

# Crystallography-driven molecularization of a two-dimensional spin-3/2 magnet

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**Abstract.** Large-spin two-dimensional magnets are generally expected to develop conventional long-range order once the dominant exchange scale becomes appreciable. The layered spin-3/2 maple-leaf compound  $\text{Na}_2\text{Mn}_3\text{O}_7$  defies this expectation: despite sizable antiferromagnetic interactions and no evident disorder, it exhibits no magnetic ordering and displays two well-separated thermodynamic crossover scales. We show that this behavior originates from a crystallography-driven molecularization of the magnetic degrees of freedom. The low-symmetry structure partitions the Mn sublattice into inequivalent exchange pathways, generating a pronounced hierarchy that nearly isolates antiferromagnetic hexagons. Magnetic correlations therefore develop in two stages: first within individual hexagons at a scale set by the dominant exchange, and only at much lower temperatures do frustrated inter-hexagon couplings attempt to establish coherence across the lattice. While isolated hexagons reproduce the two-step thermodynamic structure, the experimentally relevant temperature scales emerge only once the hexagons are embedded in the frustrated two-dimensional network. The resulting quantum ground state is magnetically disordered, characterized by strong intra-hexagon correlations and rapidly decaying inter-hexagon correlations. These results identify crystallographic inequivalence as a materials-level mechanism for stabilizing molecularized and quantum-disordered states even in large-spin two-dimensional magnets.

## Introduction

Frustrated quantum magnets are often introduced through a simple expectation: increase the spin length, and quantum fluctuations weaken, so conventional magnetic order should become more robust [1, 2]. Yet instructive counterexamples—from dimerized quantum paramagnets to proximate spin-liquid regimes—arise precisely when the lattice and exchange network reorganize the low-energy degrees of freedom into local motifs (dimers, plaquettes, or larger clusters) rather than individual spins. The paradigmatic Shastry–Sutherland model [3] illustrates how an exchange hierarchy can stabilize an exact product of singlets and how small perturbations unlock competing phases and quantum criticality [4, 5, 6, 7, 8]. This broader lesson motivates a timely question for materials-based frustrated magnetism: when a real compound refuses to order, does it realize a genuinely two-dimensional frustrated magnet, or do crystallography and exchange hierarchy repartition the degrees of freedom into emergent clusters whose thermodynamic signatures survive even when long-range order is suppressed?

The maple-leaf lattice (MLL) [9] provides a particularly sharp arena in which to pose this question. As a one-seventh site-depleted triangular lattice with coordination number five, it interpolates between triangular and kagome geometries and supports diverse classical and quantum phases [10, 11, 12, 13]. On the theory side, the MLL hosts an exact singlet product ground state for minimal anisotropy, placing it next to the Shastry–Sutherland model among exceptional uniform tilings [14]. Beyond this point, modern approaches have mapped out competing magnetic orders, magnetization plateaus, and candidate quantum-disordered regimes [10, 11, 12, 13, 15, 16, 17, 18, 19]. Experimentally, MLL realizations occur in a growing family of natural and synthetic compounds, including bluebellite [20], mojaveite [20], fuettererite [21], sabelliite [22], spangolite [23, 24, 25, 26, 27, 28], and semi-classical MLL antiferromagnets such as  $\text{MgMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$  [29]. In real materials, however, structural distortions and inequivalent exchange paths are the rule rather than the exception [20, 27, 29, 30, 31, 32, 33, 34, 35]. These developments sharpen a central puzzle: how robust are MLL phases to the structural inequivalence and further-neighbor exchanges that inevitably occur in real compounds?

A striking case is the layered manganate  $\text{Na}_2\text{Mn}_3\text{O}_7$  [36, 37]. While most attention has focused on spin-1/2 copper-based realizations [27, 32],  $\text{Na}_2\text{Mn}_3\text{O}_7$  hosts spin-3/2 moments on  $\text{Mn}^{4+}$  and would naively be expected to order once the dominant exchange scale becomes appreciable. Instead, experiments report no long-range magnetic order down to the lowest measured temperatures, accompanied by pronounced short-range correlations developing below  $\sim 100$  K [36, 37]. Its thermodynamics exhibit two clearly separated crossover scales: a broad maximum in the uniform susceptibility near 110–120 K and a lower-temperature enhancement of the magnetic specific heat around 60–70 K. Such a separation of scales is difficult to reconcile with a simple uniform lattice magnet and instead points to strong correlations forming on intermediate length scales.

More broadly,  $\text{Na}_2\text{Mn}_3\text{O}_7$  raises a conceptual question extending beyond the MLL itself: can crystallographic inequivalence reorganize a nominally two-dimensional magnet into an array of emergent magnetic “molecules,” whose internal correlations dominate thermodynamics and suppress long-range order even for large spins? In what follows, we show that this is precisely what occurs. Starting from the experimentally resolved triclinic crystal structure with three inequivalent manganese sites [38] [see

Supplementary Note 1 for why Ref. [38] is preferred over Refs. [39, 40]), we derive a microscopic Heisenberg Hamiltonian via *ab initio* energy mapping [41, 42, 43]. The resulting in-plane model is strongly nonuniform: three dominant antiferromagnetic exchanges nearly isolate hexagonal plaquettes, while weaker and mostly ferromagnetic couplings frustrate inter-hexagon coherence. This hierarchy naturally localizes strong antiferromagnetic correlations on hexagons, reminiscent of other exchange-hierarchical magnets [5, 44, 45, 46]. Magnetic correlations thus develop in two stages: first within hexagons at a scale set by the dominant intra-hexagon couplings, and only at much lower temperatures do frustrated inter-hexagon links attempt to establish lattice coherence.

We combine classical Monte Carlo, exact diagonalization of isolated spin-3/2 hexagons, and pseudofermion functional renormalization group calculations to determine the thermodynamic signatures and quantum fate of this hierarchy. While isolated hexagons robustly generate two crossover scales, the experimentally observed temperature positions emerge only once the hexagons are embedded in the frustrated two-dimensional network. Quantum fluctuations suppress the incipient classical ordering tendency and stabilize a magnetically disordered ground state with pronounced intra-hexagon correlations and rapidly decaying inter-hexagon correlations. The associated momentum-resolved correlations are consistent with available powder-averaged neutron-scattering profile [37].

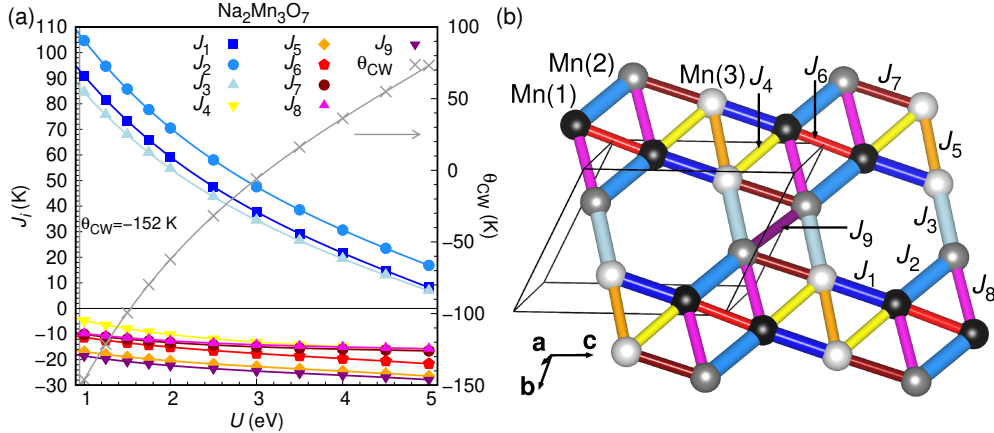
These results sharpen the broader message of current MLL research: structural inequivalence does not merely perturb the ideal phase diagram; it can qualitatively repartition the degrees of freedom and stabilize quantum-disordered behavior even for comparatively large spins. Our explanation relies on a translation-invariant Hamiltonian extracted from the experimentally resolved crystal structure and does not require quenched randomness [47, 48]. Nor is  $\text{Na}_2\text{Mn}_3\text{O}_7$  simply a weakly coupled molecular magnet: the thermodynamic maxima are strongly renormalized relative to isolated-hexagon scales, and the momentum-space correlations reflect an extended frustrated network rather than independent cluster form factors [49, 50]. Crucially, the exchange hierarchy emerges directly from crystallographic inequivalence and cannot be adiabatically deformed to a uniform two-dimensional lattice.

In  $\text{Na}_2\text{Mn}_3\text{O}_7$ , the “molecularization” of magnetism is *crystallography-enforced*: a translation-invariant, low-symmetry exchange network generates a robust hierarchy that reorganizes the low-energy degrees of freedom into emergent hexagonal units. Importantly, the experimentally relevant crossover scales are *not* set by an autonomous hexagon spectrum; they arise only once these units are embedded in the frustrated two-dimensional network, which collectively renormalizes the thermodynamic response to lower temperatures. This provides a materials-level route to cluster-dominated quantum paramagnets beyond the spin-1/2 paradigm.

## Results

### *Model Hamiltonian*

The low-temperature triclinic crystal structure of  $\text{Na}_2\text{Mn}_3\text{O}_7$  hosts three symmetry-inequivalent  $\text{Mn}^{4+}$  sites arranged on a distorted maple-leaf lattice. Starting from this experimentally resolved structure, we derive a microscopic spin Hamiltonian using Density Functional Theory (DFT)-based energy mapping [see Methods and Supplementary Note 1].



**Figure 1.** Hamiltonian of  $\text{Na}_2\text{Mn}_3\text{O}_7$  determined by DFT based energy mapping. (a) Nine exchange interactions of  $\text{Na}_2\text{Mn}_3\text{O}_7$  making up the maple leaf lattice as function of on-site interaction strength  $U$ , at fixed Hund’s rule coupling  $J_H = 0.76$  eV. The vertical line indicates the value  $U = 0.94$  eV at which the Heisenberg Hamiltonian parameters yield the Curie-Weiss temperature  $T = -152$  K determined by Venkatesh *et al.* [36] from the experimental susceptibility. (b) Structure of the  $\text{Na}_2\text{Mn}_3\text{O}_7$  lattice with the nine “nearest neighbor” exchange paths constituting the distorted maple leaf lattice. Strong antiferromagnetic couplings  $J_1$ – $J_3$  stabilize local Néel order within hexagonal plaquettes. These hexagons are coupled by weaker, predominantly ferromagnetic interactions, which frustrate coherent inter-hexagon alignment and give rise to a stripe-like classical ordering tendency at an incommensurate wave vector which is classically determined to be  $\mathbf{k}_0$  [see Eq. (3)]. The resulting classical state is only weakly stabilized, with the residual inter-hexagon coherence scale remaining small compared with the dominant intra-hexagon exchange scale.

The resulting model is well described by an isotropic Heisenberg Hamiltonian,

$$H = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where  $\mathbf{S}_i$  are  $S = 3/2$  spins on Mn sites.

The exchange network is strongly nonuniform. Three dominant antiferromagnetic couplings  $J_1$ – $J_3$  form nearly isolated hexagonal plaquettes, defining the primary energy scale  $J_h \sim 100$  K. As we show below, this hierarchy produces a *hexagon-first, network-later* regime: local correlations form at  $T_h \sim J_h$ , while the experimentally observed crossover temperatures are shifted downward by the frustrated inter-hexagon network.

All remaining interactions are substantially weaker and include mostly ferromagnetic contributions. This establishes a pronounced hierarchy

$$J_1, J_2, J_3 \gg J_{\text{inter}}, \quad (2)$$

which partitions the lattice into strongly correlated hexagonal units weakly coupled by frustrated inter-hexagon exchanges.

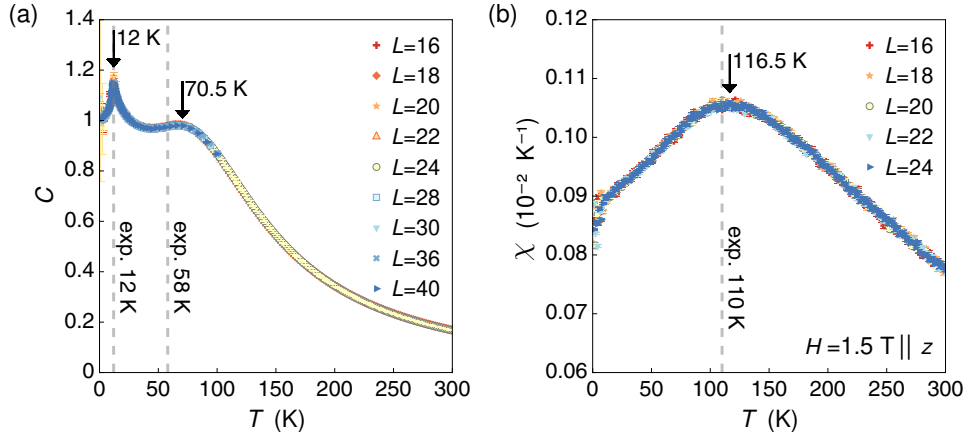
The extracted parameters reproduce the experimental Curie–Weiss temperature  $\theta_{CW}$  and are robust against moderate variations of the interaction parameters [Supplementary Note 1]. A complete list of exchange constants is provided in Table 1.

**Table 1.** Exchange paths and Heisenberg Hamiltonian couplings as determined from DFT based energy mapping. The paths are identified by Mn–Mn distance measured in the structure from Ref. [38], and they are labeled according to increasing distance. Note that interlayer couplings  $J_{22}$  to  $J_{24}$  and  $J_{31}$  to  $J_{36}$  are disregarded here. An exploratory larger-scale DFT energy-mapping calculation using a four-fold supercell with 24 inequivalent Mn spins indicates that the leading interlayer exchanges are all sub-Kelvin in magnitude, comparable to or smaller than  $J_{25}$ , thereby confirming the excellent two-dimensionality of  $\text{Na}_2\text{Mn}_3\text{O}_7$  on the energy scales considered here. Throughout this work, “nearest neighbors” refer to the nine shortest Mn–Mn bonds per Mn site identified in the experimental crystal structure and used in the DFT total-energy mapping.

	value (K)	role	$d_{\text{Mn-Mn}}$ (Å)
$J_1$	93.0788(3)	NN ( $h_1$ )	2.7887
$J_2$	107.089(2)	NN ( $h_2$ )	2.80028
$J_3$	86.5117(4)	NN ( $h_3$ )	2.805
$J_4$	-4.27245(5)	NN ( $t_1$ )	2.93047
$J_5$	-16.5873(7)	NN ( $d_1$ )	2.93479
$J_6$	-10.9994(6)	NN ( $d_2$ )	2.94347
$J_7$	-9.84737(2)	NN ( $t_2$ )	2.95048
$J_8$	-9.55351(2)	NN ( $t_3$ )	2.95498
$J_9$	-18.2468(5)	NN ( $d_3$ )	2.9606
$J_{10}$	-7.24539(2)	2NN( $\circ$ )	4.82937
$J_{11}$	-8.00611(2)	2NN( $\circ$ )	4.83238
$J_{12}$	-4.98996(5)	2NN( $\circ$ )	4.8764
$J_{13}$	-14.1377(6)	2NN	4.9108
$J_{14}$	-12.8032(7)	2NN	4.93777
$J_{15}$	-11.8711(5)	2NN	4.94802
$J_{16}$	-3.63742(2)	2NN	5.00436
$J_{17}$	-2.52701(4)	2NN	5.02042
$J_{18}$	-2.16424(2)	2NN	5.0209
$J_{19}$	-8.32332(5)	3NN( $\circ$ )	5.55231
$J_{20}$	-8.76239(7)	3NN( $\circ$ )	5.61725
$J_{21}$	-9.4215(6)	3NN( $\circ$ )	5.61771
$J_{25}$	0.445469(4)	3NN ( $J_2+J_4$ )	5.73021
$J_{26}$	3.09456(6)	3NN ( $J_1+J_6$ )	5.73072
$J_{27}$	–	3NN ( $J_1+J_7$ )	5.73843
$J_{28}$	–	3NN ( $J_3+J_5$ )	5.7395
$J_{29}$	–	3NN ( $J_3+J_8$ )	5.75864
$J_{30}$	–	3NN ( $J_2+J_9$ )	5.75961

While there is, to the best of our knowledge, no direct experimental evidence for sizeable spin-exchange anisotropy in  $\text{Na}_2\text{Mn}_3\text{O}_7$ —such as single-crystal susceptibility anisotropy, ESR constraints, or an inelastic-neutron signature requiring an anisotropic spin Hamiltonian—symmetry does not allow us to exclude Dzyaloshinskii–Moriya interactions or symmetric anisotropic exchange on all bonds. In particular, a DM vector is forbidden only when the corresponding bond has an inversion center at its midpoint; otherwise antisymmetric exchange is allowed in principle. The magnetic ion is  $\text{Mn}^{4+}$ , i.e. a  $3d^3$  ion in an octahedral crystal field, whose ground state is orbitally

nondegenerate; the orbital moment is therefore largely quenched. This provides a physical basis for using an isotropic Heisenberg model as the minimal microscopic description. Our claim is not that anisotropies are symmetry-forbidden or exactly absent, but rather that the dominant exchange hierarchy and the associated hexagon-first physics already emerge at the isotropic level. Weak anisotropic exchanges, if present, are expected primarily to affect the lowest coherence scale, where several competing classical tendencies are close in energy, while the main physics in  $\text{Na}_2\text{Mn}_3\text{O}_7$  remains controlled by the dominant hexagon-forming antiferromagnetic couplings.



**Figure 2.** Bulk thermodynamic properties obtained from cMC simulations of the full Heisenberg model given in Table 1. (a) Magnetic specific heat  $C(T)$  for several system sizes of  $L \times L$  unit cells with periodic boundary conditions. The specific heat increases upon cooling and develops a broad plateau around  $T \approx 70$  K, followed by a weak low-temperature feature near  $T \approx 12$  K. (b) dc magnetic susceptibility  $\chi(T)$  calculated under an applied magnetic field of 1.5 T along the  $z$  axis. A broad maximum appears near  $T \approx 116$  K. Dashed gray vertical markers indicate the temperatures of corresponding experimental features reported in Ref. [36].

### *Luttinger–Tisza: incommensurate order with a shallow energy landscape*

As a classical reference, we analyze the full Heisenberg Hamiltonian using the extension of Luttinger–Tisza (LT) method, which allows us to treat lattices with multiple sublattices exactly [51]. Diagonalization of the Fourier-transformed dressed exchange matrix yields a unique minimum at the incommensurate wavevector

$$\mathbf{k}_0 \simeq (0.50029, 0.04252, 0) \text{ \AA}^{-1} \quad (3)$$

with minimal eigenvalue

$$\lambda_{\min}(\mathbf{k}_0) = -206.415 \text{ K}, \quad (4)$$

corresponding to a classical energy per spin

$$E_{\text{cl}} = -103.208 \text{ K}. \quad (5)$$

The corresponding spin configuration is a single- $\mathbf{k}$  incommensurate coplanar spiral. For details see supplementary note 4.

Crucially, what is small here is *not* the classical energy per spin but the *stiffness* of the ordering tendency: the LT spectrum has a shallow curvature near  $\mathbf{k}_0$ , implying a parametrically weak coherence scale compared to the dominant intra-hexagon exchange  $J_h \sim 100$  K. The corresponding local LT dispersion is shown explicitly in Supplementary Fig. S1, where the minimum appears as a shallow, anisotropic valley rather than a sharply confined basin.

*Thermodynamics: hexagon scale vs network scale*

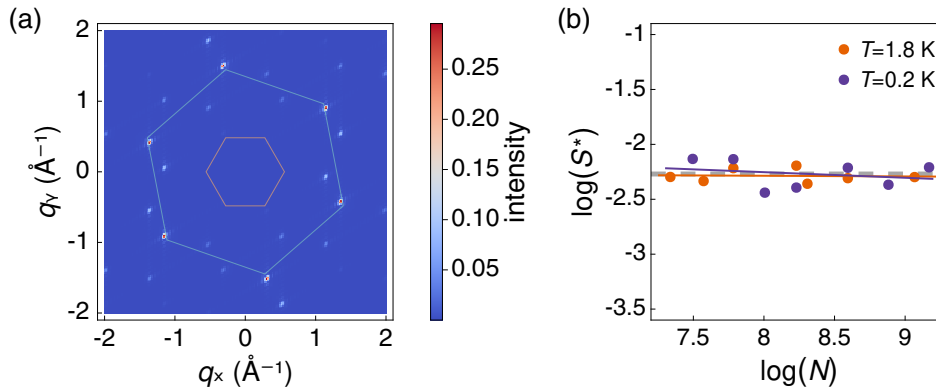
We next examine how this hierarchy manifests at finite temperature using classical Monte Carlo (cMC) simulations of the *ab initio* Hamiltonian using all couplings specified in Table 1. This parameter set reproduces the experimental Curie–Weiss temperature and therefore serves as the baseline for comparison with thermodynamic measurements.

Figure 2(a) shows the magnetic specific heat  $C(T)$  for system sizes up to  $40 \times 40$  unit cells. Upon cooling,  $C(T)$  develops a broad enhancement around  $T \approx 70$  K, followed by a weak low-temperature feature near 12 K. Increasing system size does not sharpen this feature into a true anomaly. Although the detailed shape differs from experiment, the characteristic temperature scales agree quantitatively with the broad enhancement and lower-temperature crossover reported in Ref. [36]. The finite low-temperature value of  $C(T)$  reflects the classical equipartition contribution from quadratic fluctuations. The weak 12 K feature signals the incipient classical ordering tendency associated with the shallow LT landscape.

The magnetic susceptibility exhibits a broad maximum at  $T \approx 116$  K [see Fig. 2(b)], in quantitative agreement with experiment [36, 37], confirming that the dominant exchange scale and the buildup of short-range correlations are captured already at the classical level.

The equal-time structure factor provides complementary information. Figure 3(a) shows  $S(\mathbf{q})$  at  $T = 1.8$  K. Pronounced but broadened maxima appear near the corners of the extended Brillouin zone, with weaker subdominant features inside. Their finite width and weak size dependence indicate that, at the temperatures accessible in the simulations, the correlations remain short-ranged rather than developing into resolution-limited Bragg peaks. This is illustrated by the log-log finite-size analysis of the subdominant peak near  $\mathbf{q} \simeq (1.1, -0.1) \text{ \AA}^{-1}$ , shown in Fig. 3(b), for  $T = 1.8$  K and  $T = 0.2$  K. The peak intensity shows no proportional growth with system size, supporting the interpretation of the low-temperature feature as a soft incipient coherence scale rather than a finite-temperature transition. This is consistent with the Mermin–Wagner theorem, which forbids spontaneous breaking of continuous spin-rotation symmetry at finite temperature in a strictly two-dimensional isotropic Heisenberg model. The  $T = 0$  classical limit is nevertheless controlled by the LT minimum at  $\mathbf{k}_0$ , so the finite-temperature cMC data should be viewed as probing the approach toward a very soft classical ordering tendency rather than establishing a robust ordered phase.

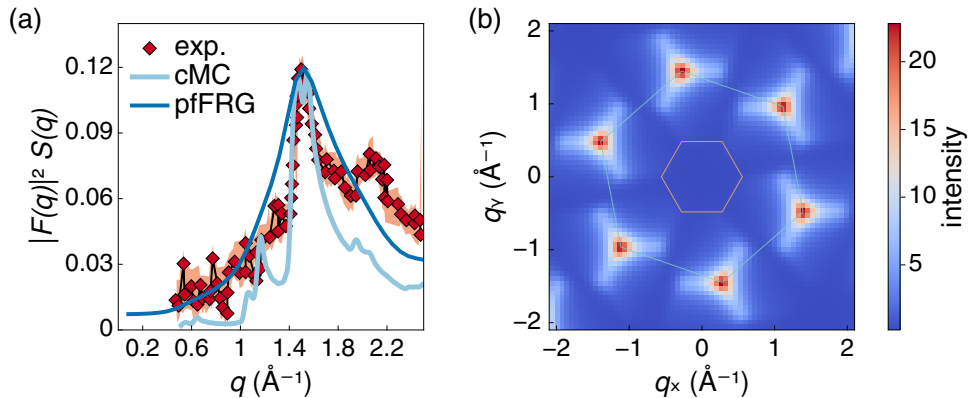
The form-factor-modulated powder average [see Fig. 4(a)] reproduces the dominant neutron-scattering peak position within experimental uncertainty [37]. This broad powder peak is dominated by the shorter-distance, stronger hexagon-scale correlations. The lower energy scale associated with frustrated inter-hexagon coherence does not generate a separate, sharply resolved powder feature in Fig. 4(a). Rather, it enters more indirectly through the low-temperature redistribution and mild sharpening of



**Figure 3.** (a) Momentum-resolved equal-time spin structure factor  $S(\mathbf{q})$  obtained from cMC simulations of the model given in Table 1 at  $T = 1.8$  K, showing broad maxima at incommensurate wave vectors. Brillouin zone and extended Brillouin zone boundaries are shown by orange and green hexagons, respectively. The tilt of the extended Brillouin zone boundary with respect to the first Brillouin zone boundary seen in the figure originates from the geometry of the ideal flat 2D maple-leaf lattice and from the chosen basis-vector pair used to define the corresponding extended zone. Put differently, the extended-zone construction is tied to the real-space orientation of the hexagon motif relative to the primitive lattice vectors. Even though a layer of the actual  $\text{Na}_2\text{Mn}_3\text{O}_7$  material is distorted, the distortions are small enough that they do not qualitatively alter this geometric tilt. (b) Finite-size scaling of the subdominant structure-factor peak associated with inter-hexagon coherence. We plot the peak intensity  $S^*$  near  $\mathbf{q} \simeq (1.1, -0.1) \text{ \AA}^{-1}$  as a function of the total number of sites  $N = 6L^2$  on a log-log scale, for  $T = 1.8$  K and  $T = 0.2$  K. The colored straight lines are linear fits to the corresponding data sets and are shown together with a zero-slope gray dashed line as a reference. The nearly flat behavior indicates that the peak intensity does not show the Bragg-like growth with system size expected for conventional long-range magnetic order. This supports the interpretation of the low-temperature cMC feature as a short-ranged incipient coherence scale rather than a finite-temperature ordering transition.

diffuse spectral weight. This is not surprising, since powder averaging washes out directional information and the lower scale here reflects a soft incipient coherence tendency rather than a distinct second local motif.

A representative cMC snapshot on a finite lattice at  $T = 0.001$  K is shown in Supplementary Fig. S2. At this very low temperature, thermal fluctuations are strongly reduced and the finite-size configuration displays a regular modulation compatible with the LT-selected incommensurate tendency. We regard this snapshot as an illustration of the fragile classical coherence tendency, not as evidence for a finite-temperature ordered phase. The absence of proportional growth in the finite-size scaling of the subdominant structure-factor peak, together with the lack of a sharp thermodynamic anomaly, supports the interpretation that the finite-temperature classical simulations remain in a short-ranged, incipient-coherence regime. Whether the physical  $S = 3/2$  quantum system condenses this fragile classical tendency requires an explicit quantum treatment, which is provided below by pf-FRG.



**Figure 4.** (a) Form-factor-modulated powder-averaged structure factor  $|F(q)|^2 S(q)$ , ( $q = |\mathbf{q}|$ ), computed from cMC and pf-FRG at  $T = 1.8$  K. Experimental neutron-scattering data and associated error profile (orange shaded region) are taken from Ref. [37]. The broad features and absence of sharp Bragg peaks reflect dominant short-range correlations and suppressed long-range magnetic order. (b) Static spin structure factor obtained from pf-FRG calculations. The structure factor displays broad maxima at wave vectors comparable to the classical results, yet remains smooth and finite, indicating that quantum fluctuations preserve the dominant short-range correlations while preventing their condensation into long-range order, consistent with a cluster-dominated quantum paramagnetic regime. The definitions of primitive lattice vectors and the basis vectors used to produce the above results are given in the Supplementary Note 3.

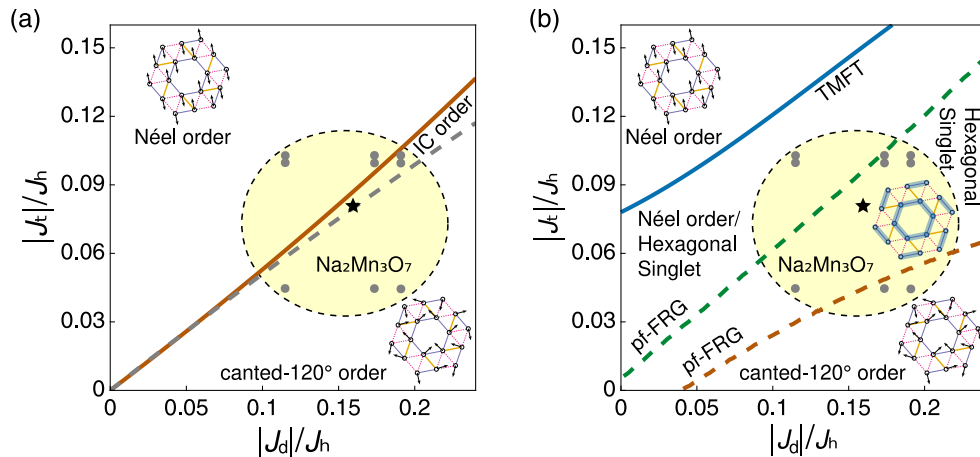
#### Cluster-dominated thermodynamics: hexagon-first physics

The *ab initio* exchange hierarchy provides a natural organizing principle for the thermodynamics. The dominant antiferromagnetic couplings  $J_1$ – $J_3$  form strongly correlated hexagonal plaquettes, while all remaining exchanges are weaker and largely ferromagnetic. Several weaker interactions act within individual hexagons ( $J_{10}$ – $J_{12}$  and  $J_{19}$ – $J_{21}$ ), reinforcing the separation between local and inter-hexagon scales.

To isolate the local building block, we solve the six-site  $S = 3/2$  hexagon by exact diagonalization. The spectrum exhibits a singlet ground state with energy  $E_0 = -277.18$  K per spin and a lowest triplet separated by  $\Delta \sim 10^2$  K. The resulting thermodynamics display two broad maxima:  $T_{\max}^{\chi_{\text{O}}} \simeq 219$  K and  $T_{\max}^{C_{\text{O}}} \simeq 148$  K. Thus, the separation of thermodynamic scales is intrinsic to a single hexagon. Including intra-hexagon diagonal exchanges yields  $E_0 = -282$  K per spin and only weakly renormalized crossover scales ( $T_{\max}^{\chi_{\text{O}}} \simeq 223$  K,  $T_{\max}^{C_{\text{O}}} \simeq 153$  K). All interactions confined to a hexagon therefore preserve the high-temperature scale separation. However, these isolated-cluster scales exceed those of the lattice response ( $\sim 116$  K in  $\chi$ ,  $\sim 70$  K in  $C$ ). The existence of two crossovers is a robust hexagon property, but their experimentally relevant positions require embedding in the frustrated two-dimensional network.

As an *illustrative* (not quantitative) way to visualize how inter-hexagon couplings renormalize cluster thermodynamics, one may write an Random Phase Approximation (RPA)-type dressing,

$$\chi_{\text{RPA}}(T) = \frac{\chi_{\text{O}}(T)}{1 - \lambda \chi_{\text{O}}(T)}, \quad (6)$$

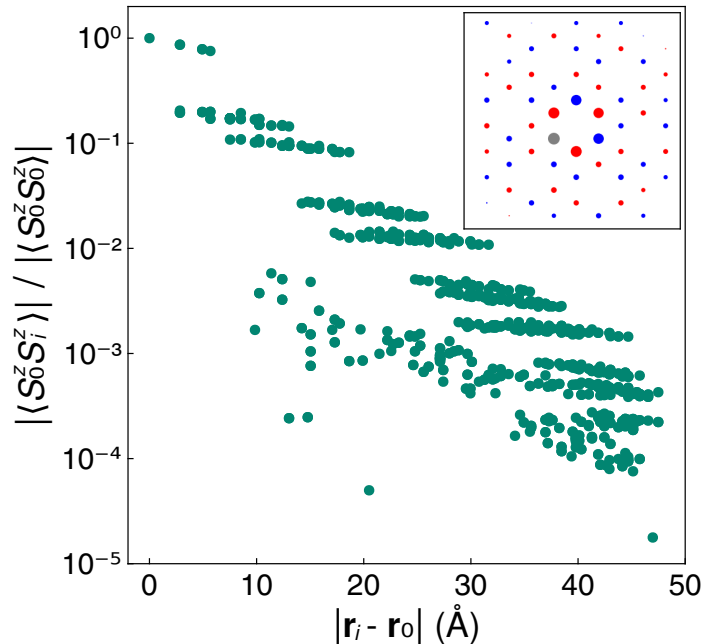


**Figure 5.** Phase boundaries of the symmetrized nearest-neighbor maple-leaf model and the location of  $\text{Na}_2\text{Mn}_3\text{O}_7$  in coupling space. The point marked as star is for the averaged nearest-neighbor couplings  $J_h, J_t, J_d$  obtained from Table 1, and the nine gray points are nine sets of nearest-neighbor  $J_t - J_d$  combinations from the Table with the three nearest-neighbor  $J_h$  averaged out. The region shaded in yellow is the best possible elliptical fit enclosing these ten coupling values. (a) Classical phase diagram (Luttinger–Tisza / energy minimization) in terms of the averaged couplings  $(J_h, J_t, J_d)$ , showing competing Néel, canted-120°, and incommensurate (IC) phases. (b) Quantum phase boundaries from triplon mean-field theory (TMFT) [see Ref. [16]] and pf-FRG. While the two approaches give different quantitative estimates for the extent of the magnetically disordered regime, both bracket a finite parameter window where dipolar order is suppressed for  $S = 1/2$ ; we use this window only as a qualitative upper bound on the corresponding regime expected for  $S = 3/2$ ; the  $\text{Na}_2\text{Mn}_3\text{O}_7$  coupling ratios fall inside this bracketed region.

where  $\lambda$  is the effective RPA parameter renormalizing the high- $T$  Curie–Weiss slope. Matching the high-temperature Curie–Weiss law  $\theta_{\text{CW}} \simeq -152$  K yields  $\lambda \simeq 403$  K. This renormalizes the Curie–Weiss slope while preserving the intrinsic two-scale structure, illustrating that lattice couplings shift the thermodynamic scales without eliminating their hexagon origin, in agreement with findings from a recent numerical linked-cluster expansion study [52]. We stress that the quantitative scale renormalization is established by the full-lattice cMC results; the RPA expression is used only to emphasize the direction and mechanism of the shift.

The resulting picture is clear: strong antiferromagnetic correlations form first on hexagons, while frustrated inter-hexagon couplings suppress coherent order and shift thermodynamic anomalies to lower temperatures. Unlike conventional molecular magnets, where clusters set the scale and the crystal embedding only fixes a much lower ordering temperature [49, 50, 53], here the frustrated network is an active ingredient that renormalizes the thermodynamics downward.  $\text{Na}_2\text{Mn}_3\text{O}_7$  thus realizes an emergent *molecularization of a two-dimensional magnet*. Here we use “molecularization” operationally to denote a strong separation of scales: robust intra-hexagon correlations form at  $T_h \sim J_h$ , whereas inter-hexagon coherence is governed by a much smaller frustrated scale  $T_{\text{net}} \ll T_h$ .

Importantly, this is *not* a weakly coupled molecular magnet. Crystallography



**Figure 6.** Real-space correlations from the pf-FRG analysis (symmetrized nearest-neighbor model, supplemented by leading further-neighbor couplings). Main panel: normalized equal-time correlations  $|\langle S_0^z S_i^z \rangle| / |\langle S_0^z S_0^z \rangle|$  as a function of separation  $|\mathbf{r}_i - \mathbf{r}_0|$ , demonstrating strong antiferromagnetic correlations confined to individual hexagons and a rapid decay beyond the hexagonal unit. Inset: map of  $|\langle S_0^z S_i^z \rangle|$  on the lattice; the reference site 0 is highlighted explicitly. The finite but rapidly decaying inter-hexagon correlations distinguish this regime from a lattice of independent magnetic molecules.

enforces a translation-invariant exchange hierarchy that places the lattice close to competing ordering tendencies, generating a parametrically small coherence scale and pushing the thermodynamic crossovers to temperatures far below the isolated-hexagon scales. It is worth noting that the two-step thermodynamic structures are not unique to extended lattices: finite antiferromagnetic clusters such as rings or polyhedral molecular nanomagnets also exhibit a susceptibility maximum at higher temperature than the dominant specific-heat maximum, reflecting discrete multiplet physics [49, 53]. In  $\text{Na}_2\text{Mn}_3\text{O}_7$ , however, the short-range correlations are strongest on hexagons but extend beyond them, and their momentum-space fingerprints correspond to a correlated lattice rather than independent molecular form factors, as addressed in the next section.

*Pseudofermion functional renormalization group: quantum melting of fragile coherence*

We now incorporate quantum fluctuations using pseudofermion functional renormalization group (pf-FRG) technique [54, 55, 56, 57, 58]. To isolate the dominant competition while preserving the hierarchy, we symmetrize the nearest-neighbor couplings as  $J_h = (J_1 + J_2 + J_3)/3$ ,  $J_t = (J_4 + J_7 + J_8)/3$ , and  $J_d = (J_5 + J_6 + J_9)/3$ . For the *ab initio* parameters,  $J_h \simeq 95.6$  K, with modest anisotropy ( $\delta_h \simeq 0.21$ ,  $\delta_{\text{NN}} \simeq 0.09$ ).

Here,  $\delta_h$  and  $\delta_{\text{NN}}$  are dimensionless anisotropy measures which quantify the deviation of the microscopic nearest-neighbor model from the symmetrized description and are defined as

$$\delta_h = \frac{\max(J_1, J_2, J_3) - \min(J_1, J_2, J_3)}{J_h}, \quad (7)$$

$$\delta_{\text{NN}} = \frac{\sqrt{(J_1 - J_h)^2 + (J_2 - J_h)^2 + (J_3 - J_h)^2}}{\sqrt{3} J_h}. \quad (8)$$

and analogous expressions for the triangular and dimer bonds. This preserves the dominant separation of scales between the different types of couplings, as described previously, retaining the hexagon-dominated physics. Classically, this model lies near multiple phase boundaries [see Fig. 5], reflecting strong frustration. This is still true, when accounting for deviations due to spatial anisotropy in the real material. Including averaged further-neighbor couplings within and between hexagons,  $J_{2\text{NN}\circ} = (J_{10} + J_{11} + J_{12})/3$  and  $J_{3\text{NN}\circ} = (J_{19} + J_{20} + J_{21})/3$ , respectively, as well as average second-nearest neighbor interaction  $J_{2\text{NN}} = (\sum_{i=13}^{18} J_i)/6$  connecting different hexagons, we compute the pf-FRG flow. The maximum static susceptibility evolves smoothly over the entire cutoff range [see Supplementary Fig. S3], with no divergence indicative of magnetic ordering. This absence of flow breakdown persists with increasing spatial truncation, demonstrating suppression of dipolar long-range order.

The momentum-resolved structure factor [see Fig. 4(b)] exhibits broad maxima at  $\mathbf{q} = \pm\mathbf{k}_0 + \mathbf{G}$ , coinciding with the cMC wavevector. Quantum fluctuations broaden but do not shift these peaks, indicating that the ordering wavevector is fixed microscopically while coherence is melted [52]. Real-space correlations [see Fig. 6] are strongest within a hexagon and decay rapidly beyond it, yet remain finite over several lattice spacings [11]. This “strong-on-hexagons but not strictly confined” pattern demonstrates an interacting network of emergent clusters rather than independent molecular units.

A direct experimental discriminator of this scenario is single-crystal diffuse neutron scattering: we predict broad intensity maxima at the symmetry-related wavevectors  $\pm\mathbf{k}_0 + \mathbf{G}$  (with  $\mathbf{G}$  reciprocal lattice vectors), with substantial intrinsic width reflecting the finite correlation length and without resolution-limited Bragg peaks.

The quantum phase boundaries for the pure  $J_t$ - $J_d$  model without further neighbor couplings have been investigated using triplon mean-field theory (TMFT) for both hexagonal singlet and dimerized ground states [16] and pf-FRG [11] for spin 1/2. As shown in Fig. 5, they bracket a finite disordered region, which we use as an upper bound for the region where we expect such physics for  $S = 3/2$ . The symmetrized  $\text{Na}_2\text{Mn}_3\text{O}_7$  coupling ratios lie inside this window, even when taking into account deviations from this idealized limit in the real couplings, indicating that the quantum-disordered state arises from competition between nearby ordered phases rather than fine tuning. Quantum fluctuations thus melt the fragile classical coherence driven by weak inter-hexagon couplings. The resulting state is a *cluster-dominated quantum paramagnet*: it is adiabatically connected to the limit of decoupled hexagons with singlet ground states, yet in the lattice it exhibits finite but short-ranged inter-hexagon correlations without dipolar long-range order. This provides the zero-temperature counterpart of the cluster-dominated thermodynamics established above. While this conclusion is based on a symmetrized model, due to the hierarchical structure of the unsymmetrized couplings, we still expect it to hold qualitatively. The quantitative extent of the disordered region in parameter space, however, would be subject to the full anisotropy of the model.

## Discussion

$\text{Na}_2\text{Mn}_3\text{O}_7$  demonstrates that crystallographic inequivalence can act as a primary organizing principle for magnetism rather than a mere perturbation of ideal lattice models. The low-symmetry structure enforces a pronounced exchange hierarchy that repartitions the low-energy degrees of freedom from individual spins into strongly correlated hexagonal units. In doing so, it stabilizes quantum-disordered behavior even for comparatively large spins and identifies crystallography itself as a practical control knob for engineering cluster-based quantum paramagnets beyond the spin-1/2 paradigm.

We have established a coherent microscopic picture for the absence of long-range magnetic order in this layered spin-3/2 maple-leaf compound. Three dominant antiferromagnetic exchanges generate robust intra-hexagon correlations at a scale  $T_h \sim J_h$ , while substantially weaker, partly ferromagnetic couplings frustrate coherent inter-hexagon order at a parametrically smaller scale  $T_{\text{net}}$ . This hierarchy naturally accounts for the experimentally observed two-step thermodynamic structure: a broad susceptibility maximum near 110–120 K and a lower-temperature specific-heat enhancement around 60–70 K.

Exact diagonalization establishes that the *existence* of two thermodynamic crossovers is an intrinsic property of a single  $S = 3/2$  hexagon. The *absolute* crossover temperatures, however, are not set by an autonomous cluster spectrum: even after including all intra-hexagon couplings, the isolated-hexagon maxima remain far above experiment. The experimentally observed scales therefore require the frustrated embedding of hexagons into the two-dimensional network, which collectively renormalizes the response to lower temperatures.  $\text{Na}_2\text{Mn}_3\text{O}_7$  is thus a *molecularized two-dimensional magnet*—cluster physics dominates over a wide window, yet the lattice remains an active ingredient rather than a passive host.

Classically, the shallow energy landscape generated by weak inter-hexagon couplings leads to an incipient ordering tendency. Quantum fluctuations, treated using pf-FRG, suppress this fragile coherence and stabilize a magnetically disordered, cluster-dominated paramagnetic regime characterized by strong intra-hexagon correlations and rapidly decaying inter-hexagon correlations. The momentum-resolved correlations retain the classical ordering wavevector but remain broadened, indicating that frustration melts long-range order without altering the underlying exchange-imposed structure. From the perspective of the symmetrized nearest-neighbor model, the extracted coupling ratios place  $\text{Na}_2\text{Mn}_3\text{O}_7$  near multiple competing ordered phases, showing that the disordered ground state arises from finely balanced competition rather than trivially weak interactions.

We do not intend this terminology to introduce a distinct new phase label; rather, it denotes a hierarchy-controlled quantum paramagnet continuously connected to the decoupled-hexagon singlet limit, while retaining measurable short-ranged inter-hexagon correlations.

Our cluster-based scenario suggests several direct experimental tests. Pressure or uniaxial strain should predominantly affect the weak inter-hexagon couplings and hence strongly modify the lowest-temperature crossover scale while leaving the high-temperature susceptibility maximum largely unchanged. Single-crystal diffuse neutron scattering would provide a sharper probe of the predicted incommensurate short-range correlations. Local probes such as  $\mu\text{SR}$  and NMR should detect persistent dynamics without static internal fields, governed primarily by intra-hexagon modes.

Field-dependent thermodynamics may further reveal signatures of cluster multiplets broadened by frustrated inter-hexagon couplings.

For a more detailed theoretical understanding, the next step would be to derive an effective low-energy theory by projecting the full Hamiltonian onto the low-lying multiplet manifold of each hexagon. Such a theory would have to retain at least the hexagon singlet and the lowest magnetic excitations, and then derive the effective inter-hexagon couplings generated within this reduced Hilbert space. The difficulty is that the inter-hexagon couplings are weak enough to preserve the cluster hierarchy but not asymptotically negligible; moreover, frustration can generate multi-hexagon terms beyond a simple RPA dressing of the isolated-hexagon susceptibility. We therefore regard the RPA expression used above only as an illustrative indication of the downward renormalization of thermodynamic scales, not as a quantitative effective theory.

More broadly, this work sharpens an emerging lesson for frustrated magnets on nonuniform lattices: structural inequivalence and exchange hierarchy can qualitatively reorganize low-energy physics into emergent clusters and stabilize quantum-disordered behavior even for sizable spin. In  $\text{Na}_2\text{Mn}_3\text{O}_7$ , this mechanism suppresses long-range order despite substantial antiferromagnetic exchange and positions the system near competing ordered states. External control parameters such as pressure, strain, or selective chemical substitution—targeting the weak inter-hexagon couplings—offer promising routes toward magnetic order, quantum criticality, or novel cluster-based phases. More generally, low crystallographic symmetry, often regarded as a complication, can instead serve as a deliberate design principle for engineering exchange hierarchy and emergent cluster physics in two-dimensional magnets.

## Methods

### *Density functional theory and exchange extraction*

All DFT calculations were performed with the all-electron full-potential local-orbital code FPLO [59] using the generalized gradient approximation (GGA) [60]. Strong electronic correlations on the Mn  $3d$  shell were treated within DFT+ $U$  [61] by varying the on-site Coulomb interaction  $U$ , while keeping the Hund’s coupling fixed at  $J_{\text{H}} = 0.76$  eV [62]. Exchange parameters were obtained from DFT total-energy mapping [see Table 1]. The value  $U = 0.94$  eV was selected because it yields a Curie–Weiss temperature consistent with experiment,  $\theta_{\text{CW}} = -152$  K [36]. All subsequent finite-temperature and quantum-many-body calculations reported in the main text use this parameter set.

### *Classical Monte Carlo*

For the cMC simulations, we considered  $L \times L$  unit-cell periodic lattices with  $L = 16, 18, 20, 22, 24, 28, 30, 36, 40$ . Updates employed standard single-spin Metropolis–Hastings rotations. A Monte Carlo sweep corresponds to  $N$  attempted single-spin updates, with  $N = L^2$  the number of spins.

Thermodynamic quantities ( $C$  and  $\chi$ ) were computed on a uniform grid of 190 temperatures spanning  $T = 1$ –300 K. At each temperature, measurements were performed after thermalization using  $15 \times 10^6$  sweeps for 300–50 K,  $25 \times 10^6$  sweeps for 50–8 K, and  $10^8$  sweeps for 8–1 K. To access low-temperature quantities ( $T \leq 1.8$  K), including equal-time correlations, structure factors, and representative

low- $T$  configurations, we supplemented the Metropolis updates by over-relaxation: after each Metropolis update at site  $i$ , the spin was rotated by  $180^\circ$  about the local effective field axis generated by its neighbors. This energy-conserving move strongly reduces autocorrelation times in the frustrated regime. For  $16 \times 16$ , the maximum autocorrelation time in the equal-time structure-factor data is  $\sim 500$  sweeps after including over-relaxation, and we therefore used a binning size of 2048 sweeps for reliable error estimates. Since  $S(\mathbf{q})$  requires  $O(N^2)$  operations per sweep, we measured it only once every  $\sim 2000$  sweeps and averaged over 1000 effectively uncorrelated samples.

We evaluated the magnetic specific heat as

$$C(T) = \frac{1}{N} \frac{\langle E^2 \rangle - \langle E \rangle^2}{T^2}, \quad (9)$$

and the dc susceptibility as

$$\chi = \frac{N}{T} (\langle M_z^2 \rangle - \langle M_z \rangle^2), \quad M_z = \frac{1}{N} \sum_i S_i^z, \quad (10)$$

with an applied field fixed to 1.5 T. The equal-time structure factor was computed as

$$S(\mathbf{q}) = \frac{1}{N} \sum_{i,j} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle, \quad (11)$$

using the Mn positions  $\mathbf{r}_i$  of the lattice convention adopted in the paper [see Supplementary Note 3], and we further computed form-factor-modulated powder averages  $|F(q)|^2 S(q)$ , with

$$F(q) = 0.3760e^{-12.5661\left(\frac{q}{4\pi}\right)^2} + 0.6602e^{-5.1329\left(\frac{q}{4\pi}\right)^2} - 0.0372e^{-0.5630\left(\frac{q}{4\pi}\right)^2} + 0.0011, \quad (12)$$

for Manganese ions [63], for direct comparison to experiment [36, 37].

### *Pseudofermion functional renormalization group*

Quantum correlations and ordering tendencies were analyzed using pf-FRG in the PFFRGsolver.jl implementation [64]. Spins were represented by Abrikosov pseudofermions and the renormalization-group flow was formulated at  $T = 0$  using a continuous infrared cutoff  $\Lambda$  in the fermionic propagator. We truncated the one-particle-irreducible vertex hierarchy at the two-particle level and used the Katanin truncation scheme [65] to feed back self-energy effects into the vertex flow [55, 56].

Spatial correlations were restricted to a finite real-space range by neglecting vertex contributions beyond a maximal bond distance  $L$ , with values up to  $L = 18$  used to assess convergence. The three-frequency dependence of the two-particle vertex was discretized on an adaptive frequency grid of size  $35 \times 40 \times 40$  (bosonic and two fermionic frequency arguments, respectively). With these parameters, the pf-FRG flow involves on the order of  $9 \times 10^7$  coupled differential equations, solved numerically using high-performance computing resources [see Ref. [57] for implementation details].

The central observable is the static susceptibility

$$\chi_{ij}^{\Lambda, \mu\nu} = \int_0^\infty d\tau \langle \hat{T}_\tau \hat{S}_i^\mu(\tau) \hat{S}_j^\nu(0) \rangle^\Lambda, \quad (13)$$

and its momentum-space form

$$\chi^{\Lambda,zz}(\mathbf{k}) = \frac{1}{N} \sum_{ij} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \chi_{ij}^{\Lambda,zz}. \quad (14)$$

For SU(2)-symmetric Heisenberg models we restrict to  $\chi^{zz}$  (all diagonal components are equal and off-diagonal components vanish). The flow was integrated down to  $\Lambda/|J| = 0.05$ , with  $|J| = \sqrt{\sum_i J_i^2}$  the overall exchange scale. Dipolar magnetic long-range order is identified by a susceptibility divergence (“flow breakdown”) at finite  $\Lambda$  [54, 56]. To avoid false positives from finite truncation, we used a conservative criterion based on the evolution of the second derivative of the maximal susceptibility: a breakdown is diagnosed when non-monotonic features emerge and become increasingly pronounced with increasing  $L$ , following established practice [11, 66, 67]. We emphasize that absence of a breakdown excludes dipolar order but may still allow non-dipolar symmetry breaking (e.g. valence-bond or spin-nematic order), which would require four-spin correlators beyond the present truncation.

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### Data Availability Statement

The data that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.20326372>.

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## Supplementary Material to “Crystallography-driven molecularization of a spin-3/2 magnet”

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Supplementary Material to “Crystallography-driven molecularization of a spin-3/2 magnet”<sup>2</sup>

### Supplementary Note 1: Crystal structure and density functional theory calculations

The microscopic origin of the anomalous magnetic behavior of  $\text{Na}_2\text{Mn}_3\text{O}_7$  lies not simply in geometric frustration, but in the low crystallographic symmetry of the material. The triclinic crystal structure hosts three symmetry-inequivalent  $\text{Mn}^{4+}$  sites, which partition the maple-leaf lattice into distinct exchange pathways already at the nearest-neighbor level. This crystallographic inequivalence is the key ingredient that generates a strong hierarchy of exchange interactions, reorganizing the low-energy degrees of freedom from individual spins into emergent hexagonal units. To quantify this hierarchy and establish a realistic microscopic Hamiltonian, we employ density-functional-theory-based (DFT) energy mapping, which provides a direct and unbiased determination of the relevant exchange couplings.

The full crystal structure of  $\text{Na}_2\text{Mn}_3\text{O}_7$  has been determined by Chang and Jansen in 1985 [1], by Raekelboom *et al.* in 2001 [2], and by Song *et al.* in 2019 [3]. Total energy calculated with the all electron full potential local orbital (FPLO) [4] and generalized gradient approximation (GGA) [5] is best for the oldest, single crystal X-ray diffraction (XRD) structure. The 2019 XRD structure is 0.2 eV/f.u. higher, the 2019 neutron diffraction structure is 0.9 eV/f.u. higher, and the 2001 structure is 1.9 eV/f.u. higher in energy. For this reason, we use the single-crystal XRD structure determined by Chang and Jansen [1] in this study. We emphasize that, within our tests, the qualitative exchange hierarchy  $J_{1,2,3} \gg |J_{4-9}|$  is a robust feature of the material and does not rely on fine structural details, although the weaker couplings naturally exhibit a stronger structure dependence.

In Fig. 1 of the main text, we show the result of the DFT energy mapping based on a  $\sqrt{3} \times 1 \times \sqrt{3}$  supercell of  $\text{Na}_2\text{Mn}_3\text{O}_7$ . Due to the low symmetry of the crystal (triclinic space group  $P\bar{1}$ ) with three symmetry inequivalent  $\text{Mn}^{4+}$  ( $S = 3/2$ ) sites, the maple leaf lattice is defined by nine distinct “nearest neighbor” bonds, nine “second nearest neighbors” (three of them inside the hexagon) and nine “third nearest neighbors” (again three of them inside the hexagon). These neighbors are all identified by Mn-Mn distance (measured in the structure of Ref. [1]) in Table I of the main text. The energy mapping results are shown for different values of the onsite interaction strength  $U$  in Fig. 1(a) of the main text, and information about the overall energy scale of the material is necessary for choosing the relevant  $U$  value. We rely on Ref. [6] that gives a value of  $\theta_{\text{CW}} = -152$  K for the Curie-Weiss temperature, based on a fit to the magnetic susceptibility  $\chi(T)$ . The resulting Heisenberg Hamiltonian, specified fully in Table I of the main text in spite of its complexity provides a clear picture for the magnetism of  $\text{Na}_2\text{Mn}_3\text{O}_7$ . The resulting exchange pattern exhibits a pronounced hierarchy: (i) three dominant antiferromagnetic couplings ( $J_1$ – $J_3$ ) forming strongly correlated hexagons, (ii) six sizable ferromagnetic interactions ( $J_4$ – $J_9$ ) coupling these hexagons, and (iii) weaker but non-negligible second- and third-neighbor interactions that further frustrate magnetic ordering. Weak interlayer couplings and longer-range in-plane interactions, which are at least an order of magnitude smaller than  $J_h$ , are neglected in the effective model and are not expected to qualitatively alter the cluster-dominated physics discussed here.

The pronounced hierarchy of exchange couplings can be traced to the low-symmetry superexchange geometry of the Mn–O network. The dominant intra-hexagon bonds are mediated by two shared oxygen ligands, enhancing antiferromagnetic superexchange, whereas the weaker inter-hexagon bonds involve single-oxygen bridges and reduced

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**Table S1.** Local superexchange geometry for the nine nearest-neighbor Mn–Mn exchange paths. For each bond class  $J_i$  (identified using the same nearest-neighbor definition as in Table I), we list the Mn–Mn distance  $d_{\text{MnMn}}$ , the number of shared (bridging) oxygens  $n_{\text{O}}^{\text{bridge}}$ , the mean Mn–O distance  $\langle d_{\text{MnO}} \rangle$  over the shared oxygens, and the corresponding Mn–O–Mn bond-angle range. While all nine bonds involve bent Mn–O–Mn geometries in a near-90° window, the dominant intra-hexagon couplings  $J_{1,2,3}$  are distinguished by double-oxygen bridges and systematically shorter Mn–O distances compared to the weaker couplings  $J_{4-9}$ , consistent with an enhanced antiferromagnetic superexchange scale.

$J_i$	$d_{\text{MnMn}}$ (Å)	$n_{\text{O}}^{\text{bridge}}$	$\langle d_{\text{MnO}} \rangle$ (Å)	$\angle \text{Mn–O–Mn}$ (deg)
$J_1$	2.7887	2	1.882	93.37–97.95
$J_2$	2.8003	2	1.871	95.26–98.64
$J_3$	2.8050	2	1.891	93.35–98.33
$J_4$	2.9305	1	1.96	~ 97
$J_5$	2.9348	1	1.97	~ 96
$J_6$	2.9435	1	1.98	~ 96
$J_7$	2.9505	1	1.97	~ 97
$J_8$	2.9550	1	1.97	~ 97
$J_9$	2.9606	1	1.97	~ 97

hybridization. While simple Goodenough–Kanamori considerations provide qualitative guidance, detailed microscopic analysis in low-symmetry environments is subtle and can be misleading if applied heuristically. The exchange hierarchy reported in Table I of the main text is therefore established directly via *ab initio* energy mapping and is robust against small variations of computational parameters.

### Supplementary Note 2: Microscopic (superexchange) origin of the exchange hierarchy

The hierarchy of exchange couplings obtained from total-energy mapping can be understood microscopically from the geometry of the Mn–O–Mn superexchange pathways. Mn<sup>4+</sup> ions in Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> have a  $3d^3$  ( $t_{2g}^3$ ,  $S = 3/2$ ) configuration, for which the magnitude of isotropic exchange is controlled primarily by the strength of Mn–O hybridization and the number and geometry of bridging ligands, in the spirit of the Goodenough–Kanamori–Anderson rules.

Using the same definition of the nearest-neighbor manifold as in the energy-mapping procedure—namely, the nine shortest Mn–Mn bonds per Mn site—we analyzed the local exchange geometry for each bond class [Table S1]. We find that the shortest Mn–Mn links, which form the hexagonal backbone of the Mn sublattice and correspond to the dominant couplings  $J_{1,2,3}$ , are mediated by two shared oxygen ligands [Table S1], with bent Mn–O–Mn bond angles in the range ~ 93°–99°. These double-oxygen bridges enhance the effective Mn–O hybridization and thus maximize the antiferromagnetic superexchange scale.

In contrast, the remaining bonds within the nine-nearest-neighbor manifold involve weaker superexchange pathways characterized by single oxygen bridges, longer Mn–O distances, and reduced effective hybridization, as summarized in Table S1. For such geometries, the antiferromagnetic hopping channel is suppressed, and competing virtual processes—including Hund’s-rule-assisted contributions—become comparably

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important, resulting in significantly weaker exchange interactions.

We emphasize that the relevant mechanism is oxygen-mediated superexchange rather than direct  $d$ - $d$  overlap. The strength of the interaction is therefore controlled not only by the Mn–Mn distance, but crucially by the Mn–O bond lengths, bond angles, and the number of bridging ligands. In the present structure, three Mn–Mn bonds are connected by double Mn–O–Mn bridges with comparatively short Mn–O distances, while the remaining six bonds are mediated by single bridges with longer Mn–O separations. This structural dichotomy naturally partitions the exchange network into two groups and provides a microscopic explanation for the hierarchy  $J_{1,2,3} \gg |J_{4-9}|$  obtained from total-energy mapping.

Even modest ( $\sim 3$ – $5\%$ ) reductions in the Mn–O distance between the double-oxygen-bridged hexagon bonds and the remaining links can translate into substantial differences in effective hopping amplitudes and hence large variations in the resulting exchange couplings, consistent with the hierarchy obtained from the *ab initio* calculations. Importantly, this hierarchy is not the result of fine tuning but follows directly from the low-symmetry crystallographic structure.

It is worth emphasizing the limitations of heuristic superexchange arguments in low-symmetry, multi-path systems such as  $\text{Na}_2\text{Mn}_3\text{O}_7$ . As illustrated by the extended discussion in Ref. [7], plausible-looking Goodenough–Kanamori–Anderson-type considerations can sometimes lead to mutually contradictory or even incorrect conclusions when applied in isolation. In the present case, the commonly invoked Mn–Mn distance argument, adopted from Ref. [8] in subsequent experimental analyses, fails to account for either the sign or the magnitude of the dominant exchange interactions. Instead, the leading antiferromagnetic couplings correlate systematically with the number and geometry of bridging oxygen ligands, with two-oxygen exchange paths consistently dominating over single-oxygen bridges.

Importantly, however, we do not regard this observation as a universal rule. Rather, it serves only as a qualitative rationalization of the exchange hierarchy obtained from *ab initio* energy mapping. The central and robust result of our analysis is the exchange hierarchy itself, which follows directly from the electronic structure calculations and does not depend on assuming the transferability of any particular superexchange heuristic to other materials or lattice geometries.

We refer to this reorganization of the magnetic degrees of freedom into strongly correlated hexagonal units as *molecularization* of the magnet: a regime in which local cluster physics dominates thermodynamics, while inter-cluster coherence is governed by weaker, frustrated couplings.

In summary, the microscopic Heisenberg Hamiltonian derived from DFT reveals a clear physical picture: strongly antiferromagnetic hexagonal building blocks are embedded in a network of competing ferromagnetic interactions, producing frustration already at the classical level. This explains both the absence of conventional magnetic order and the dominance of short-range correlations in  $\text{Na}_2\text{Mn}_3\text{O}_7$ .

**Supplementary Note 3: Lattice definition**

We use the following convention for the primitive lattice and basis vectors for a single Mn-layer in  $\text{Na}_2\text{Mn}_3\text{O}_7$  in units of Angstrom:

$$\mathbf{a}_1 = (-3.7617292, -6.5719928, 0), \quad (\text{S1a})$$

$$\mathbf{a}_2 = (7.548, 0, 0), \quad (\text{S1b})$$

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$$\mathbf{a}_3 = (0.0630616, 0.4838087, 11.1473178); \quad (\text{S1c})$$

$$\mathbf{b}_1 = (-0.2314105, -1.4489934, 0.0105900), \quad (\text{S2a})$$

$$\mathbf{b}_2 = (0.2314105, 1.4489934, -0.0105900), \quad (\text{S2b})$$

$$\mathbf{b}_3 = (2.3987910, -0.52321930, -0.0323272), \quad (\text{S2c})$$

$$\mathbf{b}_4 = (-2.3987910, 0.52321930, 0.0323272), \quad (\text{S2d})$$

$$\mathbf{b}_5 = (3.0371082, 2.3617041, 0.0089179), \quad (\text{S2e})$$

$$\mathbf{b}_6 = (-3.0371082, -2.3617041, -0.0089179). \quad (\text{S2f})$$

In this convention, a second layer is present in the unit cell, shifted by  $0.5\mathbf{a}_1 + 0.5\mathbf{a}_2 + 0.5\mathbf{a}_3$  with respect to the one given.

#### Supplementary Note 4: Classical ground state: Luttinger–Tisza analysis

Before addressing the quantum problem, it is instructive to analyze the classical ground state of the microscopic Heisenberg Hamiltonian. Beyond providing a reference point, this analysis clarifies whether the pronounced hierarchy of exchange couplings stabilizes a robust classical order or instead produces a fragile ordering tendency that is highly susceptible to fluctuations. As we show below, the latter scenario applies: while a unique classical ordering wave vector is selected, the associated stiffness is small compared with the dominant intra-hexagon exchange scale, leaving the long-wavelength coherence tendency unusually soft.

##### 4.1. Luttinger–Tisza formulation

We treat the  $\text{Mn}^{4+}$  moments as classical spins of fixed length  $|\mathbf{S}_i| = S$  and consider the classical Hamiltonian

$$H_{\text{cl}} = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (\text{S3})$$

To determine the dominant ordering tendencies, we employ the Luttinger–Tisza (LT) method, which relaxes the local hard-spin constraint to a global one and reduces the problem to minimizing the lowest eigenvalue of the Fourier-transformed exchange matrix  $\mathcal{J}_{\alpha\beta}(\mathbf{k})$ , where  $\alpha, \beta = 1, \dots, 6$  label the sublattices of the maple-leaf unit cell. All classical energies are quoted in Kelvin units, consistent with the exchange parameters in Table I of the main text. We use an extension of the method, which allows us to treat lattices with multiple sublattices exactly [9]. To achieve this, a dressed interaction matrix

$$\tilde{\mathcal{J}}_{\alpha\beta}(\mathbf{k}, \lambda) = \mathcal{J}_{\alpha\beta}(\mathbf{k}) + \lambda_{\alpha} \delta_{\alpha\beta}, \quad \sum_{\alpha} \lambda_{\alpha} = 0 \quad (\text{S4})$$

is introduced. If the hard-spin constraint is fulfilled, this does not change the energies of the system, but gives a handle on tuning the relative spin length of the sublattices for the relaxed version. In the case of a ground state determined by a single  $\mathbf{q}$ -vector, the configuration is found by maximizing w.r.t  $\lambda$ , the minimal eigenvalue of  $\tilde{\mathcal{J}}_{\alpha\beta}(\mathbf{k}, \lambda)$ , within the first Brillouin zone.

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Following the equivalence of basis sites under inversion and guided by the eigenvector-structure of  $\tilde{\mathcal{J}}_{\alpha\beta}(\mathbf{k}, \lambda = \mathbf{0})$ , we choose

$$\lambda_1 = \lambda_2 = a \quad (\text{S5})$$

$$\lambda_3 = \lambda_4 = -a - b \quad (\text{S6})$$

$$\lambda_5 = \lambda_6 = b \quad (\text{S7})$$

as an *Ansatz* for the parameters.

Diagonalizing  $\tilde{\mathcal{J}}_{\alpha\beta}(\mathbf{k}, \lambda)$  throughout the Brillouin zone yields a unique global minimum at an incommensurate wavevector

$$\mathbf{k}_0 \simeq (0.500290721994559, 0.04252249458547225, 0) \text{ \AA}^{-1}. \quad (\text{S8})$$

for  $a = 9.54$ ,  $b = -10.24$  with corresponding minimal eigenvalue

$$\lambda_{\min}(\mathbf{k}_0) = -206.415 \text{ K}. \quad (\text{S9})$$

This implies a classical energy per spin,

$$E_{\text{LT}} = \frac{1}{2} \lambda_{\min}(\mathbf{k}_0) = -103.208 \text{ K}. \quad (\text{S10})$$

The ordering wavevector lies close to one of the  $K$ -points of the Brillouin zone, but is not locked onto it, indicating that the ordering is not symmetry-enforced but instead arises from a subtle balance between the dominant antiferromagnetic couplings within the hexagonal motifs and weaker, frustrated inter-hexagon interactions.

#### 4.2. Local structure of the LT minimum

To assess the rigidity of this ordering tendency, we examine the curvature of the LT spectrum in the vicinity of  $\mathbf{k}_0$ . A fine momentum-space scan yields the Hessian

$$H_{ij} = \partial_{k_i} \partial_{k_j} \lambda_{\min}(\mathbf{k})|_{\mathbf{k}_0} = \begin{pmatrix} 371.161 & 75.406 \\ 75.406 & 152.402 \end{pmatrix}, \quad (\text{S11})$$

with eigenvalues 394.635 and 128.929. While the minimum is clearly isolated, the pronounced anisotropy of the curvature reflects a relatively shallow energy landscape, particularly along one momentum direction, as can be seen in Fig. S1. This already signals a weakly stabilized classical order.

The corresponding LT eigenvector at  $\mathbf{k}_0$ ,

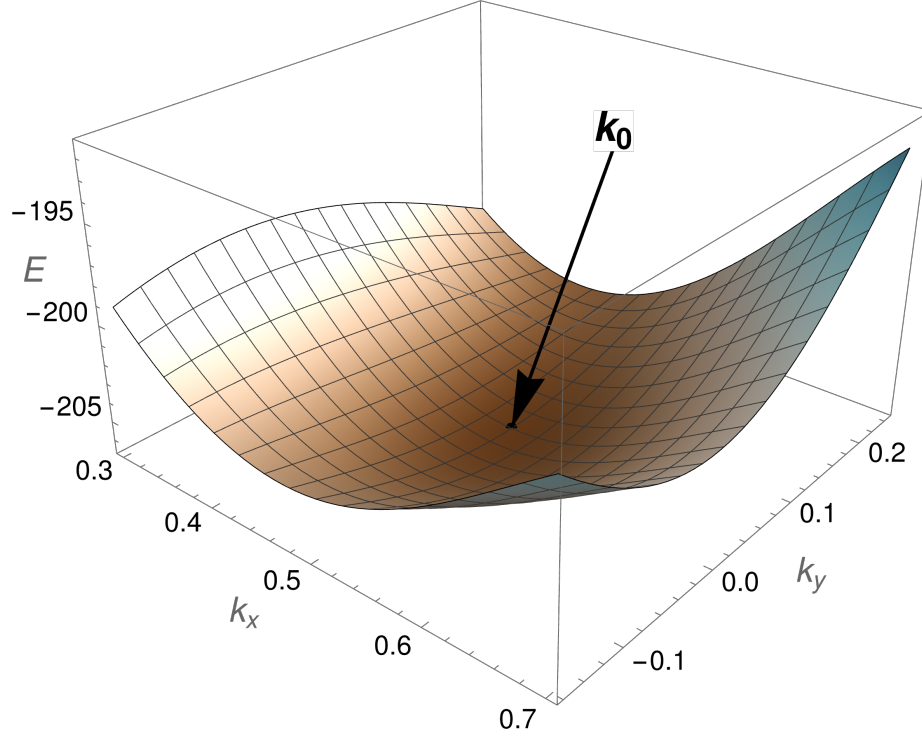
$$v_0 = (v_1, \dots, v_6), \quad (\text{S12})$$

is complex with its phases defining fixed sublattice offsets

$$\phi_\alpha = \arg(v_\alpha). \quad (\text{S13})$$

These indicate an almost perfect antiferromagnetic alignment of spins around a hexagon, canted only by a maximum of  $0.02\pi$  from the perfect antiparallel alignment.

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**Figure S1.** Luttinger–Tisza energy landscape in the vicinity of the classical ordering wave vector  $\mathbf{k}_0$ . The plot shows the lowest eigenvalue  $\lambda_{\min}(\mathbf{k})$  of the Fourier-transformed dressed exchange matrix relative to its value at  $\mathbf{k}_0$ . Although the minimum is isolated, the curvature is strongly anisotropic: one direction forms a shallow valley, while the transverse direction is considerably steeper. This illustrates that the classical ordering tendency is selected, but only weakly stabilized compared with the dominant intra-hexagon exchange scale.

#### 4.3. Physical state

The classical ground state may therefore be characterized as a weakly stabilized incommensurate spiral built from strongly, nearly antiferromagnetically correlated hexagons whose relative phases vary slowly across the lattice. The dominant couplings  $J_{1-3}$  enforce nearly collinear antiferromagnetic correlations within each hexagon, while weaker and partly frustrated inter-hexagon couplings select a unique relative phase only at a very small energy scale. Although the inter-hexagon couplings are substantially weaker than the dominant intra-hexagon exchanges, they remain essential for selecting the incommensurate ordering wavevector and for shaping the momentum-space structure of correlations. Thus, the incommensurate nature of the ordering wave-vector reflects the competition between nearly isolated hexagonal units and the frustrated network of weak inter-hexagon couplings, which cannot be simultaneously satisfied at any commensurate momentum.

From a broader perspective, the system lies in a regime where the selected classical ordering tendency is unusually fragile and highly susceptible to fluctuation effects.

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Although a specific ordering wavevector is selected at the classical level, the associated selection energy is exceedingly small and the energy landscape is shallow and anisotropic. As a result, the system is highly susceptible to both thermal and quantum fluctuations.

This conclusion provides a natural bridge to the results presented in the following section. Classical Monte Carlo (cMC) simulations capture the dominant short-range correlations and reveal only an incipient finite-size coherence tendency at the lowest temperatures, while the pseudofermion functional renormalization group (pf-FRG) indicates that quantum fluctuations suppress this fragile dipolar ordering tendency in the physical  $S = 3/2$  problem. In this sense, the LT analysis already anticipates the central message of this work:  $\text{Na}_2\text{Mn}_3\text{O}_7$  resides in a regime where a crystallography-induced exchange hierarchy produces strong local correlations, while the residual inter-hexagon coherence scale remains unusually small and therefore highly sensitive to fluctuation effects. Thus, the suppression of long-range order is not driven by an extensive classical degeneracy, but rather by the extremely small energy scale associated with an otherwise uniquely selected incommensurate spiral.

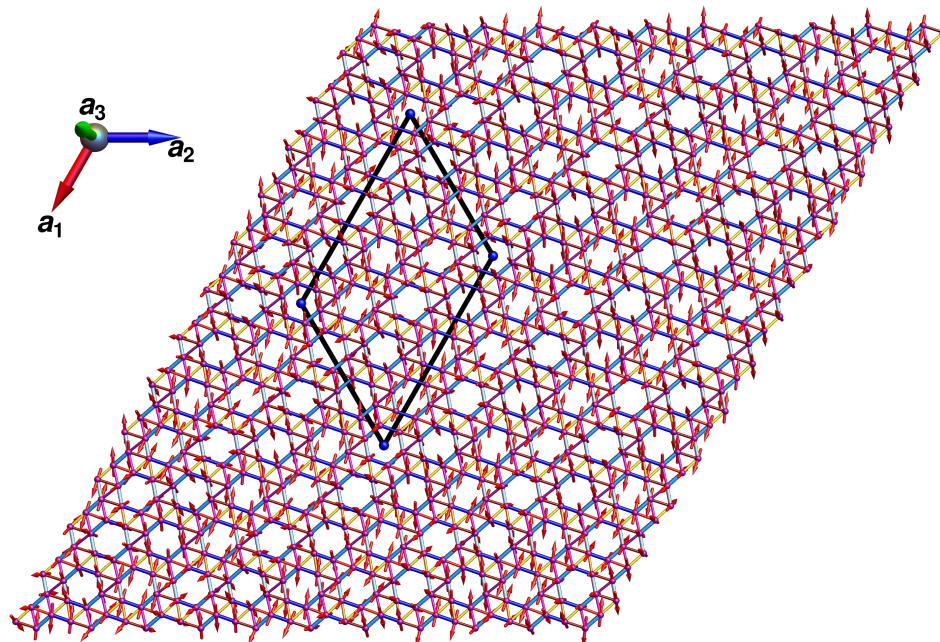
Taken together, the classical analysis identifies a uniquely selected but extremely weak incommensurate spiral. Its fragility explains why finite-temperature cMC simulations show only incipient coherence without Bragg-like scaling, and why the quantum pf-FRG flow can remain smooth, consistent with dominant short-range correlations rather than conventional dipolar long-range order. From this viewpoint, the LT analysis fixes the dominant momentum-space structure of correlations, cMC quantifies their thermal evolution, and the pf-FRG establishes their survival as short-range quantum correlations without symmetry breaking.

### **Supplementary Note 5: Low-temperature cMC spin configuration and pf-FRG flows**

The cMC calculations reveal an incipient low-temperature coherence tendency associated with the shallow LT minimum. On finite lattices and at very low temperature, this tendency can appear as a regular spin pattern whose characteristic modulation is compatible with the LT wave vector. Figure S2 shows a representative portion of a  $40 \times 40$  cMC spin configuration at  $T = 0.001$  K. Since the simulation is performed with periodic boundary conditions, the allowed modulation vectors are restricted to those compatible with the finite simulation cell; the pattern shown should therefore be understood as the finite-size wave vector closest to the incommensurate LT wave vector. We regard this configuration as an illustration of the fragile classical coherence tendency, not as evidence for a thermodynamic finite-temperature ordering transition. The fate of this fragile tendency in the physical  $S = 3/2$  system is more appropriately assessed by incorporating quantum fluctuations, which we do below using pf-FRG.

The absence of a conventional dipolar ordering instability in the quantum calculation is inferred from the pf-FRG flow of the maximum static susceptibility and its second derivative for several real-space truncation ranges, shown in Fig. S3. The curves for different truncation ranges lie essentially on top of one another and evolve smoothly as the infrared cutoff is lowered. In particular, we find no size-enhancing kink, cusp, or breakdown feature in the flow. This behavior is the pf-FRG signature of a magnetically disordered ground state with dominant short-range correlations. Within this diagnostic, the fragile classical coherence tendency is therefore suppressed by quantum fluctuations in the physical  $S = 3/2$  problem.

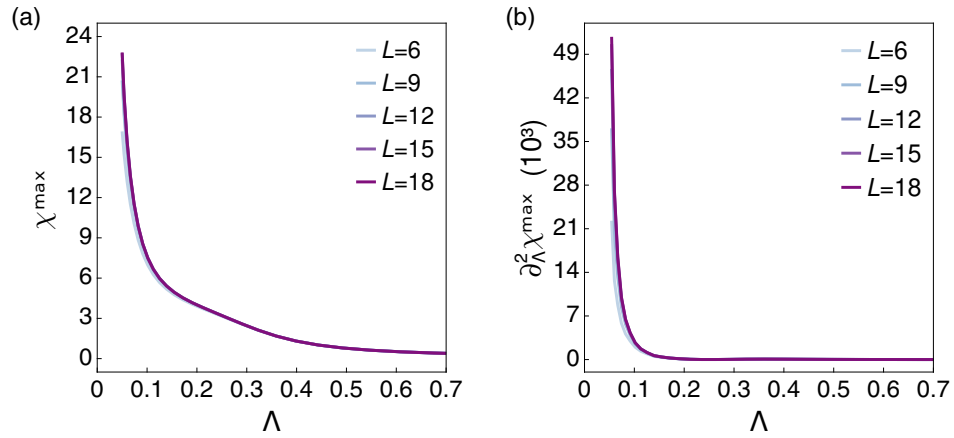
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**Figure S2.** Representative low-temperature cMC spin configuration at  $T = 0.001$  K for a portion of a  $40 \times 40$  system. Arrows indicate spin orientations, and the highlighted parallelogram marks the repeating magnetic unit cell realized in the finite simulation cell. Because of periodic boundary conditions, this pattern corresponds to the allowed wave vector closest to the incommensurate LT wave vector. The snapshot illustrates the fragile classical coherence tendency, but should not be interpreted as evidence for a thermodynamic finite-temperature ordering transition.

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**Figure S3.** pf-FRG flows demonstrating the absence of a dipolar magnetic ordering instability. (a) Flow of the maximum of the static structure factor,  $\chi^{\max}(\Lambda) = \max_{\mathbf{k}} \chi_{\Lambda}^{zz}(\mathbf{k})$ , as the infrared cutoff  $\Lambda$  is lowered, shown for several real-space truncation ranges. (b) Corresponding second derivative  $d^2\chi^{\max}/d\Lambda^2$ . The overlap of curves for different truncation ranges and the smooth, monotonic evolution without a size-enhancing nonmonotonic feature indicate no pf-FRG flow breakdown and hence no conventional long-range dipolar order.