (inset of Fig. 3). The magnetic field and temperature dependences of this anomaly were measured in $B \leq 14$ T, Fig. 4, where this feature reaches a maximum in 4 T at 0.8 K and decreases in magnitude, with a simultaneous shift to lower temperatures, until its presence is no longer resolved in fields greater than 7 T.

**B. Magnetic susceptibility in $B \leq 10$ T**

The results of isothermal ac susceptibility studies in $B \leq 10$ T are shown in Fig. 5, and no significant hysteresis was observed between the up and down sweeps. The data do not possess any sharp anomalies corresponding to a phase transition, but the appearance of a shoulder near 6 T corresponds to the field where the low temperature specific heat anomaly vanishes. Unlike the low temperature specific heat anomaly, the shoulder survives up to 1 K, suggesting that it is associated with the saturation magnetic field $B_{\text{sat}}$.

**IV. ANALYSIS AND DISCUSSION**

**A. Magnetic correlations in $B = 0$**

As stated earlier, previous specific heat studies in $B = 0$ did not indicate any magnetic phase transition down to 60 mK, and a clear quadratic dependence was observed at low temperatures. The latter coincides with the expected 2D character of short-range magnetic correlations, since the spin wave analysis of low dimensional models with $nn$ interactions predicts a $T^2$ behavior for the low temperature specific heat of square and triangular lattices and a $T$ dependence for a linear chain model. The absence of a $\lambda$-like anomaly associated with magnetic ordering is another intriguing feature of the specific heat data.
In the absence of the frustration ($J' = 0$), the ordering temperature $T_N$ of the isotropic square lattice with interlayer coupling $J''$ can be expressed as:

$$k_B T_N = J'' \left( \frac{M}{M_0} \right)^2 \left( \frac{\xi}{a} \right)^2 ,$$

where $M/M_0$ is a staggered magnetization, $a$ represents a lattice constant, and $\xi$ is an intralayer correlation length given by

$$\frac{\xi}{a} = 0.5 \exp\left( \frac{2 \pi \rho_s}{k_B T} \right) \left( 1 + \frac{k_B T}{2 \pi \rho_s} \right)^{-1} .$$

Here, $\rho_s$ is a spin stiffness, and for the isotropic square lattice with intralayer $nn$ exchange coupling $J$, it can be expressed as $\rho_s \simeq 0.18J$. Using the parameters $|J''/k_B| \approx 3$ mK, $|J/k_B| \approx 3$ K, determined in Ref. 15, and $(M/M_0)^2 \approx 0.3$, a phase transition in Cu(tn)Cl$_2$ might be expected at $T_N \approx 0.8$ K. The absence of the phase transition down to 60 mK may suggest a significant reduction of both the spin stiffness and the staggered magnetization as a consequence of frustrating $nnn$ $J'$ coupling. Apart from the aforementioned reduction of staggered magnetization, the weakness of the interlayer coupling can also lead to the absence of a detectable phase transition at finite temperatures in specific heat measurements. Recent Monte Carlo studies of the specific heat of an isotropic square lattice with various interlayer couplings revealed that, for $J''/J \lesssim 0.015$, the peak associated with the phase transition vanishes. Since $|J''/J| \approx 10^{-3}$ for Cu(tn)Cl$_2$, the ordering effects might not be observed in the specific heat even in the absence of frustration. While experimental studies of Cu(pyz)$_2$(ClO$_4$)$_2$ are consistent with this scenario, the observation of a phase transition in the specific heat of Cu(H$_2$O)$_2$(C$_2$H$_8$N$_2$)SO$_4$ with a comparable $J''/J$ ratio shows the need to consider additional effects.

### B. Magnetic correlations in $B \neq 0$

#### 1. Specific heat for $T \geq J/k_B$

After the subtraction of the phonon contribution, approximated by the specific heat of the diamagnetic isomorph Zn(tn)Cl$_2$ (Fig. 2), two different regimes can be distinguished in the behavior of $C_{\text{max}}$ for $T > 1.8$ K. For $B \lesssim 4$ T, $C_{\text{max}}$ decreases with increasing field while $T_{\text{max}}$ remains nearly unchanged, whereas for $B \gtrsim 5$ T, $C_{\text{max}}$ increases with increasing field and $T_{\text{max}}$ shifts towards higher temperatures, Fig. 6. Such a qualitative behavior has been predicted for a linear (1D) chain with $nn$ coupling $J'$, where the crossover between the two regimes occurs at a saturation field

$$g \mu_B B_{\text{sat}} = 2J .$$

For Cu(tn)Cl$_2$, this model predicts $B_{\text{sat}} = 8.4$ T, which is too high to correspond to the observed crossover region.

Using $g = 2.12$ and $J/k_B = 4$ K, which correspond to the best estimates of the parameters resulting from the linear chain model as applied to Cu(tn)Cl$_2$ in Ref. 15, Eq. 4 predicts $B_{\text{sat}} = 5.6$ T, a value that coincides rather well with the crossover region appearing between 4 T and 6 T. However, in comparison with the linear chain, which is characterized by a decrease of $T_{\text{max}}$ with increasing field for fields lower than $B_{\text{sat}}$ and an increase for higher fields, the observed shift of $T_{\text{max}}$ with respect magnetic field behaves differently. Alternatively, the effect of an external magnetic field on the short-range correlations and the thermodynamic properties of a square lattice have been theoretically investigated, and the saturation field is

$$g \mu_B B_{\text{sat}} = 4J .$$

![FIG. 6: Magnetic field dependence of the value for the maximum of the Cu(tn)Cl$_2$ magnetic specific heat, $C_{\text{max}}$, divided by the gas constant $R$ (open squares). The solid line is a guide for eyes. Magnetic field dependence of the temperature, $T_{\text{max}}$, denoting the position of $C_{\text{max}}$ (full squares). The broken line is a linear fit (see text).](image-url)
2. Specific heat for \( T \leq J/k_B 
\)

The quantitative analysis of magnetic specific heat, \( C_M \), at temperatures \( T < 0.4 \) K and \( B < 2.5 \) T reveals the \( T^2 \) dependence, as can be seen in Fig. 7, where the data are plotted as \( C_M T^2 \) vs. \( T^4 \). This approach assumes the magnetic specific heat can be expressed as a sum of \( a/T^2 \) and \( bT^2 \) terms, where the first term corresponds to the contribution of the nuclear spins and/or long-range correlations between electronic spins, and the second term is associated with 2D short-range correlations. A set of linear fits of the individual \( C_M T^2 \) vs. \( T^4 \) dependences for fixed magnetic field was performed in the temperature range from nominally 150 mK to 400 mK. The fitting procedure revealed a monotonic rise of the coefficient \( b \) (in units of \( J/(K^3 \text{ mol}) \)) with increasing magnetic field and \( a \approx 0 \). The monotonic increase can be approximated by a linear dependence

\[
b(B) = 1.36 + 0.30B ,
\]

as shown in the inset of Fig. 7. The observed low temperature \( T^2 \) behavior of \( C_M(T) \) suggests the preservation of the mainly 2D character of the magnetic correlations in \( B \neq 0 \). Furthermore, the field does not introduce an energy gap to the excitation spectrum, which remains gapless as expected for the square lattice in magnetic fields below the saturation value.\(^{16}\)

To more precisely trace the position of the low temperature peak, \( T_p \), appearing at about 0.8 K, as a function of magnetic field, the specific heat in zero magnetic field was chosen as a reference background that was subtracted from the specific heat in nonzero magnetic field, inset of Fig. 8. Using the low-field data obtained in the same way (inset of Fig. 3), the magnetic field dependence of \( T_p \) can be extracted (Fig. 8). It can be seen that a naive extrapolation to zero field provides \( T_p \approx 0.7 \) K, which is close to the value of the transition temperature \( T_X \approx 0.8 \) K estimated for the isotropic square lattice. This coincidence might support the suggestion that the weakness of the interlayer coupling prevents the observation of the phase transition in the specific heat. An extrapolation of the high-field experimental data yields \( B(T_p \rightarrow 0) \approx 6 - 7 \) T, which is lower than \( B_{\text{sat}} = 8.4 \) T calculated for the isotropic square lattice.

Finally, to determine \( B_{\text{sat}} \) from the specific heat data, we analyzed the \( C_M(T) \) data in 9 T and 14 T. While the peak height of \( C_M(T) \) in 9 T is still much lower than \( C_{\text{max}}/R = 0.438 \), the theoretical prediction for the \( S = 1/2 \) ideal paramagnet (Fig. 6), the corresponding \( B = 14 \) T value of \( C_{\text{max}}/R = 0.42 \) is close to the expected result. For \( B > B_{\text{sat}} \), a gap \( \Delta \) opens in the spin excitation spectrum, developing linearly with magnetic field as\(^{13}\)

\[
\Delta = g\mu_B(B - B_{\text{sat}}) .
\]

In the temperature region where thermal fluctuations overcome the interlayer coupling and \( T < \Delta/k_B \), a 2D character of magnon spectra can be expected, resulting in\(^{13}\)

\[
C_M(T) \approx \frac{1}{T} \exp(-\Delta/k_BT) .
\]

Fitting the \( C_M(T \leq 1 \) K, \( B = 9 \) T) and \( C_M(T < 3 \) K, \( B = 14 \) T) data yields \( \Delta/k_B = 3.4 \) K and 10.5 K, respectively, and it follows from Eq. 7 that \( B_{\text{sat}} = 6.6 \) ± 0.1 T, when assuming \( g = 2.12 \). It is important to note that the significant differences between the observed \( B_{\text{sat}} = 6.6 \) T and the 8.4 T value expected for the isotropic square

\([\text{Fig. 7: } C_M T^2 \text{ vs. } T^4 \text{ dependence for Cu(tn)Cl}_2 \text{ in } B = 0, 0.5, 0.75, 1, 1.5, 2 \text{ and } 2.5 \text{ T. Inset: Magnetic field dependence of the coefficient } b, \text{ Eq. 6. The solid line represents a linear fit.}]

\([\text{Fig. 8: Magnetic field dependence of the peak position, } T_p, \text{ of the low temperature specific heat anomalies (full squares) in Cu(tn)Cl}_2. \text{ The theoretical prediction for the field induced BKT phase transition for the isotropic square lattice is denoted by the open squares and the broken line. Inset: Temperature dependence of the difference between the specific heat in finite and zero magnetic field. The solid lines represent } B = 1, 2, 3, 3.5 \text{ and } 4 \text{ T, and the dashed lines correspond to } B = 4.5, 5, 5.5, 6 \text{ and } 7 \text{ T.}]\)
lattice indicate that Cu(tn)Cl$_2$ is indeed affected by the presence of frustrating $nnn$ interactions, since the interlayer coupling is expected to increase $B_{\text{sat}}$ as\textsuperscript{19}

$$g\mu_B B_{\text{sat}} = 4J + 2J''.$$ (9)

3. AC susceptibility for $T \leq J/k_B$

The ac susceptibility data, $\chi(T, B) = \partial M/\partial B$, can be integrated to obtain the magnetization $M(T, B)$, as shown in the inset of Fig. 5, and $M(T \to 0, B)$ data is commonly used to establish $B_{\text{sat}}$, if the saturation plateau is accessible. However, in many instances, the transition to the fully-polarized state is broadened by several effects, including issues related to finite temperature, orientation of the microcrystals, and finite size effects, so an extrapolation is used to establish a value for $B_{\text{sat}}$. Our ac susceptibility data shown in Fig. 5 suggest $B_{\text{sat}} = 6.5 \pm 0.2$ T for $T \leq 200$ mK (when considering $B_{\text{sat}}$ as the mid-point of the region where $\chi(B)$ is most strongly changing), and this value agrees with the one obtained for the extended magnetic phase diagram at 9 T and 14 T.

The crossover region, $\Delta B_{\text{sat}}$, that spans from the region from about 6 T to 7 T at low temperature, Fig. 5, merits further analysis. For example, when $k_BT \approx 0.1J$, thermal smearing of the crossover is not expected. Alternatively, the powder character of the sample might introduce a scatter of $B_{\text{sat}}$ that can be evaluated as $B_{\text{sat}}^\parallel - B_{\text{sat}}^\perp$. Previous electron paramagnetic resonance studies provided values for the anisotropic $g$-tensor of $g_\parallel = 2.25$ and $g_\perp = 2.05$.\textsuperscript{15} Assuming an ideal square lattice and taking $J/k_B = 3$ K, then

$$B_{\text{sat}}^\parallel - B_{\text{sat}}^\perp = \frac{4J}{g_\perp \mu_B},$$ (10)
yields $|\Delta B_{\text{sat}}| \leq 0.8$ T, which is less than but similar in magnitude to the observed width of the crossover. In addition, the finite size of the particles comprising the powder-like sample might cause broadening by limiting the in-plane correlation length $\xi$ at the lowest temperatures. Perhaps more fundamentally, the spatial extent of $\xi$ near $B_{\text{sat}}$ might be restricted by the underlying magnetic frustration, which suppresses the antiferromagnetic correlations.

C. Magnetic phase diagram of Cu(tn)Cl$_2$

Prior to building the magnetic phase diagram, the correlations between the shift of $T_p$ and the position of high temperature specific heat maximum $T_{\text{max}}$ with respect to magnetic field are worth noting (Figs. 6 and 8). The monotonic increase of $T_p$ with increasing magnetic field up to about 2 T corresponds to the relative field independence of $T_{\text{max}}$ in this field region. The relative field independence of $T_p$ in the field from 2 to 4 T corresponds to the slight increase of $T_{\text{max}}$, and finally, the rather rapid decrease of $T_p$ above 4 T corresponds to a linear increase of $T_{\text{max}}$.

This relationship between the low temperature anomaly and the high temperature maximum suggests that the magnetic field mainly affects the short-range correlations. This interpretation is supported by the monotonic increase of $T_p$ observed in low fields, and this behavior is typical for the Berezinski-Kosterlitz-Thouless (BKT) transition theoretically predicted in the classical limit for low dimensional magnets in uniform magnetic fields.\textsuperscript{29,30} Quantum Monte Carlo studies of the $S = 1/2$ isotropic square lattice in a magnetic field also revealed field-induced XY behavior, and a BKT transition at a finite temperature, $T_{\text{BKT}}$, was identified for sufficiently strong magnetic fields.\textsuperscript{31} Neither the presence of spatial anisotropy nor the introduction of the frustrated $nnn$ coupling are expected to qualitatively change the physical picture derived for the isotropic square lattice.\textsuperscript{32} Consequently, the measured $T_p$ vs. $B$ dependence can be compared to the theoretical prediction of $T_{\text{BKT}}$ vs. $B$ calculated for $g = 2.12$ and $J/k_B = 3$ K, and the comparison yields surprisingly good agreement between the theoretical predictions and data (Fig. 8). It should be noted that the authors of Ref. 16 identified the BKT phase transitions at $T_{\text{BKT}}$, which lies below $T_p$. However, the determination of $T_{\text{BKT}}$ directly from the experiment is not as straightforward as the determination of $T_p$. From this point of view, one must be aware that the experimental determinations of the potential $T_{\text{BKT}}$ are overestimated.

Recent quantum Monte Carlo calculations of a $B$ vs. $T$ magnetic phase diagram performed for the system of a tetragonal lattice with intralayer coupling $J$ and interlayer coupling $J''$ revealed that, for sufficiently large spatial anisotropy $J/J''$, the system preserves nonmonotonic $B$ vs. $T$ behavior typical for the BKT transition on the ideal square lattice.\textsuperscript{19} The enhancement of the critical temperatures and the saturation field with respect to the ideal 2D case is another effect of the interlayer coupling. The predictions were compared with the experimentally established phase diagram of $[\text{Cu(HF}_2\text{)}(\text{pyz})_2\text{BF}_4]$, a representative of the quasi-2D Heisenberg square lattice with a finite temperature phase transition to 3D long-range order in zero magnetic field, and excellent agreement was found.\textsuperscript{19} Unlike the phase diagram of Cu(tn)Cl$_2$, the experimental data of $[\text{Cu(HF}_2\text{)}(\text{pyz})_2\text{BF}_4]$ are significantly shifted above the theoretical prediction for the ideal square lattice model. The fact that our data lie significantly lower, i.e. below the theoretical predictions for the BKT transition (Fig. 8), supports the conjecture about the important presence of frustration.

Considering all the ac susceptibility and specific heat features together, we can identify the major regions in the extended magnetic phase diagram for Cu(tn)Cl$_2$ as a triangular magnet from the Néel phase (Fig. 9). At temperatures above 2 K, the system behaves as a paramagnet in all magnetic fields. The paramagnetic region
is separated by the line determined by the $T_{\text{max}}$ vs. $B$ dependence. At temperatures below the line, 2D antiferromagnetic correlations develop, forming free vortices (V) and antivortices (AV) in the $xy$ plane. The vortices are stabilized by the magnetic field, whose direction defines the $z$-axis in the spin space. The formation of bound V-AV pairs begins at temperatures below a line derived from the requirement that the difference of the entropy derivatives [$\delta_{T} S(T, B) - \delta_{T} S(T, 0)$] is zero.\textsuperscript{16} This quantity equals the difference of the specific heat $[C(T, B) - C(T, 0)]$ divided by temperature $T$. The intensity of the pairing process culminates at the temperatures defined by the position of the low temperature specific heat anomaly. As was shown in the theoretical studies of the BKT transition,\textsuperscript{16,19} the temperature of the BKT transition itself is about 20 – 30% lower than the position of the specific heat maximum. Consequently for Cu(tn)Cl$_2$, the potential BKT transition can be expected at temperatures lower than the critical line constructed from the $T_{p}$ vs. $B$ data.

Above the critical magnetic field region determined from the position of the high field shoulder in the isothermal ac susceptibility data, out-of-plane ferromagnetic correlations induced by the magnetic field are stabilized, while in-plane spin correlations show paramagnetic behavior.\textsuperscript{32} In this region, a spin gap appears in the excitation spectrum, and this gap was detected by the exponential character of the low temperature specific heat measured in 9 T. As shown in the phase diagram, the induced ferromagnetic correlations survive up to the temperatures on the critical line $T_{\text{max}}$ vs. $B$. Coincidence with the theoretical predictions for the square lattice,\textsuperscript{32} formation of the out-of-plane ferromagnetic correlations already begins at fields above 4 T as indicated by the linear dependence of $T_{\text{max}}$ vs. $B$ above 4 T.

The onset of quasi-long-range order (QLRO), induced by the field due to the stabilization of bound V-AV pairs expected for the unfrustrated square lattice at sufficiently low temperatures, should be reflected by the smaller entropy increase in finite magnetic field than in zero field. In other words, the presence of the V-AV pairs should lead to negative values of $[C(T, B) - C(T, 0)]$ at low temperatures. However, as can be seen from the insets of Figs. 3 and 8, in Cu(tn)Cl$_2$, the difference remains positive down to the lowest temperatures. The increasing specific heat with magnetic field can be ascribed to the combined effect of the interlayer coupling and the existence of soft spin modes, likely associated with the frustrated $nnn$ coupling, which can prevent the system from achieving full QLRO.

\section{V. SUMMARY}

The response of Cu(tn)Cl$_2$ to an externally applied magnetic field has been investigated by specific heat and ac susceptibility studies at low temperatures, $T \geq 40$ mK, and in magnetic fields up to 14 T. Specific features induced by the magnetic field in the behavior of both quantities allowed a magnetic phase diagram, whose regions are rooted in the presence of a high degree of short-range order, to be constructed. The quadratic temperature dependence of the specific heat observed below 0.4 K and in magnetic fields up to, at least, 2.5 T arises from the predominantly 2D character of magnetic correlations and identifies a gapless excitation spectrum as predicted for the isotropic square lattice. Furthermore, in finite magnetic fields up to 6 T, a field induced anomaly appears near 0.8 K, and this feature is associated with the existence of a Berezinski-Kosterlitz-Thouless (BKT) transition theoretically predicted for the isotropic square lattice.\textsuperscript{16} The dimensionality of the observed magnetic field induced transition is unresolved and will be the focus of future neutron and/or muon scattering studies. The absence of a phase transition in zero magnetic field is interpreted as a consequence of a combined effect of the weak interlayer coupling and the frustration within the magnetic layers. The saturation magnetic field value, as extracted from the specific heat and ac susceptibility data, deviates significantly from the one predicted for an isotropic square lattice, and this result is conjectured to be a consequence of the frustrating magnetic interactions, in the $bc$ layer, that have have been confirmed recently by quantum mechanical calculations.\textsuperscript{33}

Finally, it is noteworthy that a $T^2$ dependence of the
specific heat has been reported for several frustrated 2D systems in zero magnetic field and was ascribed to various scenarios. While only a weak field dependence of the low temperature specific heat has been observed in Kagome\textsuperscript{34} and triangular\textsuperscript{35} compounds, the linear increase of the $b$ coefficient, as observed in Cu(tn)Cl$_2$, points to the fact that even an infinitesimal field is able to introduce the changes. This sensitivity also supports the applicability of the BKT model to Cu(tn)Cl$_2$; however, only to some extent. In the spin wave region, the magnetic field should decrease the specific heat and, correspondingly, the $b$ coefficient, as expected for the square lattice. Since the opposite tendency was observed, our experimental data suggest the presence of soft spin modes that are possibly connected with frustration and interlayer coupling. A spin wave analysis of the triangular magnet from the Néel phase in a magnetic field would be desirable to elucidate these observed differences. Recently, the BKT description has been successfully used\textsuperscript{36} to explain the 2D spin freezing transition observed in NiGa$_2$S$_4$, a model system for the $S = 1$ isotropic triangular Heisenberg lattice.\textsuperscript{37}

In conclusion, the analysis of experimental data suggests that the $S = 1/2$ spatially anisotropic triangular magnet from the collinear Néel phase undergoes a Berezinski-Kosterlitz-Thouless transition induced by an applied magnetic field. Theoretical studies of the collinear Néel phase in a magnetic field are necessary to specify the proper range of $J$, $J'$ parameters where the BKT transition can occur. Microscopic magnetic studies of Cu(tn)Cl$_2$, possibly employing neutron and/or muon scattering techniques, are needed to clarify the nature of the ground state in zero and nonzero magnetic fields.

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