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$Ba_8CoNb_6O_{24}$: a spin-1/2 triangular-lattice Heisenberg antiferromagnet in the 2D limit

R. Rawl,[1] L. Ge,[2] H. Agrawal,[3] Y. Kamiya,[4] C. R. Dela Cruz,[3] N. P. Butch,[5] X. F. Sun,[6,7,8] M. Lee,[9,10] E. S. Choi,[10] J. Oitmaa,[11] C. D. Batista,[1,12] M. Mourigal,[2,*] H. D. Zhou,[1,10,†] and J. Ma[13,8,1,‡]

[1]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*
[2]*School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[3]*Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37381, USA*
[4]*Condensed Matter Theory Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*
[5]*NIST Centre for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*
[6]*Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[7]*Key Laboratory of Strongly-Coupled Quantum Matter Physics, Chinese Academy of Sciences, Hefei, Anhui 230026, People's Republic of China*
[8]*Collaborative Innovation Center of Advanced Microstructures, Nanjing, Jiangsu 210093, People's Republic of China*
[9]*Department of Physics, Florida State University, Tallahassee, FL 32306, USA*
[10]*National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA*
[11]*School of Physics, The University of New South Wales, Sydney, NSW 2052, Australia*
[12]*Quantum Condensed Matter Division and Shull-Wollan Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[13]*Key Laboratory of Artificial Structures and Quantum Control, Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China*

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The perovskite $Ba_8CoNb_6O_{24}$ comprises equilateral effective spin-1/2 Co^{2+} triangular layers separated by six non-magnetic layers. Susceptibility, specific heat and neutron scattering measurements combined with high-temperature series expansions and spin-wave calculations confirm that $Ba_8CoNb_6O_{24}$ is basically a two-dimensional (2D) magnet with no detectable spin anisotropy and no long-range magnetic ordering down to 0.06 K. In other words, $Ba_8CoNb_6O_{24}$ is very close to be a realization of the paradigmatic spin-$1/2$ triangular Heisenberg model, which is not expected to exhibit symmetry breaking at finite temperature according to the Mermin and Wagner theorem.

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In a celebrated 1966 paper [1], Mermin and Wagner demonstrated that thermal fluctuations prevent 2D magnets to spontaneously break their continuous spin-rotation symmetry if the interactions decay fast enough with the distance between spins. The role of thermal fluctuations is replaced by quantum fluctuations in one-dimensional (1D) systems at temperature $T = 0$; for instance, the spin-1/2 Heisenberg antiferromagnetic chain does not display long-range magnetic order in the $T = 0$ limit and instead hosts quasi-long-range correlations [2] and fractional spin excitations [3–5]. Quantum fluctuations are also expected to have a strong effect on the ground states of highly frustrated 2D and 3D Mott insulators. Indeed, the realization of *quantum spin-liquids*, quantum-entangled states of matter which do not exhibit magnetic ordering, is a major focus of modern condensed matter physics [6, 7]. While spin-liquids are an extreme case of quantum states of matter, 2D systems that *do* order at $T = 0$ can still exhibit strong deviations from semi-classical behavior. For instance, the elementary excitations of a 2D ordered magnet (magnons) become weakly bonded pairs of fractional excitations near the "quantum melting point" (QMP) that signals the transition into a spin liquid state. A clear indication of proximity to a QMP is a strong suppression of the ordered moment relative to the full moment.

The spin-1/2 2D triangular-lattice Heisenberg antiferromagnet (QTLHAF) displays non-collinear spin-order at $T = 0$ with a relative suppression of the ordered moment of more than 50% [8–13]. This makes it an ideal model for studying the effect of strong quantum fluctuations on the spectrum of magnetic excitations. In real materials, however, weak interlayer interactions and spin or spatial anisotropies are likely present. Even extremely small perturbations are sufficient to induce long-range magnetic order at a sizable Néel temperature $T_{\rm N}$, because $T_{\rm N}$ increases logarithmically in the interlayer-coupling or in the exchange anisotropy [14–18]. This is the case for well-studied compounds comprising transition-metal ions, such as Cs_2CuCl_4 ($T_{\rm N} = 0.62$ K [19]) and $Ba_3CoSb_2O_9$ ($T_{\rm N} = 3.8$ K [20]). Quantum effects remain prominent below $T_{\rm N}$ and lead to order from disorder phenomena, such as the one third magnetization plateaux [21–23], in the presence of an external magnetic field. A recent inelastic neutron scattering (NS) study of $Ba_3CoSb_2O_9$ [24] showed that even in presence of sizable perturbations [20, 25–27] relative to the pure QTLHAF, dynamical features are not captured by spin-wave theory (SWT). This observation suggests that alternative theoretical approaches are not only needed to describe spin-liquid states, but also to account for qualitative properties of the excitation spectrum of ordered magnets near their QMP [28, 29].

In this Letter, we introduce $Ba_8CoNb_6O_{24}$, a new realization of the QTLHAF model obtained from $Ba_3CoSb_2O_9$ by intercalating non-magnetic layers between the triangular

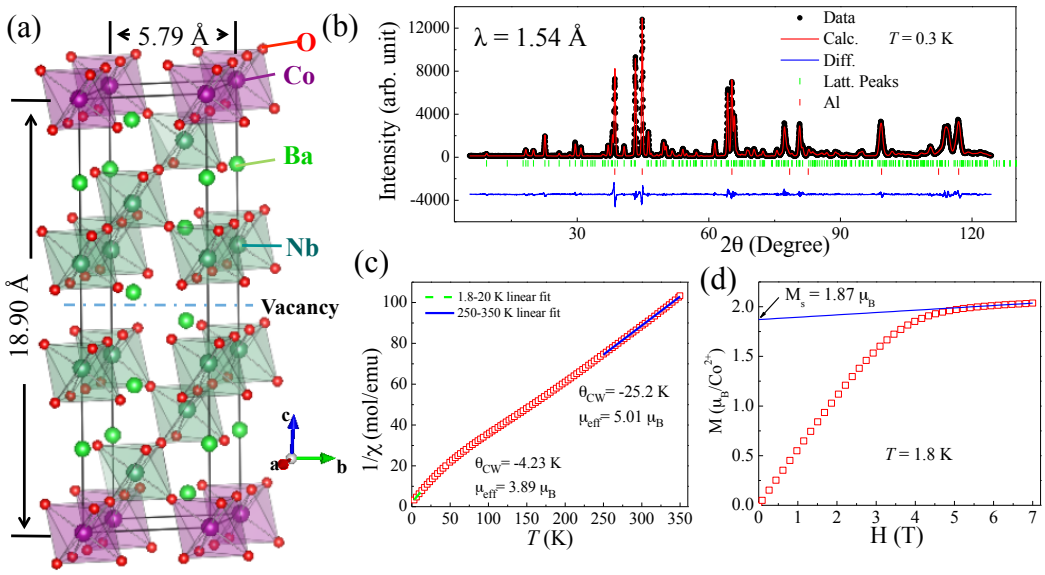

FIG. 1: (color online) (a) Stacked layer structure of $Ba_8CoNb_6O_{24}$ with Co^{2+} ions sitting on a triangular lattice. (b) Rietveld refinement of the neutron powder diffraction pattern measured at T = 0.3 K with λ = 1.54 Å. (c) Temperature dependence of the inverse DC magnetic susceptibility and corresponding Curie-Weiss fits. (d) Isothermal DC magnetization measured at T = 1.8 K and extrapolation of the saturated magnetization from the linear dependence above the saturation field (blue solid line).

planes. We present structural, thermo-magnetic, inelastic NS and theoretical results indicating that spin-space anisotropy and inter-plane interactions are both essentially absent in $Ba_8CoNb_6O_{24}$. Having a model realization of the QTL-HAF at hand, we test predictions from semi-classical spin-wave theory and investigate potential exotic phenomena arising from enhanced quantum fluctuations.

To obtain $Ba_8CoNb_6O_{24}$, we start from $Ba_3CoSb_2O_9$, a compound that comprises layers of magnetic CoO_6 octahedral stacked along the hexagonal c axis and separated by two non-magnetic SbO_6 layers. The intra-layer Co–Co distance is 5.86 Å and the interlayer Co–Co distance is 7.23 Å [20]. In the former material, the inter-layer magnetic exchange interaction, J', is ∼5% of the intra-layer exchange J [24, 26]. Moreover, $Ba_3CoSb_2O_9$ possesses a small easy-plane XXZ anisotropy (the ratio between the longitudinal and transverse exchange interactions is $\Delta \approx 0.9$). While the degree of spin anisotropy is difficult to control, one natural strategy to reduce the inter-layer interaction is to insert additional non-magnetic layers in between the magnetic layers. $Ba_8CoNb_6O_{24}$ exactly meets these requirements: it contains a vacant layer and *six layers* of non-magnetic NbO_6 octahedral between triangular layers of Co^{2+} ions [see Fig. 1(a)]. While the intra-layer Co–Co distance of 5.79 Å is comparable to $Ba_3CoSb_2O_9$, the inter-layer Co–Co distance is dramatically increased up to 18.90 Å [30]. This remarkable structure is expected to guarantee a true 2D nature for the magnetic properties of $Ba_8CoNb_6O_{24}$.

To confirm the physical outcome of our intercalation strategy, we present structural and thermo-magnetic characterization of powder samples of $Ba_8CoNb_6O_{24}$ grown from a solid-state synthesis method detailed in the supplemental information (SI) [31]. A fit to our neutron powder diffraction (NPD) pattern measured at $T = 0.3$ K with $\lambda = 1.54$ Å [Fig. 1(b)] yields the space-group $P\bar{3}m1$ with a = 5.7902(2) Å and c = 18.9026(3) Å. A Rietveld refinement yields structural parameters given in SI [31] and indicates a limited amount of disorder (< 2 %) between the Co and Nb sites, consistent with an earlier study [30]. The patterns at $T = 0.3$ K and 2.0 K are essentially identical: no additional Bragg peaks appear and broadening of existing peaks is not observed within the sensitivity and resolution of our experiment [31], suggesting the absence of a structural transition or long-range magnetic order down to $T = 0.3$ K.

The temperature dependence of the magnetic DC susceptibility, $\chi(T)$, shows no sign of magnetic ordering or spin freezing down to $T = 1.8$ K [Fig. 1(c)]. The slope of $1/\chi(T)$ changes around $T = 150$ K; Curie-Weiss fits yield $\mu_{\rm eff} = 5.01(2)\ \mu_{\rm B}$ and $\theta_{\rm CW} = -25.2(3)$ K for 200 K $< T <$ 350 K, and $\mu_{\rm eff} = 3.89(2)\ \mu_{\rm B}$ and $\theta_{\rm CW} = -4.23(1)$ K for 1.8 K $< T <$ 30 K. The effective moment reduction indicates a crossover from a high-spin state ($S = 3/2$) to a low-spin state ($S = 1/2$) and is typical for Co^{2+} ions in an octahedral environment, see *e.g.*, $ACoB_3$ (A = Cs, Rb, B = Cl, Br) [32]. The isothermal DC magnetization at $T = 1.8$ K, shown in Fig. 1(d), indicates that spins saturate above $\mu_0 H_s \approx 4$ T, while a fit to the linear magnetization observed from $\mu_0 H = 5$ T to 7 T uncovers a Van Vleck paramagnetic contribution of 0.023 $\mu_{\rm B}$.T^{-1} per Co^{2+} and yields a saturation magnetization $M_{\rm s} = 1.87\ \mu_B$. This value is comparable to that of $Ba_3CoSb_2O_9$ and corre-

sponds to a powder-averaged gyromagnetic ratio g = 3.84 for the effective $S = 1/2$ Kramers doublet.

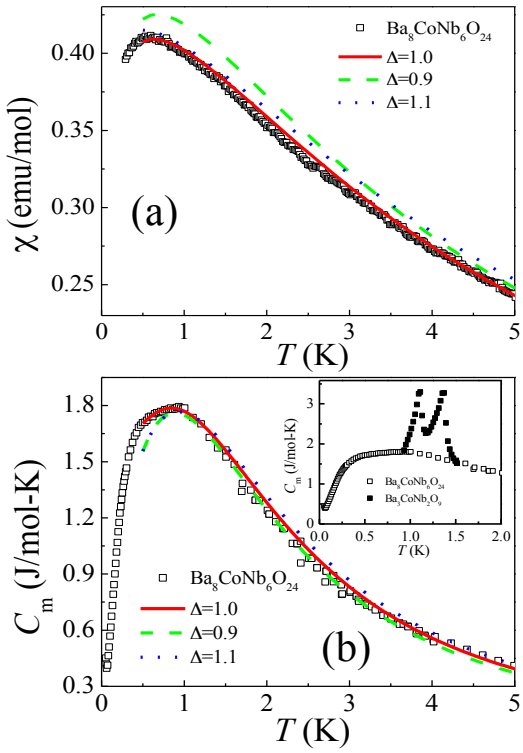

FIG. 2: (color online) (a) Temperature dependence of the magnetic AC susceptibility of $Ba_8CoNb_6O_{24}$ and corresponding high-temperature series expansion simulations for the 2D spin-1/2 triangular-lattice antiferromagnet with XXZ exchange anisotropy. Values of Δ = 0.9, 1.0, and 1.1 are used and simulations run down to a temperature of 0.5 K using Padé approximants of order [6,6]. The measurements are obtained with an AC excitation field of amplitude 0.5 Oe and frequency 300 Hz, and matched to the DC susceptibility below $T = 15$ K by an overall T-independent rescaling factor [31]. (b) Temperature dependence of the magnetic part of the specific heat of $Ba_8CoNb_6O_{24}$ and matching simulations. (Insert) Comparison to the magnetic specific heat of $Ba_3CoNb_2O_9$.

Similarly, the T-dependence of the magnetic AC susceptibility, shown in Fig. 2(a), uncovers no sharp features down to $T = 0.3$ K. Instead, it reveals a broad peak centered at $T = 0.6$ K, which we associate with the onset of short-range magnetic correlations. The presence of magnetic correlations below $T \approx 1$ K is confirmed by the heat-capacity measurements shown in Fig. 2(b). The magnetic contribution to the specific heat, $C_{\rm m}$, was isolated by subtracting the lattice contribution, $C_{\rm L}$, of the iso-structural non-magnetic compound $Ba_8ZnTa_6O_{24}$ [31]. The $C_{\rm m}(T)$ curve reveals a broad peak around $T = 0.8$ K without any sharp feature down to $T = 0.06$ K (the small increase at lower temperatures is attributed to nuclear spins), suggesting the absence of a magnetic phase transition down to $T \leq 0.06$ K. By integrating $C_m(T)/T$ from $T_{\rm min} = 0.06$ K to a target ($T \leq 8$ K), we obtain the change in magnetic entropy $\Delta S_m = S_m(T) - S_m(T_{\rm min})$ [31]. The release of entropy reaches 5.32 J mol^{-1} K^{-1} at $T = 8$ K, which is close to the value $R \ln 2$ = 5.76 J mol^{-1} K^{-1} expected for a Kramers doublet ground-state.

What is the origin of the broad peak observed in $C_{\rm m}(T)$? Previous quantum Monte Carlo studies on quasi-2D antiferromagnetic Heisenberg models have shown that the onset of long-range magnetic order yields a sharp peak in $C_{\rm m}(T)$ even for inter-layer exchange interactions as small as $J'/J = 2\times10^{-4}$ [33]. Upon further decreasing the inter-layer coupling, the sharp peak disappears and only a broad peak remains. This is precisely the behavior we observe in $Ba_8CoNb_6O_{24}$, thus exposing the practically ideal 2D nature of magnetism in this compound. This becomes even clearer when our results are compared to $Ba_3CoNb_2O_9$ [see the inset of Fig. 2(b)], which comprises only two non-magnetic layers between the magnetic planes. The specific heat of $Ba_3CoNb_2O_9$ reveals two subsequent phase transitions at $T_{\rm N1}$ = 1.10 K and $T_{\rm N2}$ = 1.36 K, indicating the presence of easy-axis anisotropy [34]. At a similar energy scale ($\approx$ 1 K), $Ba_8CoNb_6O_{24}$ only exhibits a single broad peak with no observable signs of exchange anisotropy or inter-layer coupling.

The temperature dependence of $\chi(T)$ and $C_{\rm m}(T)$ for the QTLHAF model has been well documented using high-temperature series expansions (HTSE) [35–38] up to 12th order [39]. To determine if exchange anisotropy is present in $Ba_8CoNb_6O_{24}$, we extend existing HTSE work to the XXZ Hamiltonian,

$$\mathcal{H} = J \sum_{\langle i,j \rangle} (S_i^x S_j^x + S_i^y S_j^y + \Delta\, S_i^z S_j^z), \qquad (1)$$

where $\langle i,j \rangle$ denotes nearest-neighbor spins. We obtained results for the isotropic ($\Delta = 1.0$), easy-plane ($\Delta = 0.9$), and easy-axis ($\Delta = 1.1$) models [31]. The best HTSE fit to our experimental observations, namely $\chi(T)$ and $C_{\rm m}(T)$ below $T =$ 5 K, yields $J = 0.144$ meV for $\Delta = 1.0$ with a fitting error-bar on J smaller than 10^{-3} meV [see Fig. 2]. For a fixed value of J, the fit quality becomes worse as soon as Δ deviates from 1.0 and lead to higher (respectively lower) peak heights for $\chi(T)$ (resp. $C_{\rm m}$).

With strong thermodynamic indication that $Ba_8CoNb_6O_{24}$ realizes the purely 2D and spin-isotropic QTLHAF model, we now turn to the nature of its spin excitations. NS intensity (powder-averaged) as a function of momentum transfer Q and energy transfer E allows to track the development of magnetic correlations upon lowering T. In Fig. 3(a), we present such results for $T = 0.3$ K, with additional results for 5 K $\leq T \leq$ 0.05 K included in SI [31]. The momentum dependence of the magnetic signal reveals strong ridges of intensity emerging from $Q \approx 0.7$ Å^{-1} with less intense repetitions at 1.5 Å^{-1} and 2.0 Å^{-1}. While spins appear well-correlated at $T = 0.3$ K, the low-energy signal ($E \leq 0.1$ meV) remains broader than instrumental resolution suggesting that spin correlations remain short-ranged and static magnetic order is absent. The energy dependence of the main signal reveals gapless excitations extending up to 0.35 meV with less intense

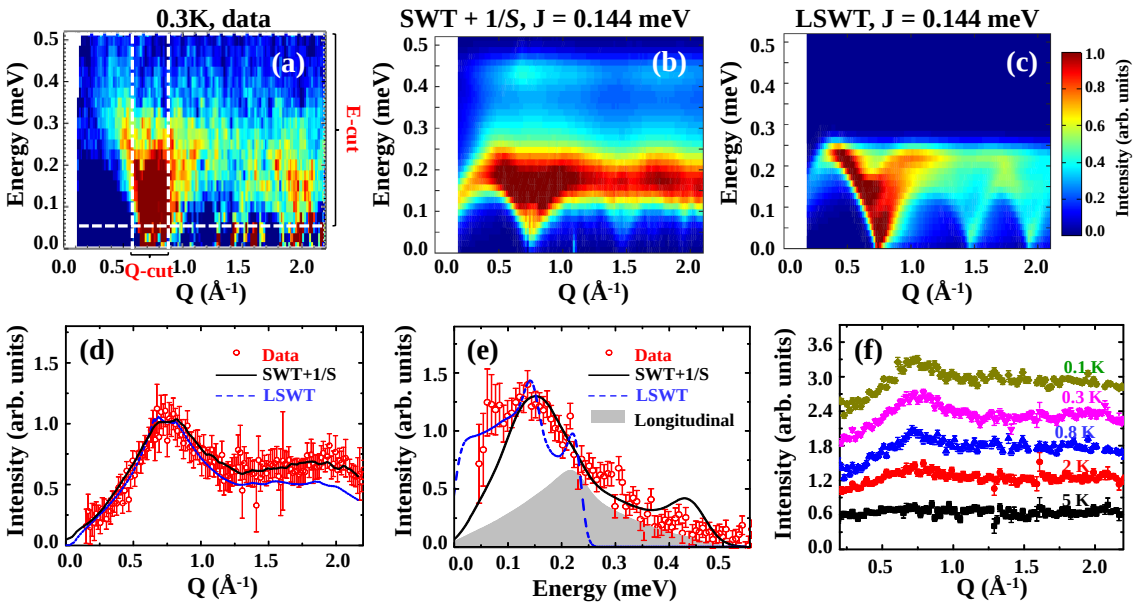

FIG. 3: (color online) (a) Powder-averaged inelastic NS spectra of $Ba_8CoNb_6O_{24}$ at $T = 0.3$ K. Data collected at $T = 10$ K is used as background. (b,c) NS intensity calculated for $J = 0.144$ meV using non-linear SWT with $1/S$-corrections and linear SWT, respectively. Calculated intensities have been convoluted by Gaussian profiles of full-width at half maximum $\Delta E = 0.025$ meV and $\Delta Q = 0.015$ Å^{-1} to approximate the effects of instrumental resolution. (d,e) Comparisons between experiment (red dots), $1/S$-SWT (solid black line) and linear SWT (dashed blue line) as energy-integrated ($0.05 \leq E \leq 0.52$ meV) and momentum-integrated ($0.6 \leq Q \leq 0.9$ Å^{-1}) cuts, respectively. The shaded (gray) area corresponds to the longitudinal (two-magnon) contribution to the NS intensity in $1/S$-SWT. The high-energy bump around E =0.45 meV in (e) is an artifact of our $1/S$ approximation [5]. (f) Temperature dependence of the energy-integrated intensity of (d) and the graphs of different temperature have been displaced each time by an Intensity of 0.6. Error bars correspond to one standard error.

signal reaching up to $E = 0.45$ meV. These features do not change significantly as T is lower than 0.5 K [31].

To model the dynamic magnetic correlations, we resort to SWT at $T = 0$; $1/S$ corrections [40] are included in Fig. 3(b) while we remain strictly at the linear level (LSWT) [41] in Fig. 3(c). We assume that the system orders in the 120° magnetic structure, at least at $T = 0$, and use $J = 0.144$ meV from the thermodynamic measurements. Our E-integrated [Fig. 3(d)] and Q-integrated [Fig. 3(e)] scans reveal a good agreement between NS measurements and powder-averaged $1/S$-SWT predictions. The most visible improvement between $1/S$ and linear SWT calculations stems from the inclusion of longitudinal spin fluctuations in the former. These excitations reflect the reduction of the ordered moment by quantum fluctuations and form a high-energy continuum also known as two-magnon scattering. The absence of notable temperature dependence for the $E \geq 0.1$ meV magnetic scattering below $T = 0.5$ K [Fig.3(f)] further supports the evidence for strong quantum fluctuations in the ground-state of $Ba_8CoNb_6O_{24}$.

It is instructive to compare the excitations of $Ba_8CoNb_6O_{24}$ with that of the quasi-2D compound $Ba_3CoSb_2O_9$, for which $J' = 0.05\ J$, $J \approx 1.7$ meV, and $\Delta \approx 0.9$. While both compounds comprise structurally similar magnetic layers with comparable Co–Co bond lengths, the ~ 2.0 meV in-plane excitation bandwidth of $Ba_3CoSb_2O_9$ is an order of magnitude larger than the present observation of ~ 0.18 meV for $Ba_8CoNb_6O_{24}$. In units of their respective J, the bandwidth $W \approx 1.18\ J$ for the former compound compares well with $W \approx 1.24\ J$ obtained by the present $1/S$-SWT analysis for $Ba_8CoNb_6O_{24}$ [see Fig. 3(b)]. While $Ba_3CoSb_2O_9$ develops long-range magnetic ordering below $T_N = 3.7$ K $\sim 0.19J$, $Ba_8CoNb_6O_{24}$ does not exhibit any magnetic ordering down to $T = 0.06$ K $\sim 0.04J$. Given that T_N increases logarithmically both in the magnitude of J' and Δ, the suppression of T_N/J by a factor of at least 4 relative to $Ba_3CoSb_2O_9$ implies that inter-plane and anisotropic exchange interactions must be extremely small in $Ba_8CoNb_6O_{24}$.

In conclusion, our powder-sample experiments reveal that $Ba_8CoNb_6O_{24}$ is virtually an ideal realization of the QTL-HAF and an unique compound to expose the consequences of the Mermin and Wagner theorem in a real triangular-lattice material. Recent studies have shown that quantum fluctuations have a non-perturbative effect on the magnetic excitations of quasi-2D quantum antiferromagnets [24, 42]. We expect even stronger quantum effects in the magnetic excitation spectrum of $Ba_8CoNb_6O_{24}$, making it an even better candidate to challenge existing semi-classical theories for the dynamic response of frustrated quantum antiferromagnets. From the materials discovery standpoint, our work devises a method for reducing dimensionality by intercalating non-magnetic layers in layered compounds that can be extended to

other lattices to reveal new physics.

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* Electronic address: mourigal@gatech.edu
† Electronic address: hzhou10@utk.edu
‡ Electronic address: jma3@sjtu.edu.cn

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