



**HAL**  
open science

# Emergent Potts order in the kagome $J_1 - J_3$ Heisenberg model

Vincent Grison, Pascal Viot, Bernard Bernu, Laura Messio

► **To cite this version:**

Vincent Grison, Pascal Viot, Bernard Bernu, Laura Messio. Emergent Potts order in the kagome  $J_1 - J_3$  Heisenberg model. *Physical Review B*, 2020, 102 (21), 10.1103/PhysRevB.102.214424 . hal-03155852

**HAL Id: hal-03155852**

**<https://hal.sorbonne-universite.fr/hal-03155852>**

Submitted on 2 Mar 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Emergent Potts order in the kagome $J_1 - J_3$ Heisenberg model

Vincent Grison,<sup>1</sup> Pascal Viot,<sup>1,\*</sup> Bernard Bernu,<sup>1,†</sup> and Laura Messio<sup>1,2,‡</sup>

<sup>1</sup>*Sorbonne Université, CNRS, Laboratoire de Physique Théorique de la Matière Condensée (LPTMC), F-75005 Paris, France*

<sup>2</sup>*Institut Universitaire de France (IUF), 1 rue Descartes, F-75005 Paris, France*

(Dated: March 1, 2021)

Motivated by the physical properties of Vesignieite  $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$ , we study the  $J_1 - J_3$  Heisenberg model on the kagome lattice, that is proposed to describe this compound for  $J_1 < 0$  and  $J_3 \gg |J_1|$ . The nature of the classical ground state and the possible phase transitions are investigated through analytical calculations and parallel tempering Monte Carlo simulations. For  $J_1 < 0$  and  $J_3 > \frac{1+\sqrt{5}}{4}|J_1|$ , the ground states are not all related by an Hamiltonian symmetry. Order appears at low temperature via the order by disorder mechanism, favoring collinear configurations and leading to an emergent  $q = 4$  Potts parameter to a finite temperature phase transition. For  $J_3$  between  $\frac{1}{4}|J_1|$  and  $\frac{1+\sqrt{5}}{4}|J_1|$ , the ground state goes through a succession of semi-spiral states, possibly giving rise to multiple phase transitions at low temperatures. Effect of quantum fluctuations are studied through linear spin wave approximation and high temperature expansions of the  $S = 1/2$  model.

## I. INTRODUCTION

The existence of competing interactions in a magnetic spin lattice model leads to the inability to satisfy all pair interactions simultaneously. The system is said to be *frustrated*. While its effects in a classical spin model can be important, they are enforced for quantum spin models, where they may induce spin liquid ground states[1]. These phases break none of the Hamiltonian symmetries and as a consequence, show no magnetic long range order. Thus, it is interesting to pick up classical models where frustration has the largest effects, in view to detect quantum models hosting highly disordered phases.

Such spin models on the bidimensional kagome lattice have a long history, both from theoretical and experimental points of view. The most studied model is definitely the first neighbor antiferromagnet, realized in Herbertsmithite[2], even if impurities and other interactions keep this compound away from its idealization. In the search of the perfect chemical realization of this specific model, many other kagome compounds were proposed, such as Kapellasite[3], Volborthite[4], Haydeite[5, 6], Ba-Vesignieite[7–10], Sr-Vesignieite[11]... although they were finally described by different interactions. Here we shall restrict our attention to the model supposed to describe the Ba-Vesignieite compound[12], with small first neighbor ferromagnetic and large third neighbor antiferromagnetic interactions.

In the Vesignieite  $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$  compound, magnetic Cu atoms form decoupled and perfect bidimensional kagome layers of  $S = 1/2$  spins. Its Curie-Weiss temperature is around  $-77\text{K}$ [7], indicating an antiferromagnetic dominant coupling that was first proposed to be first neighbor[7]. Moreover, specific heat, mag-

netic susceptibility and powder neutron diffraction measurements on Vesignieite were supporting the spin liquid ground state hypothesis[7, 13], even if more and more indications of a phase transition around 9K appeared with time[13, 14]. This transition, probably related to a small interlayer coupling, is now clearly identified in crystalline samples[8]. Finally, neutron diffraction results on crystals[13] indicated that the short range spin correlations were incompatible with antiferromagnetic first neighbor interaction ( $J_1$  in Fig. 1), but coherent with a dominant third neighbor interaction  $J_3$ . These unusual interactions in Ba-Vesignieite are our main motivation to explore this kagome model. To the best of our knowledge, the  $J_1 - J_3$  Heisenberg model on the kagome lattice[12] has still not been studied for large  $J_3$ .

In classical Heisenberg models, the interaction between two tridimensional unit spins on sites  $i$  and  $j$  is given by  $J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j$ .  $J_{i,j}$  is the coupling constant, either positive for antiferromagnetic interaction, or negative for ferromagnetic one. Unfrustrated classical Heisenberg models have collinear ground states (i.e. all the spins are oriented along a unique line, with only two possible directions). It is notably the case for ferromagnetic models, or for antiferromagnetic ones on bipartite lattices, where sites can be labelled  $A$  or  $B$  in such a way that only different types of sites interact. Frustration can induce non-collinear magnetic orders, as on the triangular lattice with antiferromagnetic interactions: three sublattices  $A$ ,  $B$  and  $C$  host spins directions  $\mathbf{S}_A$ ,  $\mathbf{S}_B$  and  $\mathbf{S}_C$  each at an angle of  $120^\circ$  from the others. In this case, spins are no more collinear but remain coplanar. Eventually, non-coplanar spin states may be found with larger unit-cells[3, 15–18]: for example, twelve site unit cells, with spins pointing towards the corners of a cuboctahedron are found with up to third neighbor interactions on a kagome lattice[3, 15, 16].

The Mermin-Wagner theorem states that no continuous symmetry of a Hamiltonian can be broken at finite (non-zero) temperature in two dimensions[19–21]. Yet, other types of finite temperature phase transitions exist,

---

\* viot@lptmc.jussieu.fr

† bernu@lptmc.jussieu.fr

‡ messio@lptmc.jussieu.fr

with or without symmetry breaking[22, 23], associated with topological defects for instance. When a Hamiltonian symmetry is broken, the Mermin-Wagner theorem implies that it is a discrete one. In Heisenberg models, global spin rotations form a continuous symmetry group, thus a broken symmetry can be a lattice symmetry[24], or the time reversal symmetry[25, 26]. In most cases, a phase transition can be inferred from the analysis of the ground state manifold: several connected components generally correspond to a broken discrete symmetry. For example, if the spins are non coplanar, the ground state manifold is isomorphic to  $O(3)$ , which has two connected components  $\pm SO(3)$ . An emergent Ising parameter  $\pm 1$  (chirality) can be defined, indicating in which connected component the spin state is. The time reversal symmetry ( $\mathbf{S}_i \rightarrow -\mathbf{S}_i$ ) is broken in the ground state but is restored at finite temperature via a phase transition[15, 25, 26].

In most cases, all the ground states are equivalent, in the sense that they are related by a symmetry of the Hamiltonian. For example, two ground states of the triangular antiferromagnetic lattice have each three different spin orientations on their sublattices:  $\mathbf{S}_A, \mathbf{S}_B, \mathbf{S}_C$  and  $\mathbf{S}'_A, \mathbf{S}'_B, \mathbf{S}'_C$ . But there exists a three dimensional rotation  $R$  such that

$$\forall \alpha \in \{A, B, C\}, \mathbf{S}'_\alpha = R \mathbf{S}_\alpha.$$

$R$  is an Hamiltonian symmetry: for any spin configuration, the  $R$ -transformed one has the same energy. When the symmetries of the Hamiltonian fail to make all of the ground states equivalent, we speak of accidental degeneracy. Different ground states then have different properties, including different density of low energy excitations. This implies that, at low temperature, some of the ground states are selected by the *order by disorder* mechanism. A connected manifold of ground states can thus be reduced to disconnected components at infinitesimal temperatures, possibly giving rise to phase transitions with an emergent discrete order parameter. It is precisely what occurs in some part of the phase diagram of the  $J_1 - J_3$  kagome Heisenberg model, and is the subject of this article.

The paper is organized as follows. In Sec. II, we present the model and its classical ground states.

In Sec. III we analyze in detail a phase called 3sub-AF, found in the range of parameters corresponding to the Ba-Vesignieite compound: we first point out an order by disorder mechanism originating a phase at finite temperature. Second, one defines an appropriate order parameter, characterizing the possible phase transition.

The finite temperature phase diagram of the classical model is explored using parallel tempering Monte Carlo simulations in Sec. IV and thermal linear spin wave calculations in Sec. VA. A phase transition is evidenced through a finite size analysis, and the critical exponents are numerically evaluated. The effects of quantum fluctuations are discussed through a linear spin wave approximation (Sec. VB) and high temperature series expansions (Sec. VI). The relevance of our approach in the case

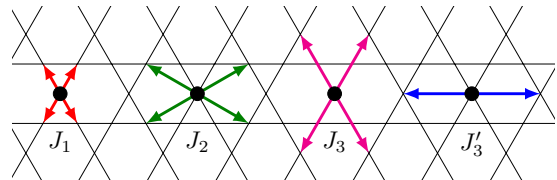


FIG. 1. Sketch of first, second and third neighbor interactions on the kagome lattice,  $J_1, J_2, J_3$  and  $J'_3$  respectively. The third neighbor interaction is split in two contributions:  $J'_3$  corresponds to interactions between spins located on two opposite corners of an hexagon, and  $J_3$  between spins located at the same distance, but on corners of two neighboring hexagons.

of the  $S = 1/2$  Ba-Vesignieite compound is discussed. In conclusion (Sec. VII), the nature of the phase transition experimentally observed in Vesignieite is discussed in light of the numerical and analytical results.

## II. THE MODEL AND ITS $T = 0$ CLASSICAL PHASE DIAGRAM

The kagome lattice consists of triangles sharing corners, with three sites per unit cell. On each site  $i$ , we place a unit vector  $\mathbf{S}_i$  (in the quantum model,  $S = 1/2$ ). We consider spin interactions between first and third neighbors, with respective strengths  $J_1$  and  $J_3$  (Fig. 1). The Hamiltonian of the system reads:

$$\mathcal{H} = J_1 \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_3 \sum_{\langle i, j \rangle_3} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the sums over  $\langle i, j \rangle$  and  $\langle i, j \rangle_3$  indicate a sum over all first and third neighbor links of the lattice.

Let us first investigate the landscape of possible ground states, presented in Fig. 2. We define an energy scale  $J = \sqrt{J_1^2 + J_3^2}$  and an angle  $\phi$  such that  $(J_1, J_3) = (J \cos \phi, J \sin \phi)$ .

The ground state determination for given  $(J_1, J_3)$  is a tough problem. No general procedure is known for such a classical Hamiltonian, outside of the case of a quadratic Hamiltonian on a Bravais lattice, that can be handled by the Luttinger-Tizsa (LT) method[27, 28]. This method can still be applied in the other cases, but then only gives a lower bound for the ground state energy (see App. A). If the energy of a trial state reaches this lower bound, it is then proved to be a ground state. Using a group-theoretical approach, a set of spin configurations called *regular magnetic orders* were defined[17], that are important trial states. In our case, regular magnetic orders are ground states for almost the whole phase diagram, with the exception of a small transition region (grey area of Fig. 2).

We now describe the phase diagram of Fig. 2, whose most phases are described on Fig. 3. When both  $J_1$  and  $J_3$  are negative, the ground state is obviously a ferromagnetic state, which survives for small positive  $J_3$ . Moving

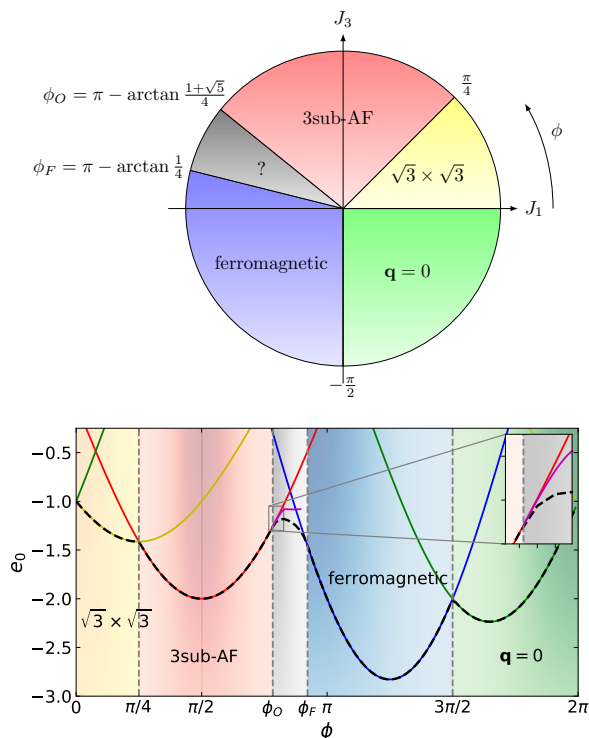


FIG. 2. Top: Ground states in the  $J_1 - J_3$  plane (see Fig. 1 for the definition of  $J_1$  and  $J_3$ ). The different orders are described in Fig. 3. Bottom: Energy per site  $e_0$  for each state named above, and Luttinger-Tizsa lower bound (dashed).  $e_0 = 2J_1 + 2J_3$  for the ferromagnetic state (blue line),  $-2J_3$  for the 3sub-AF state (red),  $-J_1 + 2J_3$  for the  $\mathbf{q} = 0$  state (green) and  $-J_1 - J_3$  for the  $\sqrt{3} \times \sqrt{3}$  state (yellow). The lower bound is reached everywhere except in the grey region. The magenta curve is the energy of the variational ground state, described in the text and in Fig. 5.

on to an antiferromagnetic coupling  $J_1 > 0$ , we encounter the kagome Heisenberg antiferromagnet for  $J_3 = 0$ . This model is known for its extensive ground-state degeneracy, which is lifted when  $J_3$  is switched on:  $J_3 < 0$  aligns spins equivalent under translations of the lattice in different triangles, giving rise to the  $\mathbf{q} = 0$  phase, while  $J_3 \gtrsim 0$  leads to the  $\sqrt{3} \times \sqrt{3}$  order, which survives up to  $J_3 = J_1$  ( $\phi = \pi/4$ ).

If  $J_1 = 0$ , the lattice is decoupled into three square sublattices (Fig. 4), each with a ferromagnetic ( $J_3 < 0$ ) or antiferromagnetic ( $J_3 > 0$ ) order, in three independent spin directions. When  $J_3 < 0$ , an infinitesimal (positive or negative)  $J_1$  completely lifts the degeneracy towards the ferromagnetic or  $\mathbf{q} = 0$  states previously discussed, but this is not the case for  $J_3 > 0$ . To see why, it is useful to consider a single spin and its nearest neighbors. The large value of  $J_3$  imposes that each spin is surrounded by pairs of anti-aligned spins, thus cancelling out nearest-neighbor energetic contributions as long as each sublattice stays ordered (Fig. 4). Thus, a small, arbitrary,  $J_1$

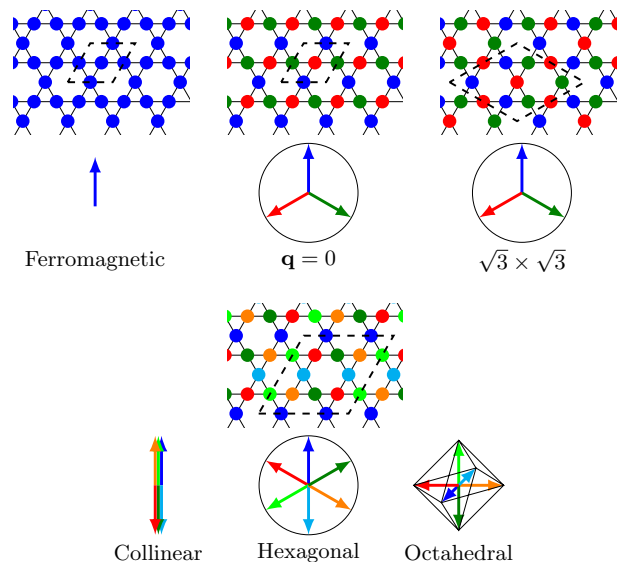


FIG. 3. Top: Three long-range orders on the kagome lattice, that are ground states in some part of the phase diagram of Fig. 2. Bottom: Collinear, hexagonal and octahedral states, that belong to the ground state manifold of the 3sub-AF states of Fig. 2.

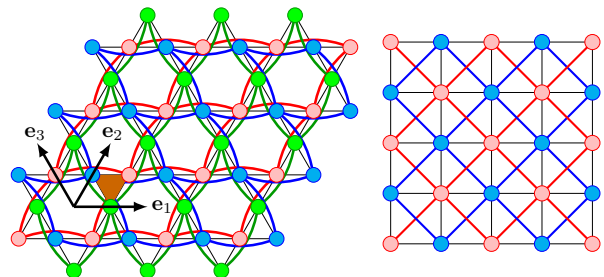


FIG. 4. Left: When only  $J_3$  interactions are present, the kagome lattice divides into three independent deformed square lattices (with blue, red and green sites and links). When  $J_3 > 0$ , an antiferromagnetic  $T = 0$  spin order sets in on each sublattice, with an arbitrary direction. A small  $J_1$  does not lift this degeneracy as it couples for example a red spin with two opposite green spins and two opposite blue spins. The same phenomena occurs on the  $J_1 - J_2$  square lattice for a strong AF  $J_2$  (right).

does not lift the degeneracy at  $T = 0$ . Among the degenerate configurations in this manifold, called the 3subAB states (some of them are illustrated in Fig. 3), we find a regular octahedral order whose spin directions correspond to the vertices of an octahedron[17]. At stronger  $J_1$ , the 3sub-AF phase breaks down in favor of other states -  $\sqrt{3} \times \sqrt{3}$  for  $J_1 > 0$ , and a succession of unconventional states with eventually several wave vectors for  $J_1 < 0$ , before reaching the ferromagnetic sector again.

We will now briefly discuss the unconventional ground states of Fig. 2, even if a detailed description is beyond

the scope of this article. In this part of the phase diagram, the LT lower bound of the energy is not reached by any spin configuration and the system has to find a compromise between the different wave vectors to minimize its energy. This situation occurs as soon as the wave vector  $\mathbf{q}_{\min}$  corresponding to the lowest eigenvalue  $\lambda_{\min}(\mathbf{q})$  becomes different from those of the simple neighboring phases. When  $\phi$  decreases from  $\pi$ , we leave the ferromagnetic state at  $\phi_F = \pi - \arctan \frac{1}{4}$ . The only  $\mathbf{q}_{\min}$ , previously the zero wave vector, splits into six  $\mathbf{q}_{\min}$  staying on lines going from the center of the BZ to its corners. When  $\phi$  increases, departing from  $\pi/2$ , we leave the 3sub-AF phase at  $\phi_O = \pi - \arctan \frac{1+\sqrt{5}}{4} \simeq 0.78\pi$  (proof in App. B, see also Fig. 19). The three  $\mathbf{q}_{\min}$  previously at the middles of the edges of the BZ split into six  $\mathbf{q}_{\min}$  staying on lines going from the middles of the edges of the BZ to its center. This part of the phase diagram is very rich. As an example, we describe here the ground state found near  $\phi_O$ , which is similar to the alternating conic spiral state of [18] and whose energy is given in Fig. 2. From numerical simulations (iterative minimization [18]), it appears that one of the three sublattices of Fig. 4 develops spin orientations in a plane, say the  $xy$  plane, whereas the other two form a cone of axis  $z$  and of small angle  $\phi$  (see Fig. 5). Note that the orientations of the two last sublattices are exactly the same, translated by a lattice spacing. Thus, this state is a spiral state, in the sense given in [17], but with an enlarged unit cell of twelve sites, reminiscent of the parent 3sub-AF phase.

### III. GROUND STATE SELECTION IN THE 3SUB-AF PHASE

#### A. Order by disorder

When  $J_1 = 0$ , the three sublattices of Fig. 4 are independent and each of them develops its own long range order at zero temperature. The ground state is then fully determined by the orientation on three reference sites (say the three sites of a reference unit cell): an element of  $\mathcal{S}_2^3$ , where  $\mathcal{S}_2$  is the unit sphere in three dimensions. The effect of a small  $J_1$  depends on the sign of  $J_3$ , as detailed in Sec. II. For a negative  $J_3$ , no accidental degeneracy survives to an infinitesimal  $J_1$ , whatever its sign. On the other hand, for positive  $J_3$ , an infinitesimal  $J_1$  has no effect on this degeneracy whatever its sign. Note that this accidental degeneracy is not extensive, i.e. does not increase with the lattice size. When temperature or quantum fluctuations are switched on, the phenomena of order by disorder occurs, lifting this degeneracy to a subset of  $\mathcal{S}_2^3$  - which will be determined below to be  $\mathcal{S}_2 \times K_4$ , where  $K_4$  is the Klein four-group.

Before considering in more detail the kagome  $J_1 - J_3$  model, let us list some models where such (simpler) accidental degeneracies are known. Historically, the order by disorder (ObD) phenomenon was described by Villain et al. on a domino model of Ising spins [29]. For a

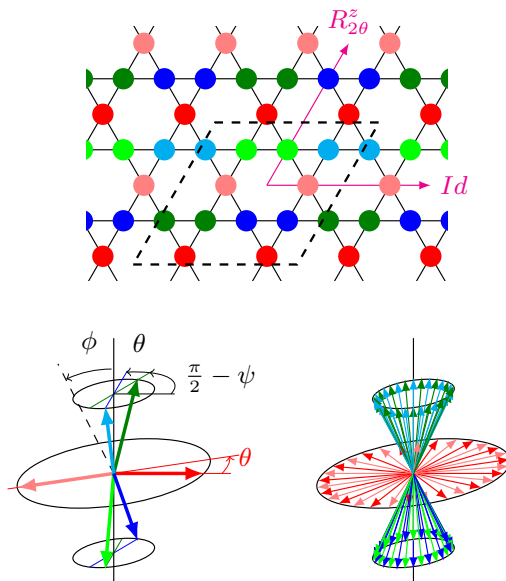


FIG. 5. Spin configuration supposed to be the ground state for  $\phi$  slightly larger than  $\phi_O$ , i.e. in the unconventional phase of Fig. 2. The spins of the dashed unit cell of 12 sites have 6 orientations, as indicated on the bottom left. The parametrization of this state is detailed in App. B. A translation in the  $\mathbf{e}_1$  direction let the spins invariant, whereas in the  $\mathbf{e}_2$  direction, they are rotated by  $2\theta$  around the  $z$  axis. Bottom right: orientation of the spins over the full lattice.

Heisenberg model, the most spectacular and most studied example of ObD is without any doubt the kagome antiferromagnet [30–38], whose degeneracy is extensive, as for the domino model. On the kagome lattice, thermal or quantum ObD selects coplanar states, whose number is still extensive, giving rise to possible further ObD effects, such as those occurring in the octupolar order [36].

We now focus our attention on other cases of bidimensional lattices, which share with the  $J_1 - J_3$  kagome model a non-extensive accidental degeneracy, with a continuous set of ground states. This situation is relatively common for Heisenberg Hamiltonians with nearest and next-nearest neighbor interaction. A well studied case is the  $J_1 - J_2$  Heisenberg model on a square lattice [39, 40], where in the case of strong AF  $J_2$ , the lattice decouples into 2 sublattices with independent antiferromagnetic orders ( $\mathcal{S}_2^2$  ground state manifold), see Fig. 4, right. Both thermal and quantum fluctuations favor collinear ordering, the ground state manifold being reduced to  $\mathcal{S}_2 \times \mathbb{Z}_2$ : the first sublattice has a free orientation ( $\mathcal{S}_2$ ) and the second one can align its reference spin with the one of the first sublattice, or set it opposite ( $\mathbb{Z}_2$ ). The effective set of ground states is now formed by two disconnected manifolds. Depending on the discrete component selected by the system, the  $T \rightarrow 0^+$  order is an horizontal or vertical columnar state. This emergent Ising variable gives rise to a phase transition at finite temperature, compatible with the Mermin-Wagner theorem.

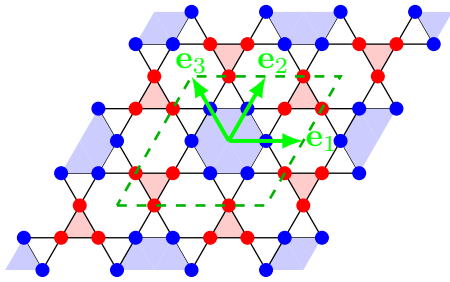


FIG. 6. In the 3sub-AF phase of Fig. 2, order by disorder effect tends to align along a unique direction the spins of the three antiferromagnetic square lattices depicted in Fig. 4. The resulting collinear spin order has a unit cell of 12 sites (in dashed green) and only two opposite spin orientations (on the blue and red sites).

The Heisenberg models on triangular[41] and honeycomb[42] lattices also develop ObD favoring collinear states (with a  $\mathcal{S}_2 \times \mathbb{Z}_3$  effective set of ground states) for some values of the  $J_1 - J_2 - J_3$  exchanges. But contrary to the square lattice, no limit of decoupled lattices allows for a simple understanding of this phenomenon. In the presence of a magnetic field, there are also many examples of ObD, where collinear configurations are stable and lead to magnetization plateaus[43, 44].

For the 3sub-AF phase of the  $J_1 - J_3$  kagome lattice, we can infer from the  $J_1 - J_2$  square lattice that the three sublattices will have a common, globally collinear, spin orientation under thermal or quantum fluctuations. The ground state manifold thus changes from  $\mathcal{S}_2^3$  to  $\mathcal{S}_2 \times K_4$ : the first sublattice has a free orientation ( $\mathcal{S}_2$ ), the second and third ones can align its reference spin with the one of the first sublattice, or set it opposite (fixing an element of  $K_4$ ) (see Fig. 6). The choice of a reference spin for each sublattice is arbitrary, which suggests to use  $K_4$  as the symmetry group labelling the different connected components, instead of the isomorphic  $\mathbb{Z}_2^2$ , since all symmetries are then explicitly treated on the same footing. Note also that the point-group symmetry of the lattice is unchanged - only the translational symmetries are broken.  $K_4$  is an unusual broken symmetry, but it has already been reported for example in an interacting electron model on the honeycomb lattice[45].

The (effective) ground-state manifold is sometimes abusively called the *order parameter space*. We take care here to distinguish them, as an order parameter taking values in another set will be defined in the coming section.

## B. Definition of an order parameter

In the previous section, it was shown that the ground-state manifold  $\mathcal{S}_2^3$  effectively reduces down to  $\mathcal{S}_2 \times K_4$  at infinitesimal temperature, i.e. when states in the limit

$T \rightarrow 0^+$  are considered. We construct in this section a local order parameter  $\Sigma$ , that will be averaged over the full lattice. We recall here that several order parameter definitions are possible, and that specific order-parameters are required for different broken symmetry.

In simple cases, the broken symmetry group is homeomorphic to the set of local configurations and the order parameter can be chosen in this set. This is for example the case for the local magnetization of ferromagnetic Ising or Heisenberg models, where the order parameter is defined on each lattice site as the spin orientation, or for the staggered magnetization of Néel orders. In these cases, the order parameter takes values in  $\mathcal{S}_2$  and can reveal a  $\mathcal{S}_2$  symmetry breaking (at  $T = 0$ , or in 3 dimensions for example).

Complications arise when the definition of a ground-state involves several sites, with constraints on the spin orientations. The antiferromagnetic triangular lattice is such an example: the sum of 3 spins of a triangle is zero at  $T = 0$ , and the orientation of two non collinear spins are required to fully determine a ground state. This ground-state manifold is homeomorphic to  $SO(3)$ [46]. For  $T \neq 0$ , the constraint on the sum of spins is no more verified and there is no direct way to chose a ground state related to this configuration. We are here quite lucky, as a local configuration on a triangle of the kagome lattice can uniquely be propagated over the full lattice to form one of the 3sub-AF states. A first possible order parameter is such a triplet of unit spins, forming an element of  $\mathcal{S}_2^3$ . However,  $\mathcal{S}_2^3$  as order parameter space does not do the job to reveal a possible symmetry breaking (Mermin-Wagner theorem). Here, the global spin rotations  $SO(3)$  form classes of equivalence in  $\mathcal{S}_2^3$  such that at infinitesimal temperature, spin waves disorder the ground state and disperse the local order parameter over the full equivalence class, when measured over the full lattice. Each such class has a zero average in  $\mathcal{S}_2^3$ , which rules out  $\mathcal{S}_2^3$  as order-parameter space to detect any finite temperature phase transition.

A  $SO(3)$  invariant description of the ground-state manifold is obtained as the quotient  $\mathcal{S}_2^3/SO(3)$ , in order to appropriately account for the possible symmetry breakings. Each point in  $\mathcal{S}_2^3$  is defined by 6 parameters, while  $SO(3)$  is a tridimensional manifold, from which we deduce that  $\mathcal{S}_2^3/SO(3)$  has dimension 3 as well. Points in this space, equivalence classes of states, must be described using  $SO(3)$  invariants built from the initial variables  $(\mathbf{S}_A, \mathbf{S}_B, \mathbf{S}_C)$  on a triangle  $ABC$ . An obvious choice is to use the dot product, giving three invariants that we group in a *vector*  $\sigma(\mathbf{S}_A, \mathbf{S}_B, \mathbf{S}_C) = (\mathbf{S}_B \cdot \mathbf{S}_C, \mathbf{S}_C \cdot \mathbf{S}_A, \mathbf{S}_A \cdot \mathbf{S}_B)$ . The  $\sigma$ 's are in a subset of  $\mathbf{R}^3$  whose shape is a slightly inflated tetrahedron. Its vertices correspond to collinear configurations, with three  $\pm 1$  vector components, and it can be shown that this shape indeed has the tetrahedral symmetry group  $T_d$ . Note that we have lost the distinction between the time-reversed spin configurations  $\mathbf{S}_i \rightarrow -\mathbf{S}_i$ . Each  $\sigma$  can be obtained from two distinct triplets of spins, except when

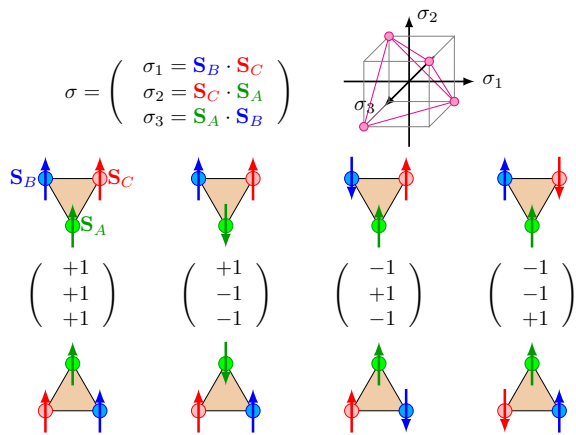


FIG. 7. Definition of a local variable  $\sigma$  on each (up and down) triangle of the kagome lattice as a function of the spin orientations ( $\mathbf{S}_A, \mathbf{S}_B, \mathbf{S}_C$ ) on the triangle vertices. Each component of  $\sigma$  is a dot product between two of these spins.  $A, B$  and  $C$  labels are chosen as indicated by the colors. In collinear configurations (expected in the  $T \rightarrow 0^+$  limit), each component of  $\sigma$  takes the value  $\pm 1$  with a constraint of an even number of  $-1$ . Then, the 4 possible  $\sigma$  values are horizontally listed, together with the corresponding collinear configuration (up to a global spin rotation) on up and down triangles. These four values point toward the vertices of a tetrahedron (drawn in magenta) in the  $(\sigma_1, \sigma_2, \sigma_3)$  space.

they are coplanar (as spin inversion is equivalent to a rotation of  $\pi$  in this case). Thus,  $\sigma$  is unable to describe the breaking of the  $\mathbb{Z}_2$  inversion subgroup of the  $O(3)$  global spin transformations.

Returning to ObD, the alignment of all spins can now be easily identified using  $\sigma$ . The tendency to collinearity of neighboring spins can be visualized as free energy barriers effectively pushing the ground-state configurations towards the vertices of the inflated tetrahedron, points of high symmetry, describing perfect (anti)-alignment in spin triplets. By considering vertices only, one can quickly observe that each vertex is invariant under the permutation of the three others,  $\mathcal{S}_3$ , while the whole symmetry group is isomorphic to the permutation group of four points  $\mathcal{S}_4$ . Consequently, our points may be described as the quotient space  $\mathcal{S}_4/\mathcal{S}_3 \simeq K_4$ , a genuine group since  $\mathcal{S}_3$  is normal in that case. This group provides the set of transformations that allows us to navigate between the different collinear ground states, by flipping pairs of spins (or not flipping any for the neutral element), and is thus the actual symmetry broken by this phase transition - they simply represent the action of translations of the lattice on a ground state. As a time-reversal spin transformation ( $\mathbf{S}_i \rightarrow -\mathbf{S}_i$ ) let the elements of this group invariant, the impossibility to distinguish states breaking this symmetry, evocated above, does not evince  $\sigma$  as an appropriate order parameter.

Up to now, we have considered a single reference triangle  $ABC$ . Depending on the choice of the labels  $A, B$

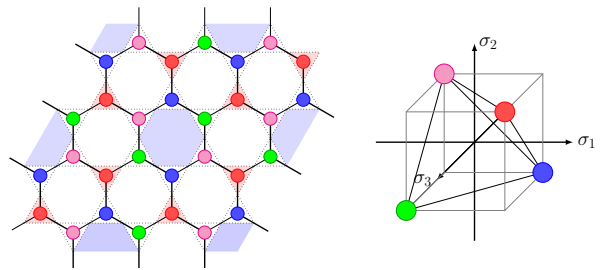


FIG. 8. Honeycomb lattice of effective spins, i.e. values of the tri-dimensional order parameter locally defined on each triangle of the kagome lattice. Shared vertices between triangles are edges between sites of the honeycomb lattice. Each effective-spin color corresponds to a value of  $\sigma$ , as shown on the right panel. Vertices of red triangles and blue hexagons are sites with opposite spin directions, as in Fig. 6. Each value of  $\sigma$  exists both on up and down triangles (see for example the red triangles).

and  $C$  of the triangle vertices (4 possibilities),  $\sigma$  undergoes a transformation. To fix the definition of  $\sigma$ , its  $i$ th component  $\sigma_i$  is defined as the dot product of spins on a link directed along the vector  $\mathbf{e}_i$  of Fig. 6. This unambiguously defines  $\sigma$  on all the pointing-down as well as pointing up triangles (see Fig. 7).

The four possible triplets for collinear configurations are represented on Fig. 7. The centers of up and down triangles on the kagome lattice form a honeycomb lattice, and  $\sigma$  is an effective (non unit) spin on these sites, oriented alternately as indicated on Fig. 8 in a collinear ground state configuration. Note that once  $\sigma$  is chosen on one of the kagome triangle in a collinear ground state configuration (or equivalently on one of the honeycomb lattice sites),  $\sigma$  on any other triangle can be deduced from elementary operations belonging to the Klein group  $K_4$ : an  $\mathbf{e}_i$  translation of the spins rotates  $\sigma$  by  $\pi$  around the  $\sigma_i$  axis. The tetrahedra of  $\sigma$  orientations falls in one of four possible orientations, corresponding to a  $q = 4$  Potts variable[47].

By analogy with the alternate order parameter used for antiferromagnetic long-range order, we define an alternate order parameter  $\Sigma$ , homogeneous over the full lattice. The evolution of its average over the full lattice as a function of the temperature and of the system size will now be studied below using Monte Carlo simulations. Note that in a collinear ground state,  $\Sigma$  is homogeneous, and only four ground states are possible. In this aspect, the effective model for the  $\Sigma$  variables resembles more to the ferromagnetic  $q = 4$  Potts model than to the antiferromagnetic one, whose degeneracy on the honeycomb lattice would be extensive.

## IV. MONTE CARLO SIMULATIONS AT FINITE TEMPERATURE

### A. The method

To investigate the phase diagram of the  $J_1 - J_3$  model, we perform Monte Carlo simulations by implementing a parallel-tempering method[48]. In the case of first-order phase transitions, this method enables to overcome the associated free-energy barriers by considering  $N_p$  replicas of the system at different temperature  $T_i$ , with  $i = 1, \dots, N_p$ . Each replica constitutes a separate, parallel, simulation box whose state evolves independently via local spin updates, but can also periodically be swapped with that of its immediate neighbors. Hence, higher temperature simulation boxes allow lower temperature ones to sample their phase space much more efficiently. The temperature interval  $[T_{\min}, T_{\max}]$  is chosen in order to cover the region where a putative phase transition is expected, and the difference of inverse temperature between two adjacent replicas  $\Delta\beta$  is kept constant (we also also tried a geometric progression for the inverse temperatures in the range, without noticing significant changes for the convergence of the method).

In order to satisfy a detailed balance for this process, the probability  $P_{PT}$  of accepting an exchange of configurations between boxes  $i$  and  $i + 1$  is chosen with a Metropolis rule

$$P_{PT}(i \leftrightarrow i + 1) = \text{Min}(1, \exp(\Delta\beta\Delta E)), \quad (2)$$

with  $\Delta\beta = \beta_i - \beta_{i+1}$  and  $\Delta E = E_i - E_{i+1}$ . The double arrow means that the probability  $P_{PT}$  is symmetric to the reverse exchange.

The mean acceptance probability  $P_A(i \leftrightarrow i + 1)$  between boxes  $i$  and  $i + 1$  is the average of  $P_{PT}(i \leftrightarrow i + 1)$  over thermalized configurations, and writes:

$$P_A(i \leftrightarrow i + 1) = \int dE_i dE_{i+1} P_{\beta_i}(E_i) P_{\beta_{i+1}}(E_{i+1}) P_{PT}(i \leftrightarrow i + 1), \quad (3)$$

where  $P_{\beta_i}(E_i)$  denotes the equilibrium probability of the box  $i$  to have an energy  $E_i$ . Eq. (3) is merely a weighted sum over all possible energetic configurations for two given neighboring boxes. In order to optimally schedule the temperatures, we check that the acceptance probability of swaps between neighboring replicas is near 0.5[48].

We choose an even number of replicas  $N_p$  and at constant time intervals, two kinds of exchanges between neighboring boxes are proposed: either exchanges between all pairs  $(2k - 1, 2k)$  where  $k = 1, \dots, N_p/2$  or exchanges between all pairs  $(2k, 2k + 1)$  where  $k = 1, \dots, N_p/2 - 1$ , which preserves the ergodicity of the process. Otherwise, we perform local updates of spins for each simulation box according to a Metropolis rule.

In simulations on a lattice of linear size  $L$ , we store the histograms of the energy and of the order parameter modulus  $|\sum_{\nabla, \Delta} \Sigma|$  for each temperature, giving directly

$\alpha$	$\gamma$	$\beta$	$\delta$	$\nu$	$\eta$
$\frac{2}{3}$	$\frac{7}{6}$	$\frac{1}{12}$	15	$\frac{2}{3}$	$\frac{1}{4}$

TABLE I. Critical exponents of the two-dimensional  $q = 4$  Potts model. For  $q \leq 4$ , they have a conjectured exact expression[47].

access to the mean energy  $\langle E \rangle(\beta, L)$ , and the mean Potts magnetization  $\langle \Sigma \rangle(\beta, L)$ . The specific heat  $C_V$ , the susceptibility of the order parameter  $\chi_\Sigma$ , and the associated Binder parameter  $B_\Sigma$ [49] are given per lattice site as:

$$C_V(\beta, L) = \frac{\beta^2}{N} (\langle E^2 \rangle - \langle E \rangle^2) \quad (4a)$$

$$\chi_\Sigma(T, L) = N_\Delta (\langle \Sigma^2 \rangle - \langle \Sigma \rangle^2) \quad (4b)$$

$$B_\Sigma(\beta, L) = 1 - \frac{\langle \Sigma^4 \rangle}{3\langle \Sigma^2 \rangle^2}. \quad (4c)$$

where  $N_\Delta$  is the number of up and down triangles.

Moreover, by using the reweighing method[50], and the histograms obtained in simulations, one builds for each box  $i$  all estimated above quantities within a temperature interval  $[(\beta_i + \beta_{i-1})/2, (\beta_i + \beta_{i+1})/2]$ . Collecting all datas, one can build a global graph from  $T_{\min}$  to  $T_{\max}$ . The convergence for all temperatures of the parallel tempering method is confirmed when the curve is continuous at each boundary between two temperature intervals.

In order to perform a finite-size scaling analysis, we simulated different system sizes of the kagome lattice with periodic boundary conditions.  $L$  is the linear size of the lattice, and the number of sites is  $N = 3L^2$ . From simulation data, we determine the maxima  $C_V^{\max}(L)$  and  $\chi_\Sigma^{\max}(L)$  of these quantities, occurring at temperatures  $T_c^{C_V}(L)$  and  $T_c^{\chi_\Sigma}(L)$ . For a continuous phase transition, the finite size scaling at the lowest order of these quantities is given by[49]:

$$C_V^{\max}(L) \simeq aL^{\alpha/\nu} + b, \quad (5a)$$

$$\chi_\Sigma^{\max}(L) \simeq cL^{\gamma/\nu} + d, \quad (5b)$$

$$T_c^{C_V, \chi}(L) \simeq eL^{-1/\nu} + T_c(\infty), \quad (5c)$$

where  $\alpha$ ,  $\nu$  and  $\gamma$  are critical exponents whose values for the ferromagnetic  $q = 4$  Potts model are recalled in Tab. I and  $T_c(\infty)$  is the critical temperature of the phase transition. For a first-order phase transition in  $D$  dimensions, and when the linear size of the simulation box  $L$  is larger than the correlation length, the magnetization and the energy distributions become bimodal[49], which leads to a finite size scaling given by:

$$C_V^{\max}(L) \simeq aL^D + b, \quad (6a)$$

$$\chi_\Sigma^{\max}(L) \simeq cL^D + d, \quad (6b)$$

$$T_c^{C_V, \chi}(L) \simeq eL^{-D} + T_c(\infty). \quad (6c)$$



$\frac{J_3}{ J_1 }$	0	1/4	1/2	0.68	3/4	0.809	1	2	$\infty$
$\phi/\pi$	1	0.922	0.852	0.810	0.795	0.783	0.750	0.648	1/2

TABLE II.  $J_3/|J_1|$  versus  $\phi$  for  $J_1 = -1$ .  $\phi_F \simeq 0.922\pi$  and  $\phi_O \simeq 0.783\pi$  are the boundaries of the unconventional phase, whose exact value is given in Fig. 2.

## B. Results for ferromagnetic $J_1$

The linear size of the lattice  $L$  goes in the simulations from 12 to 104. The interaction between nearest neighbors is set to  $J_1 = -1$ , and  $J_3$  is varied from 0.2 to 2. By considering the  $T = 0$  phase diagram (top of Fig. 2), this corresponds to a vertical line in the upper left quarter, which intersects three ground state sectors: ferromagnetic, unconventional and 3sub-AF. One leaves the ferromagnetic phase when  $J_3 = \frac{1}{4}$  and enters the degenerate 3sub-AF phase for  $J_3 = \frac{1+\sqrt{5}}{4} \simeq 0.809$ , where one expects a finite temperature phase transition due to emergence of the discrete  $K_4$  order parameter. Note that Tab. II gives a one-to-one mapping between the coupling ratio  $J_3/|J_1|$  and the parameter  $\phi$  introduced in the preceding section.

$C_V$  and/or  $\chi_\Sigma$  show a maximum increasing with  $L$  for some  $J_3$  values, revealing a phase transition. The resulting finite temperature phase diagram is displayed in Fig. 9, while Fig. 10, 11 and 12 illustrate the specific points  $J_3 = 0.67$ ,  $J_3 = 1$  and  $J_3 = 1.5$ .

Blue points indicate both a  $C_V$  and  $\chi_\Sigma$  divergence, whereas green points indicate that only  $C_V$  diverges. For the blue points,  $C_V^{\max}$  and  $\chi_\Sigma^{\max}$  have been collected on Fig. 13, for different values of  $L$  and  $J_3$ , together with the temperature  $T_c^{C_V}$  and  $T_c^{\chi_\Sigma}$ .

We now discuss in more detail our results by considering the three different regions (ferromagnetic, unconventional and 3sub-AF ground states).

### 1. Ferromagnetic region: no transition

For  $J_3 = 0.2$  (let us recall that  $J_1$  is set to  $-1$  in simulations), no phase transition was observed, at any temperature. There is no evolution of the specific heat with the system size. Hence our results are in line with the predictions of the Mermin-Wagner theorem for this phase, as expected.

### 2. Non $K_4$ phase transitions in the unconventional phase

When  $0.25 < J_3 < 0.809$ , the ground state is not easily determined and seems to be very dependent of  $J_3$ , as explained in Sec. II (for example, with a succession of various types of wave vectors). The following values of  $J_3$  have been explored: 0.3, 0.4, 0.5, 0.6, 0.65, 0.67, 0.69,

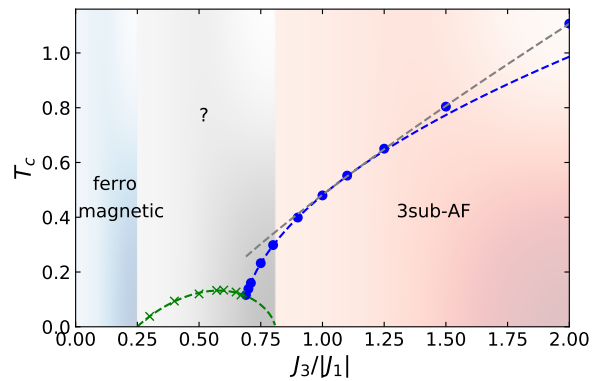


FIG. 9. Phase diagram of the  $J_1 - J_3$  Heisenberg model on the kagome lattice. A phase transition with both  $C_V$  and  $\chi_\Sigma$  divergence (blue points) is evidenced by Monte Carlo classical simulations, restoring the  $K_4$  symmetry. Blue (res. grey) dashed line fits the low- $T$  (resp. high- $T$ ) points with the function  $a(J_3/|J_1| - c)^b$  with  $a = 0.851$ ,  $b = 0.516$ ,  $c = 0.670$  (resp.  $a = 0.7547$ ,  $b = 0.832$ ,  $c = 0.417$ ). Green points are phase transitions with no  $\chi_\Sigma$  divergence. The green dashed line is a guide to the eyes. Error bars are smaller than the symbol size.

0.7, 0.71, 0.75, 0.8, all a divergence of  $C_V(\beta, L)$  with  $L$  at a unique temperature.

For  $0.25 \leq J_3 \leq 0.67$ , the  $K_4$  Potts parameter  $\Sigma$  remains close to zero at all temperatures. However, the specific specific heat displays a peak at low temperature, whose size increases with  $L$ . The approximative limit of  $T_c^{C_V}$  when  $L$  increases seems to be a continuous function of  $L$  and is indicated as green points on Fig. 9: it increases from zero for  $J_3 = 1/4$  up to  $T_c = 0.134(1)$  for  $J_3 \simeq 0.60(3)$ , and slightly decreases down to  $0.116(1)$  up to  $J_3 = 0.67(2)$ . Due to the nature of the ground state, it is possible that transitions associated with various broken symmetries occur in this range of parameters. It is for example probable that the three-fold spatial rotation is broken at low  $T$  for  $J_3 \simeq 0.67$  as the order of Fig. 5 particularizes one of the three sublattices. We did not try to identify the order parameter associated with these phase transitions as the focus of this study is the 3sub-AF phase.

For  $0.5 \leq J_3 \leq 0.67$ , the mean energy per site at low  $T$  depends on the system size even quite far from the critical temperature. Moreover the temperature of  $C_V^{\max}$  varies non monotonously with the system size (see Fig. 10). These features are the signature of a phase transition thwarted by the incommensurability of the lattice size with the periodicity of the order, inducing frustration. The phenomenon weakens when  $L$  increases, and could be handled using twisted boundary conditions.

Lastly, the energy distribution is unimodal for  $J_3 < 0.5$ , but becomes bimodal for system sizes of  $L \geq 32$  (24) and  $J_3 = 0.6$  (0.65), which is in favor of a first-order phase transition. For  $J_3 = 0.67$ , the energy distribution

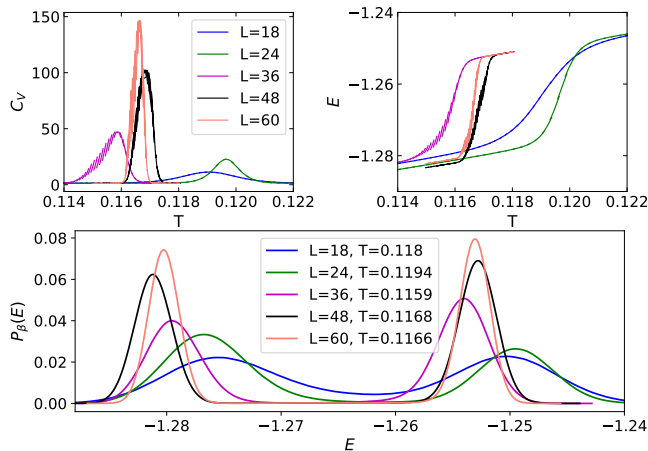


FIG. 10. Specific heat  $C_V$ , average energy  $E$  and distribution of the energies for  $J_1 = -1$  and  $J_3 = 0.67$ , for different lattice sizes.  $T_c^{C_V}$  is non-monotonic, which corresponds to variations of  $E$  with the size  $L$  over a large temperature range. The energy distribution at  $T_c^{C_V}$  is clearly bimodal, sign of a first order transition. The  $K_4$  order parameter remains very low and no divergence of its susceptibility develops in this range of temperature.

consists in two well separated peaks near  $T_c$ , even at low  $L$  and the phase transition is clearly first order (bottom of Fig. 10).

For  $0.69 \leq J_3 \leq 0.809$ ,  $\Sigma$  has large values in the low  $T$  phase and its susceptibility shows a peak which increases with  $L$ . For this reason, this transition will be discussed in the next paragraph, on the  $K_4$  transition. Such  $K_4$  transition is surprising here as the  $T \rightarrow 0$  state is not supposed to break the  $K_4$  symmetry:  $\Sigma$  should be zero in the non-3sub-AF ground state. Another phase transition thus seems unavoidable at lower  $T$ , restoring  $K_4$ . In this hypothesis, the green dashed line of Fig. 9 was extended up to 0.809, implying a reentrance of the  $K_4$ -breaking phase in the unconventional phase. The low- $T$  phase transition would be first-order, as it relates phases with different broken symmetries. However, we did not succeed to evidence such a low- $T$  phase transition, probably because of metastable states breaking  $K_4$ , in which the simulations remains stuck despite the parallel tempering.

### 3. $K_4$ phase transition, in the unconventional and 3sub-AF regions

For  $J_3 \geq 0.69$ , a transition occurs with both a  $C_V^{\max}$  and a  $\chi_{\Sigma}^{\max}$  divergence with  $L$ , occurring at temperatures converging towards the same value  $T_c(J_3)$ . The Binder cumulant associated with  $\Sigma$  also indicates a phase transition: it tends to  $2/3$  below  $T_c$  when  $L$  increases and its curves cross at the same temperature for different  $L$ . Fig. 11 shows several quantities as a function of  $T$  for

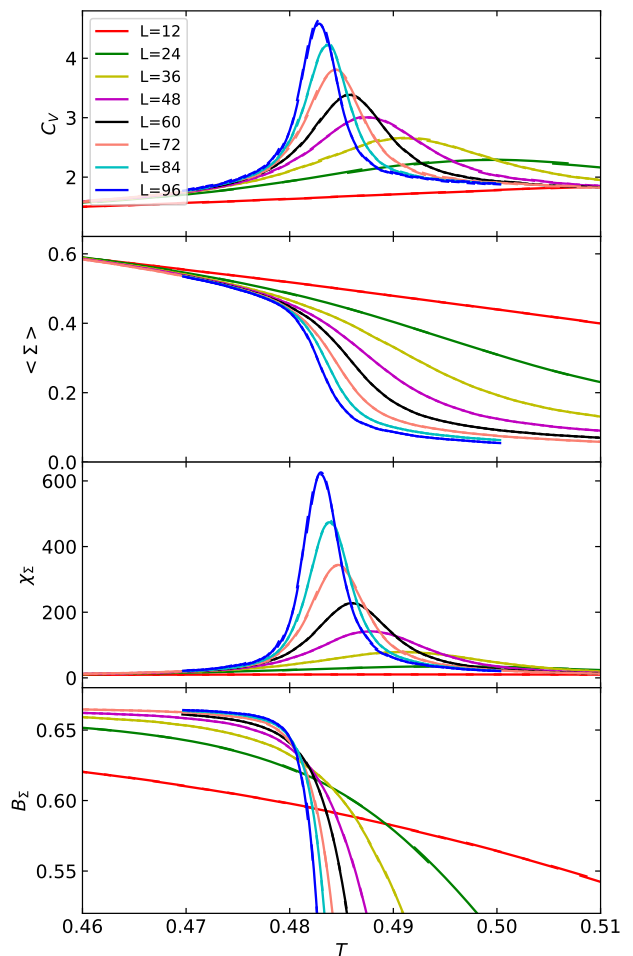


FIG. 11. Specific heat  $C_V$ ,  $K_4$  order parameter  $\Sigma$ , susceptibility  $\chi_{\Sigma}$  and Binder parameter  $B_{\Sigma}$  versus  $T$  for different system sizes  $L$  for  $J_1 = -1$  and  $J_3 = 1$ .

different system sizes, for  $J_3 = 1$ , as an illustration of a finite size scaling.

This phase transition separates a low- $T$  phase with large  $\Sigma$  from a high- $T$  one with nearly zero  $\Sigma$  and corresponds to the restoration of the  $K_4$  Potts symmetry. Thus, we have the proof that the order by disorder favors collinear states among the ground state manifold at low temperature.

The critical temperature  $T_c(J_3)$  increases with  $J_3$  (Fig. 9) and is fitted by the three-parameter function  $T_c(J_3) = a(J_3 - c)^b$ . When the fit is restricted to low  $J_3$ 's (blue dashed line of Fig. 9), the exponent  $b$  is nearby  $1/2$ , and increases up to  $b = 0.88$  for only large  $J_3$ 's (grey dashed line).  $b$  seems to tend to 1 for large  $J_3$ , what would be similar to the results of Weber et al. [51] on the  $J_1 - J_2$  square lattice: a square root behavior near the transition with the competing phase and a linear behavior in the large  $J_2$  ( $J_3$  here) limit.

At low  $J_3 \lesssim 1$ , the energy distribution is weakly bimodal near  $T_c$ , which means that the two peaks are not well separated at low  $L$ . Both  $C_V$  and  $\chi_{\Sigma}$  show a nice

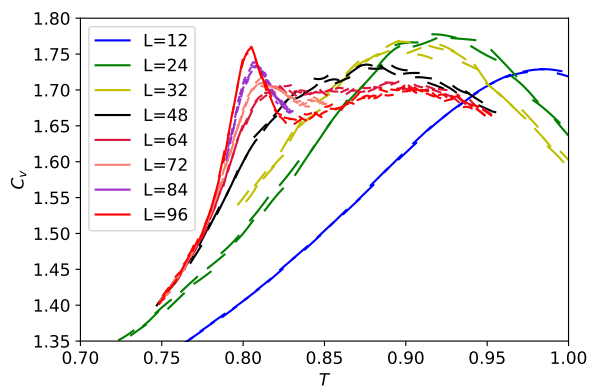


FIG. 12. Specific heat for different system sizes  $L$  for  $J_1 = -1$  and  $J_3 = 1.5$ , with the development of a slowly increasing secondary peak. The disjoint lines are an effect of the reweighting method at the junction between two temperature intervals and give an indication of the error bars.

divergence, at a temperature that extremely rapidly converges, making the determination of the exponents related to it impossible due to precision issue. The exponents of the growth of  $\chi_\Sigma$  is very near 2, which supports the hypothesis of a first order transition, but the one for  $C_V$  remains near 1, against 2 expected. It may be as a consequence of the unclear separation of the two peaks in the energy distribution, revealing a finite, but very large correlation length at the critical temperature, that would require simulations with larger lattice size. Another explanation would be that the transition becomes second ordered. Then, if it is in the universality class of the  $q = 4$  Potts model, the exponents should be  $\alpha/\nu = 1$  and  $\gamma/\nu = 7/4$ . These values are possible, but cannot be confirmed in view of our calculations.

The energy distribution at  $T_c$  becomes unimodal for  $J_3 \gtrsim 1$  up to the explored lattice sizes. Together with this change, the maximum of the specific heat needs much larger lattice sizes to convincingly increase with  $L$  (Fig. 13). This is more and more pronounced when  $J_3$  increases: for  $J_3 \gtrsim 1.25$ , we even see the appearance at large size of a secondary peak in  $C_V$ , that develops itself on the side of the main broad peak. For  $J_3 = 1.5$ , it only catches up the broad-peak maximum value at  $L \simeq 64$ , as illustrated on Fig. 12. It can also be seen on Fig. 13, where it translates in a dropout of  $T_c^{C_V}$  with  $L$ . It becomes tedious to extract critical exponents for  $C_V$  because the prefactor of the scaling behavior is very small. The signature of the transition is still present in the scaling behavior of the order parameter:  $\chi_\Sigma$  displays clear sign of divergence, even at small lattice sizes, with an exponent that remains near 2. This behavior at large  $J_3$  explains the absence of points for  $J_3 > 2$  on the phase diagram of Fig. 9, where the extraction of the critical temperature would require too large lattice size.

To conclude, we observe a phase transition for  $J_3 >$

0.69 associated with  $\Sigma$ , that is weakly first order for small  $J_3$ . With increasing  $J_3$ , the first order transition still weakens, up to a point where it could be a second order transition. However, the critical exponents are difficult to determine due to the large sizes required to observe the leading order behavior of the maximum of  $C_V$ , but could correspond to those of the  $q = 4$  Potts model. In the case of the antiferromagnetic  $J_1 - J_2$  square lattice, where order by disorder tends to align spins for  $J_2 > J_1/2$ , the same difficulty was observed[51] when the sublattices become less coupled (when  $J_2$  increases for the square lattice,  $J_3$  for the kagome).

### C. Results for antiferromagnetic $J_1$

In order to explore the full 3sub-AF phase of the phase diagram, we have also investigated the model with an antiferromagnetic interaction between the first nearest spins ( $J_1 = 1$ ). However, this situation is not supposed to describe the Ba-Vesignieite compound. Simulation are performed for various positive values of  $J_3$  and the transition temperatures are displayed on Fig. 14, which translates Fig. 9 in terms of  $\phi$  and extends it to positive  $J_1$  values. An astonishing similarity with the ferromagnetic  $J_1$  is found: the transition temperature does not depend on the sign of  $J_1$  for  $J_3 > 1$ , as emphasized on Fig. 14. It suggests that the critical temperature is only a function of  $\sin \phi$  in the whole 3sub-AF phase. The grey curve of Fig. 14:  $T_c = a(J_3/|J_1| - c)^b$ , with  $b = 0.88$  has a limit  $\lim_{\phi \rightarrow \pi/2} T_c(\phi) = 0$  as  $b < 1$ , which seems coherent as in this limit, the three sublattices are completely independent and no order is expected, at any temperature. A linear behavior with  $b = 1$  is however not excluded for large  $J_3$  if logarithmic corrections restore this limit.

For  $J_3 < 1$ , the ground state is in the  $\sqrt{3} \times \sqrt{3}$  phase and at low  $T$ ,  $\Sigma$  is effectively very low. However, for  $0.95 < J_3 < 1$  ( $0.242 < \phi/\pi < 0.25$ ), it sharply increases above a first critical temperature, and goes down again at a second one (grey dots of Fig. 14). This shows the existence of a reentrance of the  $K_4$  symmetry broken phase in the  $\sqrt{3} \times \sqrt{3}$  phase. This behavior is here more easily detected than in the unconventional phase, where it was only conjectured. This is probably due to the nature of the  $\sqrt{3} \times \sqrt{3}$  low  $T$  phase, that here does not break any symmetry and must cause less thermalization issue.

## V. QUANTUM AND THERMAL FLUCTUATIONS: LINEAR SPIN WAVE APPROXIMATION

An analytical approach to understand the emergence of a discrete order parameter, leading to a phase transition, consists in departing from one of the classical ground states, and perturbing it by adding infinitesimal thermal or quantum fluctuations. We thus expect to lift the degeneracy between them. Thermal and quantum per-

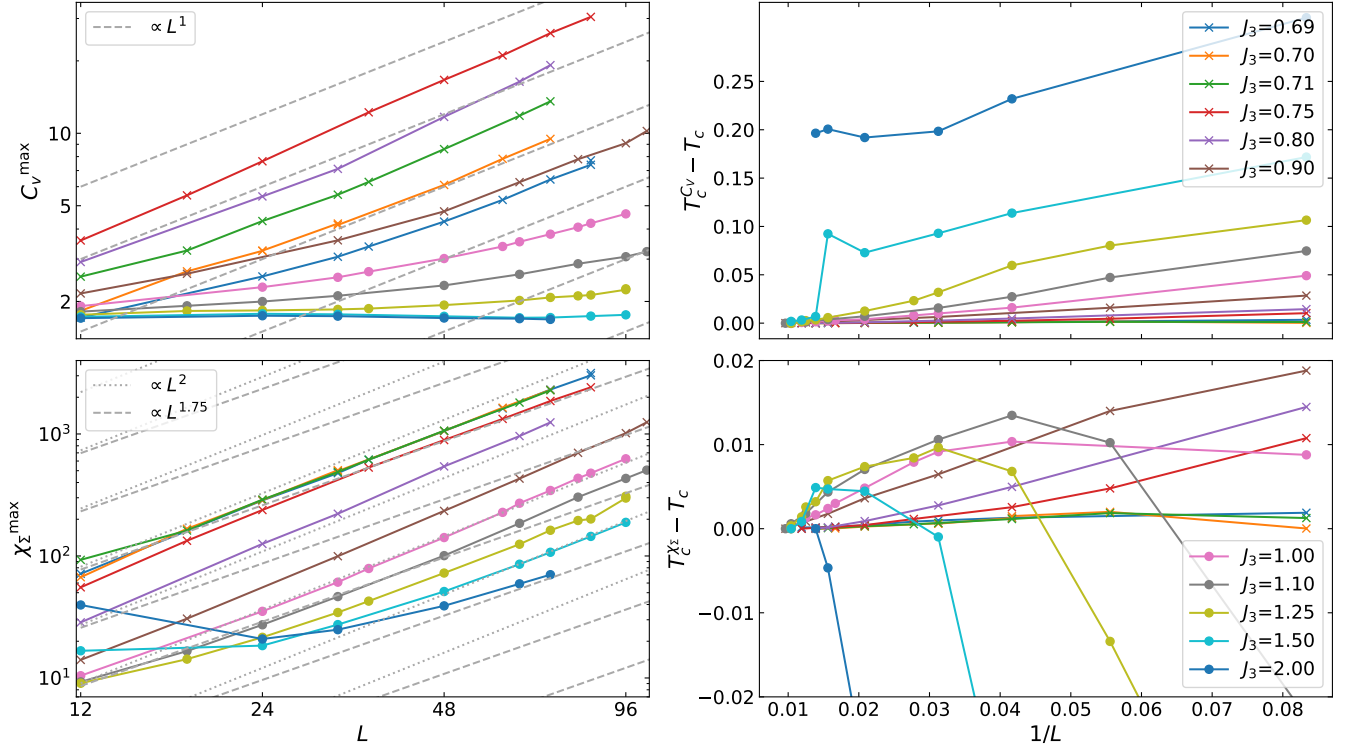


FIG. 13. Maximum of  $C_V$  and of  $\chi$  versus the lattice size  $L$  for  $J_1 = -1$  and various  $J_3$ , and temperature of their maxima.  $T_c$  has been extracted from  $\chi_{\Sigma}$ .

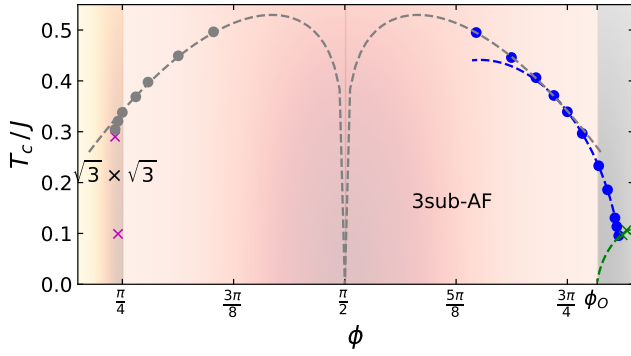


FIG. 14. Phase diagram of the  $J_1 - J_3$  Heisenberg model on the kagome lattice as a function of  $\phi$ . Phase diagram obtained by Monte-Carlo simulation of the  $J_1 - J_3$  model, in the  $T - \phi$  plane.  $T_c$  is in unit of  $J = \sqrt{J_1^2 + J_3^2}$ . The blue and green points are those of Fig. 9, for  $J_1 < 0$ , with the same fits (blue and grey dashed lines). Grey and blue dots indicate a phase transition from a  $K_4$  ordered low- $T$  phase and green crosses: between two  $K_4$  symmetric phases. The grey dashed line is symmetric with respect to  $\phi = \pi/2$ . The magenta crosses indicate a transition from a low- $T$   $K_4$  symmetric phase towards an intermediate- $T$   $K_4$  ordered phase: the  $K_4$  order only exists at intermediate temperature over this small range of  $\phi$ .

turbations can be handled through the same linear spin wave formalism. It will be developed in the two next subsections. But let us first develop the part common to both perturbations and define a set of eigen energies  $\omega_{\mathbf{q},l}$  which will be exploited differently in each case.

First, a reference ground state is chosen, whose spin orientation on site  $i$  is  $\mathbf{S}_i^0$ . Then, we chose a rotation  $R_i$  such that  $R_i \mathbf{S}_i^0 = \mathbf{e}_z$  and label by  $\mathbf{S}'_i$  the spin in the newly defined basis:  $\mathbf{S}'_i = R_i \mathbf{S}_i$ , whatever its orientation.  $\mathbf{S}'_i$  is either a real vector in the classical case, or an operator vector in the quantum case. In both cases, its norm is constrained by the spin length  $S$ . Using  $S'_i{}^{\pm} = S'_{ix} \pm iS'_{iy}$ , a vector  $\mathbf{U}_i$  is defined as:

$$\mathbf{U}_i = \begin{pmatrix} S'_i{}^+ \\ S'_i{}^- \\ S'_i{}^z \end{pmatrix} = V \mathbf{S}'_i \quad V = \begin{pmatrix} 1 & i & 0 \\ 1 & -i & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (7)$$

The Hamiltonian written in terms of  $\mathbf{U}_i$  is:

$$H = \frac{1}{2} \sum_{i,j} \mathbf{U}_i \cdot \underbrace{(V R_i J_{i,j} R_j^{-1} V^{-1})}_{M_{i,j}} \mathbf{U}_j \quad (8)$$

We now expand the Hamiltonian with respect to a small parameter related to the distance of the actual state with the reference ground state:  $S - S'^z_i$ . We need here to focus

successively on the low- $T$  classical case and on the zero- $T$  quantum case, to finally get the same eigen modes in both situations.

To describe the quantum ground state, a Holstein-Primakoff transformation of the  $\mathbf{S}'_i$  spins is performed. It defines  $a_i^\dagger$  and  $a_i$  bosonic creation and annihilation operators on each site  $i$ . They are subject to a constraint on their number  $n_i = a_i^\dagger a_i \leq 2S$ , in order to respect the spin length.  $n_i$  is supposed to be  $\mathcal{O}(1)$  in  $S$ :

$$\mathbf{U}_i = \begin{pmatrix} \sqrt{2S - a_i^\dagger a_i} \\ a_i^\dagger \sqrt{2S - a_i^\dagger a_i} \\ S - a_i^\dagger a_i \end{pmatrix} = \begin{pmatrix} \sqrt{2S} a_i + \mathcal{O}(S^{-1/2}) \\ \sqrt{2S} a_i^\dagger + \mathcal{O}(S^{-1/2}) \\ S - a_i^\dagger a_i \end{pmatrix} \quad (9)$$

The Hamiltonian now describes interacting bosons on the lattice.

On the classical side, by choosing as small complex parameter  $z_i = \frac{S_i'}{\sqrt{2S}}$  and assuming it in  $\mathcal{O}(1)$  (which is unjustified, as explained below), we get:

$$\mathbf{U}_i = \begin{pmatrix} \sqrt{2S} z_i \\ \sqrt{2S} z_i^* \\ \sqrt{S^2 - 2S|z_i|^2} \end{pmatrix} = \begin{pmatrix} \sqrt{2S} z_i \\ \sqrt{2S} z_i^* \\ S - |z_i|^2 + \mathcal{O}(S^{-1}) \end{pmatrix}. \quad (10)$$

The Hamiltonian of Eq. (8) is now expanded in powers of  $1/\sqrt{S}$ . The first term is the energy of the reference classical ground state, in  $S^2$ . The next term, in  $S^{3/2}$ , is zero if the reference ground state has correctly been chosen, as a stationary point of the reference energy with respect to the  $R_i$ 's. Finally, the first interesting term is in  $S$ , and has exactly the same form from Eq. (9) or from (10): it is a quadratic Hamiltonian either in  $a_i$  and  $a_i^\dagger$  or in  $z_i$  and  $z_i^*$ :

$$H^S = \frac{1}{2} \sum_{i,j} \mathbf{v}_i^\dagger M_{i,j}^S \mathbf{v}_j \quad (11)$$

where  $M_{i,j}^S$  is a  $2 \times 2$  matrix and  $\mathbf{v}_i$  is the two-component vector containing either  $a_i$  and  $a_i^\dagger$  or  $z_i$  and  $z_i^*$ .

Depending on the periodicity of  $M_{i,j}^S$ , an eventually large unit-cell of  $m$  sites is chosen to perform a Fourier transform  $\tilde{\mathbf{v}}_{\mathbf{q}}$  of  $\mathbf{v}_i$ , of components:

$$\tilde{\mathbf{v}}_{\mathbf{q}} = \begin{pmatrix} \tilde{a}_{\mathbf{q},1} \\ \tilde{a}_{\mathbf{q},2} \\ \dots \\ \tilde{a}_{\mathbf{q},m} \\ (\tilde{a}_{-\mathbf{q},1})^\dagger \\ (\tilde{a}_{-\mathbf{q},2})^\dagger \\ \dots \\ (\tilde{a}_{-\mathbf{q},m})^\dagger \end{pmatrix}, \quad \begin{pmatrix} z_{\mathbf{q},1} \\ z_{\mathbf{q},2} \\ \dots \\ z_{\mathbf{q},m} \\ (z_{-\mathbf{q},1})^* \\ (z_{-\mathbf{q},2})^* \\ \dots \\ (z_{-\mathbf{q},m})^* \end{pmatrix}. \quad (12)$$

The Hamiltonian rewrites:

$$H^S = \frac{1}{2} \sum_{\mathbf{q}} (\tilde{\mathbf{v}}_{\mathbf{q}})^\dagger \cdot \tilde{M}_{\mathbf{q}}^S \tilde{\mathbf{v}}_{\mathbf{q}} + E_{\text{class}}, \quad (13)$$

where  $i$  and  $j = 1 \dots m$  are now the indices of sites in the large unit cell and  $\mathbf{q}$  are wave vectors of a reduced Brillouin zone. The constant  $E_{\text{class}}$  results from commutation relations used in the quantum case, and has no effect in the classical expansion.

The eigen energies  $\omega_{\mathbf{q},l}$  are determined via a Bogoliubov transformation, that preserves the bosonic commutation relations in the quantum case, and the conjugation relations between  $z_i$  and  $z_i^*$  in the classical case. We thus define new vectors  $\tilde{\mathbf{w}}_{\mathbf{q}}$  from a matrix  $P_{\mathbf{q}}$  such that  $P_{\mathbf{q}} \tilde{\mathbf{w}}_{\mathbf{q}} = \tilde{\mathbf{v}}_{\mathbf{q}}$ , with properties similar to the  $\tilde{\mathbf{v}}_{\mathbf{q}}$ , that are eigen modes of the Hamiltonian (the transformed  $\tilde{M}_{\mathbf{q}}^S$  matrix is diagonal). The information that we can extract from  $P_{\mathbf{q}}$  and  $\omega_{\mathbf{q},l}$  in the quantum and classical cases will be described in the next subsections.

We now apply this formalism to the  $J_1 - J_3$  model, in the 3sub-AF part of the phase diagram (Fig. 2). A generic ground state is chosen, parametrized by three angles  $\theta_B$ ,  $\theta_C$  and  $\phi_C$  where spins in the origin unit cell (on the green, blue and red sites of the brown triangle of Fig. 4) are:

$$\mathbf{S}_A^0 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{S}_B^0 = \begin{pmatrix} \sin \theta_B \\ 0 \\ \cos \theta_B \end{pmatrix}, \quad \mathbf{S}_C^0 = \begin{pmatrix} \sin \theta_C \cos \phi_C \\ \sin \theta_C \sin \phi_C \\ \cos \theta_C \end{pmatrix}. \quad (14)$$

This parametrization describes all the ground states, up to a global spin rotation (equivalent to an appropriate choice of the basis in the spin space). Moreover, up to a lattice translation, we can fix  $0 \leq \theta_B, \theta_C \leq \pi/2$ ,  $0 \leq \phi_C \leq \pi$ . The three states of the bottom of Fig. 3 are given from left to right by  $(\theta_B, \theta_C, \phi_C) = (0, 0, 0)$  (collinear state),  $(\pi/3, \pi/3, \pi)$  (hexagonal) and  $(\pi/2, \pi/2, \pi/2)$  (octahedral).

To perform the Fourier transformation of Eq. (13), a unit-cell of 12 sites has to be chosen (as on Fig. 6), which results in  $24 \times 24$   $\tilde{M}_{\mathbf{q}}^S$  matrices. The dispersion relations for  $\phi = 3\pi/4$  ( $J_3 = -J_1 > 0$ ) are given in Fig. 15 for the collinear, hexagonal and 3sub-AF states.

### A. Linear thermal spin wave approximation

In two dimensions, we cannot expect to have a valid expansion at finite temperature: the Mermin-Wagner theorem predicts that a continuous order parameter (here the spin orientation), cannot survive to infinitesimal temperature. The hypothesis done on the small fluctuations around the classical ground state is false. However, short range correlations survive, and their nature can still be inferred from entropic selection of the maximally fluctuating ground state at low temperatures[39, 52].

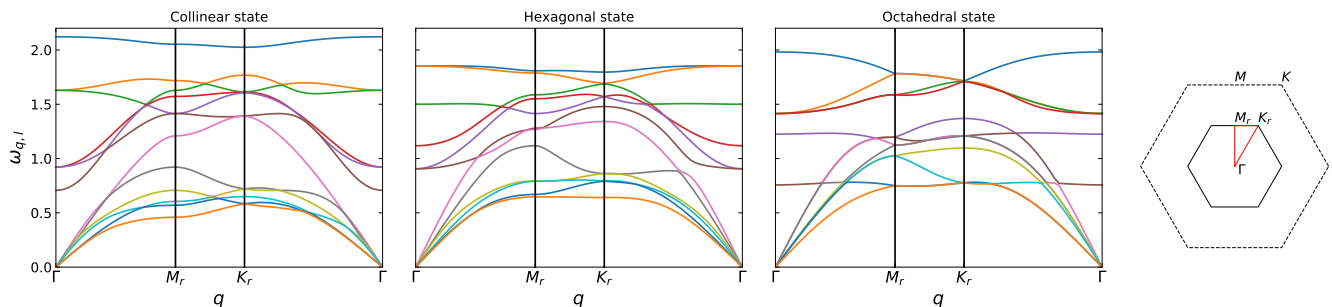


FIG. 15. Dispersion relations  $\omega_{\mathbf{q},l}$  along a cut in the Brillouin zone (red line on the right) from linear spin wave approximation for  $\phi = 3\pi/4$  ( $J_3 = -J_1 > 0$ ) for the  $J_1 - J_3$  kagome model, for the three ground states of Fig. 3. As a unit cell of 12 sites has been chosen, there are 12 energy bands in the reduced Brillouin zone (full black line on the right).

Classical spins are described, in the linear spin wave approximation, by a collection of independent harmonic oscillators of frequencies  $\omega_{\mathbf{q},l}$ . There are two modes for each couple  $(\mathbf{q}, l)$ , associated with the real ( $x$  spin component) and imaginary ( $y$  spin component) part of  $z_i$  in Eq. (10). At finite temperature, the free energy  $F = E - TS$  depends on the reference ground state which has been chosen.  $E$  is the same for all of them, thus, it is the entropy that lifts the degeneracy. For a classical harmonic oscillator of frequency  $\omega$ , the entropy is  $S = \text{const} - \ln \frac{T}{\omega}$ . A zero point energy is necessary to forbid negative values of the entropy at low temperature. The entropies of different reference ground states are parametrized by the angles  $S(\theta_B, \theta_C, \phi_C)$  of Eq. (14), or more conveniently, by the vector of spin dot-products  $\boldsymbol{\sigma}$ , defined in Sec. III B. The difference  $\Delta S(\theta_B, \theta_C, \phi_C) = S(\theta_B, \theta_C, \phi_C) - S(0, 0, 0)$ , or equivalently  $\Delta S(\boldsymbol{\sigma}) = S(\boldsymbol{\sigma}) - S(\boldsymbol{\sigma}_0)$ , where  $\boldsymbol{\sigma}_0 = (1, 1, 1)$ , does not depend on the temperature and is represented on Fig. 16 for  $\phi = 3\pi/4$ . The maximum is reached in the collinear state, and the minimum in the octahedral state, as expected.

### B. Linear quantum spin wave approximation

In quantum materials, the spin has a finite value ( $S = 1/2, 1, 3/2, \dots$ ), which differs from the classical case corresponding to the limit  $S \rightarrow \infty$ . In Ba-Vesigneite, the spin on the copper sites has the most quantum value of  $1/2$ . We now discuss the consequences in light of the previous classical considerations. Quantum fluctuations tend to disorder the system: a model with a magnetically ordered ground state in the classical limit generally has an order parameter  $m$  that decreases when  $S$  decreases. We thus face two possibilities: either the order parameter remains finite ( $m > 0$ ) when quantum fluctuations are switched on, or it reaches zero and the ground state is no more long-range ordered.

The linear spin wave approximation expands to first non trivial order quantum observables (as the energy or an order parameter) in  $1/\sqrt{S}$  at zero temperature and

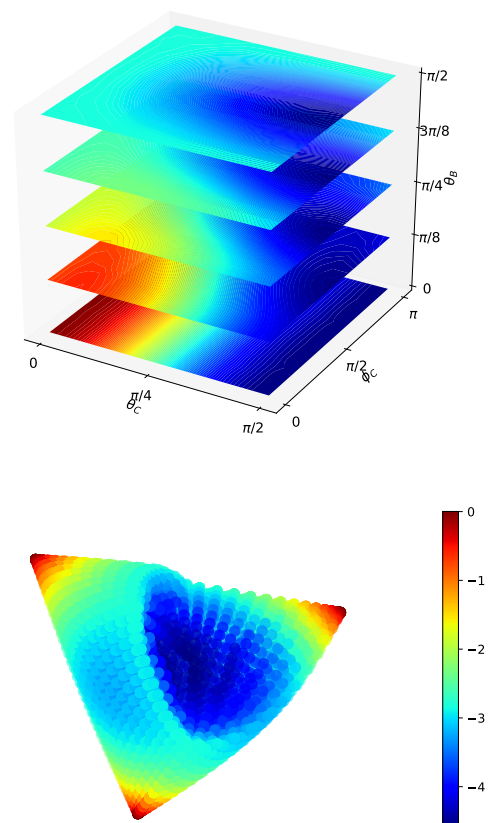


FIG. 16. Low energy entropy  $\Delta S(\theta_B, \theta_C, \phi_C)$  (top) and  $\Delta S(\boldsymbol{\sigma})$  (bottom), where the angles were defined in Eq. (14) and  $\boldsymbol{\sigma}$  in Sec. III B, for  $J_1 < 0$  and  $J_3 = -J_1$ . The maximal entropy (in dark red) is for  $\theta_B = \theta_C = 0$ : the collinear state, and the minimum (in dark blue) for  $\theta_B = \theta_C = \phi_C = \pi/2$ : the octahedral state, corresponding respectively to the vertices and to the center of the inflated tetrahedron formed by the set of  $\boldsymbol{\sigma}$  values.

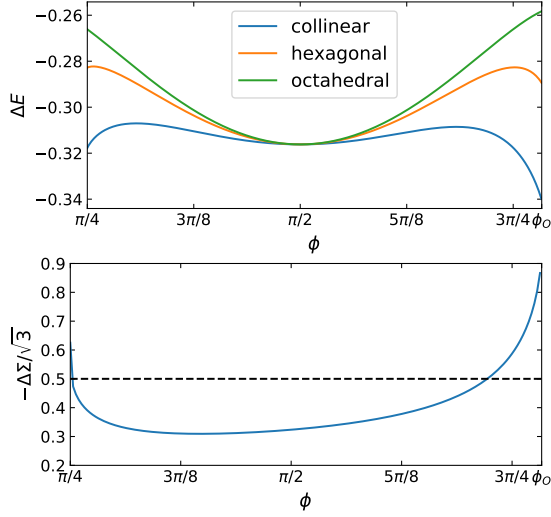


FIG. 17. Results of quantum linear spin wave approximation for  $(J_1, J_3) = (\cos \phi, \sin \phi)$ , in the 3sub-AF phase of Fig. 2. Top: correction  $\Delta E$  of order  $S$  to the energy around the three classical states depicted in Fig. 3. Bottom: correction  $\Delta \Sigma$  of order  $S$  to the order parameter for the collinear phase. The dashed line indicates an approximative value of  $-\Delta \Sigma / \sqrt{3}$  above which quantum fluctuations restore the  $K_4$  symmetry for  $S = 1/2$ .

around a specific ground state. When several ground states exist, as occurs here in the  $J_1 - J_3$  model, the expansion can be performed around any of them, giving different correction to the energy that eventually lifts the degeneracy. The first terms of the energy are:

$$E = S(S+1)E_{\text{class}} - \frac{S}{2} \sum_{\mathbf{q}, l} \omega_{\mathbf{q}, l} + \mathcal{O}(\sqrt{S}), \quad (15)$$

where  $E_{\text{class}} = -2J_3$  in the 3sub-AF phase. The term of order  $S$ :  $\Delta E = E_{\text{class}} - \frac{1}{2} \sum_{\mathbf{q}, l} \omega_{\mathbf{q}, l}$ , depends on the angles  $(\theta_B, \theta_C, \phi_C)$  and on the coupling  $\phi$ . It can be represented in the same way as  $\Delta S$  in Fig. 16 for a fixed  $\phi$ . The same qualitative behavior is obtained, and the same conclusion: the collinear state is the most favored by quantum fluctuations, whereas the octahedral one has the weakest quantum energy correction. It is quite expected that quantum and thermal fluctuations favor the same order, even if counter-examples exist[53]. For completeness, the curve of  $\Delta E$  is given versus  $\phi$  in Fig. 17, for the three ground states of Fig. 3. Whatever  $\phi$  (except  $\phi = \pi/2$  where the three sublattices are completely decoupled), quantum fluctuations always favor the collinear state.

The order parameter  $\Sigma$  can be expanded as the energy:  $\Sigma = S^2 \Sigma_{\text{class}} + S \Delta \Sigma + \mathcal{O}(\sqrt{S})$ , which can be used as an indication of the critical spin where its average cancels, excluding the occurrence of a phase transition at finite temperature. The classical value is  $\Sigma_{\text{class}} = \sqrt{3}$ . Thus,  $S_c \sim -\frac{\Delta \Sigma}{\sqrt{3}}$ .  $S_c$  is below 1/2 in all the 3sub-AF phase, except near the boundary with the unconventional phase

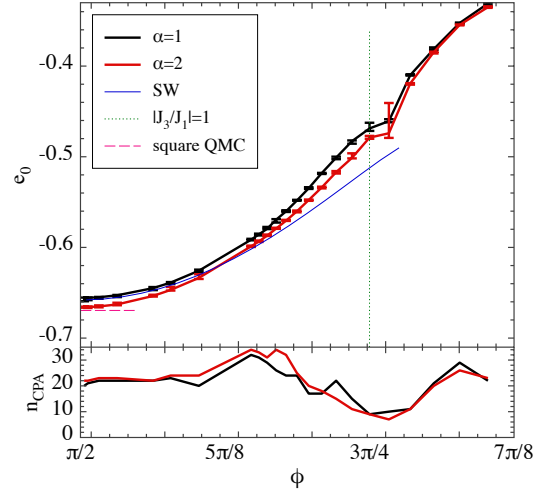


FIG. 18. Ground state energy per site  $e_0$  as a function of  $\phi$ , with  $(J_1, J_3) = (\cos \phi, \sin \phi)$  on the kagome lattice.  $e_0$  is obtained via the method described in Bernu et al. [54], using high temperature series expansions up to order 15, assuming no finite temperature phase transition. The red and black points are the results with the hypothesis that  $C_V \sim A(\phi)T^\alpha$ , with  $\alpha = 1$  and 2. The blue curve is the linear spin wave energy up to order  $S$ , approximated for  $S = 1/2$ .  $n_{\text{CPA}}$  is the number of coinciding Pade approximants, whose large value indicates a good quality of the result.

(Fig. 17). It suggesting that the  $K_4$  symmetry could be broken even in the  $S = 1/2$  case.

## VI. HIGH TEMPERATURE SERIES EXPANSIONS (HTSE)

After a look at the behavior of the model from the classical limit ( $S = \infty$ ) towards finite spins, the extreme quantum case of  $S = 1/2$  can be investigated through high temperature series expansions. The logarithm of the partition function  $\frac{\ln Z}{N}(\beta)$  is expanded in powers of the inverse temperature  $\beta$  directly in the thermodynamic limit:

$$\lim_{N \rightarrow \infty} \frac{\ln Z}{N}(\beta) = \ln 2 + \sum_{n=1}^{\infty} \left( \sum_{i=0}^n Q_{i,n} J_1^i J_3^{n-i} \right) \beta^n, \quad (16)$$

where  $N$  is the number of lattice sites. Enumerating connected clusters on the  $J_1 - J_3$  kagome lattice, we exactly calculate the coefficients of this series up to order 15 in  $\beta$ , each of them being an homogeneous polynomial in  $J_1$  and  $J_3$ .

A direct use of the truncated series to evaluate thermodynamical functions is doomed to fail, as the series only converges for  $T \gtrsim J_1, J_3$ . An extrapolation technique called the entropy method (HTSE+ $s(e)$ ) has been developed[55, 56], that extrapolates functions from infinite down to zero temperatures, under the hypothesis

of the absence of finite temperature phase transition (so that the functions are analytical over the full temperature interval). First, we apply it to the  $J_1 - J_3$  model assuming that this hypothesis is verified. Incoherent results are found near  $J_3 = |J_1|$  for  $J_1 < 0$ . Thus, in a second part, we will adapt the method to account for finite temperature phase transitions.

**Without finite temperature phase transition:** the HTSE+ $s(e)$  method also requires some inputs: the ground state energy per site  $e_0$  and the low temperature behavior of  $C_V$  (in power law  $C_V \sim T^\alpha$ , or exponential for example), what can be understood as the need to constrain the thermodynamical functions both from the  $T = \infty$  side, which is ensured by the series coefficients, and from the  $T = 0$  one.

The need for  $e_0$  is a real problem, as no generic method exist to determine it in the case of frustrated quantum models. In Bernu et al. [54], a self-consistent method has been developed that proposes an  $e_0$ . Although no rigorous argument says that this energy is near the real one, it has been shown to give extremely coherent results on the first neighbor kagome model. With the hypothesis that no finite-temperature phase transition occurs, the ground state energy  $e_0$  obtained by this method is shown in Fig. 18, for  $C_V \sim_{T \rightarrow 0} AT^\alpha$  with  $\alpha = 2$  (which is the case for  $\phi = \pi/2$ ) and  $\alpha = 1$ . The minimal  $\phi = \pi/2$  on Fig. 18 corresponds to the three decoupled square sublattices, whose ground state energy is accessible through quantum Monte Carlo simulations in this unfrustrated case:  $e_0 = -0.6695$ [57, 58]. HTSE+ $s(e)$  results give still better results than the linear spin wave approximation at  $\phi = \pi/2$ . The quality of the results is bad in the neighborhood of  $\phi_O$  (convergence issue of the method: small number of coinciding Pade approximants), at the point where a slope breaking occurs in  $e_0(\phi)$ .

**With a finite temperature phase transition:** In view of the previous sections, this behavior can be attributed to the existence of a phase transition at finite temperature  $T_c$  near  $\phi_O$ . In the Supp. Mat. of [56], the possibility to detect a phase transition thanks to HTSE+ $s(e)$  was proposed for a ferromagnetic BCC lattice, where  $e_0$  was exactly known and the extrapolation was performed down to  $T = 0$  despite the singularity at  $T_c$ . Here, the method tends to deviate  $e_0$  from its real value to get ride of eventual singularities. We propose a new adaptation of HTSE+ $s(e)$  to models with phase transitions, that will be detailed elsewhere[59]. The extrapolation is only done on the temperature interval  $[T_c, \infty]$ , requiring as supplementary input parameters  $T_c$ , the energy  $e_c$  and the entropy  $s_c$  at  $T_c$ . We also characterize the behavior of  $C_V$  near the transition by an exponent  $\alpha$ :

$$C_V(T) \sim_{T \rightarrow T_c^+} \frac{A}{(T - T_c)^\alpha}. \quad (17)$$

Because of the sum rules on  $C_V(T)/T$ ,  $\alpha$  must be lower or equal to 1. For  $J_1 = -1$  and  $J_3 = 1$ , the four parameters  $T_c$ ,  $e_c$ ,  $s_c$  and  $\alpha$  giving the higher quality of result were

looked for. Interesting values are found in a tiny valley of the 4 dimensional space, with a transition at  $T_c = 0.42(1)$  and an exponent of  $\alpha = 0.29(1)$ ,  $e_c = -0.405(5)$  and  $s_c = 0.35(1)$ .

Even if still exploratory, this section on HTSE confirm the possibility of a phase transition in the  $S = 1/2$  model, in the domain of parameter where it is the more easily detected in the classical model:  $J_3 \simeq |J_1|$ .

## VII. CONCLUSION

Motivated by the Ba-Vesignieite compound, this article has explored the  $J_1 - J_3$  model on the kagome lattice, in the domain of large  $J_3$ . The classical phase diagram has revealed interesting phases: for ferromagnetic  $J_1$  and moderate  $J_3$ , an unconventional phase displays conical, spiral, and probably other unusual phases, whereas for large  $J_3$ , whatever the sign of  $J_1$ , a 3sub-AF phase possesses an accidental degeneracy. Thermal or quantum fluctuations lift this degeneracy via the order by disorder mechanism, favoring collinear configurations, labelled by an element of the  $K_4$  group. An order parameter  $\Sigma$  was constructed by analysing the symmetries of the model, to detect this discrete  $K_4$  symmetry breaking.

Classical Monte Carlo simulations have evidenced an order-by-disorder induced phase transition associated with  $\Sigma$ . The transition is first order for low  $J_3$ 's, and either weakly first order or second order for large ones. Other phase transitions were found in the unconventional phase, associated with one or several other order parameters.

Linear spin wave formalism have shown that both thermal and quantum fluctuations favor the collinear states. But quantum fluctuations can be so strong that they completely disorder the system, preventing the occurrence of a phase transition, notably near the boundary with the unconventional phase  $\phi = \phi_O$ . Finally, HTSEs also confirm the possibility of a phase transition, this time in the  $S = 1/2$  model.

What are the implication of this phase transition on Ba-Vesignieite ? First of all, the dominant coupling was proposed to be  $J_3$  in [12], but the one coming next was  $J'_3$ , then  $J_1$ , and  $J_2$ . We did not considered  $J'_3$  as it did not couple the three kagome sublattices, and have focused on  $J_1$ . Note that  $J_2$  would have led to the same order by disorder effect as  $J_1$ . One could argue that many perturbations other than next nearest neighbor interactions can lift the degeneracy of the 3sub-AF phase. Among them, a slight distortion of the lattice is know, of less than 1% of the Cu-Cu distance and causes a coupling anisotropy[13]. Some impurities are unavoidable, whose effect has been studied on the  $J_1 - J_2$  square lattice. Their effect is opposite to the one of thermal fluctuation, selecting orthogonal configurations[39, 52], and penalizing collinear ones. If this occurs here, the octahedral state of Fig. 3 would be favored, possibly leading to a chiral phase transition. Dzyaloshinskii-Moriya interactions must also be



present[60], as well as Ising spin anisotropy[12] but eventually very small. Lastly, a small coupling between spins in successive kagome planes exists and is suspected to induce the phase transition observed at  $T = 9K$ [12].

However, despite this whole set of deviations from the  $J_1 - J_3$  model, the transition discussed in this article remains meaningful. At temperature larger than the energy scale of these deviations, their effect is crushed, and the  $K_4$  order can still be present.

Lastly, the theoretical investigation of such an emerging  $q = 4$  Potts order parameter and of its phase transition illustrate in an original way the order by disorder mechanism.

## ACKNOWLEDGEMENTS

We thank Bjorn Fåk for discussions on the experimental results on Vesignieite. This work was supported by the French Agence Nationale de la Recherche under Grants No. ANR-18-CE30-0022-04 LINK.

Numerical simulations were performed on the highly parallel computer of the LJP, LKB and LPTMC.

### Appendix A: The Luttinger-Tizsa (LT) method

To use the LT method[27, 28], we perform a Fourier transform on  $H$ . With this in mind, we rewrite Eq. (1)

$$H = \frac{1}{2} \sum_{\mathbf{r}} \sum_{\mathbf{v}} \sum_{i,j} J_{i,j}(\mathbf{v}) \mathbf{S}_{i,\mathbf{r}} \cdot \mathbf{S}_{j,\mathbf{r}+\mathbf{v}}, \quad (\text{A1})$$

where  $\mathbf{r}, \mathbf{r} + \mathbf{v}$  are vectors from a Bravais lattice locating the unit-cells of the interacting spins,  $i$  and  $j$  label inequivalent sites in each unit-cell. Next, we introduce the Fourier modes of a spin  $i$  in cell  $\mathbf{r}$ :

$$\mathbf{S}_{i,\mathbf{r}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \tilde{\mathbf{S}}_i(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (\text{A2})$$

to rewrite the Hamiltonian as:

$$H = \frac{1}{2} \sum_{\mathbf{q}} \sum_{i,j} \tilde{\mathbf{S}}_i(\mathbf{q}) \tilde{J}_{i,j}(\mathbf{q}) \tilde{\mathbf{S}}_j(-\mathbf{q}) \quad (\text{A3})$$

where  $\tilde{J}_{i,j}(\mathbf{q}) = \sum_{\mathbf{v}} J_{i,j}(\mathbf{v}) e^{i\mathbf{q}\cdot\mathbf{v}}$  is akin to a Fourier transform of the couplings of  $H$ . The Hamiltonian itself is now expressed as a bilinear form in the Fourier modes  $\tilde{\mathbf{S}}_i(\mathbf{q})$ .

If the lattice is a Bravais lattice (with one site per unit cell), its ground state may easily be found by diagonalizing  $\tilde{J}(\mathbf{q})$  and minimizing its lowest eigenvalue  $\lambda_{\min}(\mathbf{q})$  with respect to  $\mathbf{q}$ . This, in turn, leads us to a generally discrete set of wave vectors  $\mathbf{q}_i$  of the Brillouin zone respecting the lattice symmetries[61]. The desired ground state is then obtained by solely populating the eigen modes corresponding to  $\lambda_{\min}(\mathbf{q}_i)$  and performing

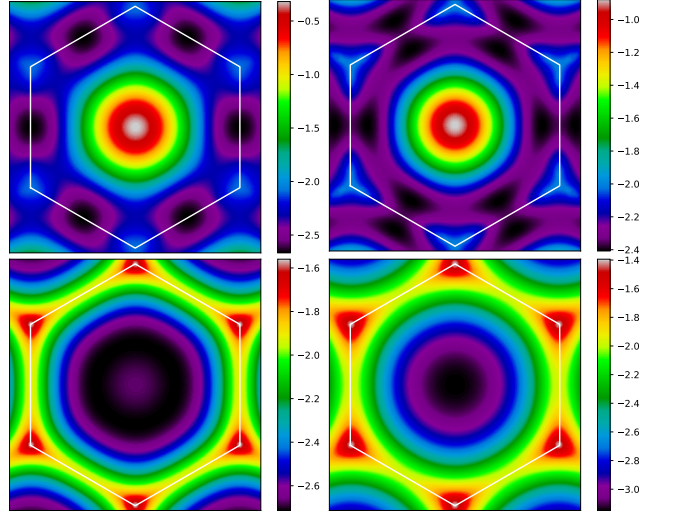


FIG. 19.  $\lambda_{\min}(\mathbf{q})$  for the  $J_1 - J_3$  model on the kagome lattice with  $\phi = \phi_O - 0.05$  (top left),  $\phi_O + 0.05$  (top right)  $\phi = \phi_F - 0.05$  (bottom left),  $\phi_F + 0.05$  (bottom right).

an inverse Fourier transform.

However, for non-Bravais lattices (with more than one site per unit cell), we have to take into account an unmentioned constraint: at each site we have a unit spin  $\mathbf{S}_i$ , with  $\|\mathbf{S}_i\| = 1$ . For Bravais lattices this is not an issue, since there always exists a spiral state, defined by a single wave vector, which is a ground state of the Hamiltonian. For non-Bravais lattices, however, such as the kagome lattice we are working on, this constraint prevents us from applying the last step, as naively populating a mode with the lowest energy generally does not respect the constraint on all sites of a unit cell. Thus, other modes can be used to recover the constraint, increasing the energy as compared with  $\lambda_{\min}$ , which is then only a lower bound.

### Appendix B: Determination of the value of $\phi_O$

We present here a derivation of the value of  $\phi_O$ , where the transition between the orthogonal and unconventional phase occurs in the  $J_1 - J_3$  model on the kagome lattice (see Fig. 2). The proof rests on the LT method presented in App. A. The  $\tilde{J}(\mathbf{q})$  matrix of Eq. (A3), multiplied by the overall  $\frac{1}{2}$ , writes:

$$\begin{pmatrix} J_3(c_1^2 + c_2^2 - 1) & \frac{J_1}{2}c_1 & \frac{J_1}{2}c_2 \\ \frac{J_1}{2}c_1 & J_3(c_1^2 + c_3^2 - 1) & \frac{J_1}{2}c_3 \\ \frac{J_1}{2}c_2 & \frac{J_1}{2}c_3 & J_3(c_2^2 + c_3^2 - 1) \end{pmatrix}, \quad (\text{B1})$$

where  $c_1 = \cos \frac{q_x}{2}$ ,  $c_2 = \cos \frac{q_y}{2}$  and  $c_3 = \cos \frac{q_x - q_y}{2}$ .

In the 3sub-AF phase, the minimal eigenvalue  $\lambda_{\min}(\mathbf{q})$  of  $\tilde{J}(\mathbf{q})$  occurs for three  $\mathbf{q}$ :  $\mathbf{M}_{1,2,3}$ , the middles of the

edges of the Brillouin zone (see Fig.19). At the transition toward the unconventional phase, each of the three minima splits in two, giving six new minima evolving with  $\phi$  along the line  $M_i - \Gamma$ .

The characteristic polynomial  $C(\lambda)$  of the  $\tilde{J}_{i,j}(\mathbf{M}_1 + \delta_{\mathbf{q}})$  matrix is expanded to the first order in  $\epsilon = \lambda + 2J_3$ , as we look for the minimal root of  $C(\lambda)$ , which is nearby  $-2J_3$  (the energy of an 3sub-AF state) in the neighborhood of  $\mathbf{M}_1 = (\pi, 0)$  and for the values of  $J_3$  and  $J_1$  of interest. The root of the first order degree polynomial approximating  $C(\lambda)$  is expanded to the second order in  $\delta_{\mathbf{q}}$ . Increasing from  $\phi = \pi/2$ , the quadratic form thus obtained changes at  $\phi = \phi_t = \pi - \arctan \frac{1+\sqrt{5}}{4}$  from a positive one, with a minima at  $\delta_{\mathbf{q}} = \mathbf{0}$ , to a non-positive one, with a saddle point at  $\delta_{\mathbf{q}} = \mathbf{0}$ , indicating that the energy of the 3sub-AF states is no more the lower bound, and that  $\phi_O \geq \phi_t$  (they are unequal if the 3sub-AF phase remains the ground state in the area where it does not have the LT lower bound energy).

It remains to exhibit a state that has a lower energy than the 3sub-AF states for  $\phi > \phi_t$  to prove that  $\phi_t$  is effectively the transition value. This is done using the conical state of Fig. 5. We parametrize it by four angles  $(\theta, \phi, \psi)$ . A unit cell of 12 sites is defined as indicated on Fig. 5, with three different spin orientations  $\mathbf{S}_{1,2,3}$ . A translation in the  $\mathbf{e}_1$  direction has no effect on the spin

orientation, whereas a translation in the  $\mathbf{e}_2$  ( $y$  coordinate) rotates the spins of  $\phi$  and inverse them:

$$\begin{aligned} \mathbf{S}_1 &= (-1)^y \begin{pmatrix} \cos 2y\psi \\ \sin 2y\psi \\ 0 \end{pmatrix}, \\ \mathbf{S}_2 &= (-1)^y \begin{pmatrix} -\sin \phi \sin((2y-1)\psi) \\ \sin \phi \cos((2y-1)\psi) \\ \cos \phi \end{pmatrix}, \\ \mathbf{S}_3 &= (-1)^y \begin{pmatrix} -\sin \phi \sin((2y-1)\psi) \\ \sin \phi \cos((2y-1)\psi) \\ -\cos \phi \end{pmatrix} \end{aligned} \quad (\text{B2})$$

The energy per site thus reads:

$$\begin{aligned} E &= \frac{2J_1 \sin \phi}{3} (\sin \psi (1 - \cos 2\psi) - \cos \psi \sin 2\psi + \sin \phi) \\ &\quad + \frac{2J_3}{3} (2 \sin^2 \phi \sin^2 \psi - \cos 2\psi - 2 \cos^2 \phi) \end{aligned}$$

The minimum of this energy (numerically obtained) is effectively between the lowest bound and the energy of the 3sub-AF states for  $\phi \gtrsim \phi_O$  (see the inset of Fig. 2, bottom)

- 
- 1 L. Savary and L. Balents, Quantum spin liquids: a review, *Reports on Progress in Physics* **80**, 016502 (2017).
  - 2 M. A. de Vries, J. R. Stewart, P. P. Deen, J. O. Piatek, G. J. Nilsen, H. M. Rønnow, and A. Harrison, Scale-free antiferromagnetic fluctuations in the  $s = 1/2$  kagome antiferromagnet herbertsmithite, *Phys. Rev. Lett.* **103**, 237201 (2009).
  - 3 B. Fåk, E. Kermarrec, L. Messio, B. Bernu, C. Lhuillier, F. Bert, P. Mendels, B. Koteswararao, F. Bouquet, J. Ollivier, A. D. Hillier, A. Amato, R. H. Colman, and A. S. Wills, Kapellasite: A Kagome Quantum Spin Liquid with Competing Interactions, *Phys. Rev. Lett.* **109**, 037208 (2012).
  - 4 Z. Hiroi, H. Yoshida, Y. Okamoto, and M. Takigawa, Spin-1/2 kagome compounds: Volborthite vs Herbertsmithite, *J. Phys.: Conf. Ser.* **145**, 012002 (2009).
  - 5 R. Colman, A. Sinclair, and A. Wills, Comparisons between Haydeeite,  $\alpha$ - $\text{Cu}_3\text{Mg}(\text{OD})_6\text{Cl}_2$ , and Kapellasite,  $\alpha$ - $\text{Cu}_3\text{Zn}(\text{OD})_6\text{Cl}_2$ , Isostructural  $S = 1/2$  Kagome Magnets, *Chem. Mater.* **22**, 5774 (2010).
  - 6 R. H. Colman, A. Sinclair, and A. S. Wills, Magnetic and Crystallographic Studies of Mg-Herbertsmithite,  $\gamma$ - $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Cl}_2$ -A New  $S = 1/2$  Kagome Magnet and Candidate Spin Liquid, *Chem. Mater.* **23**, 1811 (2011).
  - 7 Y. Okamoto, H. Yoshida, and Z. Hiroi, Vesignieite  $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$  as a Candidate Spin-1/2 Kagome Antiferromagnet, *J. Phys. Soc. Jpn.* **78**, 033701 (2009).
  - 8 H. Yoshida, Y. Michiue, E. Takayama-Muromachi, and M. Isobe, Vesignieite  $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$ : a structurally perfect  $S = 1/2$  kagomé antiferromagnet, *J. Mater. Chem.* **22**, 18793 (2012).
  - 9 Y. Okamoto, M. Tokunaga, H. Yoshida, A. Matsuo, K. Kindo, and Z. Hiroi, Magnetization plateaus of the spin-1/2 kagome antiferromagnets volborthite and vesignieite, *Phys. Rev. B* **83**, 180407 (2011).
  - 10 H. Ishikawa, T. Yajima, A. Miyake, M. Tokunaga, A. Matsuo, K. Kindo, and Z. Hiroi, Topochemical Crystal Transformation from a Distorted to a Nearly Perfect Kagome Cuprate, *Chem. Mater.* **29**, 6719 (2017).
  - 11 A. Verrier, F. Bert, J. M. Parent, M. El-Amine, J. C. Orain, D. Boldrin, A. S. Wills, P. Mendels, and J. A. Quilliam, Canted antiferromagnetic order in the kagome material Sr-vesignieite, *Phys. Rev. B* **101**, 054425 (2020).
  - 12 D. Boldrin, B. Fåk, E. Canévet, J. Ollivier, H. C. Walker, P. Manuel, D. D. Khalyavin, and A. S. Wills, Vesignieite: An  $S = \frac{1}{2}$  Kagome Antiferromagnet with Dominant Third-Neighbor Exchange, *Phys. Rev. Lett.* **121**, 107203 (2018).
  - 13 R. H. Colman, F. Bert, D. Boldrin, A. D. Hillier, P. Manuel, P. Mendels, and A. S. Wills, Spin dynamics in the  $S = \frac{1}{2}$  quantum kagome compound vesignieite,  $\text{Cu}_3\text{Ba}(\text{VO}_5\text{H})_2$ , *Phys. Rev. B* **83**, 180416 (2011).
  - 14 J. A. Quilliam, F. Bert, R. H. Colman, D. Boldrin, A. S. Wills, and P. Mendels, Ground state and intrinsic susceptibility of the kagome antiferromagnet vesignieite as seen by  $^{51}\text{V}$  NMR, *Phys. Rev. B* **84**, 180401 (2011).
  - 15 J.-C. Dometge, P. Sindzingre, C. Lhuillier, and L. Pierre, Twelve sublattice ordered phase in the  $J_1 - J_2$  model on

- the kagomé lattice, *Phys. Rev. B* **72**, 024433 (2005).
- 16 L. Messio, B. Bernu, and C. Lhuillier, Kagome Antiferromagnet: A Chiral Topological Spin Liquid?, *Phys. Rev. Lett.* **108**, 207204 (2012).
  - 17 L. Messio, C. Lhuillier, and G. Misguich, Lattice symmetries and regular magnetic orders in classical frustrated antiferromagnets, *Phys. Rev. B* **83**, 184401 (2011).
  - 18 S. R. Sklan and C. L. Henley, Nonplanar ground states of frustrated antiferromagnets on an octahedral lattice, *Phys. Rev. B* **88**, 024407 (2013).
  - 19 N. D. Mermin and H. Wagner, Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models, *Phys. Rev. Lett.* **17**, 1133 (1966).
  - 20 N. D. Mermin, Absence of ordering in certain classical systems, *J. Math. Phys.* **8**, 1061 (1967).
  - 21 A. Klein, L. J. Landau, and D. S. Shucker, On the absence of spontaneous breakdown of continuous symmetry for equilibrium states in two dimensions, *J. Stat. Phys.* **26**, 505 (1981).
  - 22 J. M. Kosterlitz and D. J. Thouless, Ordering, metastability and phase transitions in two-dimensional systems, *J. Phys. C: Solid State Phys.* **6**, 1181 (1973).
  - 23 H. W. J. Blöte, W. Guo, and H. J. Hilhorst, Phase Transition in a Two-Dimensional Heisenberg Model, *Phys. Rev. Lett.* **88**, 047203 (2002).
  - 24 M. E. Zhitomirsky and K. Ueda, Valence-bond crystal phase of a frustrated spin-1/2 square-lattice antiferromagnet, *Phys. Rev. B* **54**, 9007 (1996).
  - 25 J.-C. Domenge, C. Lhuillier, L. Messio, L. Pierre, and P. Viot, Chirality and  $\mathbb{Z}_2$  vortices in a Heisenberg spin model on the kagome lattice, *Phys. Rev. B* **77**, 172413 (2008).
  - 26 L. Messio, J.-C. Domenge, C. Lhuillier, L. Pierre, P. Viot, and G. Misguich, Thermal destruction of chiral order in a two-dimensional model of coupled trihedra, *Phys. Rev. B* **78**, 054435 (2008).
  - 27 J. M. Luttinger and L. Tisza, Theory of dipole interaction in crystals, *Phys. Rev.* **70**, 954 (1946).
  - 28 T. A. Kaplan and N. Menyuk, Spin ordering in three-dimensional crystals with strong competing exchange interactions, *Philos. Mag.* **87**, 3711 (2007).
  - 29 Villain, J., Bidaux, R., Carton, J.-P., and Conte, R., Order as an effect of disorder, *J. Phys. France* **41**, 1263 (1980).
  - 30 G.-W. Chern and R. Moessner, Dipolar order by disorder in the classical heisenberg antiferromagnet on the kagome lattice, *Phys. Rev. Lett.* **110**, 077201 (2013).
  - 31 M. E. Zhitomirsky, Field-induced transitions in a kagomé antiferromagnet, *Phys. Rev. Lett.* **88**, 057204 (2002).
  - 32 S. Schnabel and D. P. Landau, Fictitious excitations in the classical heisenberg antiferromagnet on the kagome lattice, *Phys. Rev. B* **86**, 014413 (2012).
  - 33 A. L. Chernyshev and M. E. Zhitomirsky, Quantum selection of order in an  $xxz$  antiferromagnet on a kagome lattice, *Phys. Rev. Lett.* **113**, 237202 (2014).
  - 34 A. L. Chernyshev, Strong quantum effects in an almost classical antiferromagnet on a kagome lattice, *Phys. Rev. B* **92**, 094409 (2015).
  - 35 E. F. Shender, V. B. Cherepanov, P. C. W. Holdsworth, and A. J. Berlinsky, Kagomé antiferromagnet with defects: Satisfaction, frustration, and spin folding in a random spin system, *Phys. Rev. Lett.* **70**, 3812 (1993).
  - 36 M. E. Zhitomirsky, Octupolar ordering of classical kagome antiferromagnets in two and three dimensions, *Phys. Rev. B* **78**, 094423 (2008).
  - 37 M. Taillefumier, J. Robert, C. L. Henley, R. Moessner, and B. Canals, Semiclassical spin dynamics of the antiferromagnetic heisenberg model on the kagome lattice, *Phys. Rev. B* **90**, 064419 (2014).
  - 38 C. L. Henley, Long-range order in the classical kagome antiferromagnet: Effective hamiltonian approach, *Phys. Rev. B* **80**, 180401 (2009).
  - 39 C. L. Henley, Ordering due to disorder in a frustrated vector antiferromagnet, *Phys. Rev. Lett.* **62**, 2056 (1989).
  - 40 C. Weber and F. Mila, Anticollinear magnetic order induced by impurities in the frustrated heisenberg model of pnictides, *Phys. Rev. B* **86**, 184432 (2012).
  - 41 T. Jolicoeur, E. Dagotto, E. Gagliano, and S. Bacci, Ground-state properties of the  $S = 1/2$  heisenberg antiferromagnet on a triangular lattice, *Phys. Rev. B* **42**, 4800 (1990).
  - 42 J. Fouet, P. Sindzingre, and C. Lhuillier, An investigation of the quantum  $J_1$ - $J_2$ - $J_3$  model on the honeycomb lattice, *Eur. Phys. J. B* **20**, 241 (2001).
  - 43 B. Schmidt and P. Thalmeier, Frustrated two dimensional quantum magnets, *Phys. Rep.* **703**, 1 (2017), frustrated two dimensional quantum magnets.
  - 44 M. V. Gvozdikova, P.-E. Melchy, and M. E. Zhitomirsky, Magnetic phase diagrams of classical triangular and kagome antiferromagnets, *J. Phys.: Condens. Matter* **23**, 164209 (2011).
  - 45 G.-W. Chern, R. M. Fernandes, R. Nandkishore, and A. V. Chubukov, Broken translational symmetry in an emergent paramagnetic phase of graphene, *Phys. Rev. B* **86**, 115443 (2012).
  - 46 H. Kawamura and S. Miyashita, Phase transition of the heisenberg antiferromagnet on the triangular lattice in a magnetic field, *J. Phys. Soc. Jpn.* **54**, 4530 (1985).
  - 47 F. Y. Wu, The Potts model, *Rev. Mod. Phys.* **54**, 235 (1982).
  - 48 E. Bittner and W. Janke, Parallel-tempering cluster algorithm for computer simulations of critical phenomena, *Phys. Rev. E* **84**, 036701 (2011).
  - 49 K. Binder, Applications of monte carlo methods to statistical physics, *Rep. Prog. Phys.* **60**, 487 (1997).
  - 50 A. M. Ferrenberg and R. H. Swendsen, New monte carlo technique for studying phase transitions, *Phys. Rev. Lett.* **61**, 2635 (1988).
  - 51 C. Weber, L. Capriotti, G. Misguich, F. Becca, M. Elhadj, and F. Mila, Ising transition driven by frustration in a 2d classical model with continuous symmetry, *Phys. Rev. Lett.* **91**, 177202 (2003).
  - 52 C. L. Henley, Ordering by disorder: Ground-state selection in fcc vector antiferromagnets, *J. Appl. Phys.* **61**, 3962–3964 (1987).
  - 53 T. A. Tóth, A. M. Läuchli, F. Mila, and K. Penc, Three-sublattice ordering of the  $su(3)$  heisenberg model of three-flavor fermions on the square and cubic lattices, *Phys. Rev. Lett.* **105**, 265301 (2010).
  - 54 B. Bernu, L. Pierre, K. Essafi, and L. Messio, Effect of perturbations on the kagome  $s = \frac{1}{2}$  antiferromagnet at all temperatures, *Phys. Rev. B* **101**, 140403 (2020).
  - 55 B. Bernu and G. Misguich, Specific heat and high-temperature series of lattice models: Interpolation scheme and examples on quantum spin systems in one and two dimensions, *Phys. Rev. B* **63**, 134409 (2001).
  - 56 B. Bernu and C. Lhuillier, Spin Susceptibility of Quan-

- tum Magnets from High to Low Temperatures, *Phys. Rev. Lett.* **114**, 057201 (2015).
- 57** J.-K. Kim and M. Troyer, Low Temperature Behavior and Crossovers of the Square Lattice Quantum Heisenberg Antiferromagnet, *Phys. Rev. Lett.* **80**, 2705 (1998).
- 58** M. Calandra Buonaura and S. Sorella, Numerical study of the two-dimensional Heisenberg model using a Green function Monte Carlo technique with a fixed number of walkers, *Phys. Rev. B* **57**, 11446 (1998).
- 59** B. Bernu and L. Messio, Detecting and characterizing a phase transition in spin systems using high temperature expansions, in preparation.
- 60** A. Zorko, F. Bert, A. Ozarowski, J. van Tol, D. Boldrin, A. S. Wills, and P. Mendels, Dzyaloshinsky-Moriya interaction in vesignieite: A route to freezing in a quantum kagome antiferromagnet, *Phys. Rev. B* **88**, 144419 (2013).
- 61** Villain, J., A magnetic analogue of stereoisomerism : application to helimagnetism in two dimensions, *J. Phys. France* **38**, 385 (1977).