Specific Heat Study of 1D and 2D Excitations in the Layered Frustrated Quantum Antiferromagnets $Cs_2CuCl_{4-x}Br_x$

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We report an experimental and theoretical study of the low-temperature specific heat C and magnetic susceptibility χ of the layered anisotropic triangular-lattice spin-1/2 Heisenberg antiferromagnets $Cs_2CuCl_{4-x}Br_x$ with $x = 0$, 1, 2, and 4. We find that the ratio J'/J of the exchange couplings ranges from 0.32 to ≈ 0.78, implying a change (crossover or quantum phase transition) in the materials' magnetic properties from one-dimensional (1D) behavior for $J'/J < 0.6$ to two-dimensional (2D) behavior for $J'/J \approx 0.78$. For $J'/J < 0.6$, realized for $x = 0$, 1, and 4, we find a magnetic contribution to the low-temperature specific heat, $C_m \propto T$, consistent with spinon excitations in 1D spin-1/2 Heisenberg antiferromagnets. Remarkably, for $x = 2$, where $J'/J \approx 0.78$ implies a 2D magnetic character, we also observe $C_m \propto T$. This finding, which contrasts the prediction of $C_m \propto T^2$ made by standard spin-wave theories, shows that Fermi-like statistics also plays a significant role for the magnetic excitations in spin-1/2 frustrated 2D antiferromagnets.

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Introduction.—Spin-1/2 frustrated antiferromagnets are considered a source of intriguing phenomena. The interplay of geometric frustration and strong quantum fluctuations is known to weaken or even destroy magnetic order and may give rise to novel liquidlike states, so-called quantum spin liquids [1,2], or nontrivial quantum phase transitions; see, e.g., Ref. [3]. The theoretical understanding of the phases involved and their experimental identification pose major challenges in current research on correlated quantum many-body systems. In this respect, specific heat measurements play an important role [4–6] for characterizing the nature of the excitations of these phases and for the determination of the entropy associated with them.

Layered spin-1/2 Heisenberg antiferromagnets with an anisotropic triangular arrangement of spins which interact by exchange coupling constants J and J' (see Fig. 1) represent an interesting family of such correlated systems, where the possibility of a frustration-induced quantum phase transition has been discussed [7–9]. Moreover, when close enough to the Mott metal-insulator transition [2,10] where additional interactions, such as ring exchange, become relevant, these systems may also support a quantum spin liquid state. In triangular-lattice spin-1/2 Heisenberg antiferromagnets, the geometric frustration supports an effective decoupling of the spin chains, defined by the dominant coupling constant J, thus extending the range where 1D behavior dominates to relatively high J'/J values. Whether the 2D state is reached by a crossover or by a quantum phase transition [7,9,11,12] is still under debate.

There is general consensus [1,7–9,13,14] that for $J'/J < 0.6$ the 1D behavior prevails where fractionalized $S = 1/2$ spinon excitations with fermionic character propagate along the chains. As rigorously shown by Bethe-ansatz calculations [15,16] for the antiferromagnetic Heisenberg chain, these spin-1/2 excitations are reflected in a low-temperature contribution to the magnetic specific heat, C_m, which (in good approximation) varies linearly with

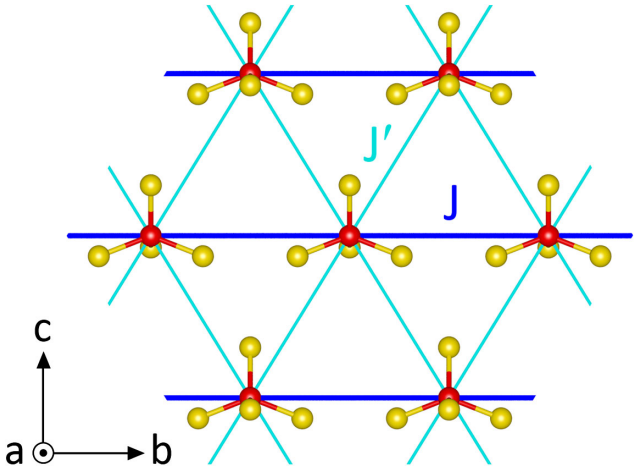

FIG. 1. Spin-coupling scheme of the anisotropic triangular-lattice Heisenberg antiferromagnet as realized in $Cs_2CuCl_{4-x}Br_x$ where the $S = 1/2$ spins of the Cu^{2+} ions (red spheres) are tetrahedrally coordinated by the halide ions (yellow spheres).

temperature T, i.e., $C_m \propto T$. On the other hand, for 2D quantum antiferromagnets, expected for $J'/J > 0.65$ [7,9,17–22], the situation is less clear. At first glance, this seems surprising considering that the specific heat is a sensitive quantity for probing the dimensionality of the low-lying excitations, as, e.g., verified for lattice excitations [23–25]. The difficulty for 2D antiferromagnets lies in the quantum nature of $S = 1/2$ spin operators which commute on different sites (like bosons) but, locally, on the same site satisfy the $SU(2)$ algebra including a Fermi-like anticommutation relation between spin-ladder operators. Thus, depending on the model applied, different results have been obtained for $C_m(T)$. According to modified spin-wave [26] and Schwinger-boson-based mean-field [27] theory, a $C_m \propto T^2$ behavior was proposed. This contrasts with $C_m \propto T^\nu$ and $0.67 \leq \nu \leq 1$, obtained using the resonating valence bond theory [28,29], Wigner-Jordan fermions [30], Gutzwiller projection of fermionic mean-field states [10], and a recent spin Hartree-Fock approach [31].

Thus, low-temperature specific heat measurements on triangular-lattice Heisenberg antiferromagnets, covering the range from $J'/J < 0.6$ (1D) to J'/J significantly above 0.6 (2D), are of great interest for identifying the character of the low-energy excitations in frustrated 2D antiferromagnets, thereby settling this fundamental issue. Here we report an experimental study of the low-temperature specific heat on $Cs_2CuCl_{4-x}Br_x$ single crystals with $x = 0$, 1, 2, and 4, where J'/J is found to span a wide range from 0.32 to ≈ 0.78. This system thus offers the possibility to study, on a series of isostructural compounds, the character of the low-lying excitations in the different regimes and to test the theoretical predictions.

The chosen quantum-spin system.—The two border compounds of the $Cs_2CuCl_{4-x}Br_x$ system ($x = 0$ and 4), where Cu^{2+} ions carry well-localized $S = 1/2$ spins, have been studied intensively for more than 15 years. A comprehensive characterization was provided by neutron-scattering experiments which revealed the geometry and size of the spin-spin interactions [32–35]. According to these studies, both compounds are good realizations of a layered anisotropic triangular-lattice Heisenberg antiferromagnet. The dominant interaction J runs along the b direction, thereby forming chains. These chains interact with each other via the weaker diagonal interaction J' in the bc plane; cf. Fig. 1. For the two border compounds values of $J/k_B = 4.34$ K, $J'/k_B = 1.48$ K (Cs_2CuCl_4) [32] and $J/k_B = 13.9$ K, $J'/k_B = 6.49$ K (Cs_2CuBr_4) [34] were found. Besides the dominant couplings J and J', a weak Dzyaloshinskii-Moriya interaction with components D_a and D_c was observed ($D_a/k_B = 0.23$–0.33 K, $D_c/k_B = 0.36$ K for $x = 0$) [32,36] along with a weak interlayer interaction $J_\perp$ ($J_\perp/k_B = 0.20$ K for $x = 0$ [32] and $J_\perp/k_B < 0.64$ K for $x = 4$ [34]).

The small ratio $J_\perp/J$ for the $x = 0$ and 4 compounds implies low-dimensional magnetic behavior over a wide range of temperatures $T \gg J_\perp/k_B$. However, $J_\perp$ is still strong enough to generate 3D antiferromagnetic ordering with Néel temperatures T_N of 0.6 ($x = 0$) [37] and 1.4 K ($x = 4$) [34]. On the other hand, as shown in Ref. [38], partial substitution of Cl for Br in Cs_2CuBr_4 can lower T_N significantly to at least 0.6 K and possibly even further, suggesting that for certain Br concentrations T_N values much smaller than 0.6 K might be possible. An ordering temperature as low as possible is desirable in order to search for signatures of genuine 1D or 2D behavior and its dependence on J'/J.

Crystals.—Single crystals of $Cs_2CuCl_{4-x}Br_x$ were grown from aqueous solutions at temperatures of about 50 °C and then characterized by structural and energy-dispersive x-ray investigations (see Ref. [39]). Under these conditions, the substitution of Br for Cl (and vice versa) is site selective [39–41], an important aspect which ensures a well-ordered halide sublattice. Note that for crystals grown by the Bridgman method (as in Ref. [38]), the high temperatures of about 600 °C used there imply a random distribution of Br and Cl on the halide sites. Thus, the growth from an aqueous solution provides crystals with a regular halide sublattice structure not only for the two border compounds ($x = 0$, 4) but also for the two intermediate systems with $x = 1$ and 2. For $x = 3$, the site-selective occupation does not lead to a well-ordered halide sublattice, as there are two Cl(3) sites in each copper-halide tetrahedron, both occupied by Br and Cl with equal probability.

Magnetic susceptibility.—For characterizing the single crystals of $Cs_2CuCl_{4-x}Br_x$ used in our study and for determining their coupling constants J and J', we have measured the low-field ($\mu_0 H = 0.1$ T) molar magnetic susceptibility $\chi_{\mathrm{mol}} = (1/n)M/H \approx (1/n)\partial M/\partial H$ (n being the amount of substance) in the temperature range $2\ \mathrm{K} \leq T \leq 100$ K for various Br concentrations x covering the whole concentration range from $x = 0$ to 4 [39]. A Quantum Design superconducting quantum interference device magnetometer was used for this purpose. After correcting for the temperature-independent diamagnetic core contribution and the magnetic contribution of the sample holder, the data were analyzed by using theoretical calculations of $\chi(T)$ for the anisotropic triangular-lattice $S = 1/2$ Heisenberg antiferromagnet based on the finite-temperature Lanczos method [42,43]. The g factor and the coupling constants J and J' were used as free parameters in the fits. The so-obtained results are presented in Fig. 2 for the Br concentrations $x = 0$, 1, 2, and 4. The agreement between the model calculations and the experimental data is very good above the temperatures where the fit curves show their maxima. For temperatures significantly below the maximum, which is of relevance only for $x = 4$, the fits are slightly affected by finite-size effects leading to a rapid decrease of the calculated susceptibility for $T \to 0$. In the case of the $x = 2$ compound, where the χ data lack a

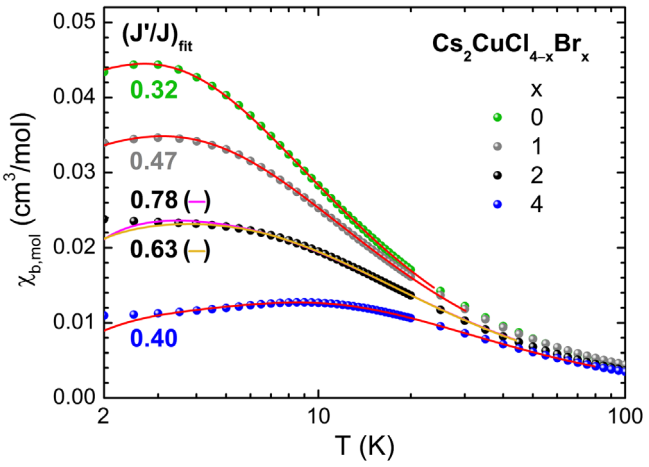

FIG. 2. Magnetic susceptibility (in cgs units) measured along the b axis of $Cs_2CuCl_{4-x}Br_x$ as a function of the temperature. Circles, experimental data; lines, fit curves based on the model of the $S = 1/2$ Heisenberg antiferromagnet with an anisotropic triangular lattice using the finite-temperature Lanczos method. Colored numbers are J'/J values obtained by this method. The corresponding values of J/k_B and g for $x = 0$, 1, 2, 4 are 4.52, 5.46, 7.44–6.88 K, and 14.78 K and 2.09, 2.11, 2.09–2.10, and 2.06, respectively.

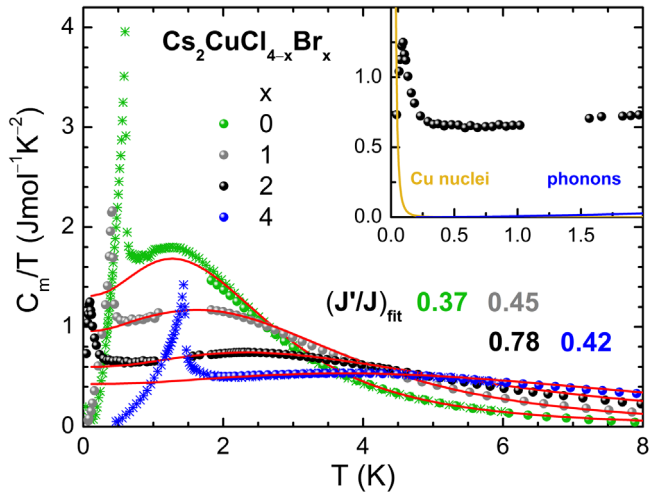

FIG. 3. Magnetic specific heat divided by temperature C_m/T of $Cs_2CuCl_{4-x}Br_x$ as a function of the temperature. Circles (crosses), experimental data of this work (from Ref. [45] for $x = 0$ and Ref. [38] for $x = 4$); lines, fit curves based on the model of the $S = 1/2$ Heisenberg antiferromagnet with an anisotropic triangular lattice using the spin Hartree-Fock approach. The colored numbers are the J'/J values which have been obtained by this method. The values of J/k_B for $x = 0$, 1, 2, 4 are 4.29, 6.06, 8.69, and 13.37 K, respectively. Inset: C_m/T of $Cs_2CuCl_2Br_2$ below 2 K. Yellow (blue) line: Contribution from the copper nuclei (phonons).

well-pronounced maximum [44], fits of comparable quality could be obtained for J'/J values ranging from 0.63 up to 0.78.

Specific heat.—The results for the magnetic specific heat C_m (divided by the temperature) are shown in Fig. 3 for single crystals of all compounds with a well-ordered halide sublattice ($x = 0$, 1, 2, 4). Data were taken from 40 mK to about 20 K. The high-temperature data ($T > 1.8$) were obtained with a physical properties measuring system relaxation calorimeter (Quantum Design), whereas for the low-temperature range a self-constructed relaxation calorimeter adapted to a ^{3}He-^{4}He dilution refrigerator was used ($x = 1$, 2). In the case of the two border compounds ($x = 0$, 4) and low temperatures, data from the literature [38,45] were taken which overlap with our results in the temperature range from 1.8 to 6 K. The agreement between both datasets is very good except for $x = 0$ and 1.8 K $\leq T \leq$ 3.0 K, where our data lie somewhat below (maximally 7%) those of Ref. [45]. The magnetic specific heat C_m was obtained from the total specific heat C by subtracting the nuclear contribution $C_n = A/T^2$, caused by the hyperfine interaction of the copper ions, as well as the phonon contribution C_{ph}. As described in detail in Ref. [17] and shown exemplarily for the $x = 2$ compound (inset in Fig. 3), the nuclear contribution becomes relevant only below about 100 mK, whereas the phonon contribution starts to become significant above about 2 K.

The data in Fig. 3 represent the central result of this study and contain three important pieces of information. Besides the identification of phase transition anomalies for the recently discovered intermediate compounds $x = 1$ and 2, the data can be used for an independent determination of the J'/J values for all crystals under investigation. In addition, and of particular interest here, is the determination of the temperature dependence of C_m, i.e., the identification of a potential power-law behavior at low temperatures $T < T_{\mathrm{max}}$, with T_{max} the temperature where C_m adopts a broad maximum. Note that T_{max} primarily depends on the dominant energy scale J; see Ref. [17] for a detailed discussion of C_m and its dependence on J and J'/J.

Figure 3 reveals clear evidence for phase transition anomalies in C_m/T also for the intermediate compounds with $x = 1$ and 2. In analogy to the border compounds $x = 0$ and 4, we assign these transitions to the onset of long-range antiferromagnetic order at $T_N = 0.41$ ($x = 1$) and 0.095 K ($x = 2$). Remarkably, for the $x = 2$ compound, T_N is strongly suppressed as compared to the other compounds (see Fig. 4), reflecting a particularly high degree of frustration for this material. For a quantitative determination of the J'/J values from the data in Fig. 3, we performed model calculations for C_m. Instead of using the Lanczos method, which becomes too inaccurate at such low temperatures ($T \ll T_{\mathrm{max}}$), we use the recently proposed spin Hartree-Fock approach [31]. This new method has been successfully applied in Ref. [31] to the case of an antiferromagnetic Heisenberg chain, for which the specific heat is known with high accuracy [16]. The spin Hartree-Fock approach well reproduces the Bethe-ansatz results at $T < 0.9T_{\mathrm{max}}$ but yields a slightly too high (15%) value for

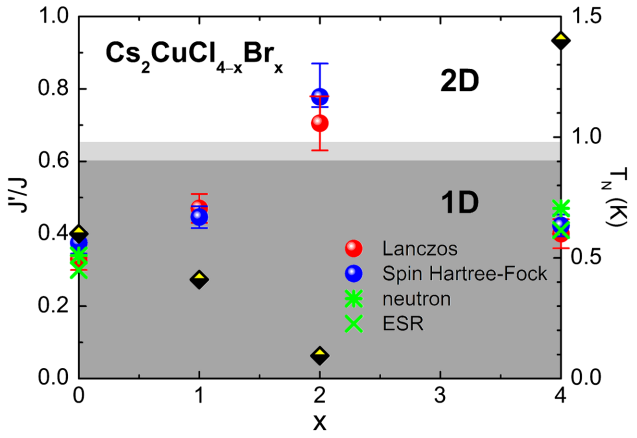

FIG. 4. Coupling ratio J'/J and Néel temperature T_N (diamonds) of $Cs_2CuCl_{4-x}Br_x$ as a function of the Br concentration x. Red (blue) spheres, values obtained with the Lanczos method (spin Hartree-Fock approach) using the susceptibility (magnetic specific heat) data; green crosses, literature data obtained by neutron scattering [32,34] or ESR [46] experiments. At a critical value of J'/J, which is close to 0.6, a crossover or quantum phase transition from 1D to 2D magnetic behavior is expected.

C_m around $T_{\max}$. However, as we apply this method only for fitting $C_m(T)$ up to about $0.7T_{\max}$, this limitation is of no relevance here.

The so-derived fit curves for the specific heat, included as red lines in Fig. 3, provide an excellent description of the experimental data above T_N in the temperature range shown in Fig. 3. In addition, the J'/J values obtained from the least-squares fits are very close to those revealed by the Lanczos fits to the susceptibility data (see Fig. 2). For a comparison of the spin Hartree-Fock approach with the Lanczos method, as far as results of the specific heat and the magnetic susceptibility are concerned, see Ref. [17].

A compilation of the J'/J values of all compounds studied here are shown in Fig. 4. In addition, Fig. 4 demonstrates that for $x = 0$ and 4 the J'/J values derived from the spin Hartree-Fock description are in good agreement with the values obtained by neutron scattering [32,34] and ESR [46] studies. For $x = 2$, however, the spin Hartree-Fock result yields $J'/J = 0.78^{+0.09}_{-0.03}$, which lies at the upper end of the range $J'/J = 0.63$–0.78 obtained from the least-squares Lanczos fits. In view of the considerable uncertainties involved in pinpointing the J'/J value for $x = 2$ from fits to the $\chi(T)$ data, and given the fact that a description of the specific heat for this compound with values $J'/J < 0.75$ is of distinctly less quality [17], we consider $J'/J = 0.78^{+0.09}_{-0.03}$ to be reliable. This holds true also in the presence of a Dzyaloshinskii-Moriya interaction of the size reported in Ref. [47]. Taking the dominant component $D_a/k_B = 0.45$ K [47] of this interaction into account, the spin Hartree-Fock approach yields a change in $C(T)$ of less than 1.5% [17], which is below the experimental uncertainty of the data.

Discussion.—In discussing the low-temperature specific heat data with regard to potential power-law behavior, it is obvious that the occurrence of a phase transition at T_N due to a weak interlayer coupling $J_\perp$ imposes some limitations. These restrictions are more severe for the $x = 0$ compound but of less relevance for $x = 1$, 2, and 4. At the same time, as the model calculations based on the spin Hartree-Fock approach provide a very good description of $C_m(T)$ for $T_N \le T \lesssim 0.7T_{\max}$, we can include these theoretical results in the discussion.

First, we focus on the compounds with $J'/J < 0.6$, realized for $x = 0$, 1, and 4 with $J'/J = 0.37$, 0.45, and 0.42, respectively. For these compounds we find a low-temperature specific heat which approaches a $C_m/T =$ const behavior for $T \to 0$. This observation is consistent with the 1D magnetic behavior expected for $J'/J < 0.6$ [1,7–9,13,14]. Remarkably, as shown in the inset in Fig. 3 on expanded scales, a $C_m/T =$ const behavior over a rather wide temperature range is also revealed for the $x = 2$ compound, which is already far inside the 2D regime. This experimental finding clearly contradicts the prediction of $C_m/T \propto T$ made by bosonic spin-wave theories [26,27]. Such a behavior is counterintuitive at first sight. However, it can be rationalized by considering the nontrivial statistics of magnetic excitations in the fully quantum case of spin 1/2, which are usually highly entangled states in low-dimensional quantum magnets involving many spins. Note that on different lattice sites $i \neq j$ the spin-1/2 operators commute, e.g., $S_i^\alpha S_j^\beta - S_j^\beta S_i^\alpha = 0$, like bosons, but on the same lattice site the spin ladder operators $S_i^\pm$ obey the anticommutation relation $S_i^- S_i^+ + S_i^+ S_i^- = 1$. Thus, the many-body states consisting of a great number of magnetic excitations have a structure that is neither entirely symmetric with respect to permutation of two particles (Bose-like) nor entirely antisymmetric (Fermi-like). The $C_m/T \approx$ const behavior observed in this experiment for a 2D antiferromagnet can be interpreted as a consequence of the Fermi-like part of the statistics (see details in Ref. [17]) which is taken into account by the theories in Refs. [10,28–31].

In the 2D regime, realized in the $x = 2$ compound, the frustration effects of a triangular lattice are generally expected to be strong, since the antiferromagnetic couplings to the neighboring spins cannot be satisfied simultaneously, resulting in a macroscopically degenerate ground state. Using the standard thermodynamic relation ($dS = CdT/T$) between the change of the entropy, dS, and the heat capacity, we can estimate the change of the total entropy $\Delta S = S(T = \infty) - S(T = 0)$ by integrating the experimental C_m/T data from $T_1 = 40$ mK up to $T \le T_2 = 20$ K and then extrapolating the so obtained $\Delta S(T) = S(T) - S(T_1)$ to $T = \infty$ and $T_1 = 0$. We find $\Delta S = (0.95 \pm 0.05)R \ln 2$ with R the gas constant (see Ref. [17] for details) which is almost identical to the full entropy of $R \ln 2$ expected for $S = 1/2$ spins. This result implies an upper bound of

$S(0) \leq 0.05R \ln 2$ for the residual entropy of the ground state. It is interesting to compare this value with the well-established result for the isotropic triangular-lattice Ising model yielding a residual entropy of $S(0) = 0.34R$ [48]. This marked difference in the geometrical frustration can be attributed to the dominant role of quantum fluctuations in spin-1/2 Heisenberg systems as opposed to Ising systems. The quantum uncertainty of a spin 1/2 is of the order of its size and can result in a fully nondegenerate ground state.

We note that layered triangular-lattice spin-1/2 systems with similar ratios $J'/J \approx 0.74$ to 0.84 are realized in the organic charge-transfer salts κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ and $EtMe_3Sb[Pd(dmit)_2]_2$. These systems, where the low-temperature specific heat also varies linearly in T [4,5], are considered as prime candidates for a quantum spin liquid [49,50]. In contrast to the present $Cs_2CuCl_2Br_2$ compound, described by well-localized spins, these organic materials are located rather close to the Mott transition so that a description based on a pure spin Hamiltonian appears inappropriate [2,10].

Conclusions.—Measurements of the low-temperature specific heat have been performed on four members of the layered anisotropic triangular-lattice spin-1/2 Heisenberg antiferromagnets $Cs_2CuCl_{4-x}Br_x$, all of which show a structurally well-ordered halide sublattice. The materials span a wide range of the ratio of coupling constants $0.32 \leq J'/J \lesssim 0.78$, implying a change from 1D magnetic behavior for $J'/J < 0.6$ ($x = 0$, 1, 4) to 2D behavior for $J'/J \approx 0.78$ ($x = 2$). Our central finding is that, for the frustrated 2D case, the magnetic specific heat varies linearly in temperature, $C_m \propto T$, reflecting a significant role of Fermi-like statistics in this 2D quantum antiferromagnet. Moreover, at variance with a naive expectation for such a strongly frustrated system, no indication of residual entropy is found within the experimental uncertainty. This observation, which is in marked contrast to the triangular-lattice Ising model, is attributed to the importance of quantum fluctuations in low-dimensional spin-1/2 Heisenberg systems.

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