Magnetic frustration and multiferroics

Virginie Simonet

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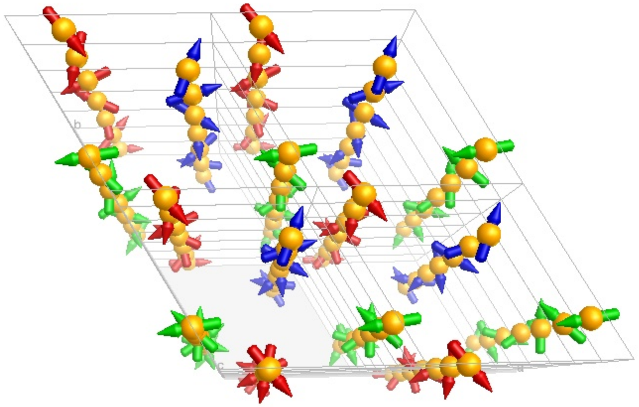
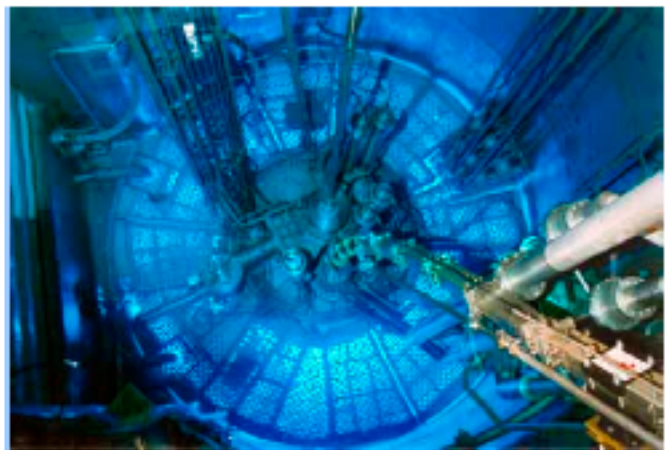
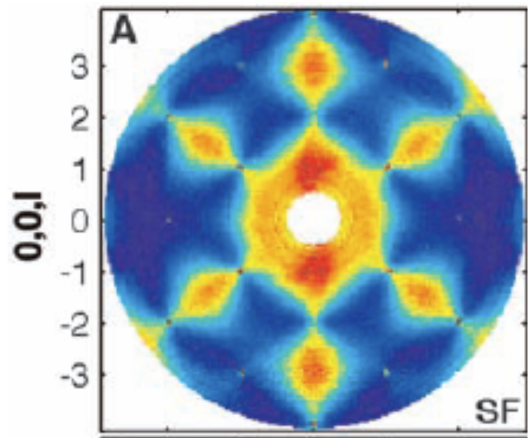






Outline of the lecture

Reminder: Conventional Magnetism

Magnetic frustration

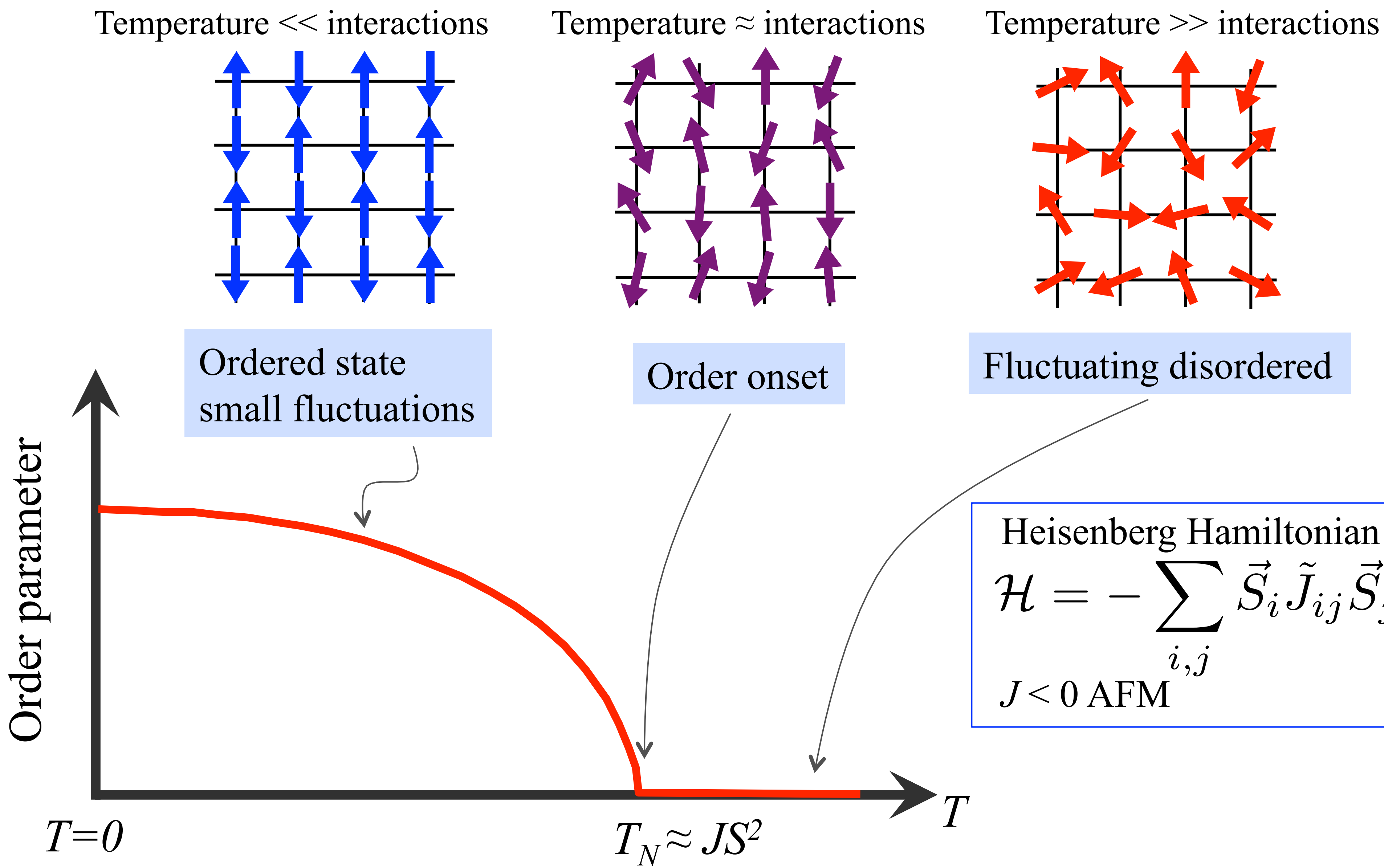
- Introduction
- Competition of interactions
- Geometrical frustration
- Quantum case
- Role of the anisotropy

Multiferroism

- Introduction
- About symmetries and chirality
- Examples

Sorry, I will only speak about neutron scattering!

Reminder: conventional magnetism



Heisenberg Hamiltonian

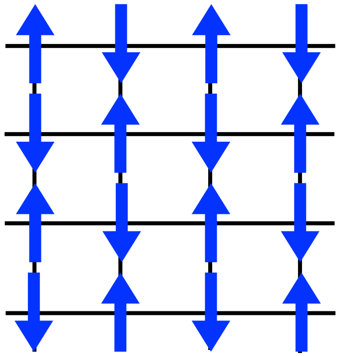
$$\mathcal{H} = -\sum_{i,j} \vec{S}_i \tilde{J}_{ij} \vec{S}_j$$

$J < 0$ AFM

Reminder: conventional magnetism

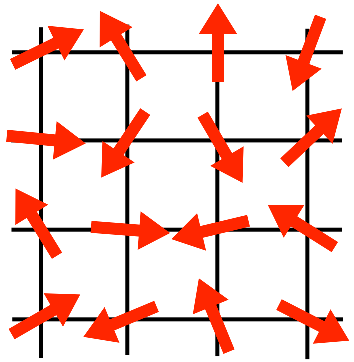
Temperature << interactions

Ordered state



Temperature >> interactions

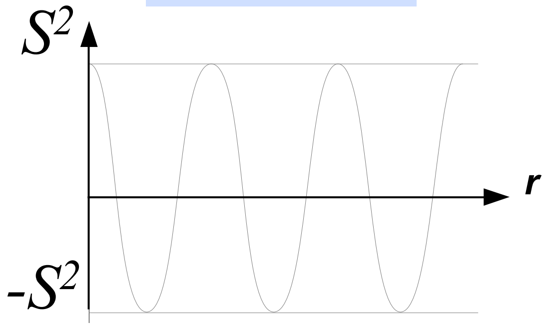
Disordered state



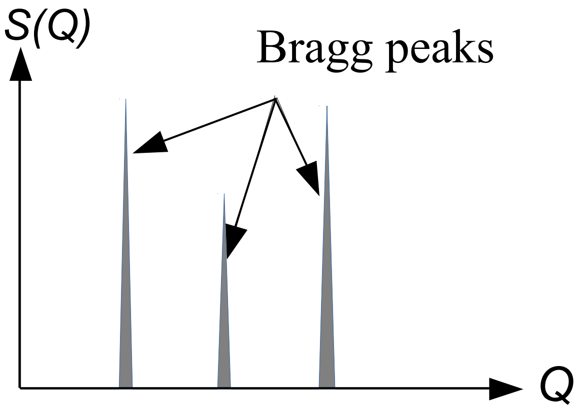
- **Spin pair correlation function** $< S_i(0)S_j(r) >$

$< S_i(0)S_j(r) >= S^2\delta_{ij}$

Real space



Reciprocal space



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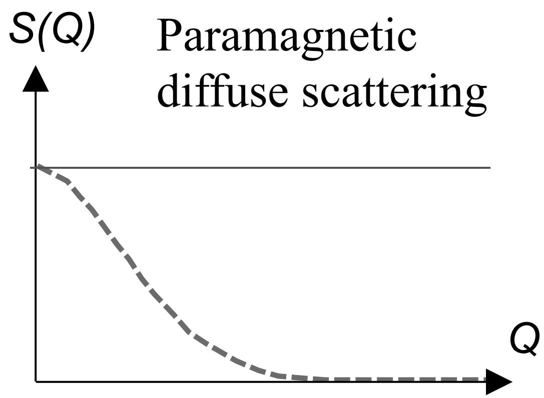

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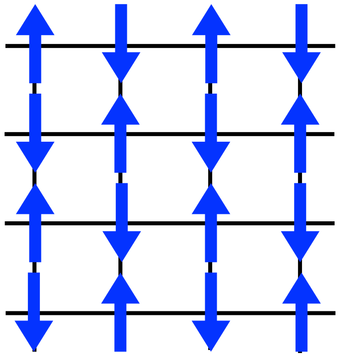

Temperature >> interactions

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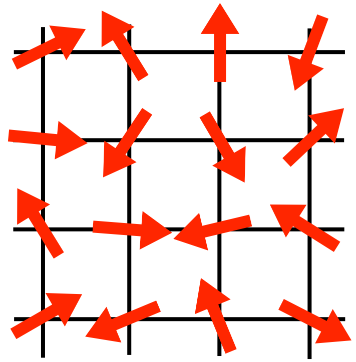
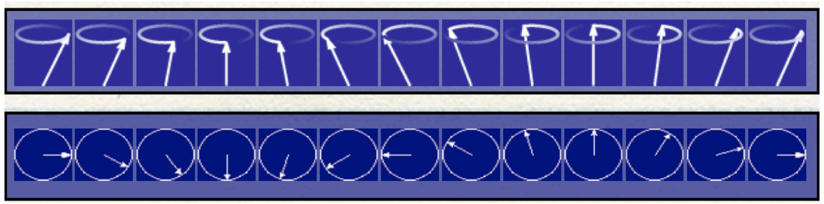
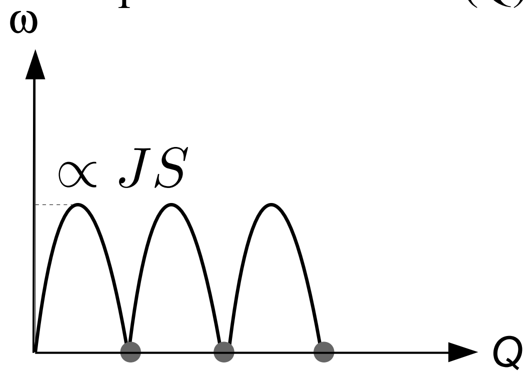


- **Spin pair correlation function** $< S_i(0)S_j(r) >$ $\quad < S_i(0)S_j(r) >= S^2\delta_{ij}$

- **Excitations**:
  spin waves (magnons)



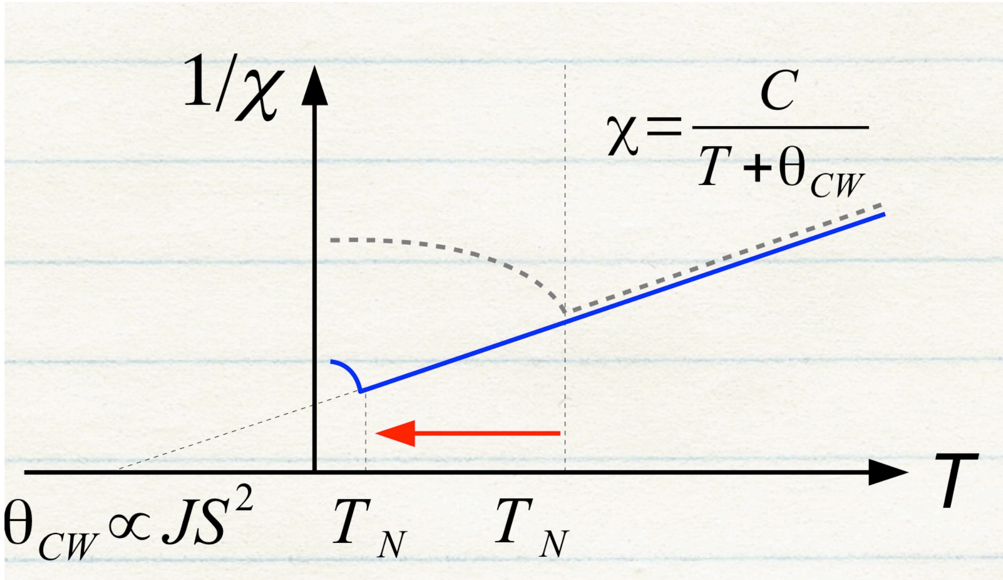
dispersion relation ω(Q)



Magnetic frustration: introduction

Is it possible to impede the onset of magnetic ordering?

➔ Yes, through dimensional effects, introduction of disorder and **frustration**
Consequences on spin pair correlations, excitations, neutron signatures?



Frustration index $f = \frac{\theta_{CW}}{T_N}$

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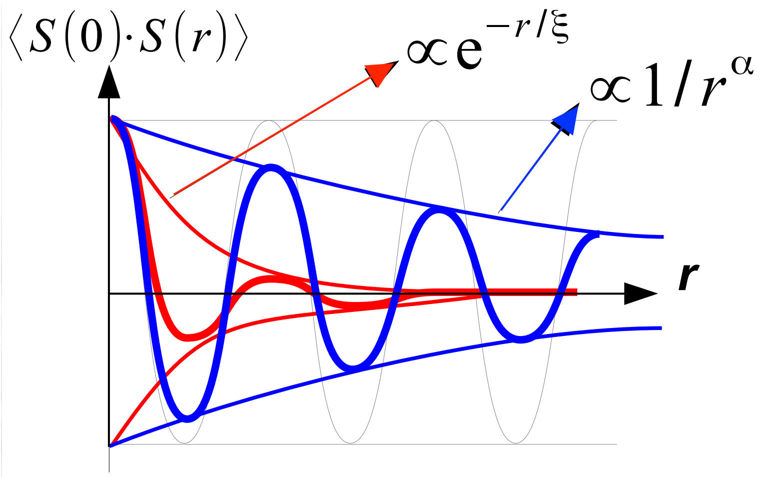

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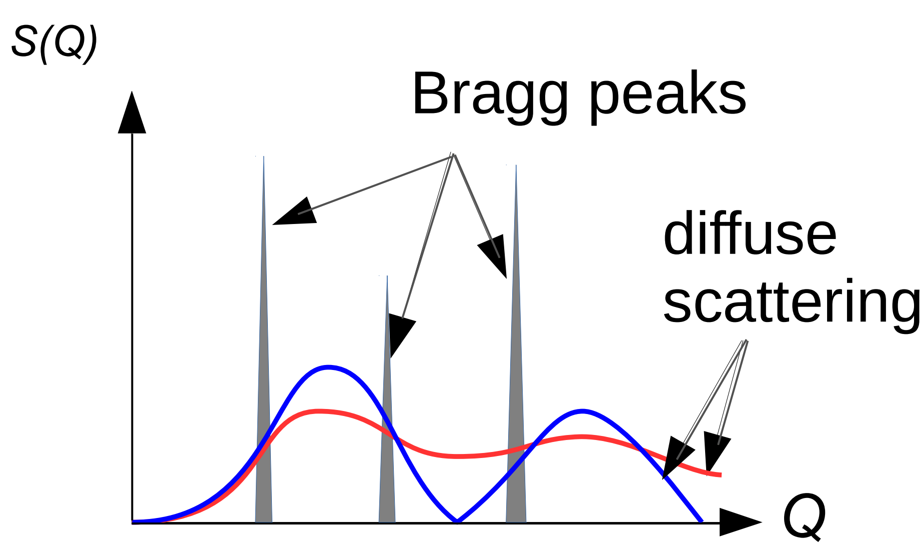
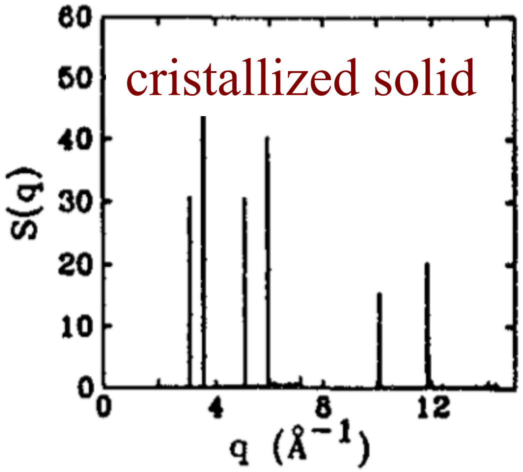
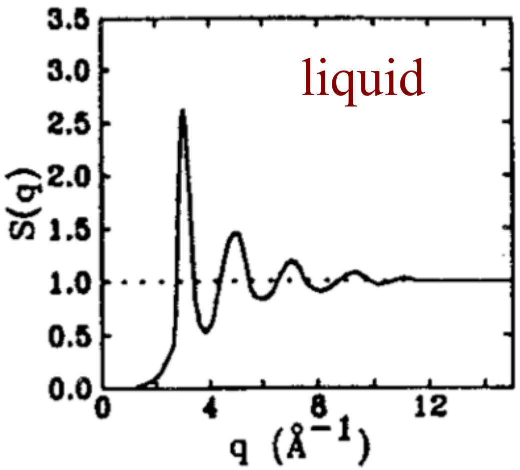
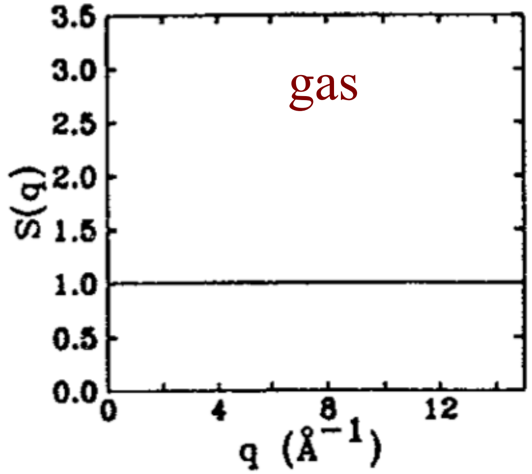


Magnetic frustration: introduction

atomic states





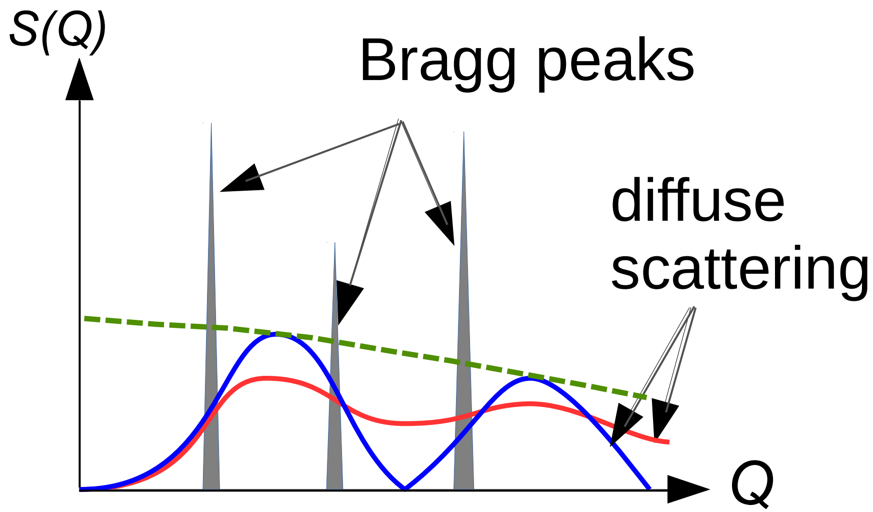


Magnetic order

Spin liquid

paramagnet

Magnetic states

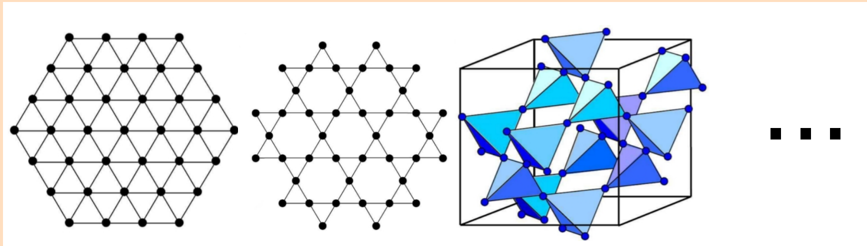


Magnetic frustration: introduction

One or several competing constrains can not be satisfied simultaneously

Important ingredients:

- Topology of the lattice



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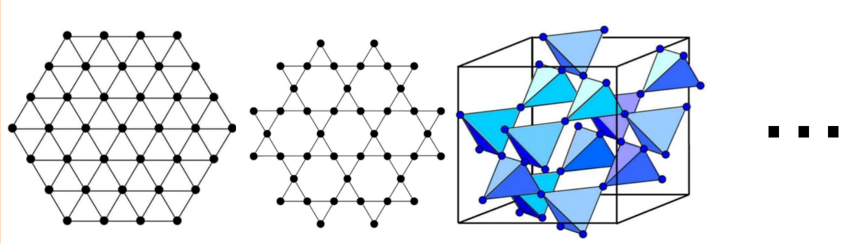

- Competing interactions: superexchange (nearest/further neighbors) dipolar, DM

$$\mathcal{H} = -\sum_{i,j} \vec{S}_i \tilde{J}_{ij} \vec{S}_j$$

$$\vec{D}_{ij}.(\vec{S}_i \times \vec{S}_j)$$

$$Dr_{nn}^3 \sum_{i>j} \left[\frac{\mathbf{S}_i \cdot \mathbf{S}_j}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5} \right]$$

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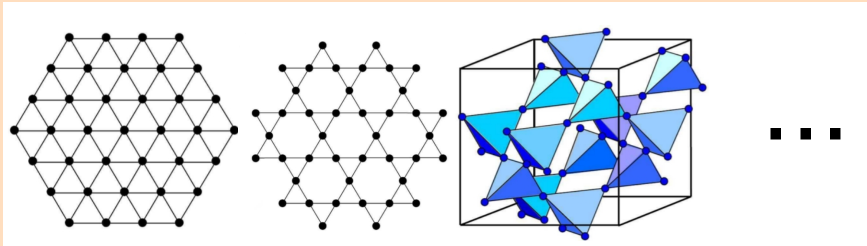

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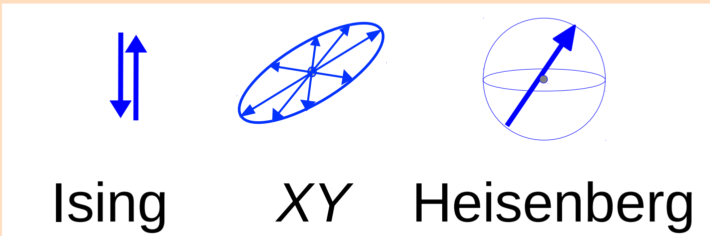
- Anisotropy, spin dimension and norm (classical versus quantum)



S=1/2, 1, 3/2, …, ∞

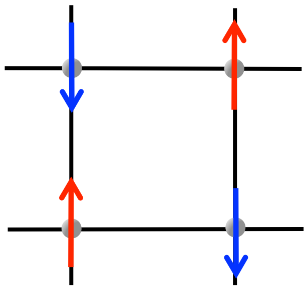
- Disorder, thermal and quantum fluctuations

Magnetic frustration: competition of interactions

One or several competing constrains can not be satisfied simultaneously

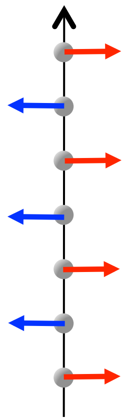
Through competing interactions:

Square lattice with Ising spins



AFM J_1

Spin chain with Ising spins



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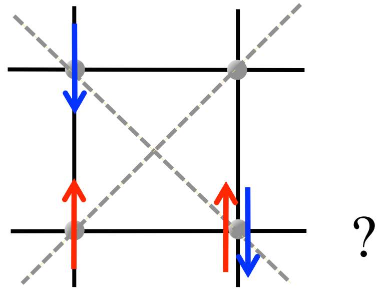
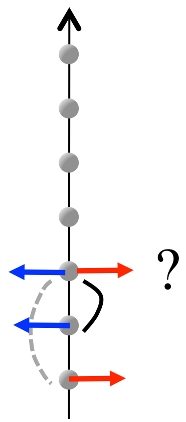


AFM J_1

≈AFM J_2

Spin chain with Ising spins



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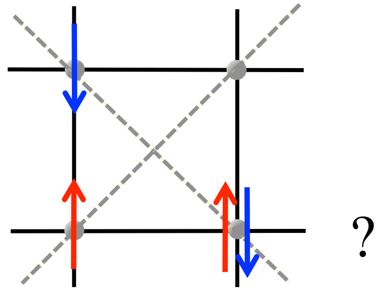
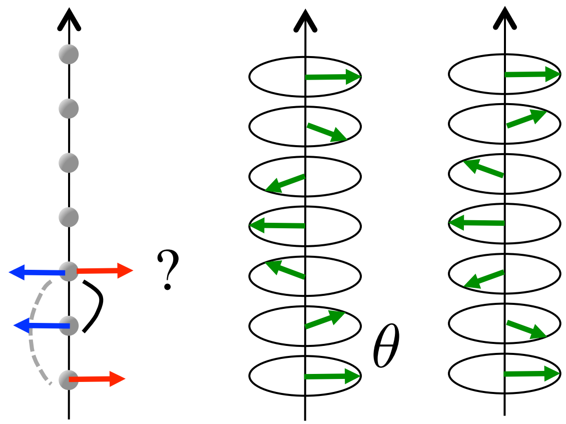


Spin chain from Ising to Heisenberg (XY) spins

AFM J_1

≈AFM J_2



Helical order for $J_1 \leq 4J_2$

with $\theta = \arccos(\frac{-J_1}{4J_2})$

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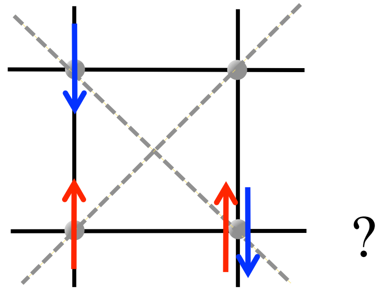

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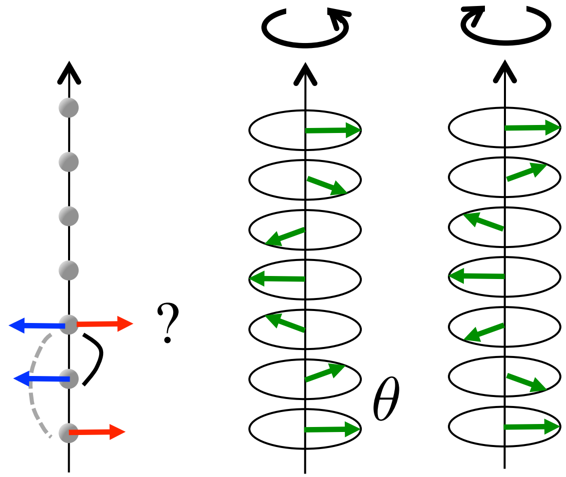

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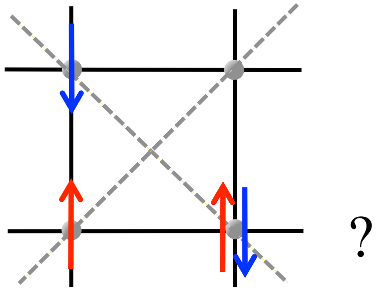

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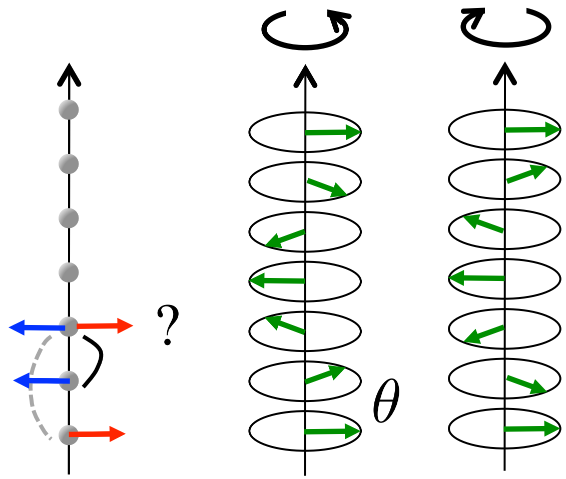


➔ Prevents magnetic order or find a compromise with exotic magnetic orders (non collinear)

Geometrical frustration

One or several competing constrains can not be satisfied simultaneously

Through the geometry of the lattice:

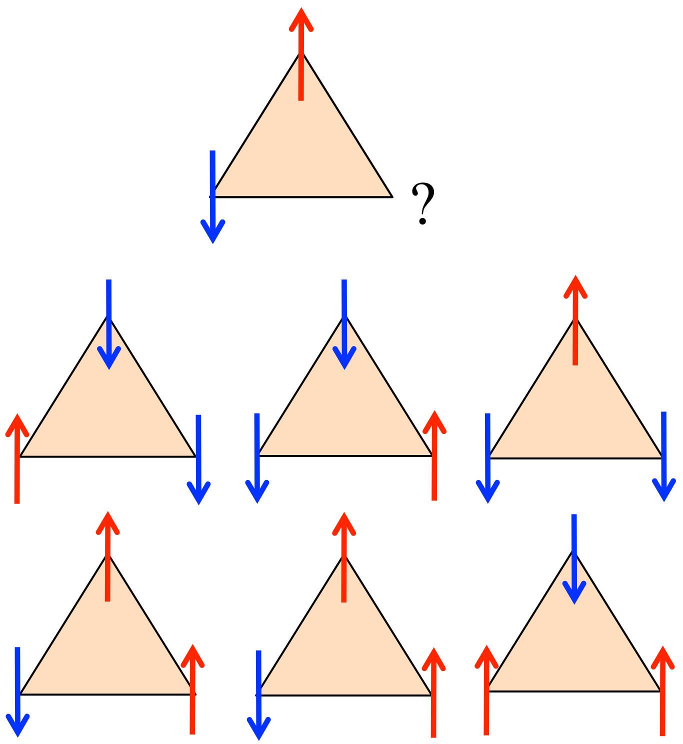
Polygons with odd number of edges

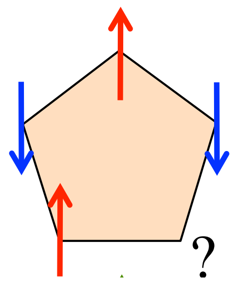
Ex. triangles,

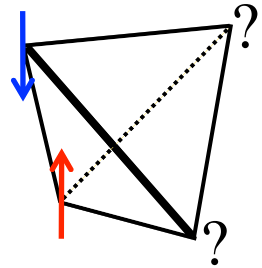
Pentagons, tetrahedron

Antiferromagnetic interactions

Ising







Degeneracy
(measured by finite entropy)

Geometrical frustration

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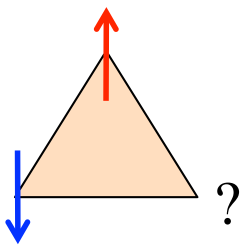
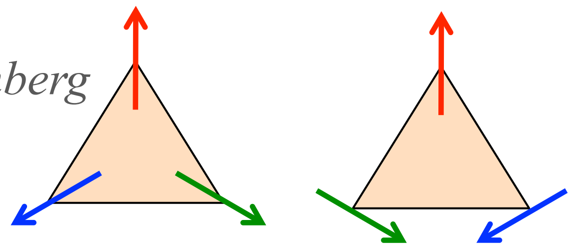
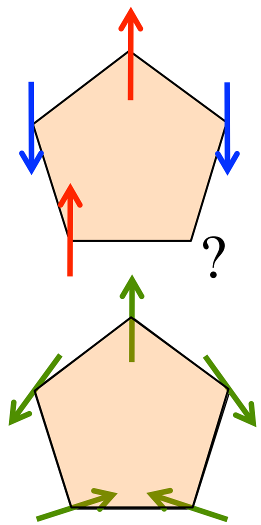
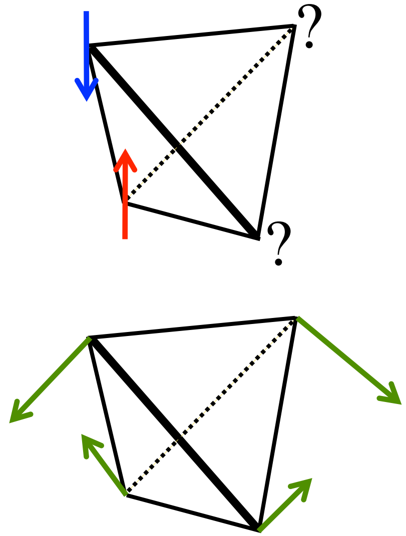


XY or Heisenberg







$$\mathcal{H} = -J(S_1.S_2 + S_2.S_3 + S_3.S_1)$$
$$= -\frac{J}{2}(S_1 + S_2 + S_3)^2 + cst$$

Geometrical frustration

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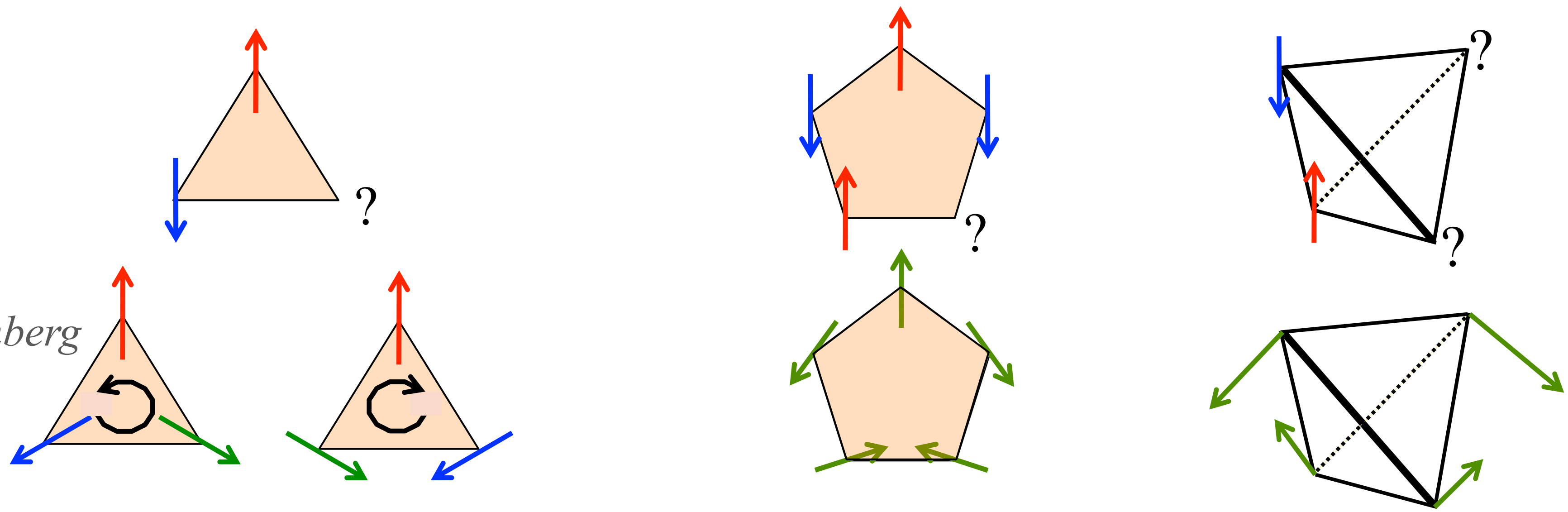
Ising

XY or Heisenberg



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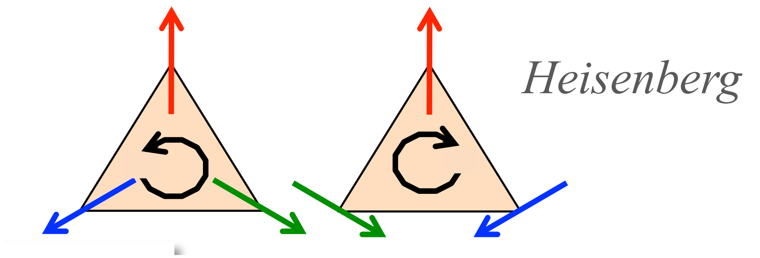
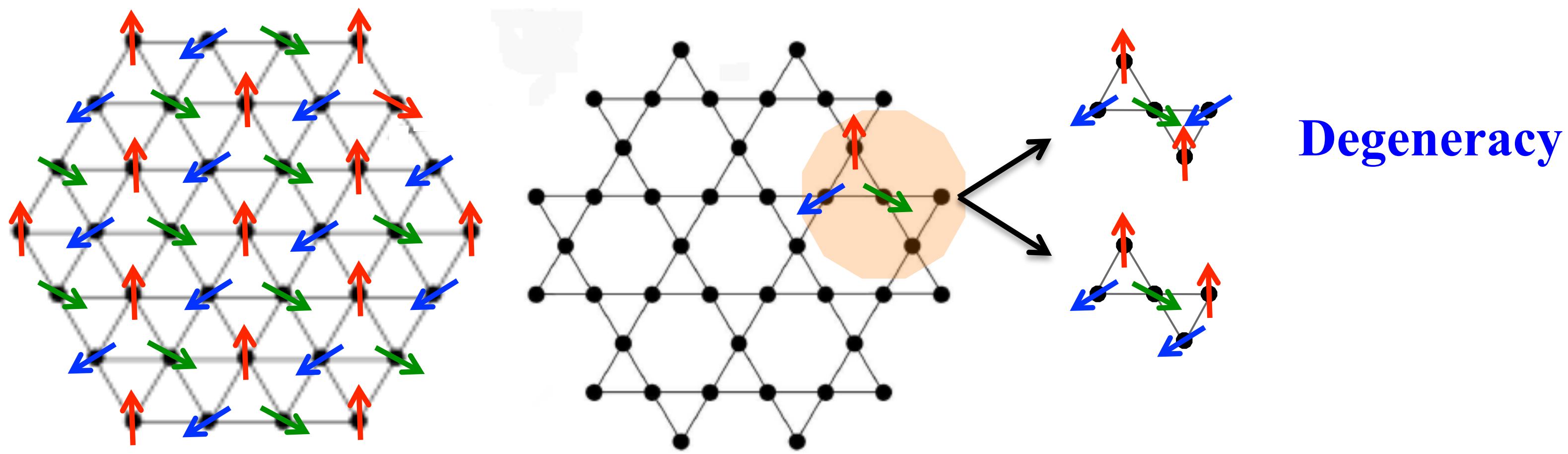
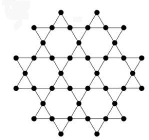


role of connectivity: **triangular** (Néel order) vs **kagomé** (spin liquid)





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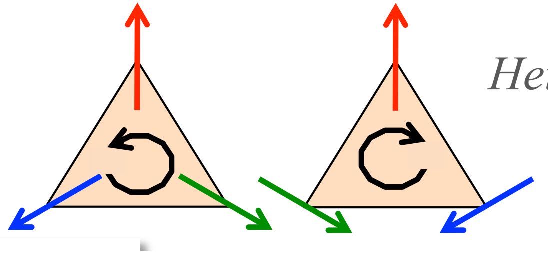
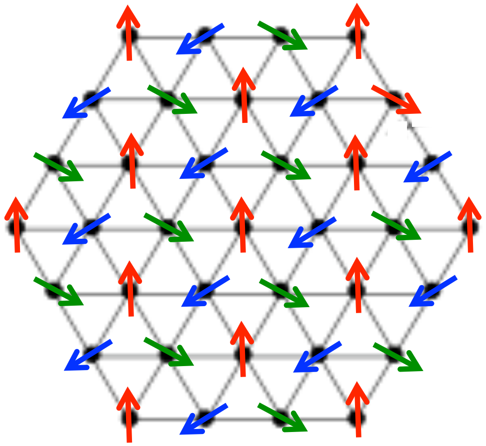
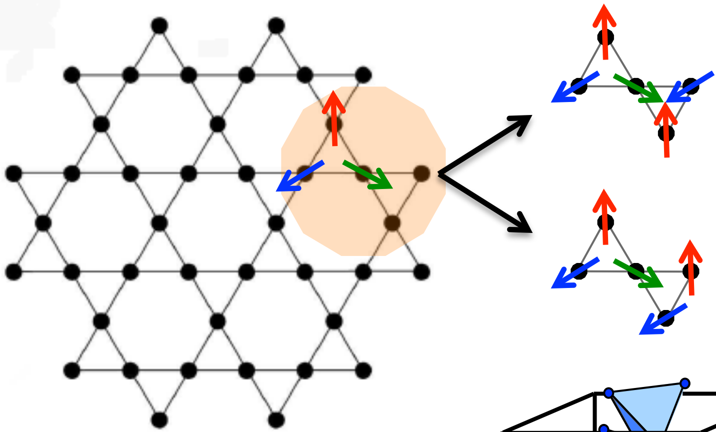


Heisenberg

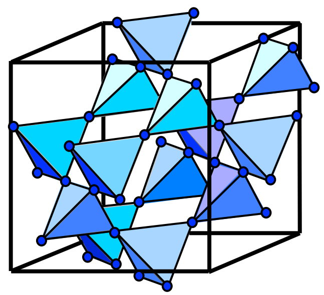
role of connectivity: **triangular** (Néel order) vs **kagomé** (spin liquid)





Degeneracy

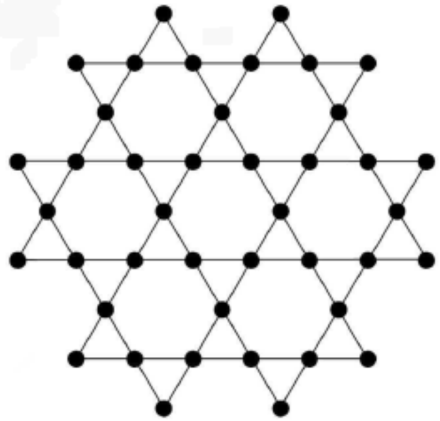
Macroscopic degeneracy
also for the 3D **pyrochlore** (corner-sharing tetrahedra) lattice



Geometrical frustration

One or several competing constrains can not be satisfied simultaneously

Spin liquids: exotic excitations



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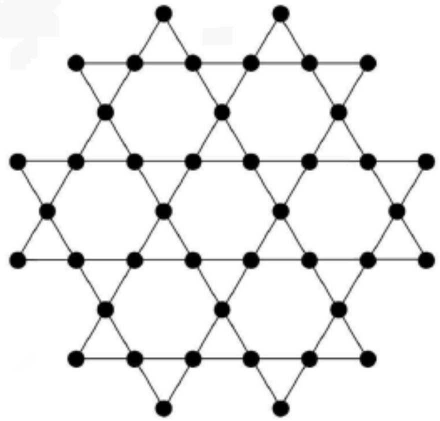

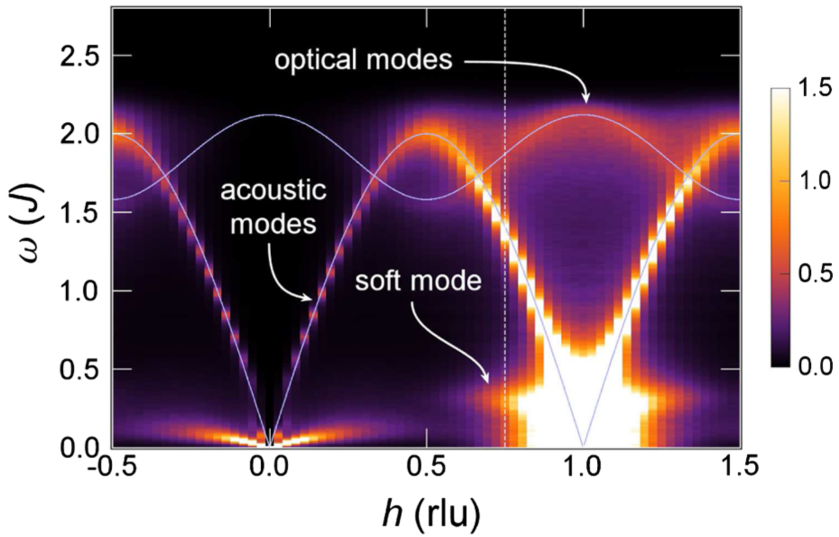

Robert et al. PRL 2008

Well defined excitations in the spin liquid state

Geometrical frustration

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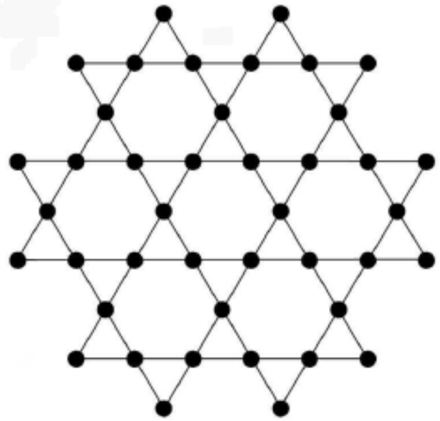
Spin liquids: exotic excitations



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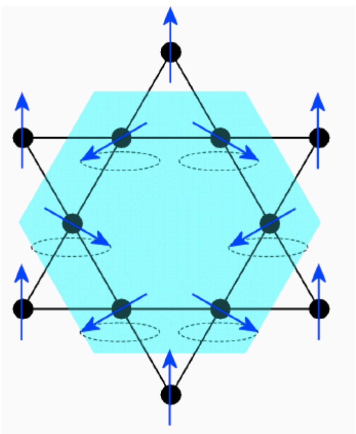
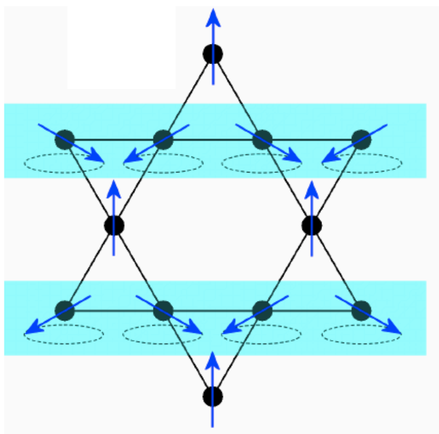
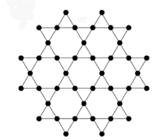
Heisenberg spins : weathervane modes
➔ flat modes in ordered states



$\sqrt{3} \times \sqrt{3}$



$q = 0$



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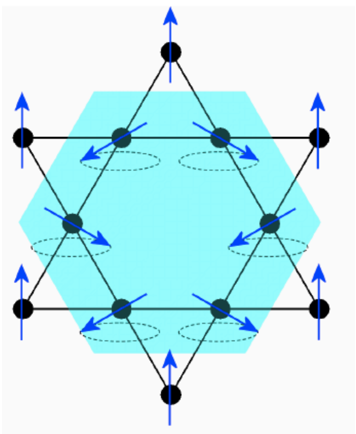
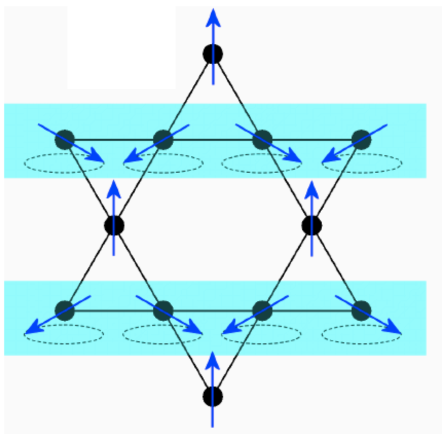
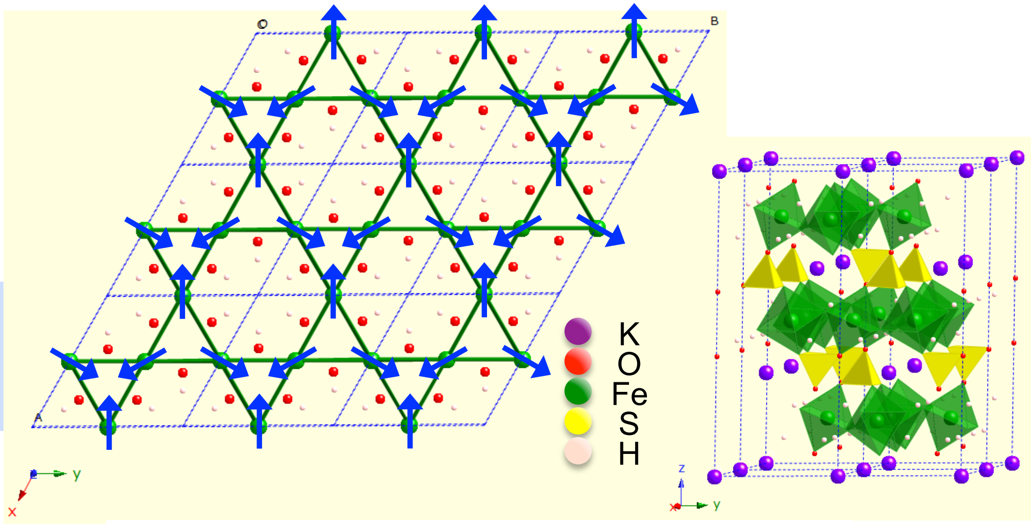


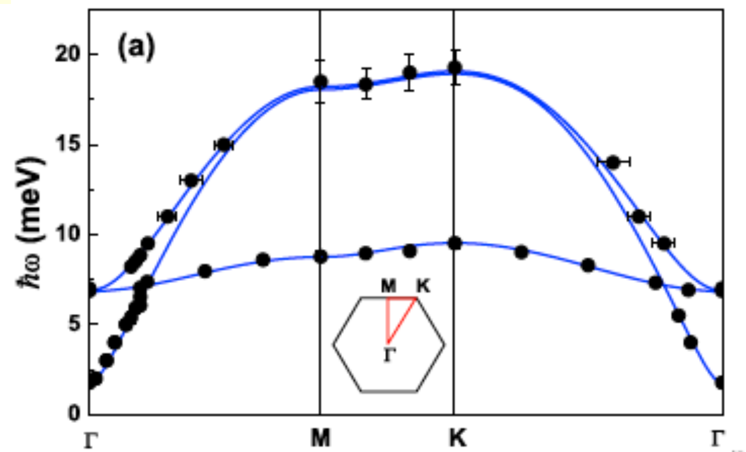
$\sqrt{3} \times \sqrt{3}$



$q = 0$

Example Fe jarosite





Matan et al. PRL 2006

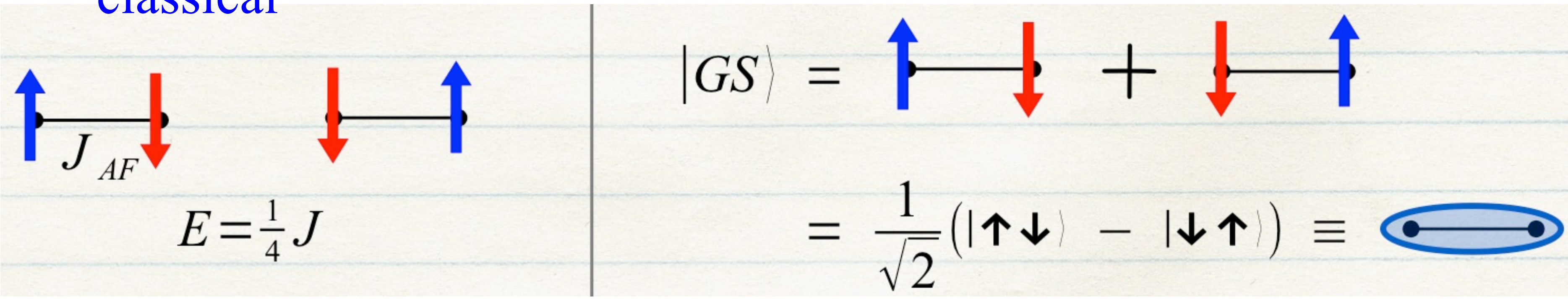
Magnetic frustration : quantum case

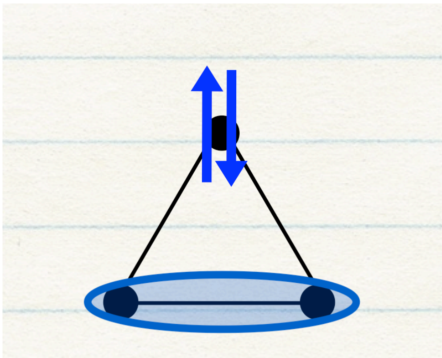
valence bond, entanglement of 2 spins 1/2

$$\mathcal{H} = -J S_1 . S_2$$

classical

quantum

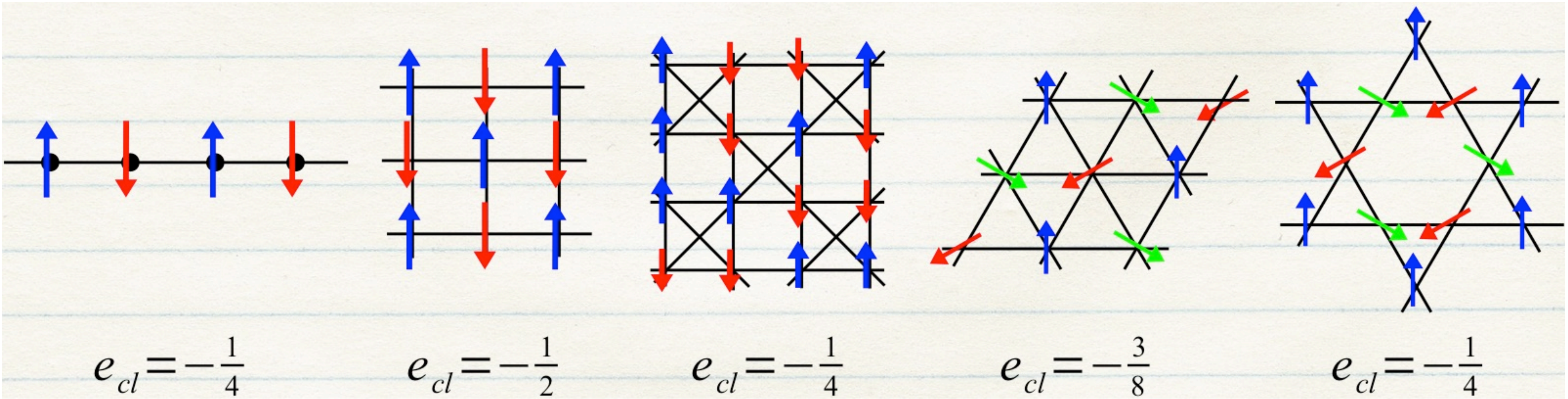


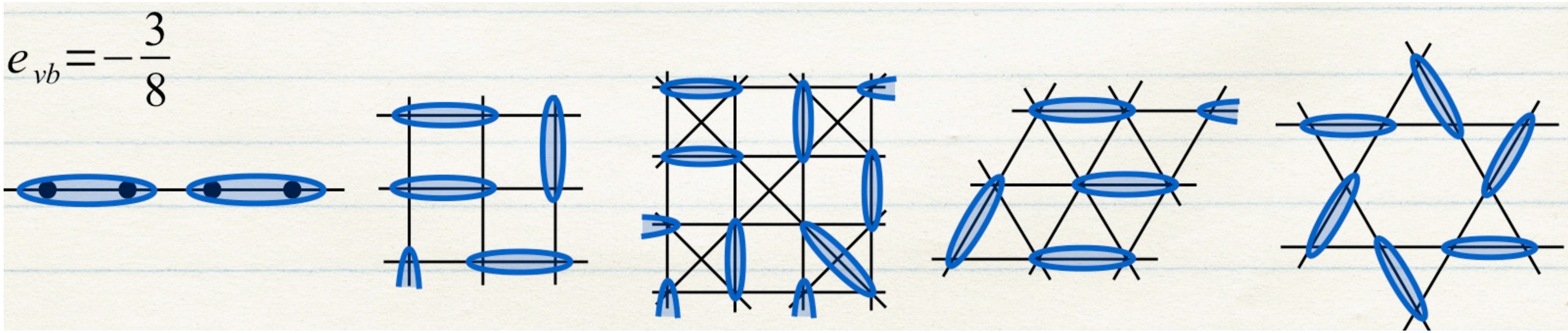


4 ground states

Magnetic frustration : quantum case

Rough comparison of the energies : classical vs quantum ground states





Magnetic frustration : quantum case

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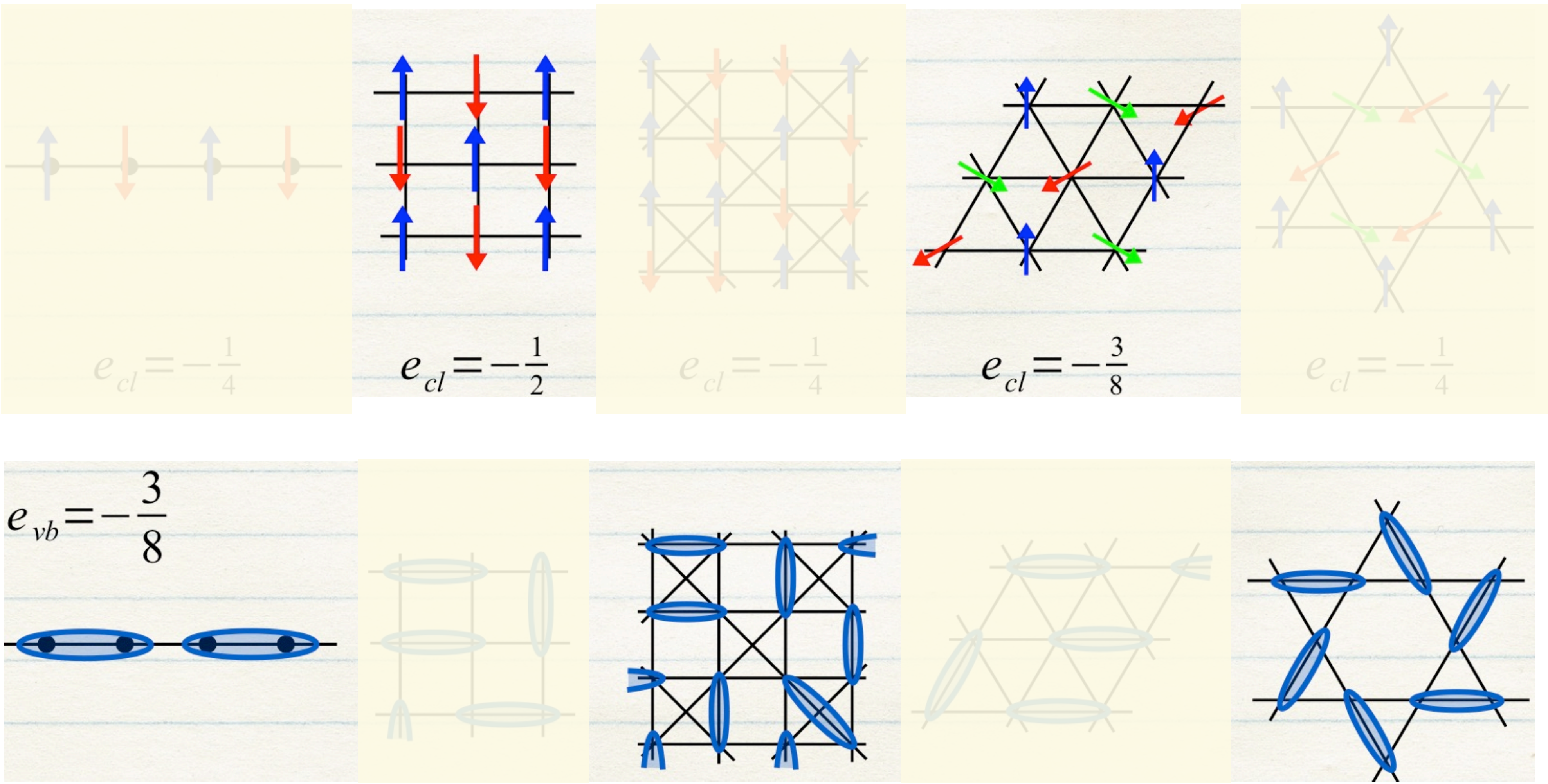
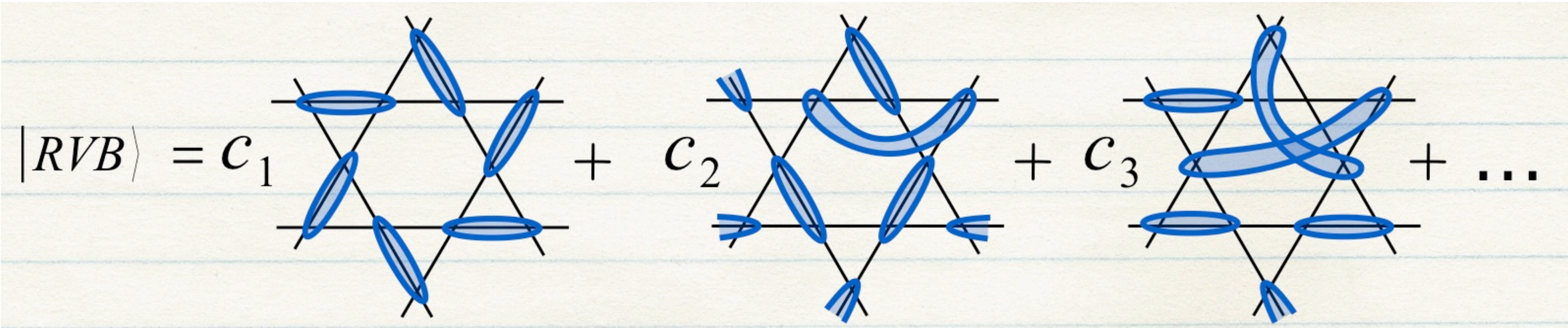
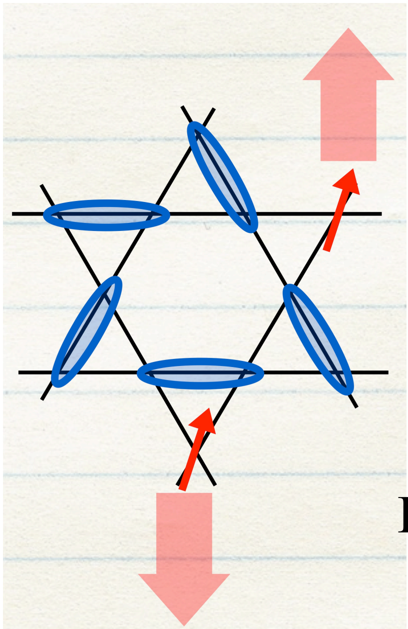


Magnetic frustration : quantum case

Quantum spin liquid on a kagome lattice: resonating valence bond model

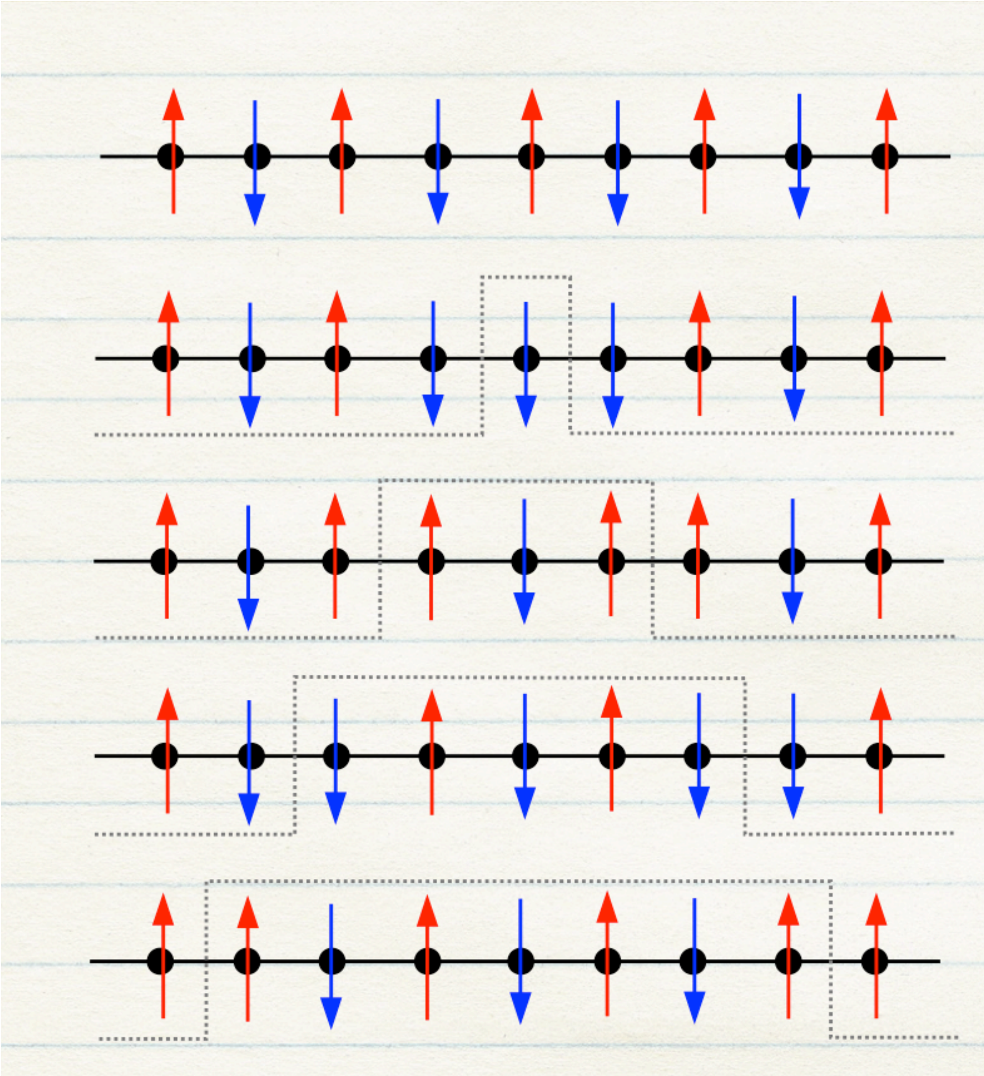


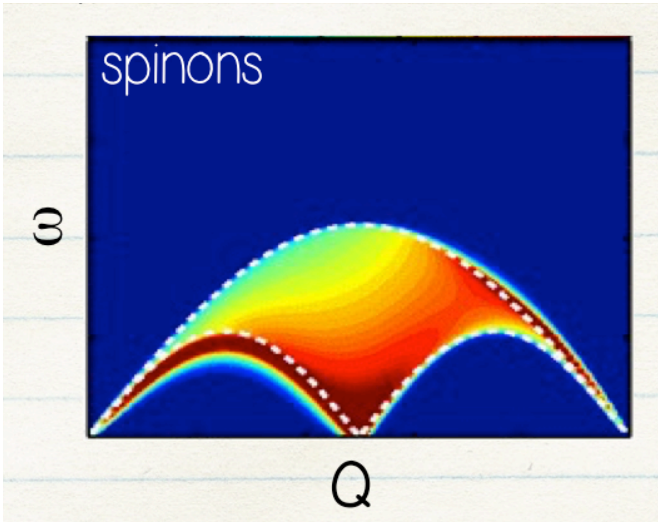


Excitations : deconfined spinons (continuum)

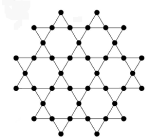
Magnetic frustration : quantum case

Fractionalized excitations: spinons continuum





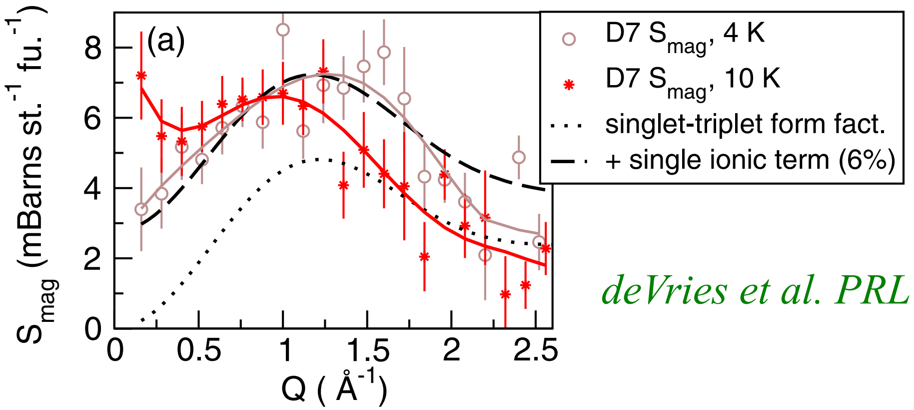
Magnetic frustration : quantum case



Quantum spin liquid on a kagome lattice: resonating valence bond model

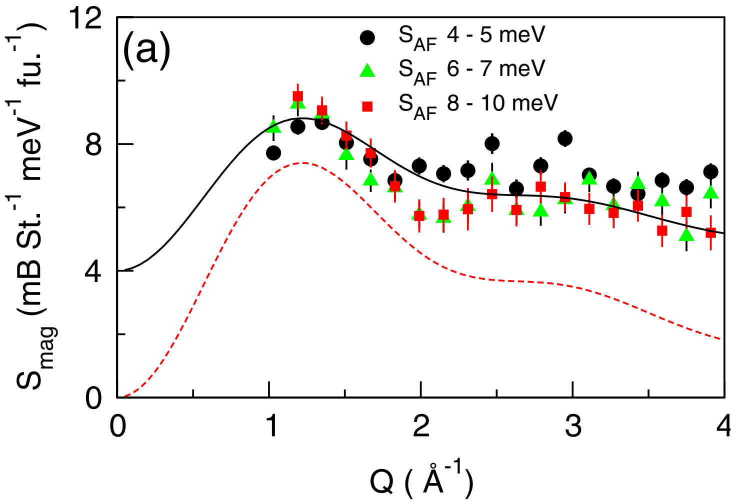
Experimental search for kagome quantum spin liquid : one candidate **Herbertsmithite**,

- powder measurements : diffuse spin correlations, dynamics weakly dependent of energy and temperature : signature of spin liquid with spinon excitations?



deVries et al. PRL 2009

Polarized neutron spectrometer D7@ILL
XYZ polarization analysis



Time-of-flight spectrometer IN4@ILL

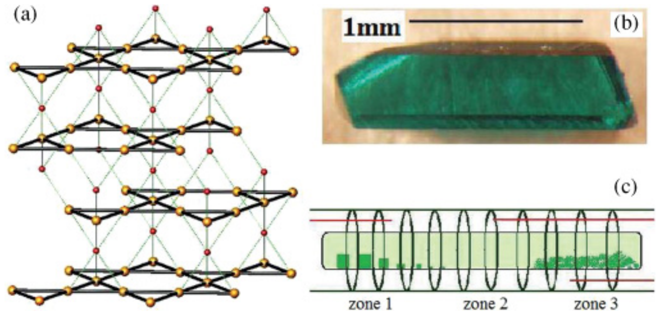
Magnetic frustration : quantum case

Quantum spin liquid on a kagome lattice: resonating valence bond model

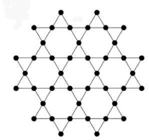
Experimental search for kagome quantum spin liquid : one candidate **Herbertsmithite**,

- 14 years to succeed in growing a single crystal!

Han et al. PRB 2011



Magnetic frustration : quantum case



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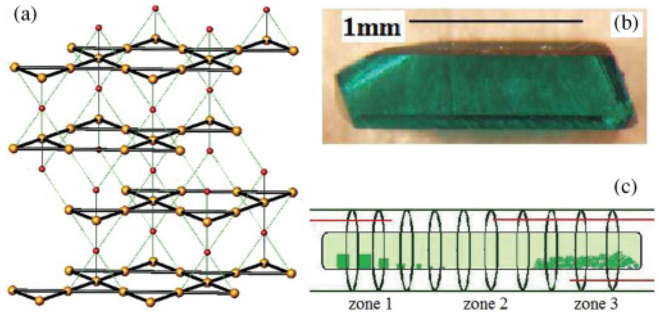
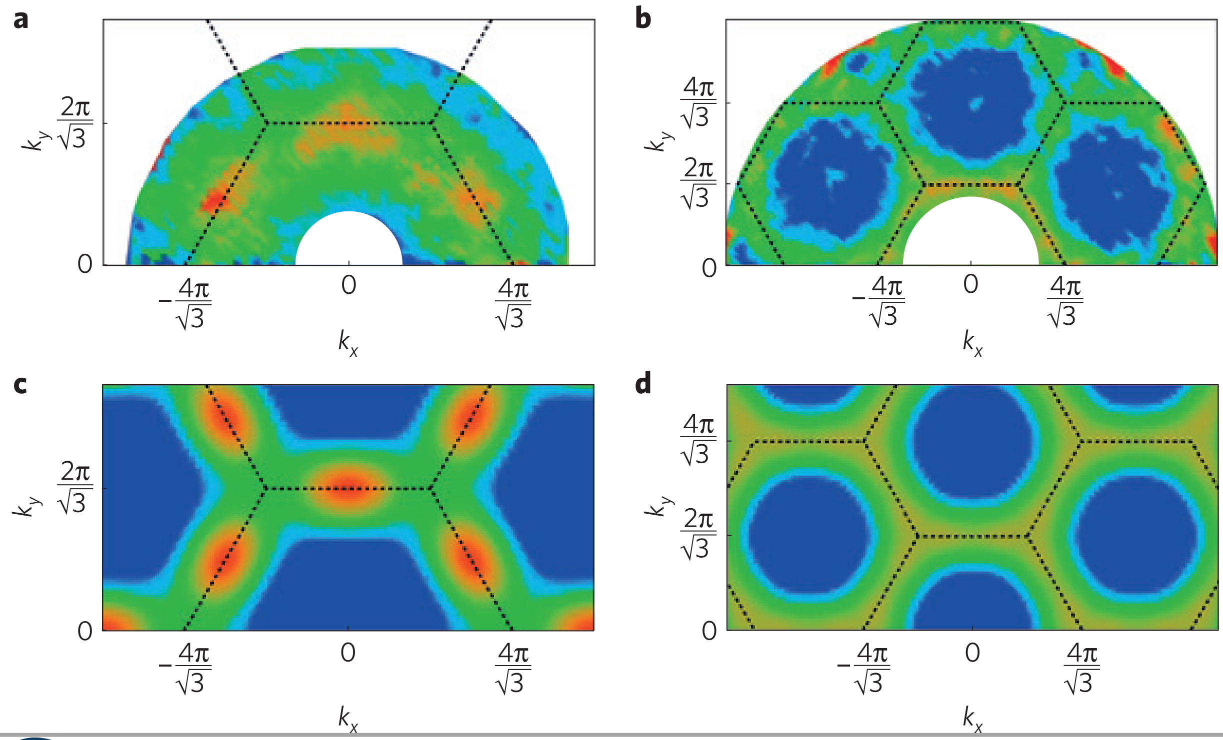


Dynamical structure factor



Experiment: Han et al. Nature 2012

Calculations: Punk et al. Nat. Phys. 2014

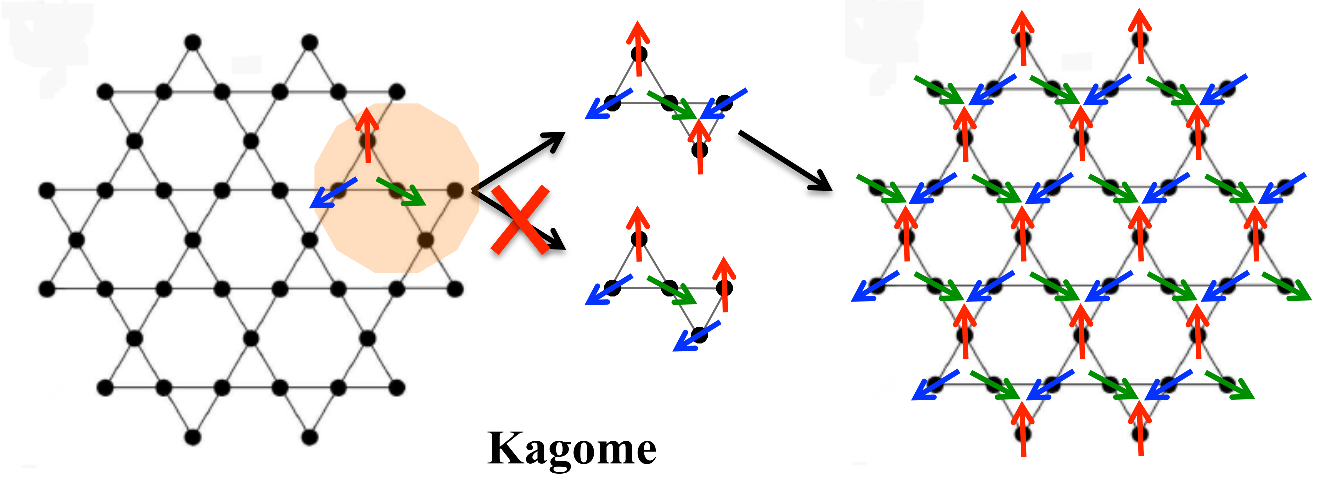
Cl: Quantum spin liquid with complex fractionalized excitations

Magnetic frustration: role of anisotropy

Spin liquids : fragile state with strong degeneracies, spin-spin liquid-like pair correlation, flat modes
➔easily destabilized by small perturbations (DM, dipolar, second neighbor interactions, disorder…)

Antiferromagnetic interactions

Example: Release of degeneracy by the multiaxial anisotropy



Kagome

Ising spins // triangle bisectors

$q = 0$ order

Magnetic frustration: role of anisotropy

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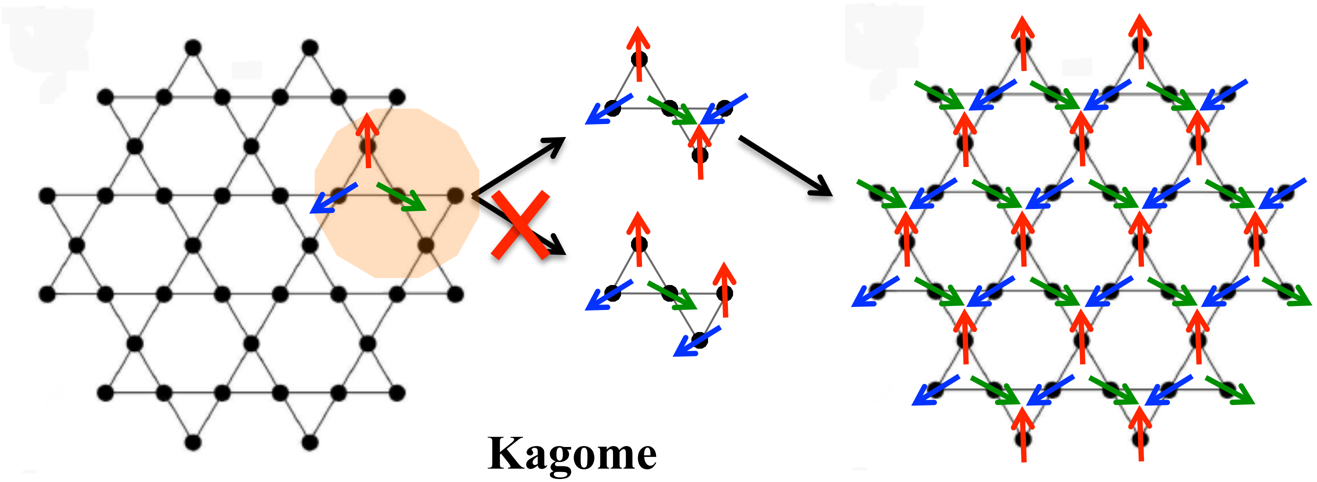

Kagome

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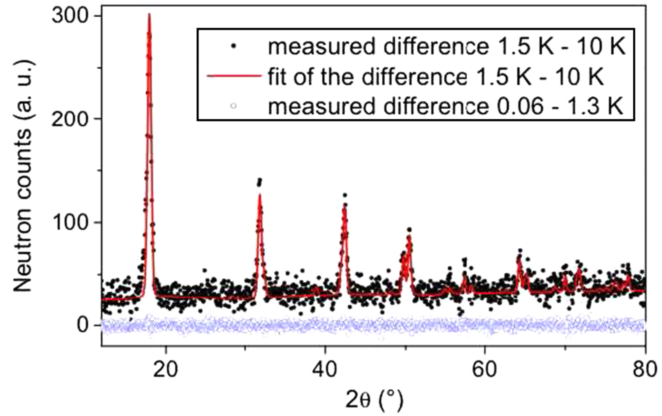

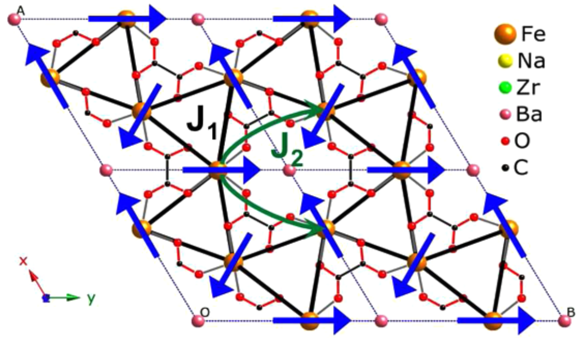

Ex: $Na_2Ba_3[Fe^{II}_3(C_2O_4)_6][A^{IV}(C_2O_4)_3]$

Lhotel et al. PRL 2011

Magnetic frustration: role of anisotropy

Spin liquids : fragile state with strong degeneracies, spin-spin liquid-like pair correlation, flat modes
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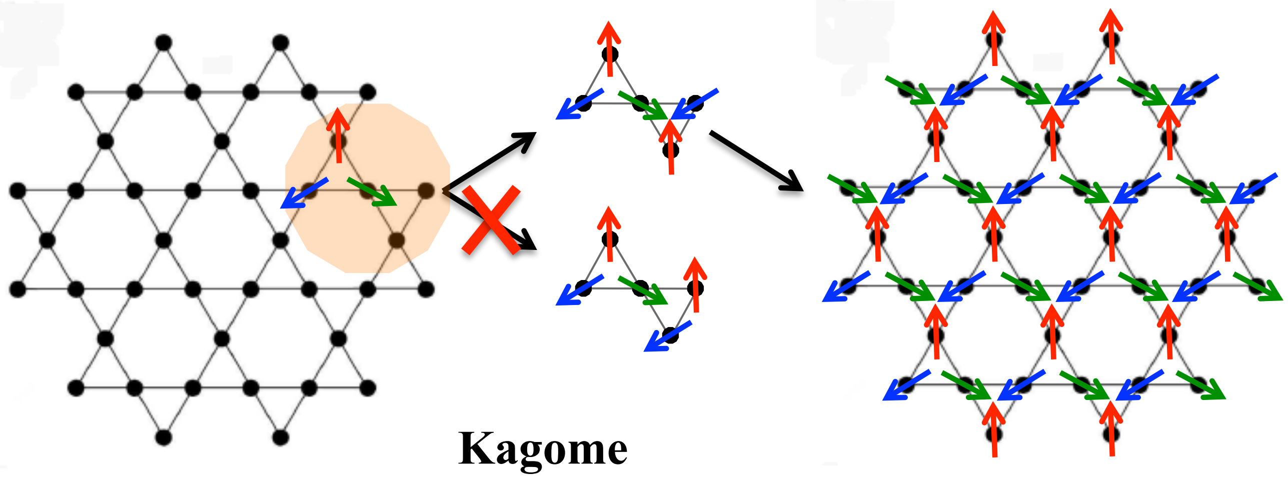
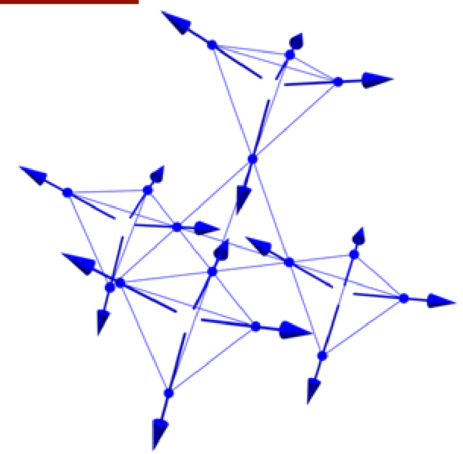


Kagome
Ising spins // triangle bisectors

q = 0 order



Pyrochlore
Ising spins // <111> directions

all-in all-out order

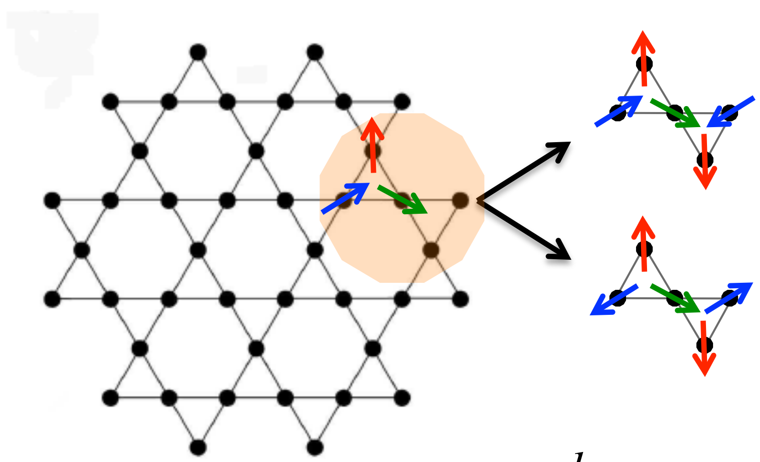
Magnetic frustration: role of anisotropy

Spin liquids : fragile state with strong degeneracies, spin-spin liquid-like pair correlation, flat modes
➔easily destabilized by small perturbations (DM, dipolar, second neighbor interactions, disorder…)

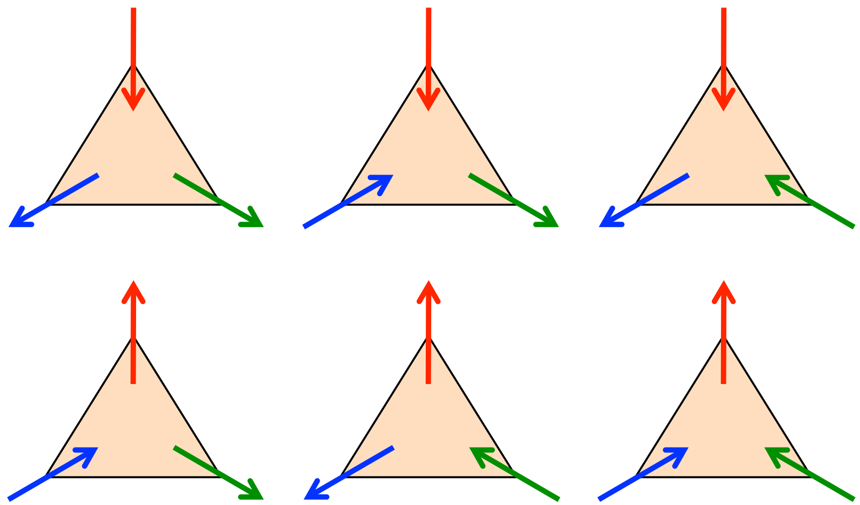
What about ferromagnetic interactions + multiaxial anisotropy?

⇩

Degenerate ground state



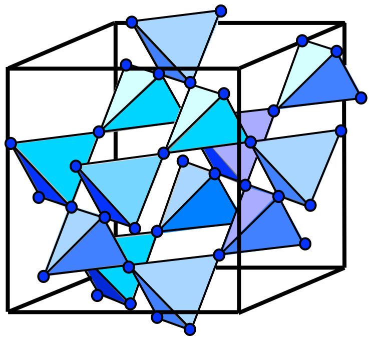
kagome



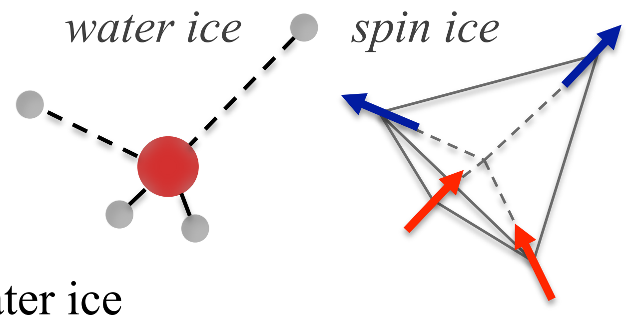
Two-in one-out or two-out on-in ice rule

Spin ice = special case of spin liquids

Magnetic frustration: role of anisotropy



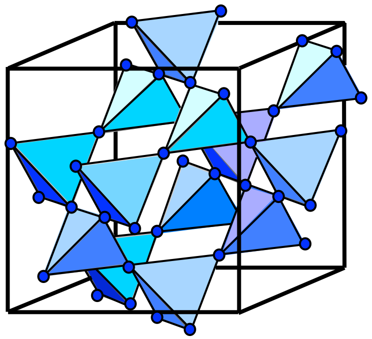
Spin ices in pyrochlores
Multiaxial anisotropy + ferromagnetic interactions



Analogy with proton position in water ice
(2 close, 2 far)

Ice-rules: 2 spins in, 2 spins out

Magnetic frustration: role of anisotropy



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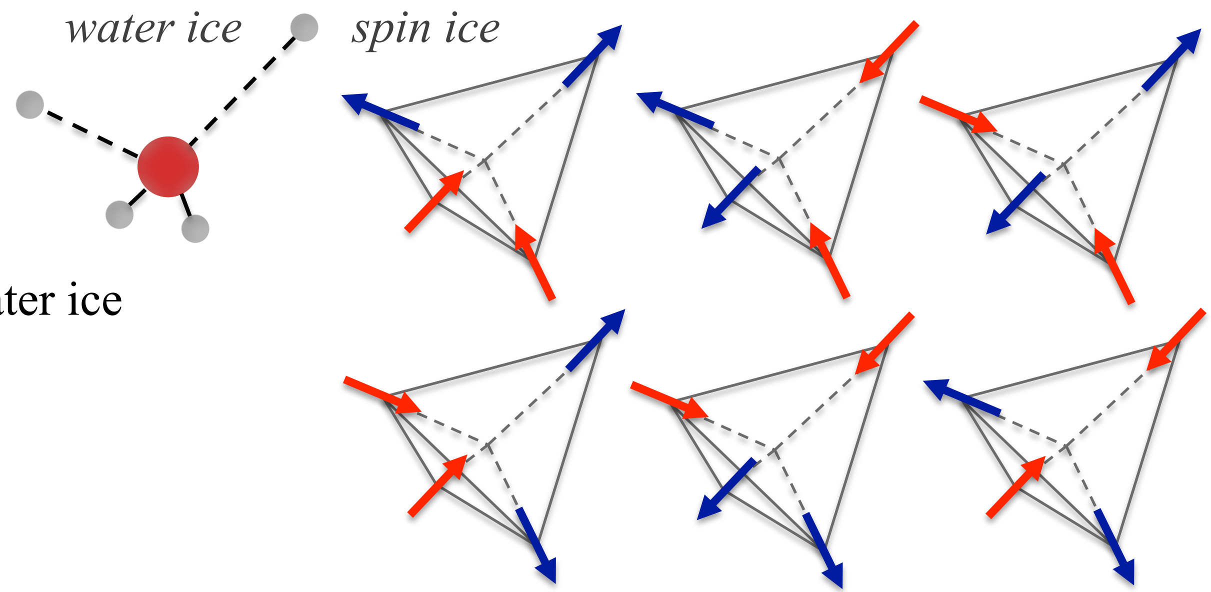


Analogy with proton position in water ice
(2 close, 2 far)

Ice-rules: 2 spins in, 2 spins out
6 possible states / tetrahedron
=> **Macroscopic degeneracy**

Harris et al., PRL 1997

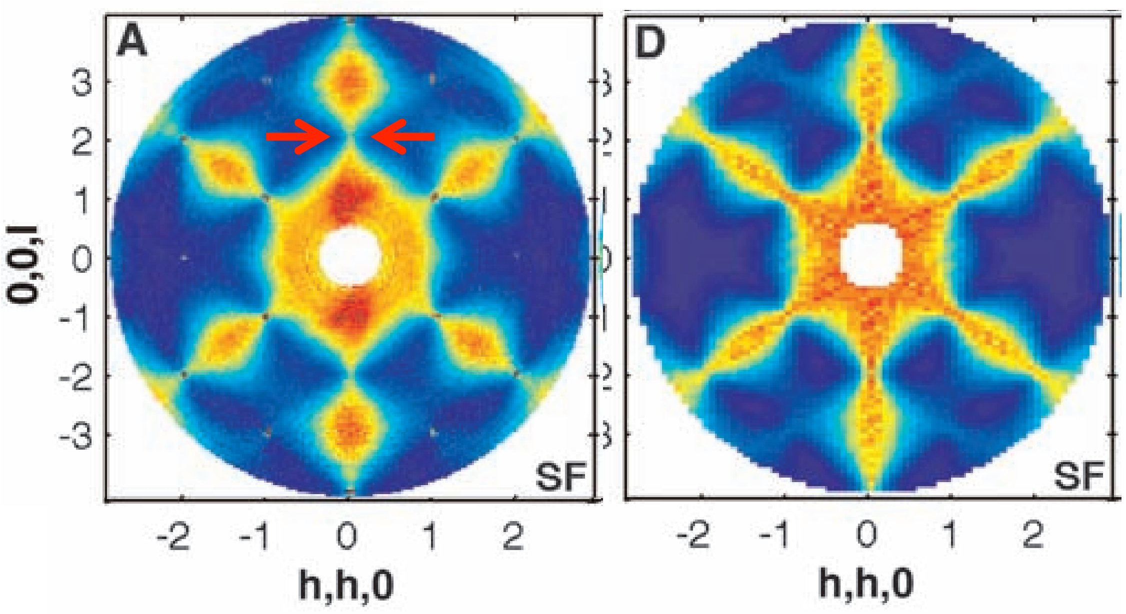
Magnetic frustration: role of anisotropy

Spin ices in pyrochlores
Multiaxial anisotropy + ferromagnetic interactions

Ice-rules

➔ power-law correlations and pinch-points in reciprocal space

Experiment at 1.7 K *Calculations*



Fennell et al., Science 2009

Single-crystal spin-flip diffuse scattering map on D7@ILL

Magnetic frustration: summary

Magnetic frustration = wonderful playground to observe new magnetic behaviors:
Macroscopic degeneracy, spin liquid, spin ice, fractionalized excitations …

Easily destabilized towards complex magnetic orders:
order by disorder, additional interactions, anisotropies, classical and quantum fluctuations …
➔non collinear, chiral, partially fluctuating magnetic order with complex (H,T) phase diagram…

Why neutron scattering is a suitable tool?

Small magnetic signal at very low temperature,
access to spin correlation functions and diffuse scattering,
use of polarized neutrons,
inelastic probe,
complex magnetic order,
complex (H, P, T) phase diagram