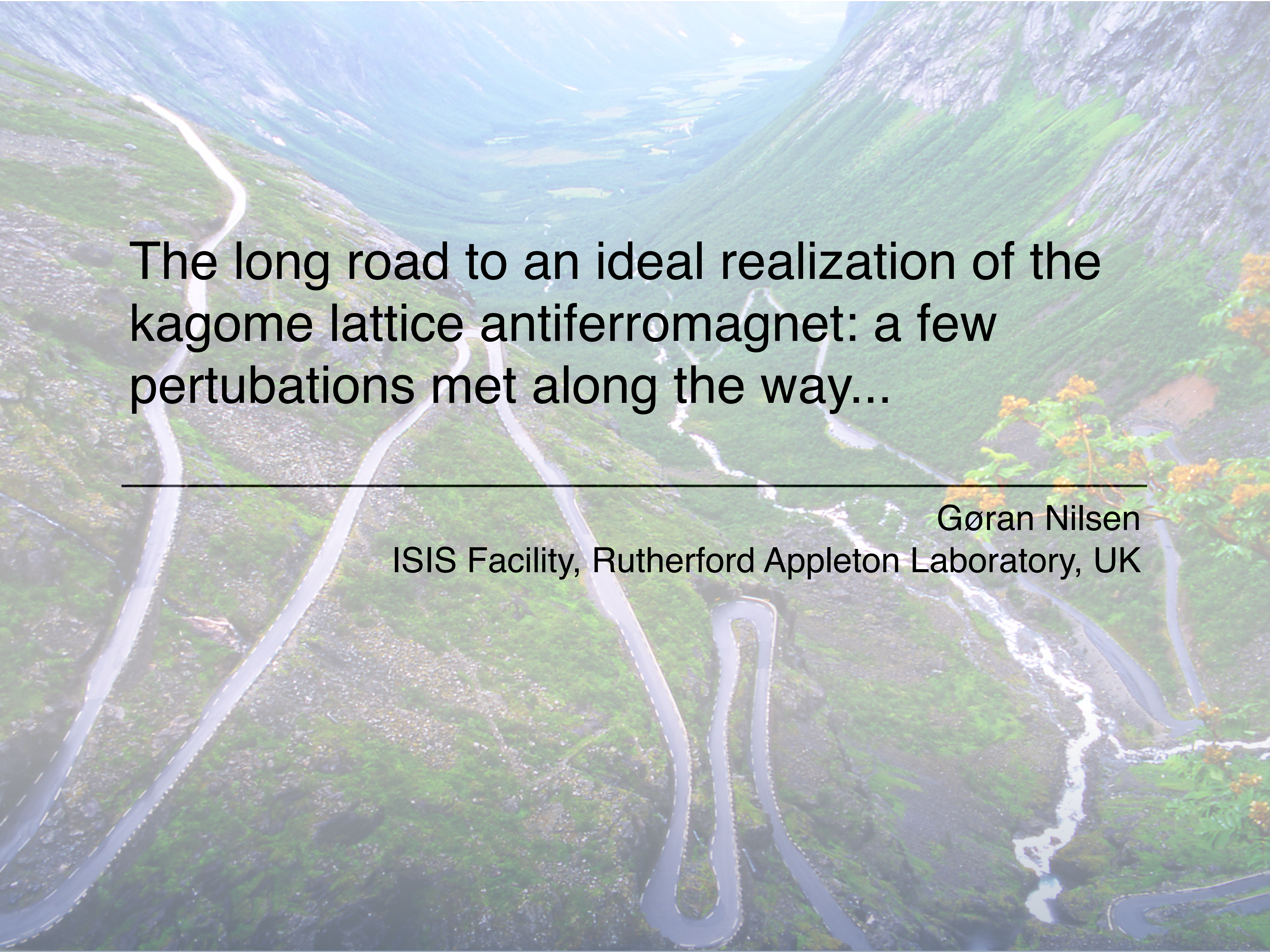


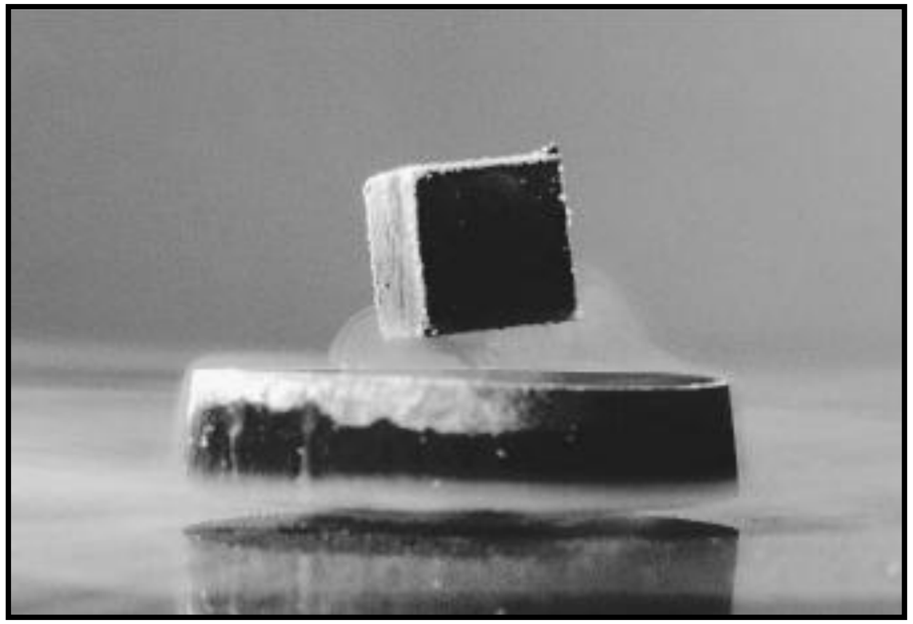
The long road to an ideal realization of the kagome lattice antiferromagnet: a few pertubations met along the way...

Gøran Nilsen
ISIS Facility, Rutherford Appleton Laboratory, UK

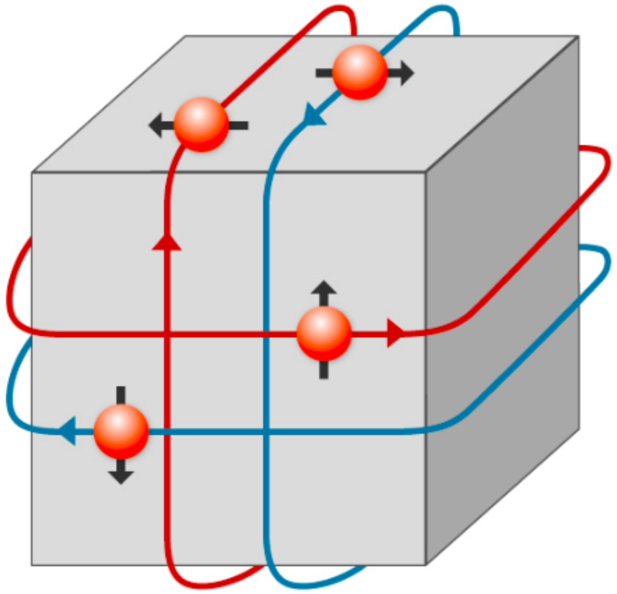
Motivation: Quantum Materials

Materials that show macroscopic quantum behaviour because of electron correlations and/or geometry/dimensionality

e.g. high-T_c superconductors



e.g. topological insulators

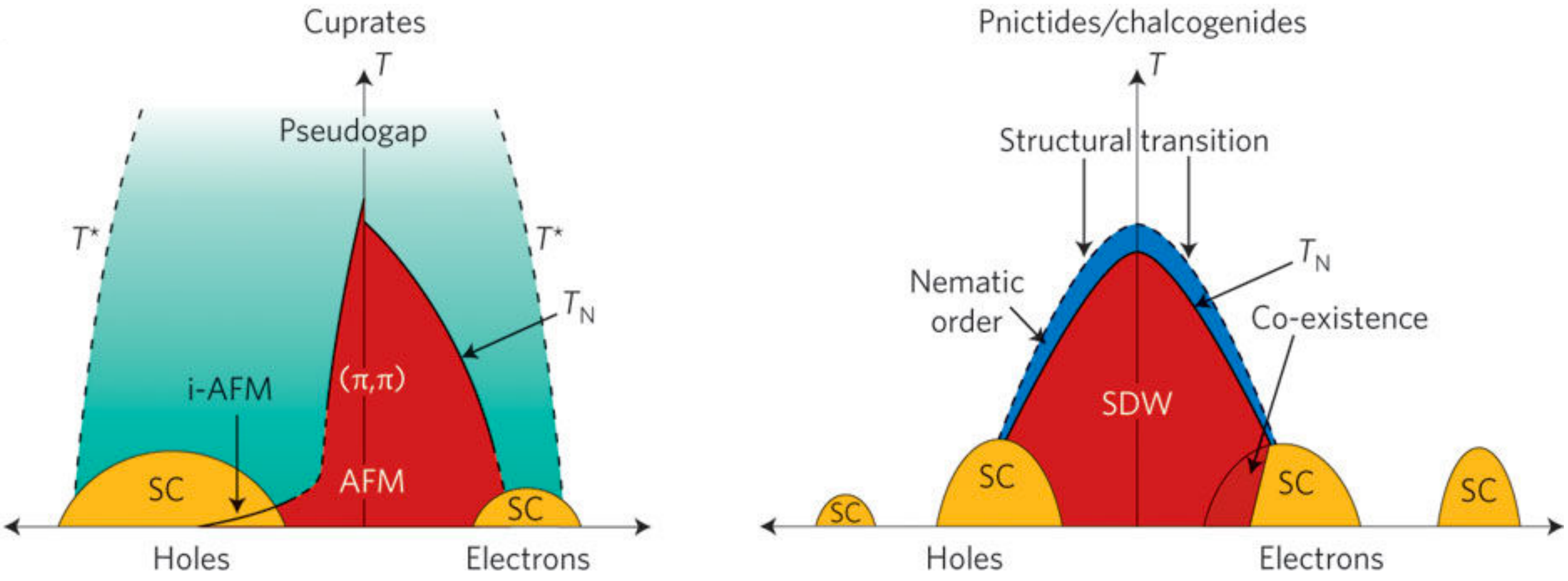


Keimer et. al. Nature Phys. **13** 1046; Tokura et. al. Nature Phys. **13** 1056

Enormous promise for future energy transport, sensing, computing etc.

Magnetic quantum materials

The first class of quantum materials are generally magnetic, and in many cases, their novel properties are intimately related with their magnetism…

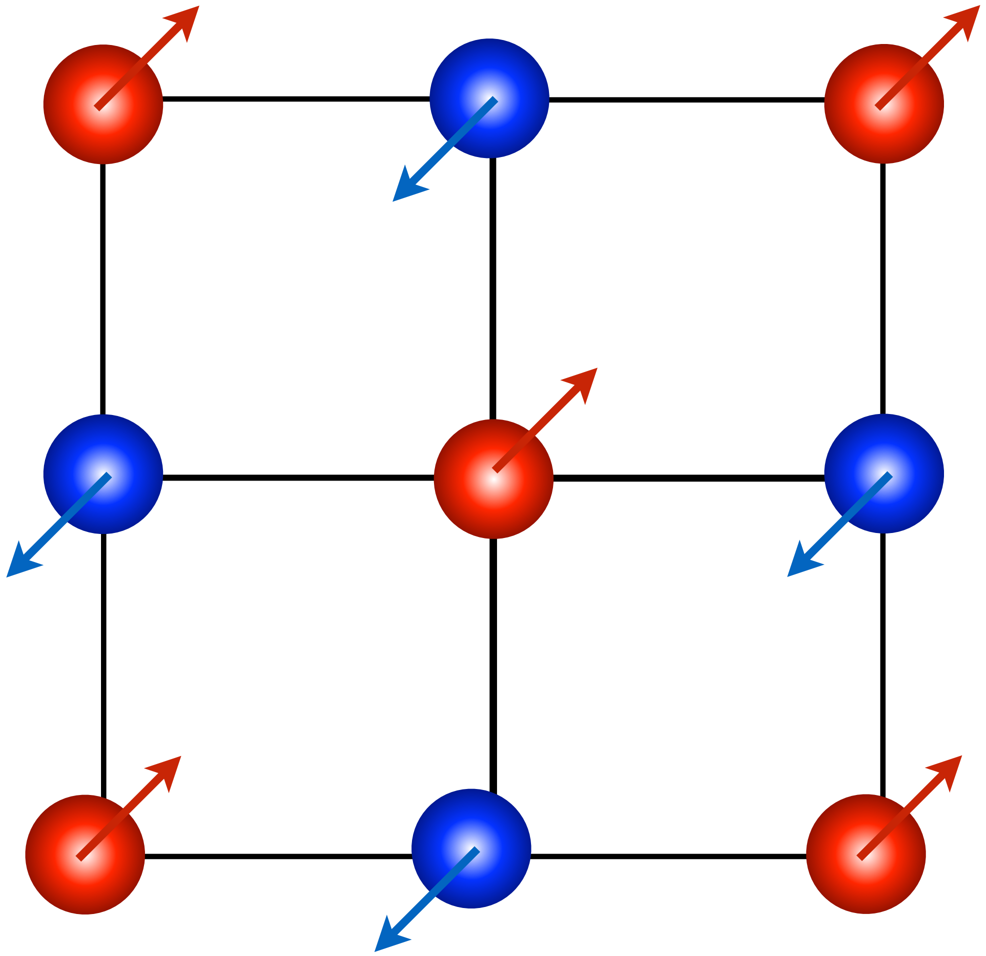


Basov and Chubukov Nature Phys. **7** 272

However, these are complex systems with spin, charge, and orbital degrees of freedom, which makes them difficult to deal with theoretically.

Magnetic quantum materials

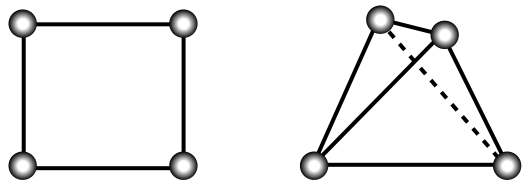
Can exotic states be achieved without chemical doping (and all the ensuing complexity)? Yes, in magnetic systems…



… however, most of these order at high temperature. Need to find a way to enhance quantum fluctuations and destroy conventional magnetic order.

The path to quantum spin liquids

Lattice
Dimensionality
Topology

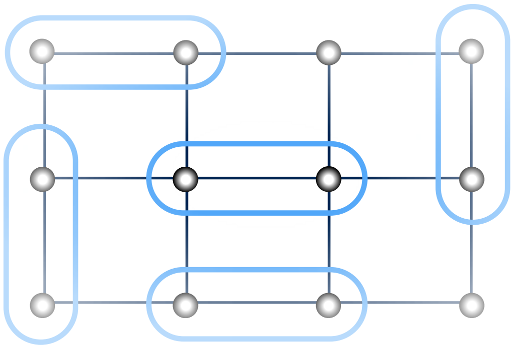


Interactions
Antiferro, ferro
Superexchange
RKKY
Anisotropic
Magneto-elastic

Spin
Quantum $S \lesssim 1$
Classical $S > 1$
Heisenberg
XY
Ising

Frustration, antiferromagnetism, quantum spins, low D

Quantum Spin Liquids

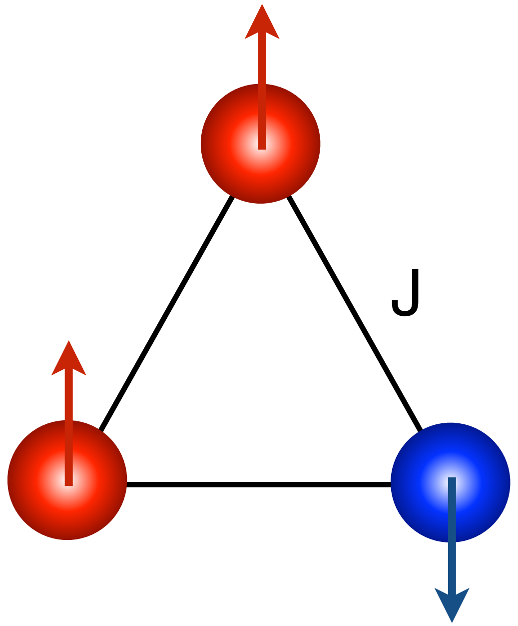


Outline

- Magnetic frustration
- QSL in the kagome lattice antiferromagnet
  - Ground state
  - Excitations - inelastic neutron scattering
- Neutron scattering on kagome lattice materials
  - Overview of Cu^{2+} minerals
  - Herbertsmithite: our best shot at a QSL so far
  - Volborthite: orbital order and trimerization
  - $KCu_3As_2O_7(OD)_3$: multiferroicity in a material far from the QSL limit
- Conclusion

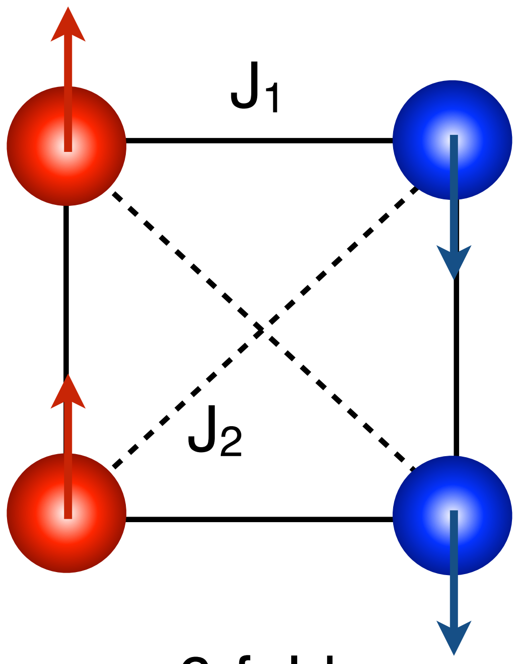
What is frustration?

Geometric



6-fold

Non-geometric

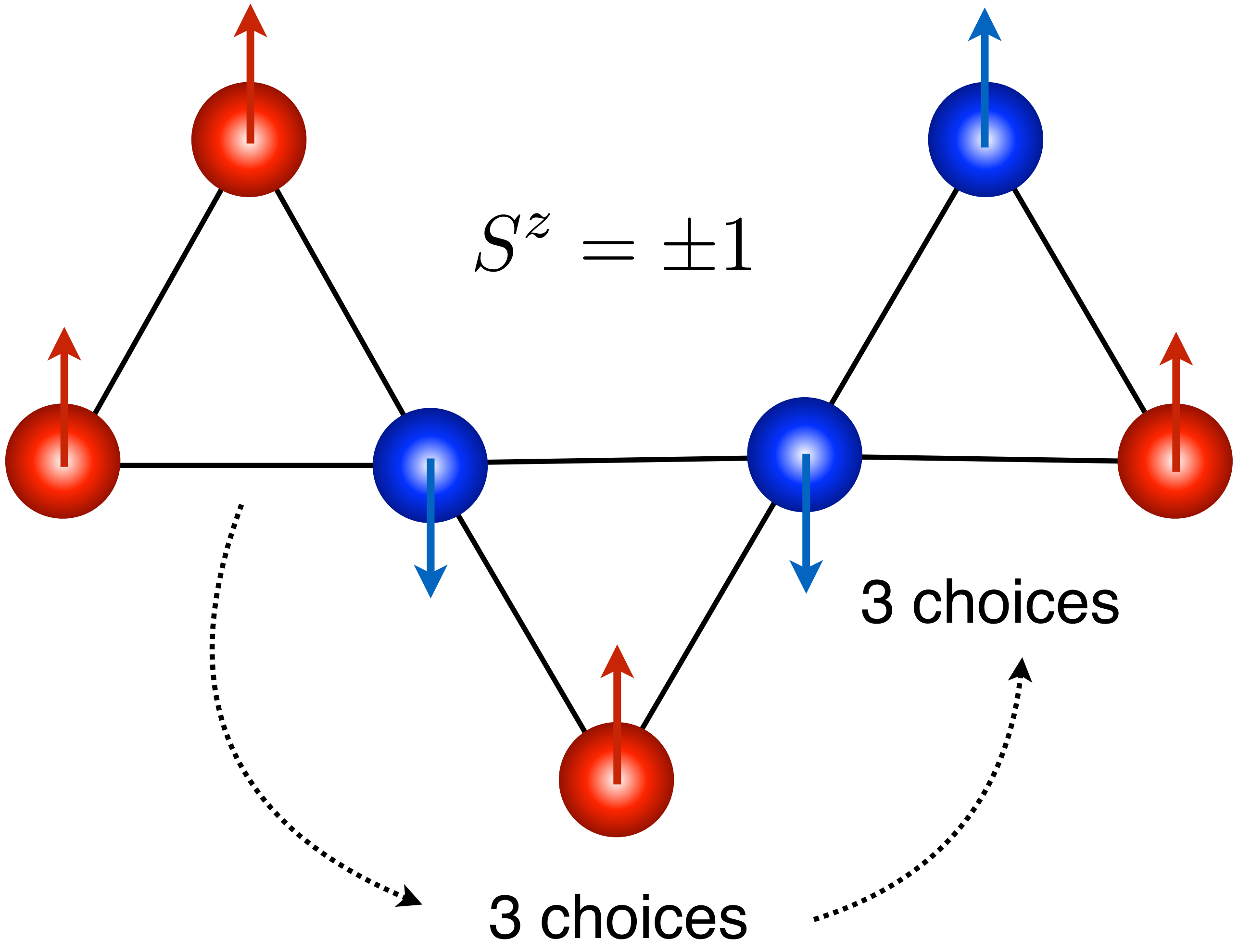


6-fold

$$S^z = \pm 1$$

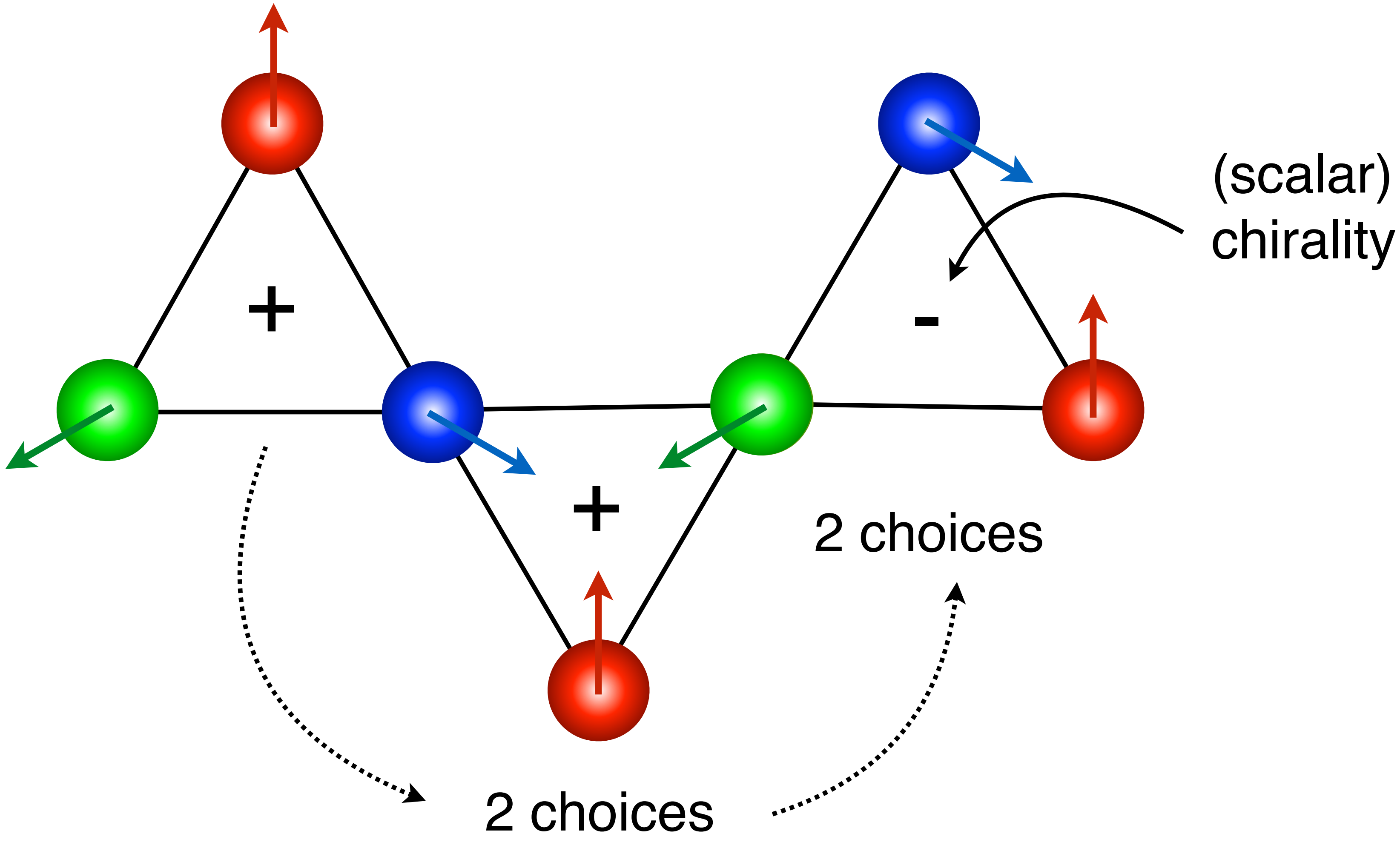
$$\mathcal{H} = J \sum_{i,j} S_i^z S_j^z$$

Consequence 1: degeneracy



Husimi and Syozi Prog. Theor. Phys. **5** 117 (1950)

Consequence 1: degeneracy



(scalar) chirality

2 choices

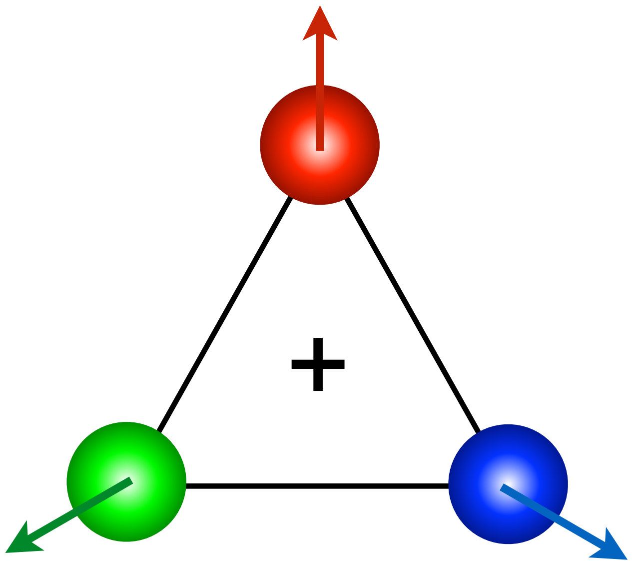
2 choices

In both cases, huge degeneracy in GS (sometimes lifted by fluctuations)
Large barrier to conventional magnetic order

Consequence 2: competition

Science & Technology Facilities Council

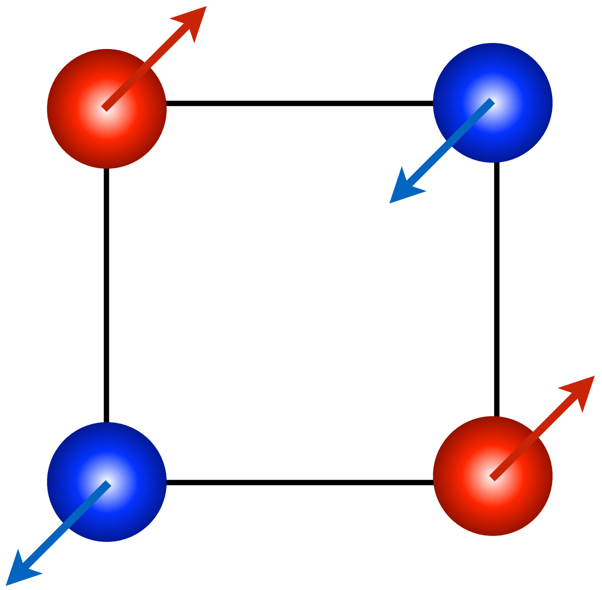
Frustrated



120°

$$\langle E_{ij} \rangle = JS^2 \cos\theta = -\frac{JS^2}{2}$$

Unfrustrated



“Néel”

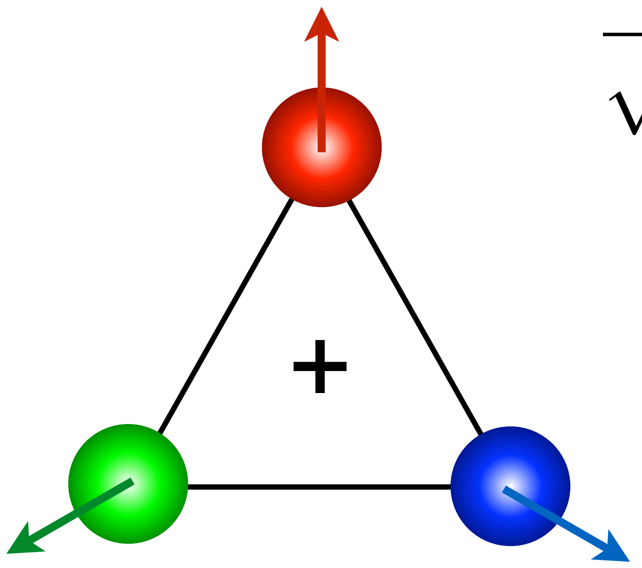
$$\langle E_{ij} \rangle = -JS^2$$

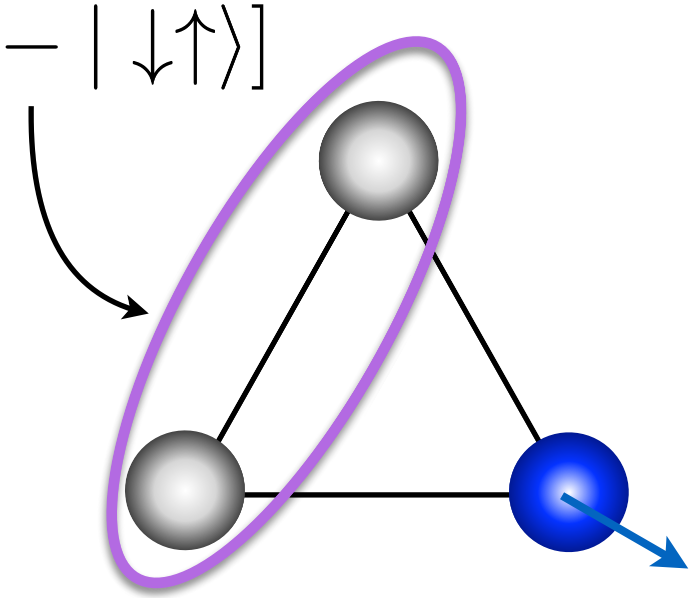
Consequence 2: competition

Classical (vector)

Quantum (operator)

$$\frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$





120°

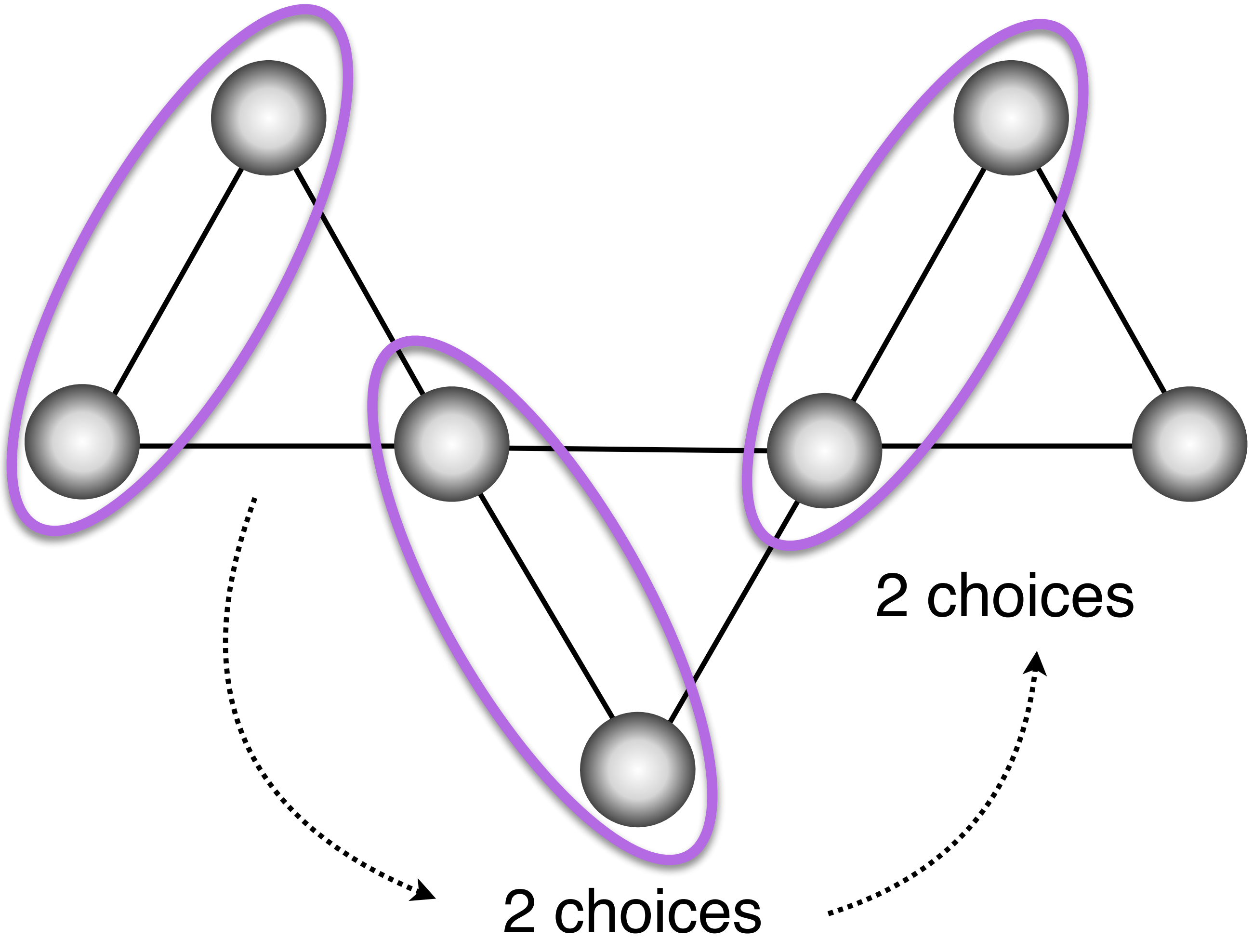
“Valence bond”

$$\langle E_{ij}\rangle = JS^2\cos\theta = -\frac{JS^2}{2}$$

$$\langle E_{ij}\rangle = -\frac{JS(S+1)}{3}$$

Valence bond states

Just like in the classical case, there is an exponentially large number of dimer coverings of the lattice…

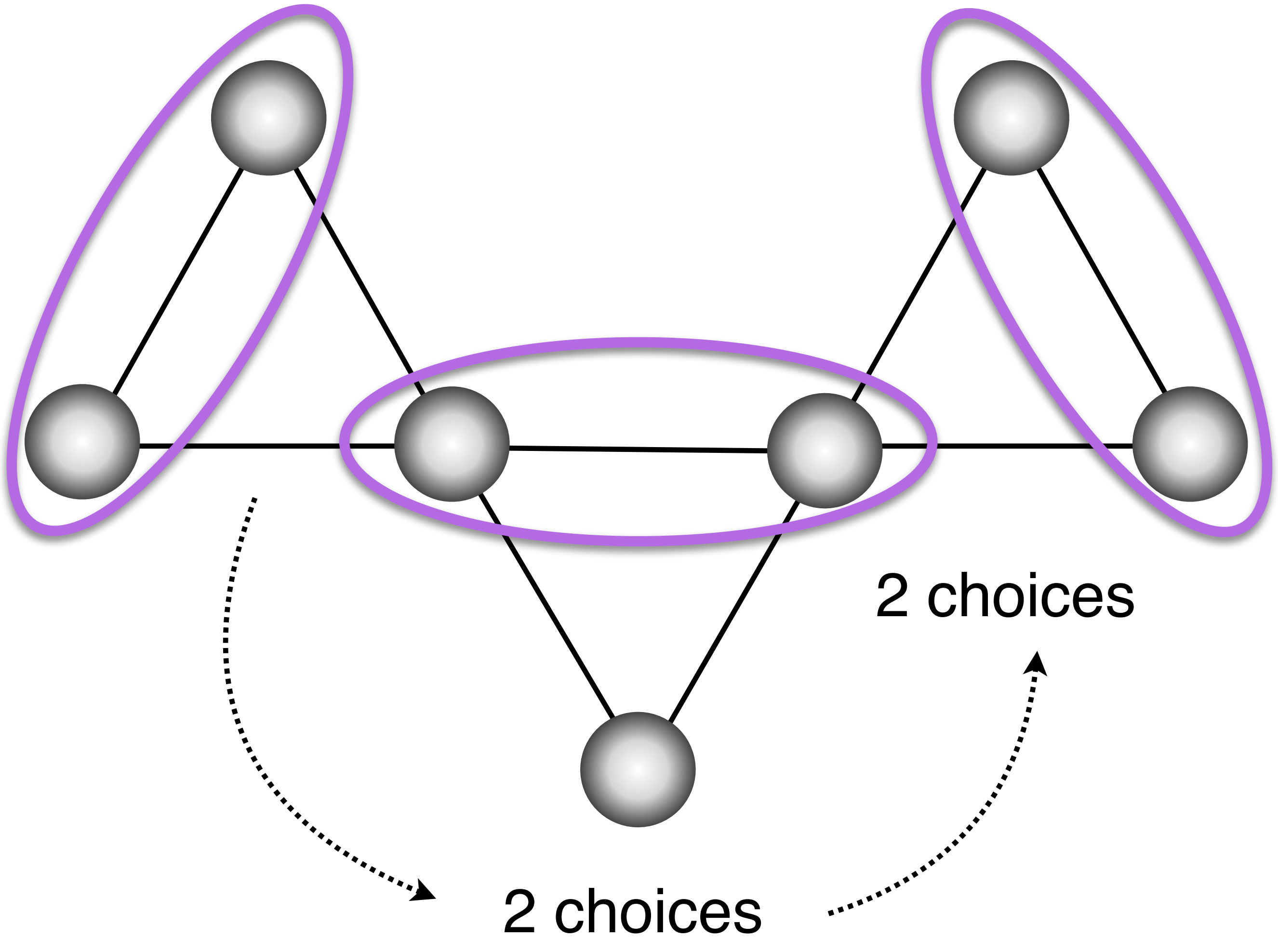


2 choices

2 choices

Resonating Valence bond

Just like in the classical case, there is an exponentially large number of dimer coverings of the lattice…



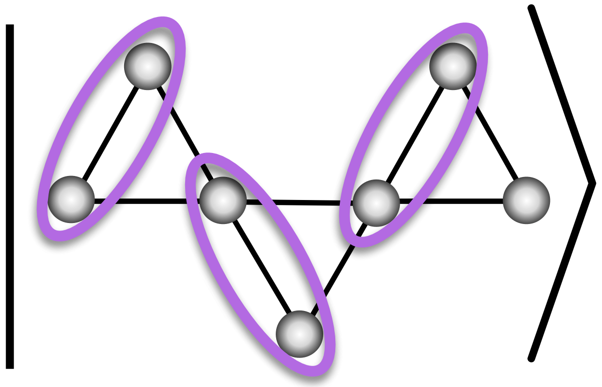
2 choices

2 choices

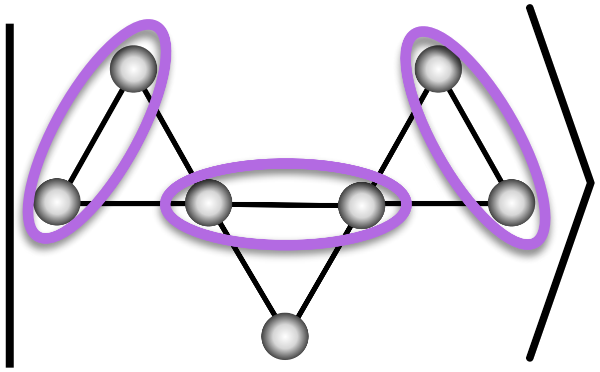
Resonating Valence bond

The system can gain energy by fluctuating between these configurations, as well as ones with longer-ranged bonds:

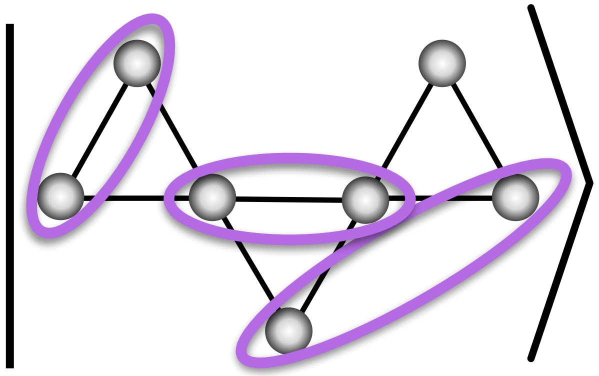
$|\Psi\rangle = c_1$



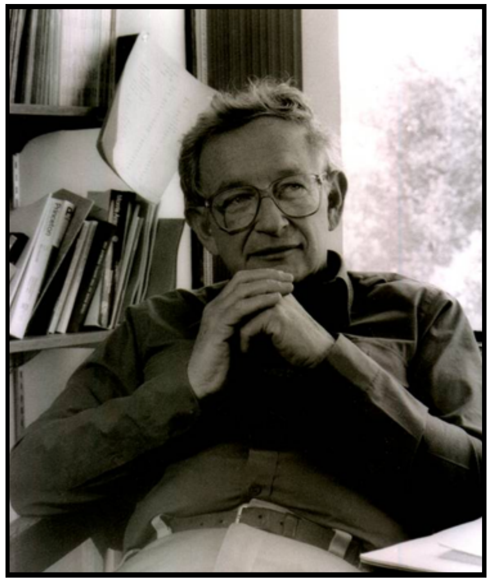
$+ \; c_2$



$+ \; c_3$



$\ddots$

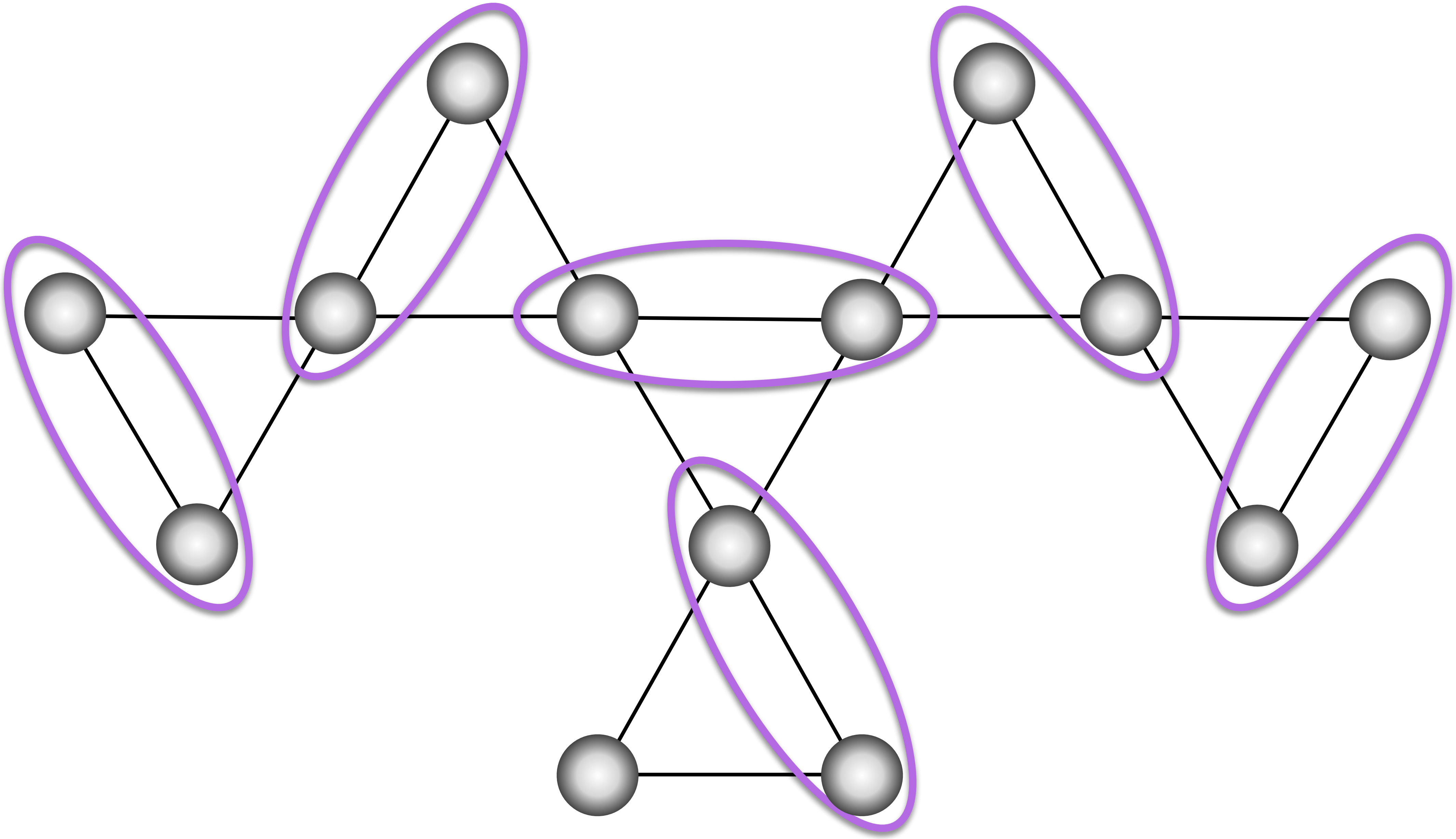


RVB + charges
= superconductivity

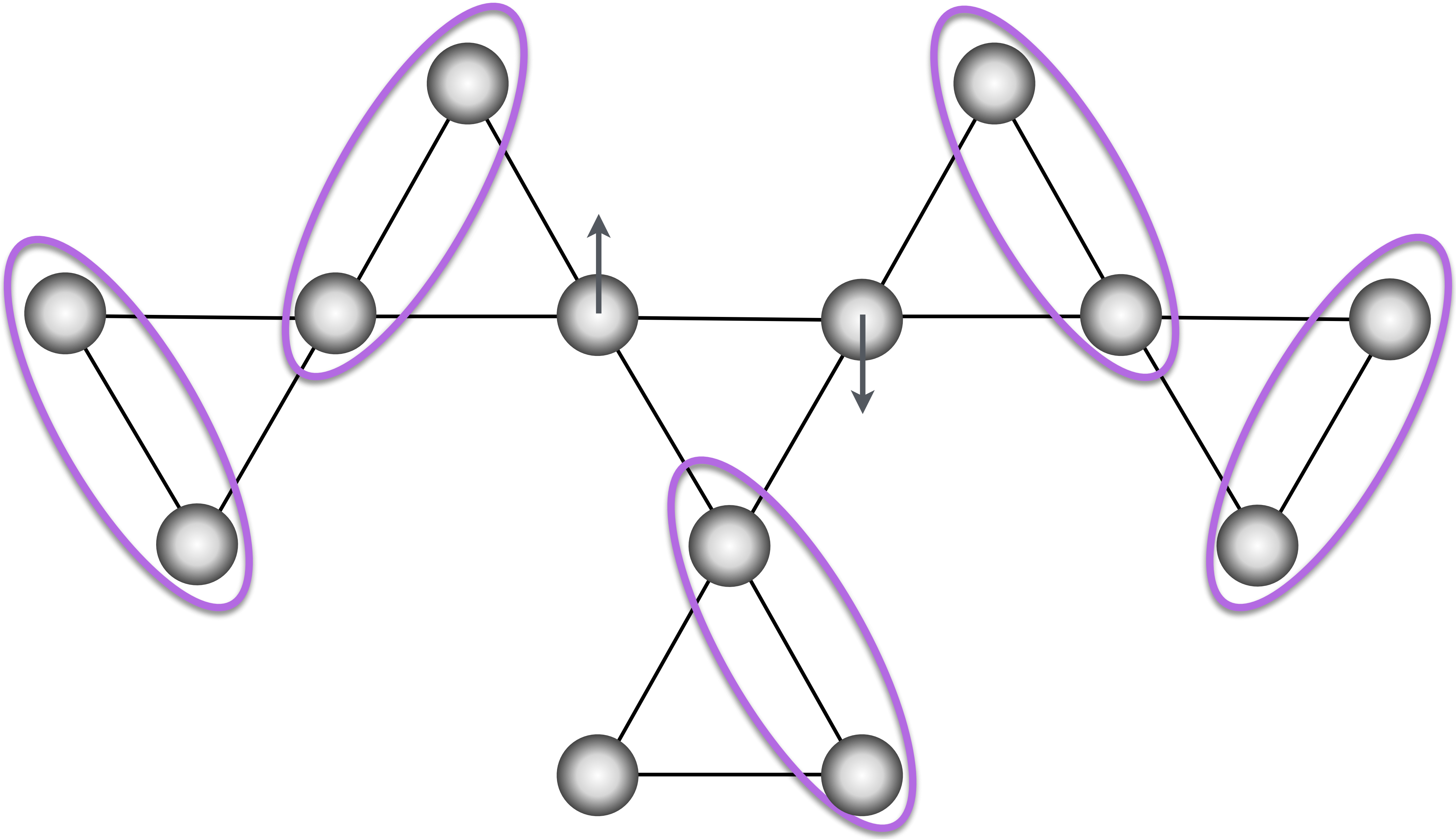
Anderson Science **235** 1196

Excitations: spinons

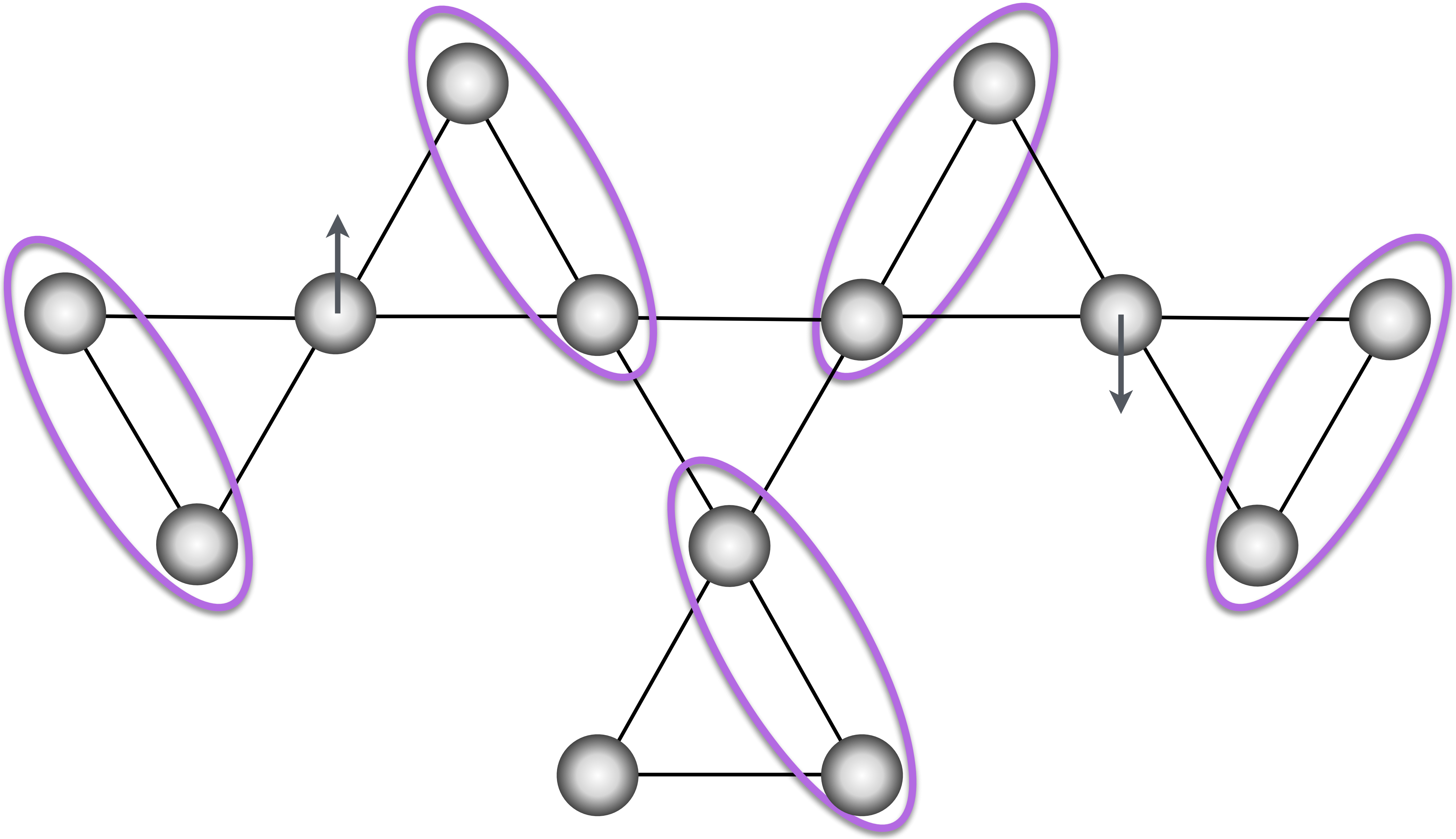
If one of the singlets is broken,



Excitations: spinons

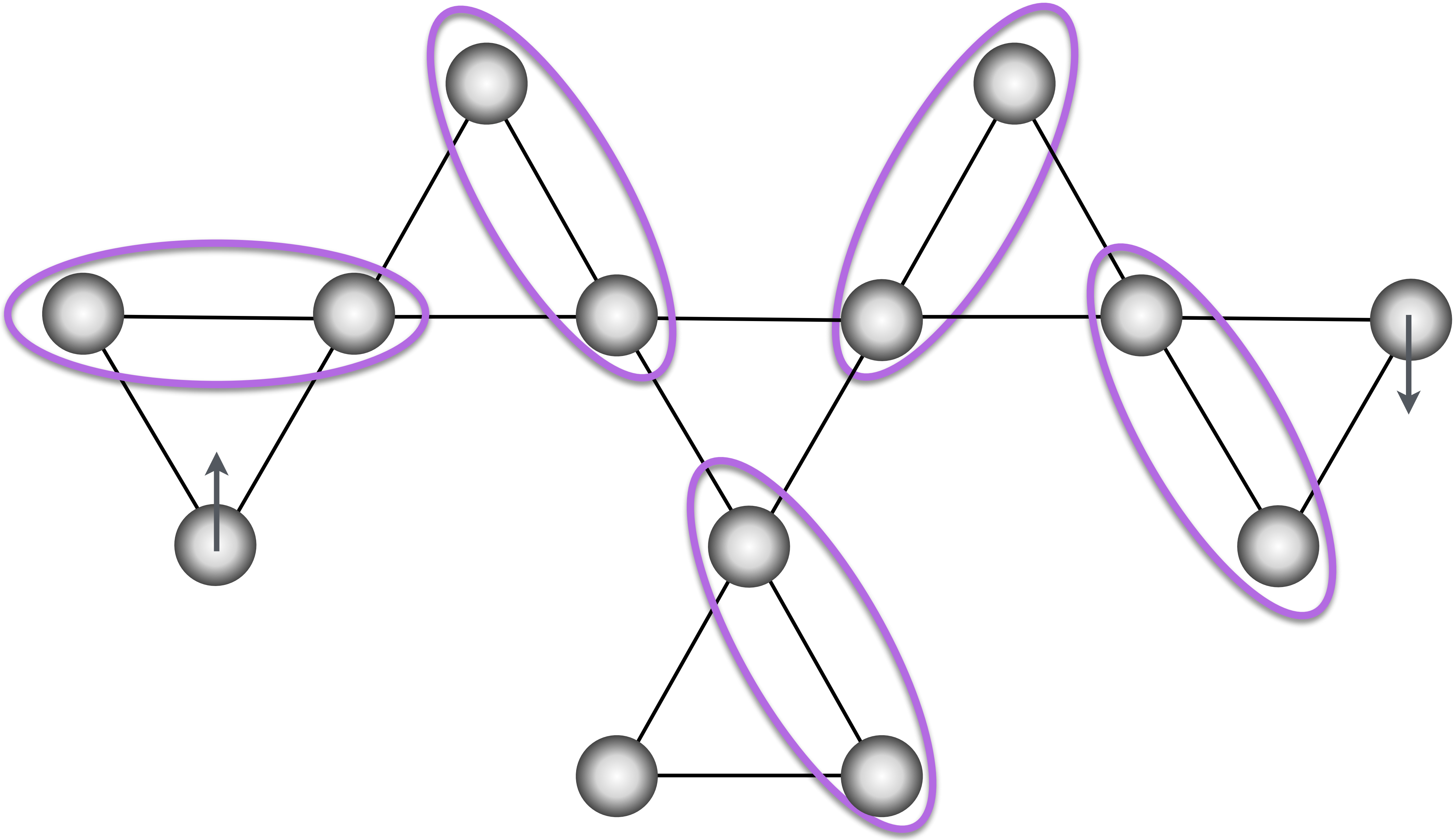


Excitations: spinons



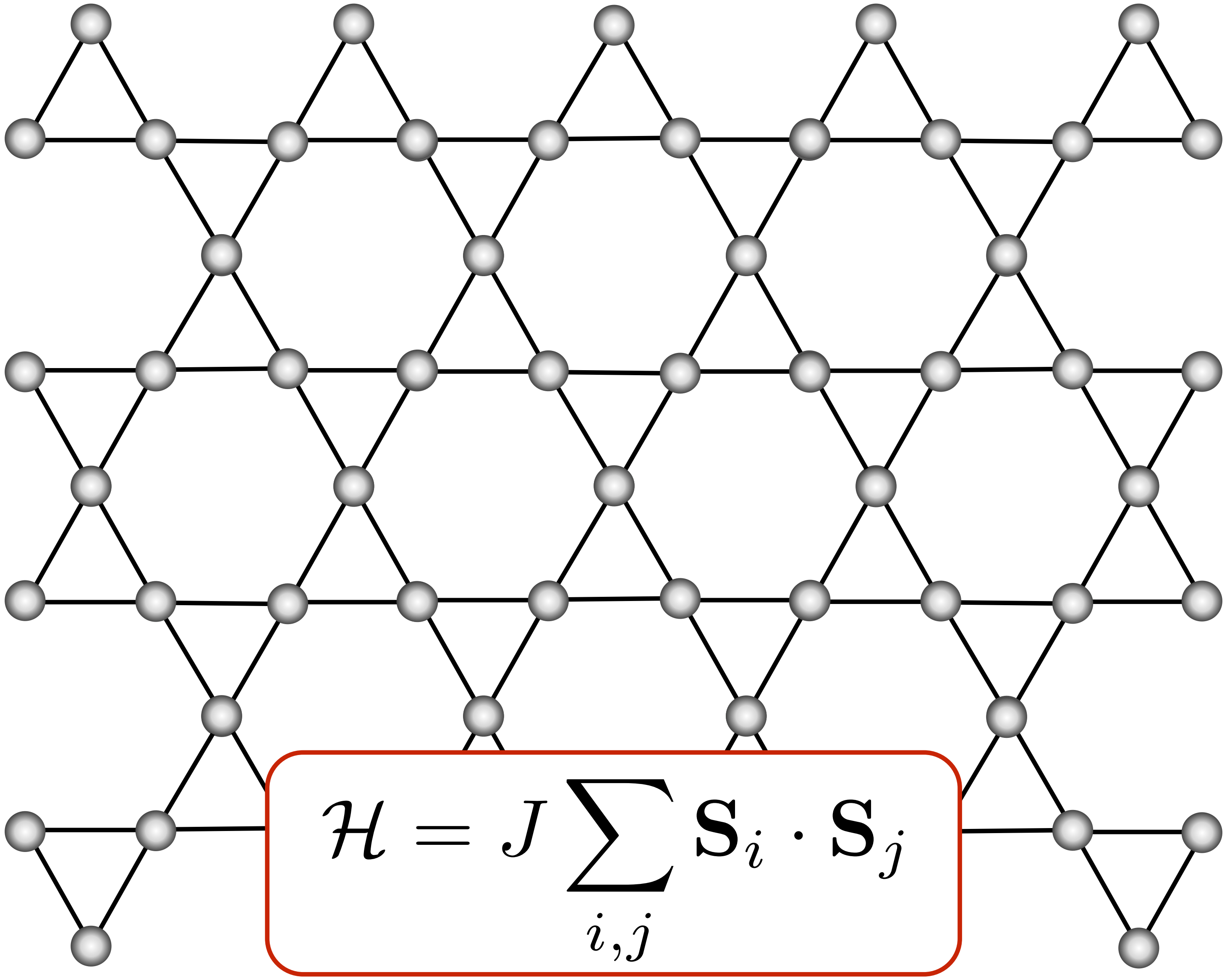
Excitations: spinons

Fractionalized, (potentially) deconfined quasiparticles…



Kagome lattice

The S = 1/2 kagome lattice antiferromagnet is **THE** model of frustration in 2D:

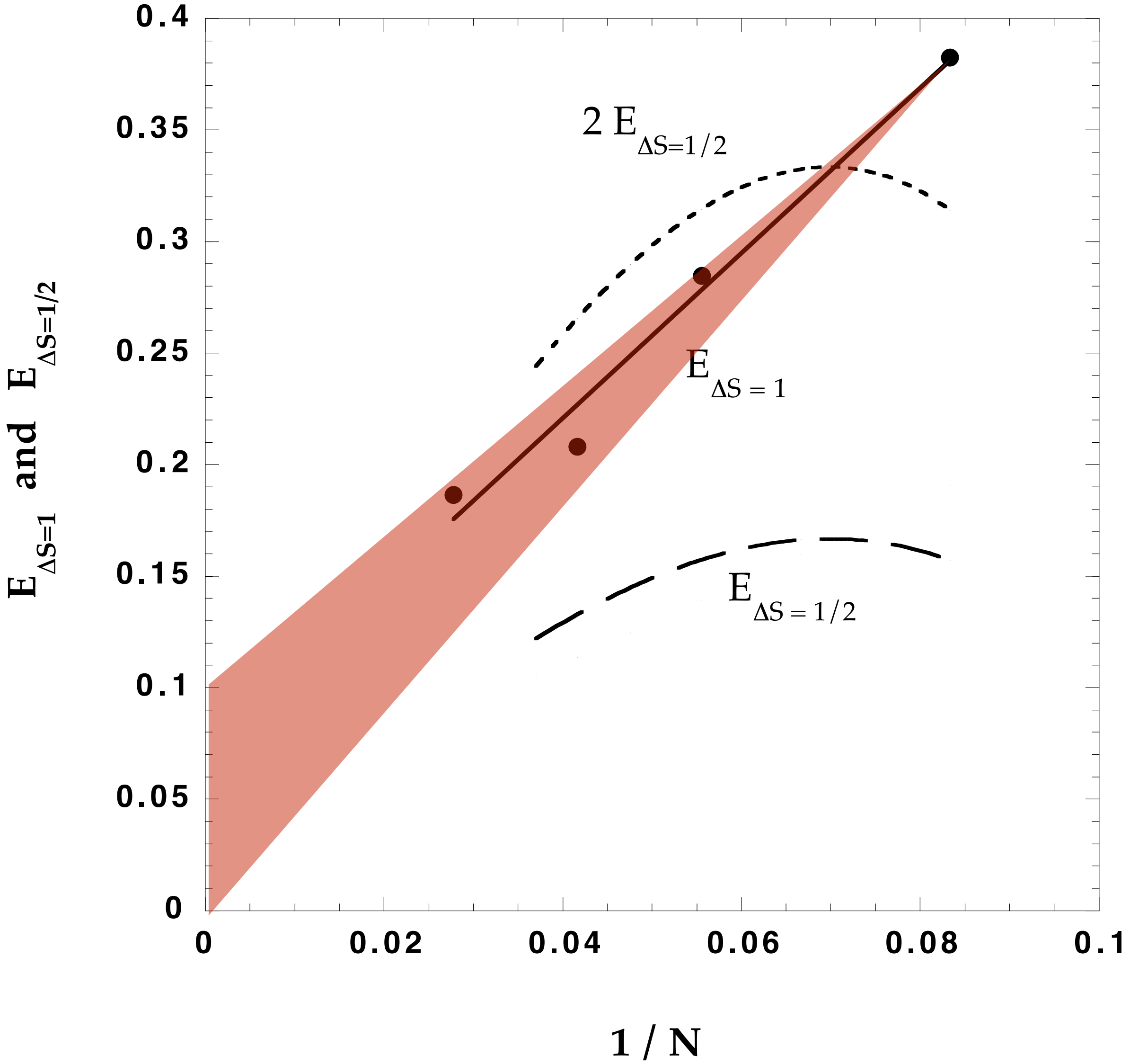


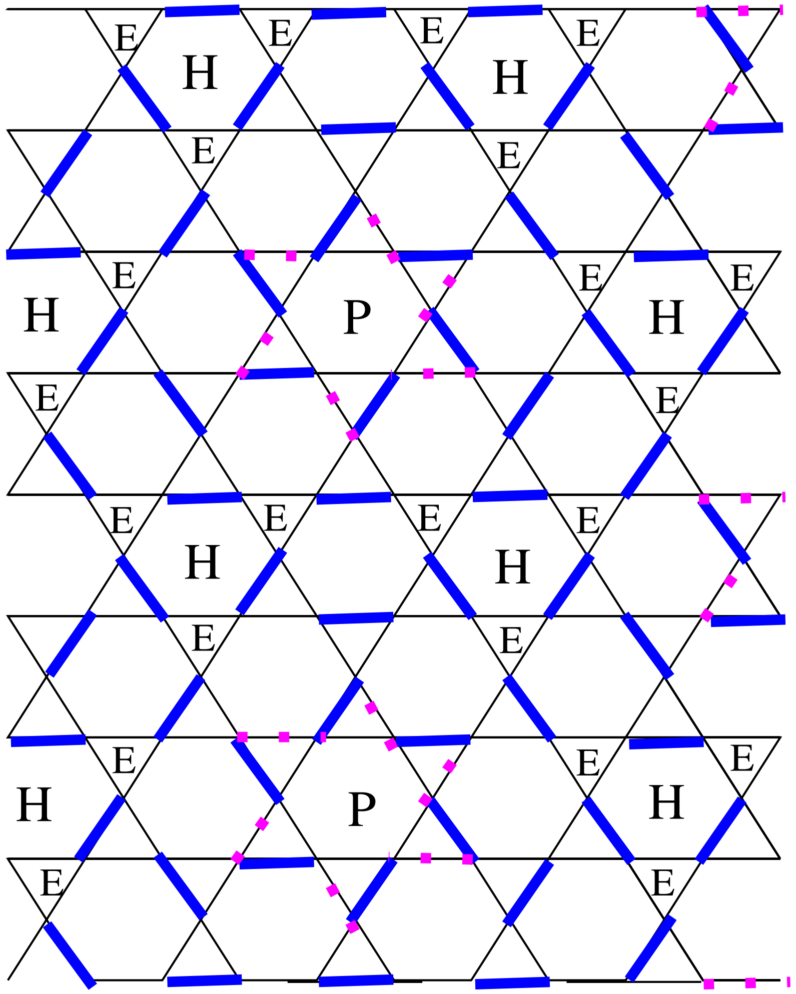
$$\boxed{\mathcal{H} = J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j}$$

Is its ground state the long-sought RVB state?

Kagome lattice: history of the ground state

Its ground state was initially proposed to be a gapless QSL, then a gapped VBS:



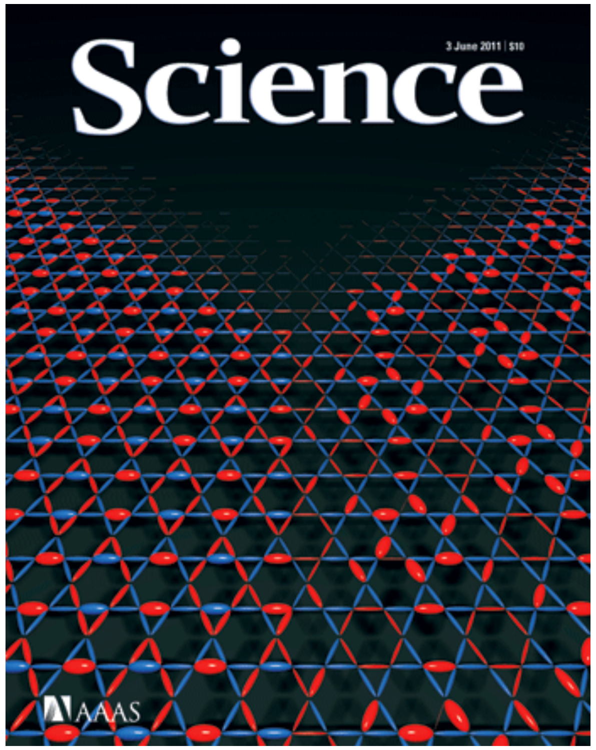


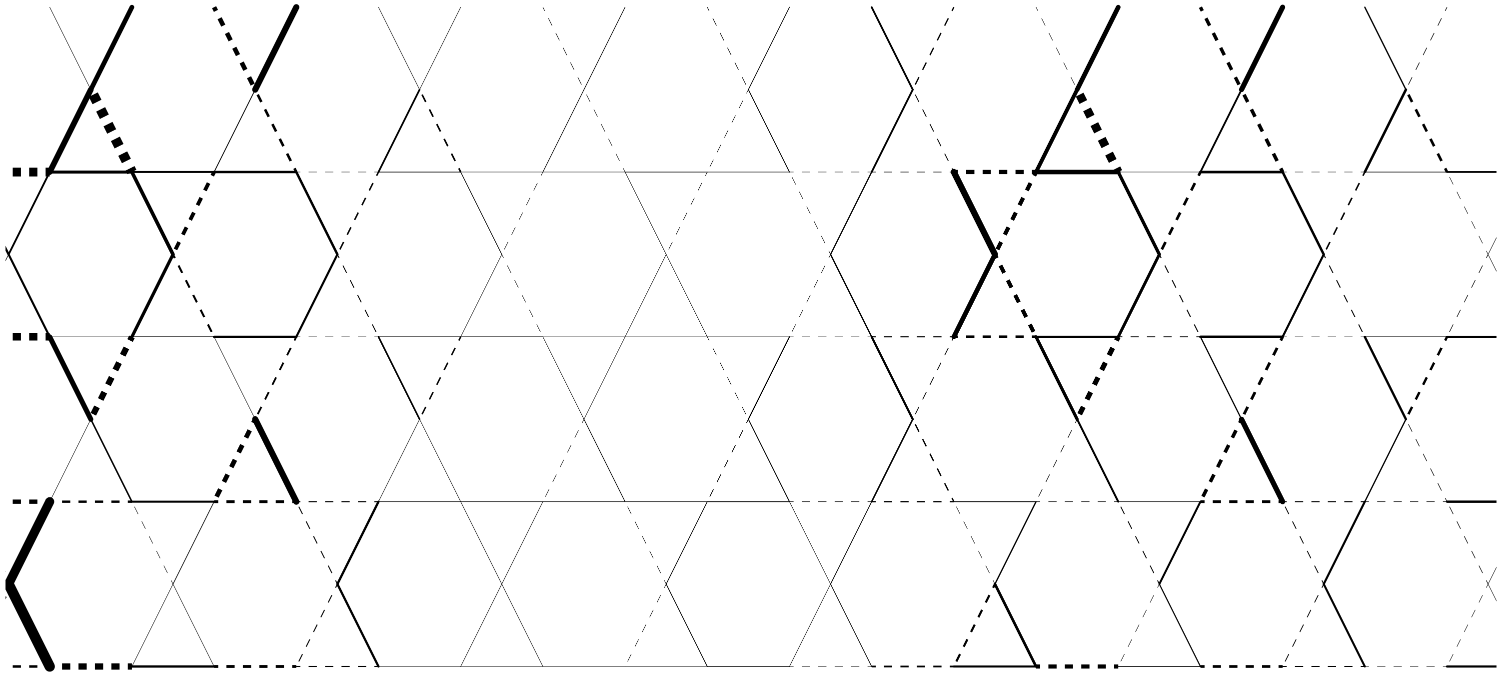
Lecheminant et. al. PRB **56** 2521
Waldtmann et. al. EPJB **2** 501

Singh and Huse PRB **76** 180407 (R)

Kagome lattice: history of the ground state

In 2011, state-of-the art DMRG simulations suggested strongly fluctuating SL with weak dimer correlations:





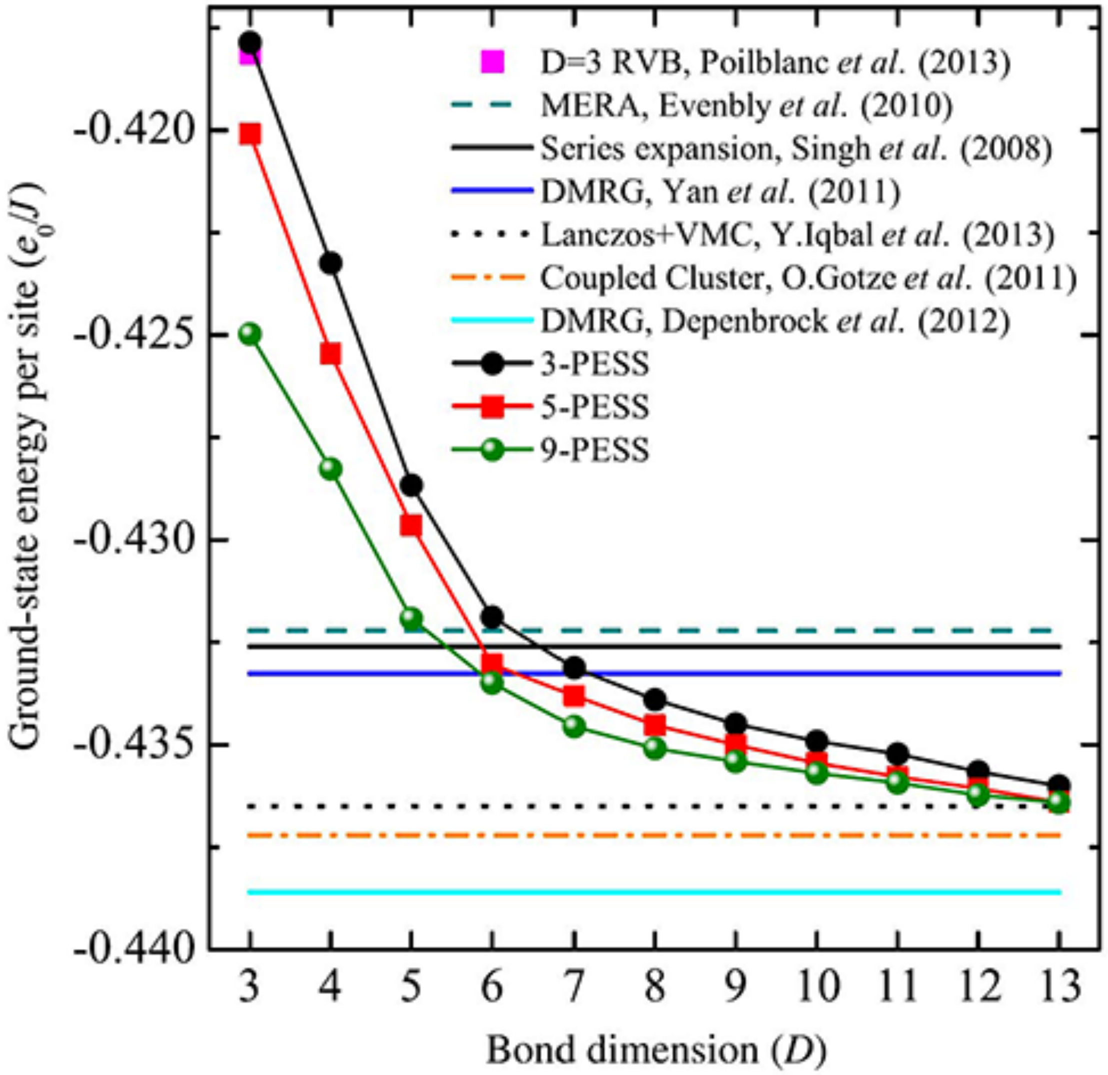
Yan, Huse and White Science **332** 1173

Still considerable debate, however: not SU(2) (uniform RVB) — either U(1) or Z_2 — in the RVB picture, these correspond to different weightings of bonds

Kagome lattice: ground state

Science & Technology
Facilities Council

States separated by minute energies (near a QCP), so interactions beyond J can drastically alter the ground state. These are inevitable in real systems…

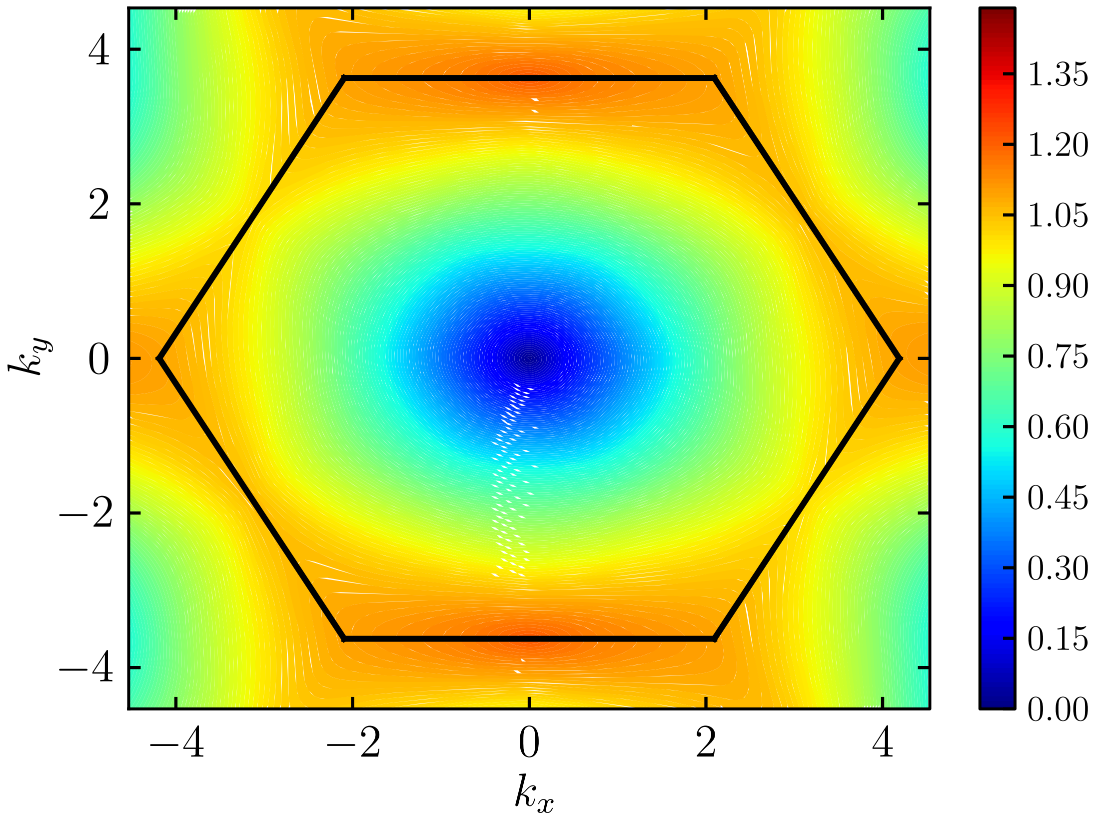


Liao et. al. PRL **118** 137202

Kagome lattice: S(Q)

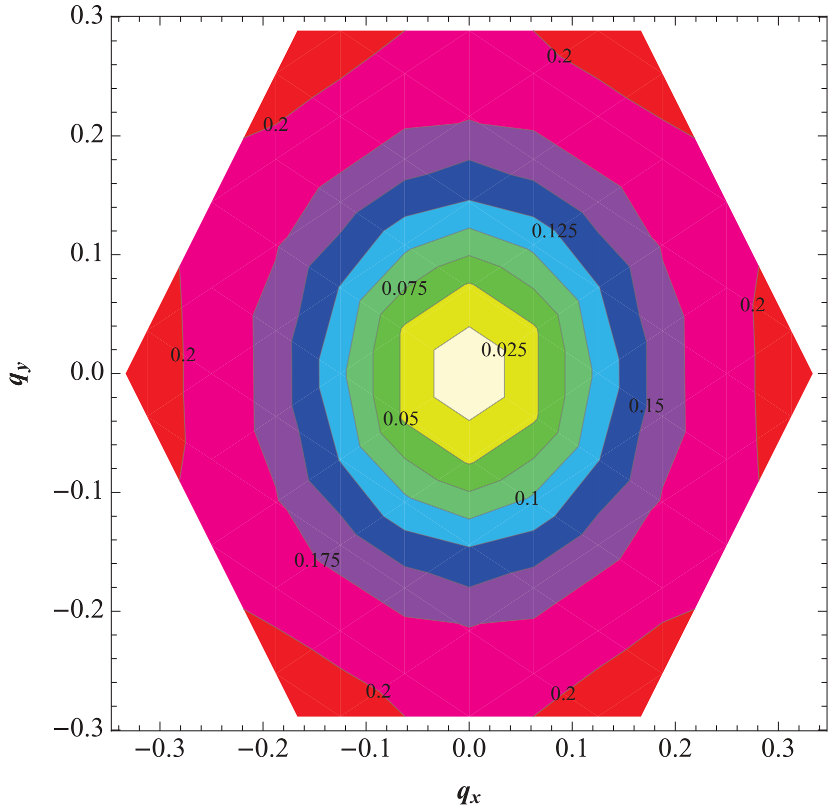
Regardless what the actual ground-state is, the static structure factors are nearly identical:

Z_2 QSL S(Q)



Depenbrock et. al. PRL **109** 067201

U(1) QSL S(Q)



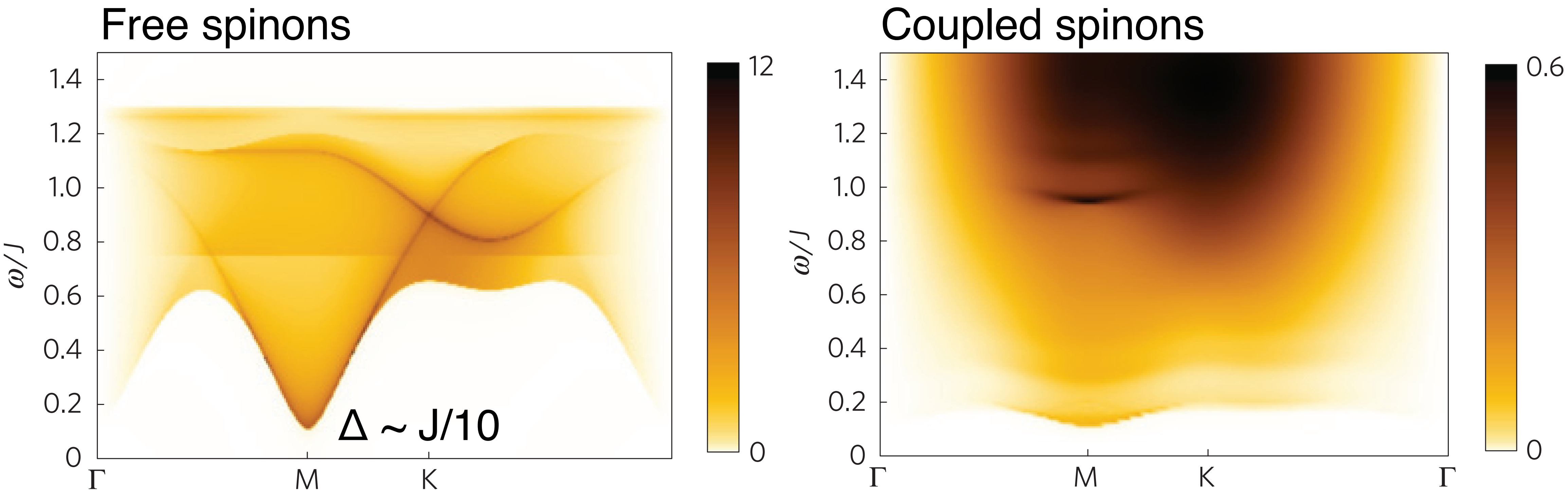
Iqbal et. al. **87** 060405

However, the Z_2 QSL is associated with a small gap Δ in the excitation spectrum, while the U(1) should be gapless…

Kagome lattice: dynamical structure factor

Non-interacting spinon limit: strongly dispersing continuum (one neutron, two spinons). Introduce interactions between spinons and other excitations: broaden.

Z_2 QSL S(Q,ω)



Free spinons

Coupled spinons

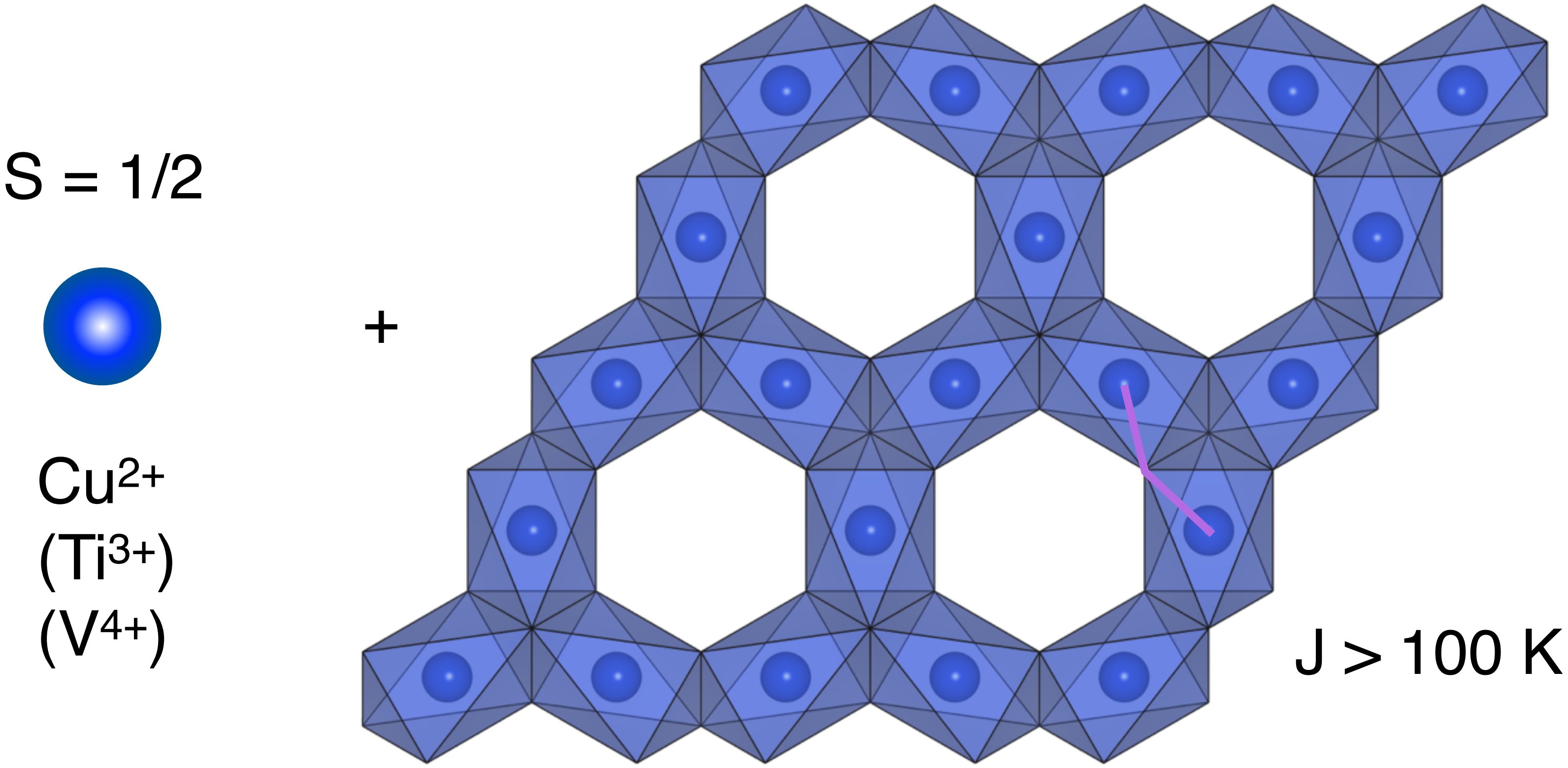
Punk et. al. Nature Phys. **10** 289; Dodds et. al. PRB **88** 224413

Spinons coupled to visons - topological singlet excitations.

Cu^{2+} minerals as realisations of the kagome lattice antiferromagnet

Kagome lattice materials

How can we realize a kagome lattice material? If we consider inorganic materials with TM octahedra…



S = 1/2

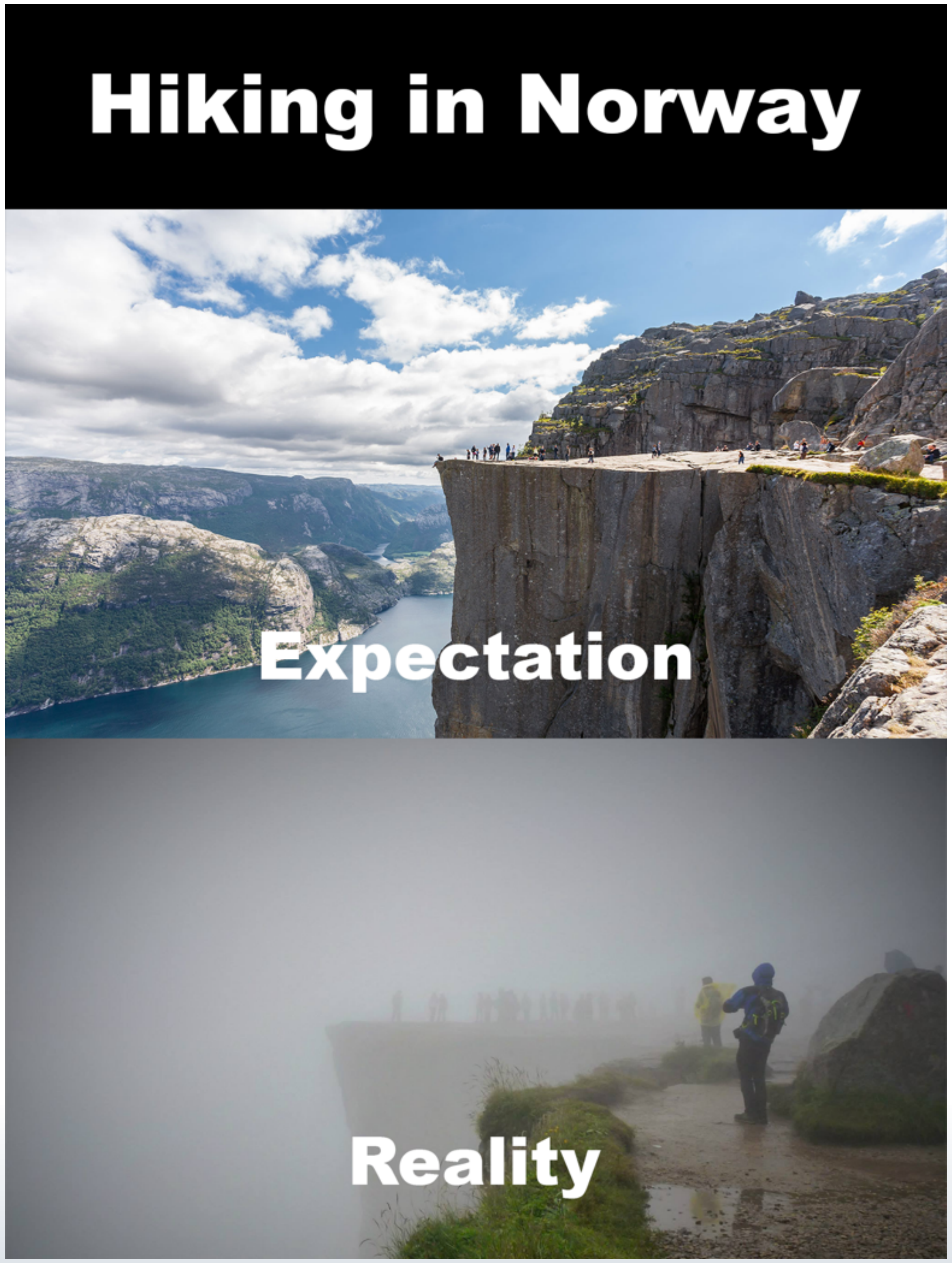
Cu^{2+}
(Ti^{3+})
(V^{4+})

+

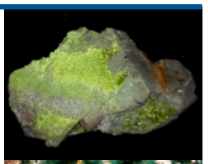
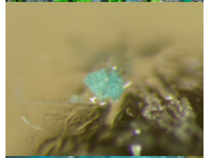
J > 100 K AFM

Most materials studied so far contain some variation on this motif…

Sometimes nature gets in the way…



Kagome lattice materials

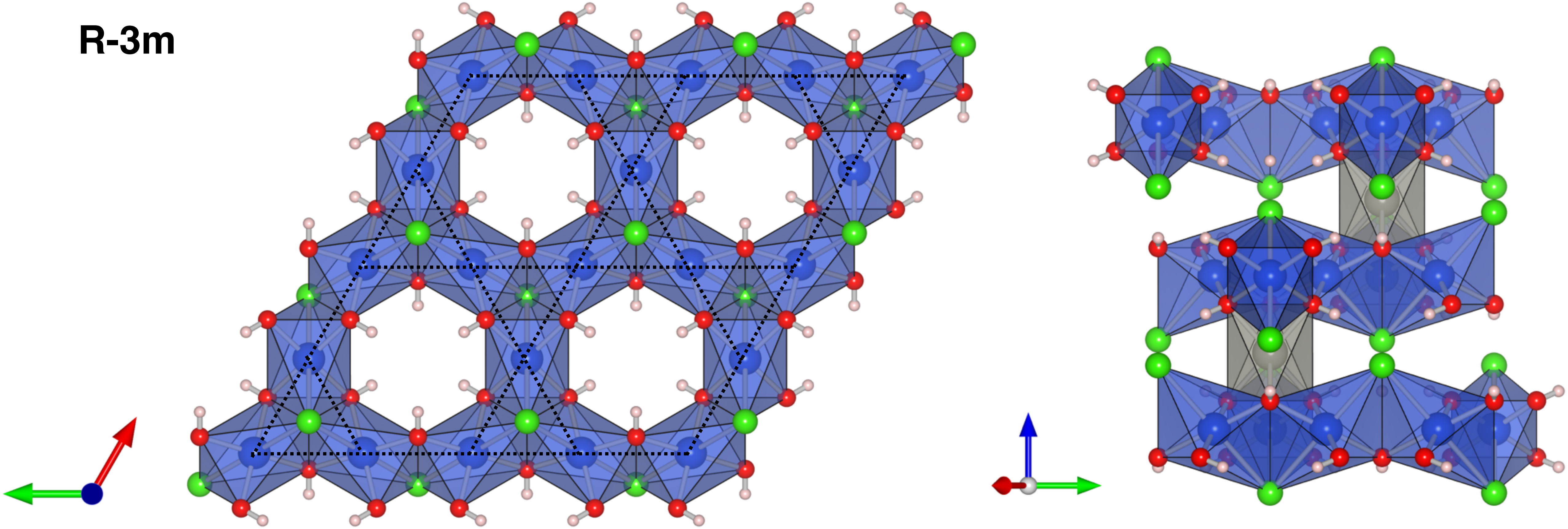
Material	SG	θ	Order	Reference(s)	
Volborthite $Cu_3V_2O_7(OH)_2.2H_2O$	*C2/m*	-115 K	1 K	Z. Hiroi *et. al.*, JPSJ **70**, 3377 M. Yoshida *et. al.*, PRL **103**, 077207 G. J. Nilsen *et. al.*, PRB **84**, 172401	
Herbertsmithite β-$Cu_3Zn(OH)_6Cl_2$	$R\bar{3}m$	-240 K	< 50 mK	M. P. Shores *et. al.* JACS **127**, 13462 de Vries *et. al.* PRL **103**, 237201 T. Han *et. al.* Nature **492**, 406	
$KCu_3As_2O_7(OD)_3$	*C2/m*	+13.4 K	7 K	Y. Okamoto *et. al.* JPSJ **81**, 033707	
Bayldonite $PbCu_3(AsO_4)_2(OH)_2$	*C2/c*	+49 K	< 2 K ?	Unpublished (H. Ishikawa, Y. Okamoto)	
Vesignieite $BaCu_3(VO_4)_2(OH)_2$	*C2/m*	-59 K	7 K	Y. Okamoto *et. al.*, JPSJ **78**, 033701 M. Yoshida *et. al.*, JPSJ **82**, 013702	
Edwardsite $Cu_3Cd_2(SO_4)_2(OH)_6.4H_2O$	$P2_1/c$	- 50 K	4.3 K	H. Ishikawa et. al. JPSJ **82**, 063710	
Kapellasite α-$Cu_3Zn(OH)_6Cl_2$	$R\bar{3}m$	0 K	< 50 mK	Colman *et al.*, Chem. Mater **20** 6897 Fåk *et. al.* PRL, **109** 137208	
$Cu_3Zn(OH)_6(SO_4)$	$P2_1/a$	- 79 K	< 50 mK	Y. Li et. al., cond-mat:1310.2795	

What is the nature of the QSL in Herbertsmithite?

Herbertsmithite, $Cu_3Zn(OH)_6Cl_2$

$\theta = -240$ K, $J = 180$ K, $T_N < 50$ mK

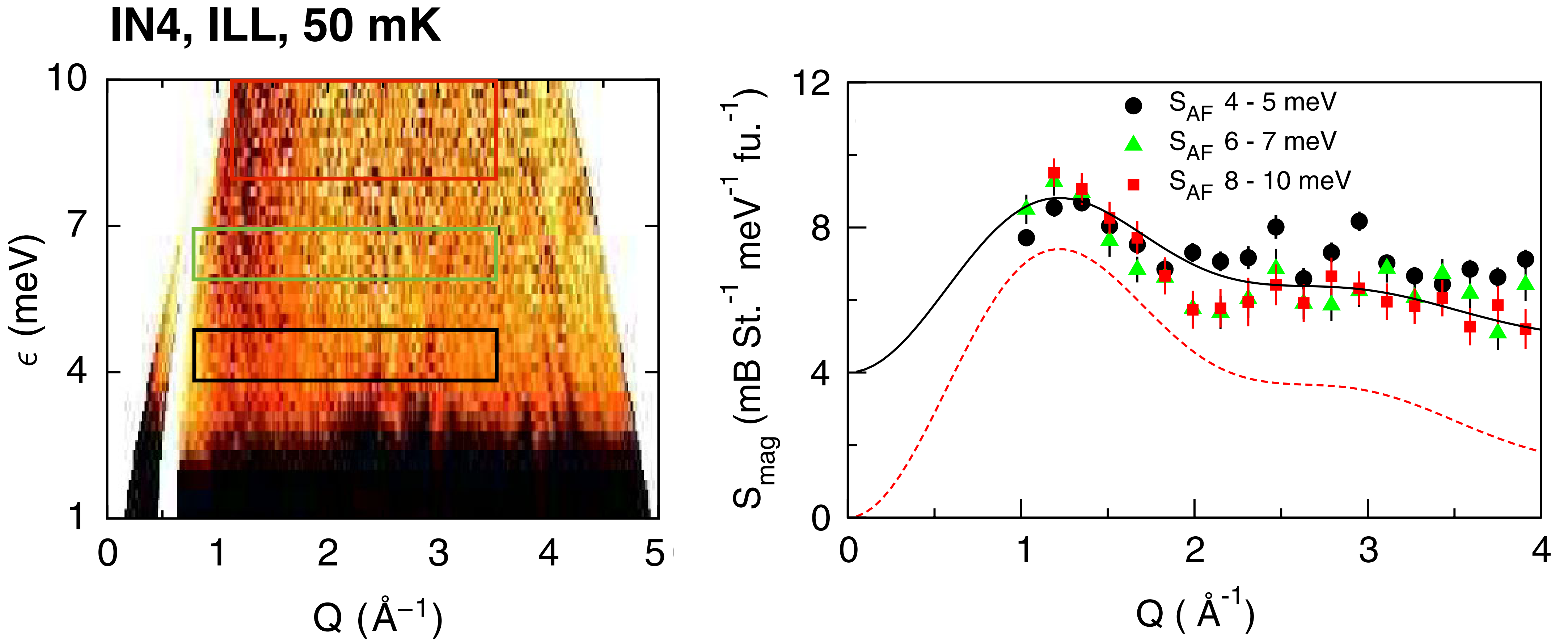
R-3m



M. P. Shores et. al. JACS **127** 13462

Herbertsmithite: high-energy excitations

High-energy S(Q,ω) consistent with very short-range correlations even at 50 mK!

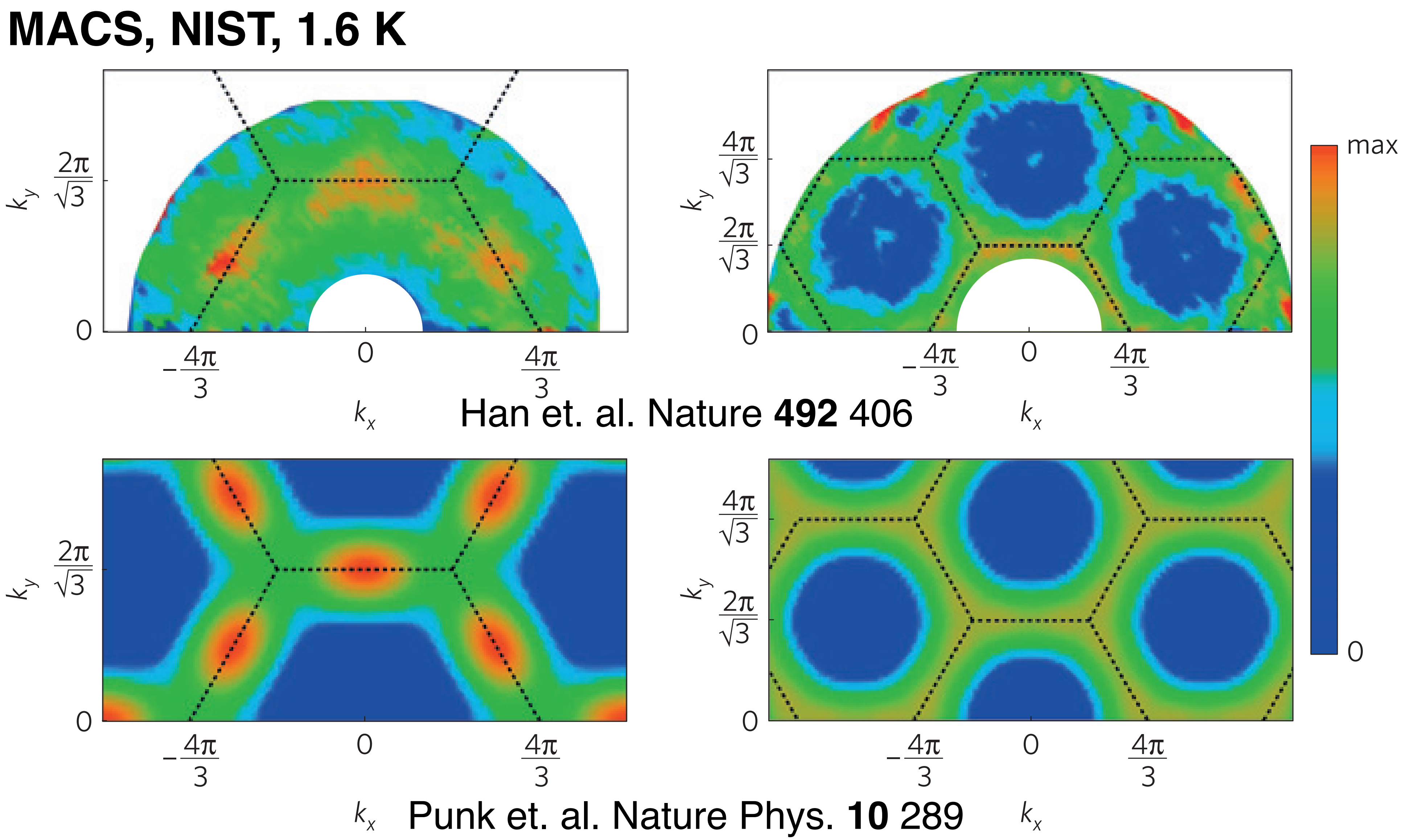


M. A. de Vries GJN et. al. PRL **103** 237201

No sign of gap down to ~ 3 meV.

Herbertsmithite: high-energy excitations

High-energy S(Q,ω) consistent with very short-range correlations even at 50 mK!



MACS, NIST, 1.6 K

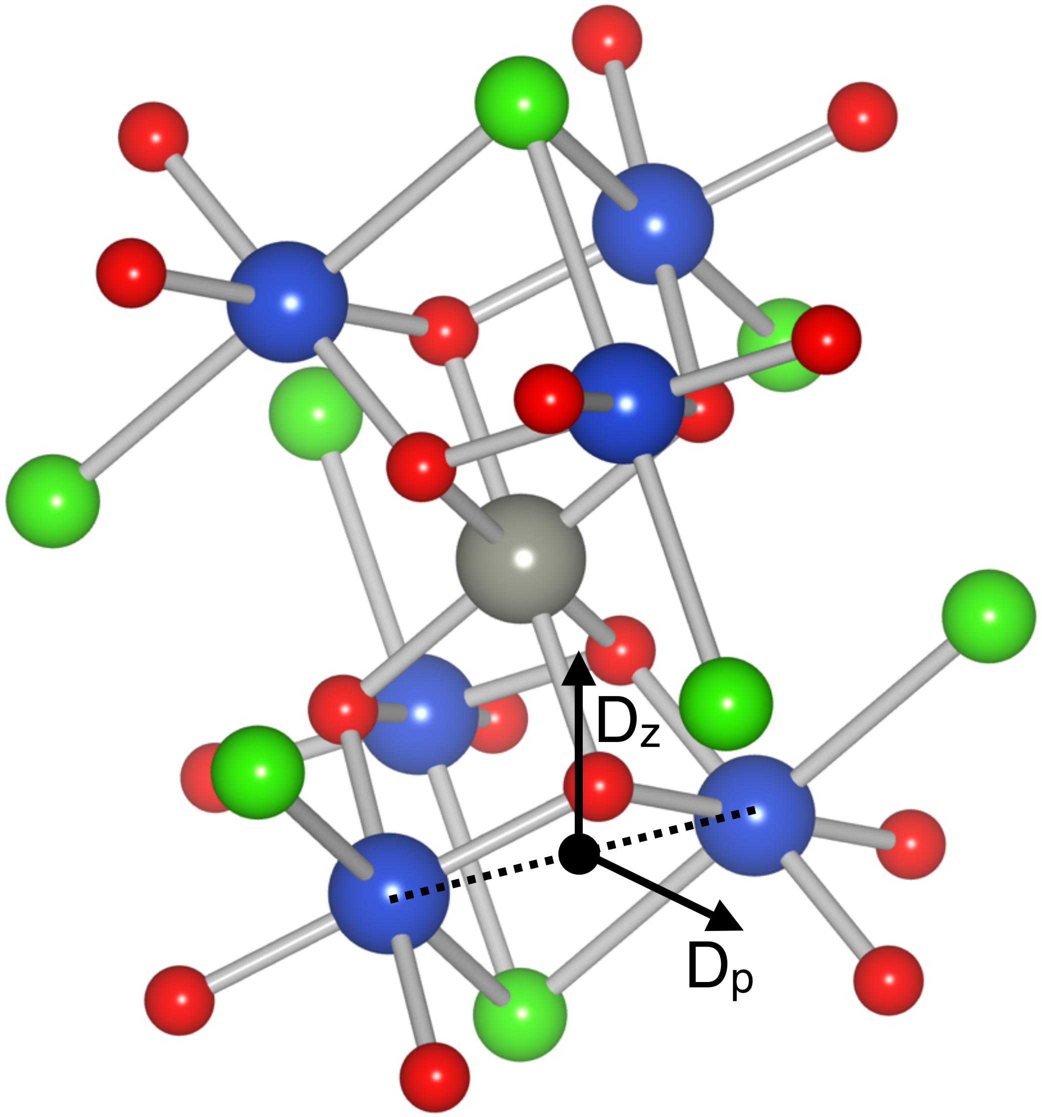
Han et. al. Nature **492** 406

Punk et. al. Nature Phys. **10** 289

Calculation for Z_2 spin liquid with spinon-vison interactions agrees qualitatively!

Herbertsmithite: a true QSL?

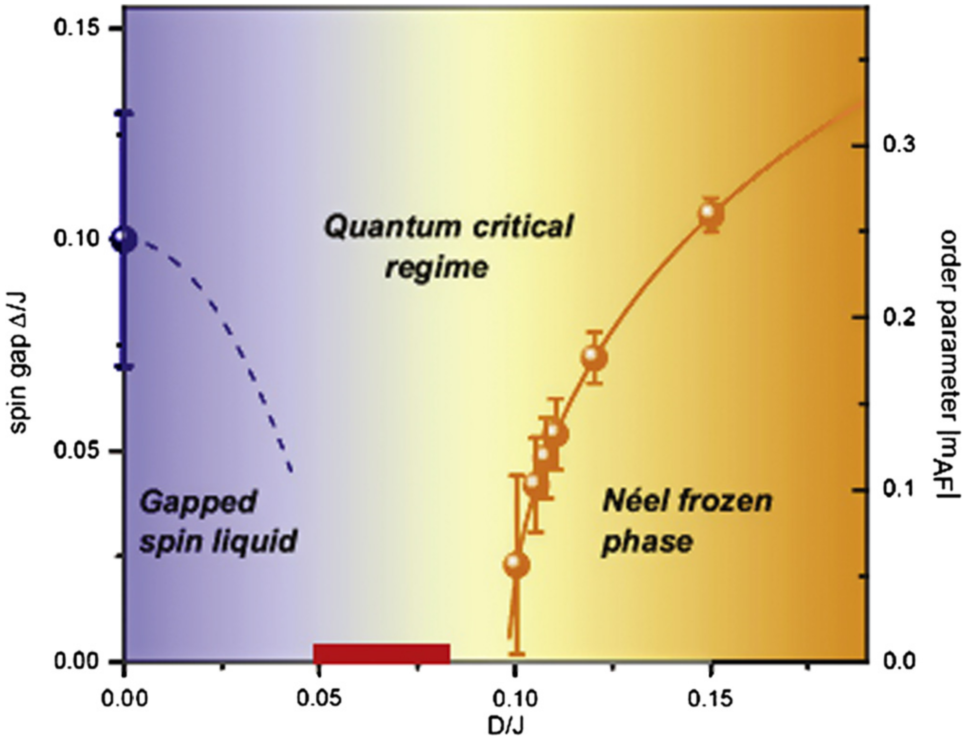
These look like encouraging signs of a QSL, but there are a few caveats…



Lack of inversion centre means Dzyaloshinskii-Moriya allowed:

$$\mathbf{D} \cdot \mathbf{S}_i \times \mathbf{S}_j$$

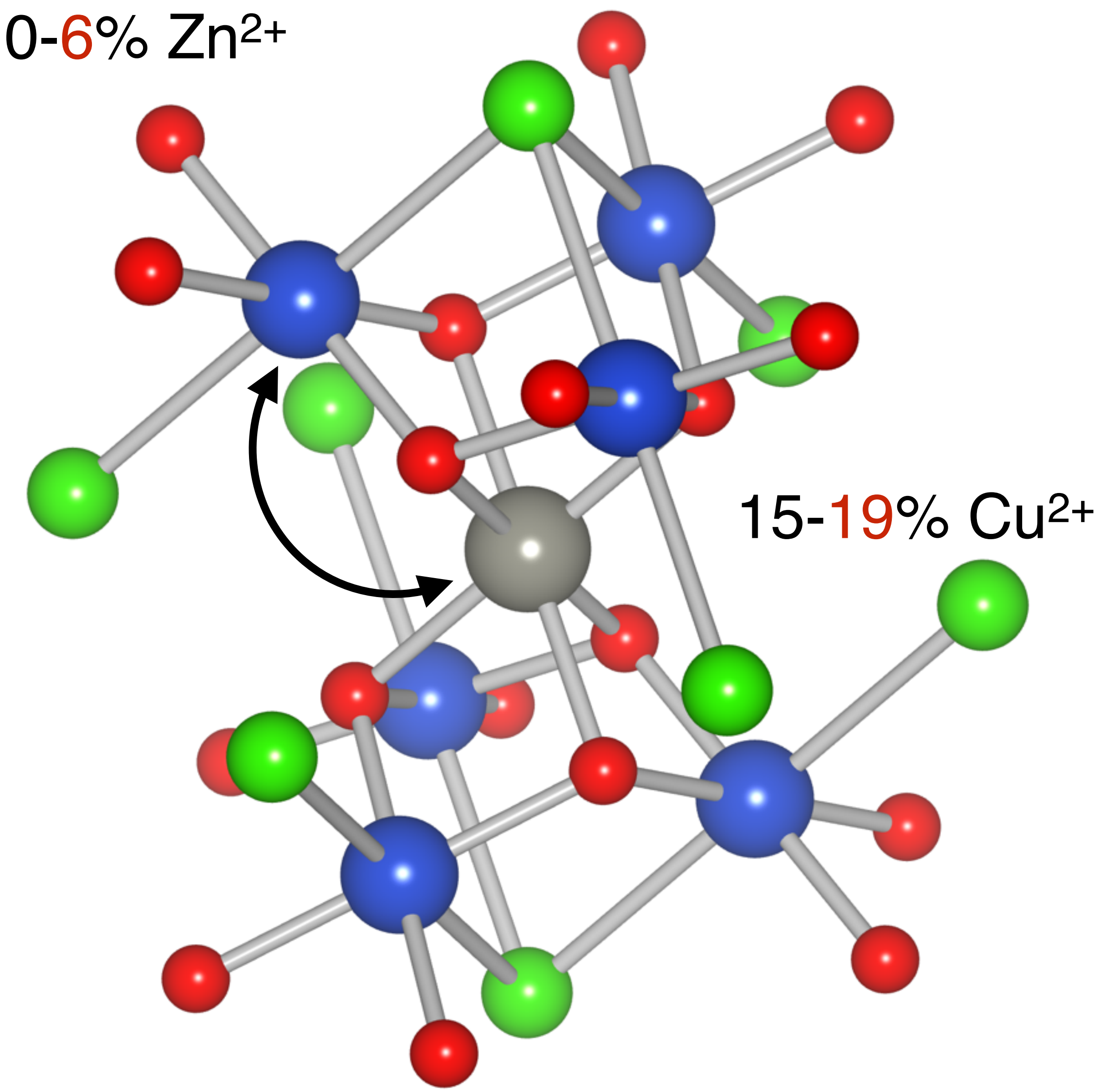
ESR suggests D_z = 15 K ~ 0.08 J



Zorko et. al. PRL **101** 026405; Bert et. al. Reflets Phys. **37** 4; Cepas et. al. PRB **78** 140405

Herbertsmithite: a true QSL?

These look like encouraging signs of a QSL, but there are a few caveats…

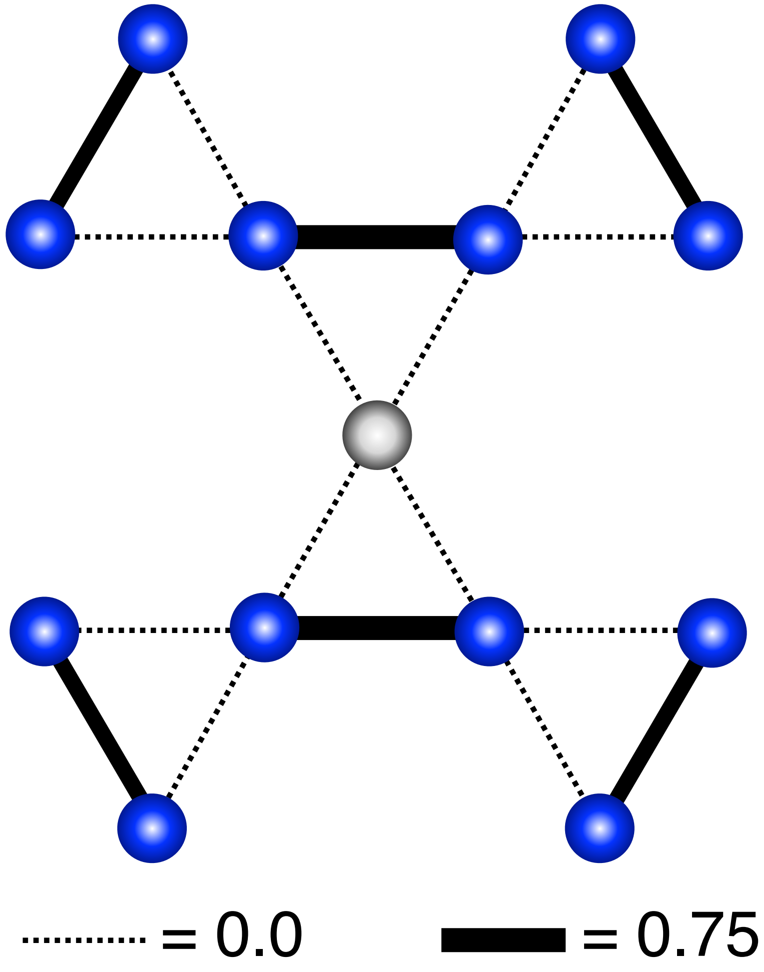


0-6% Zn^{2+}

15-19% Cu^{2+}

Freedman et. al. JACS **132** 16185
de Vries et. al. PRL **100** 157205

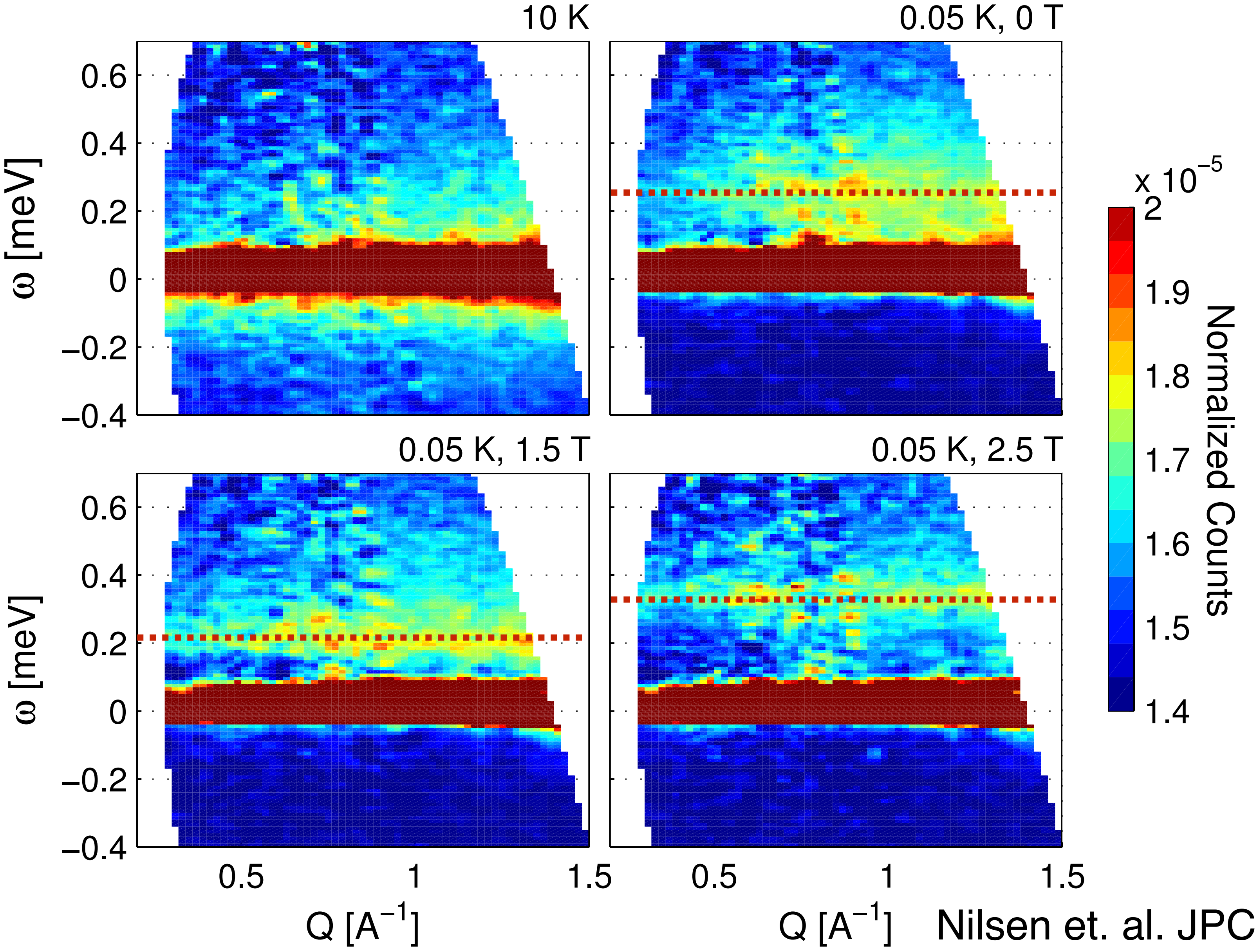
~1 %, valence bond glass



Singh, PRL **104** 177203

Herbertsmithite: low-energy excitations

Low-energy $S(Q,\omega)$ looks ungapped, although dominated by interplane defects

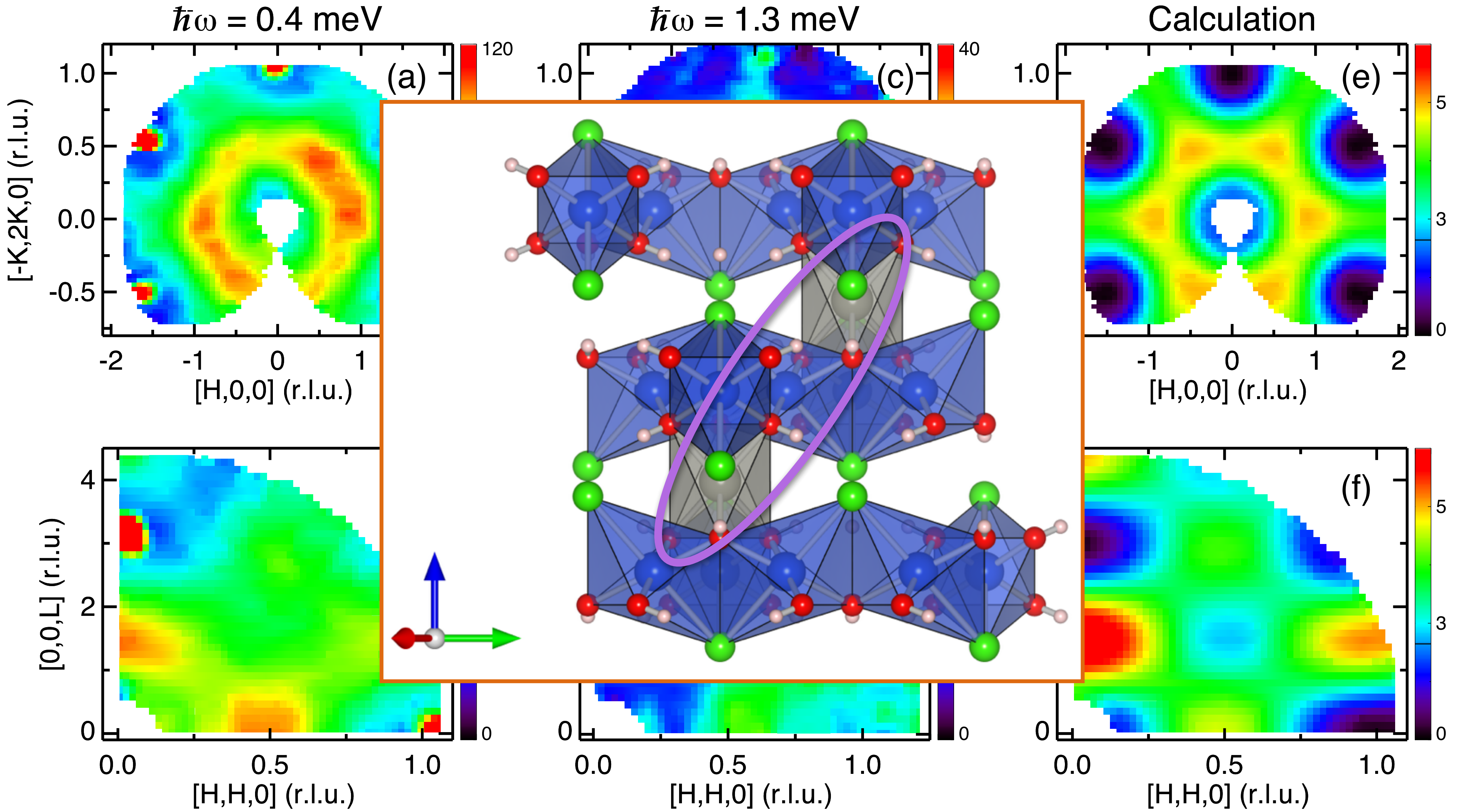


Nilsen et. al. JPCM **25** 106001

Defects weakly correlated, but can be decoupled with small magnetic field.

Herbertsmithite: low-energy excitations

Single crystals add some detail to this picture.

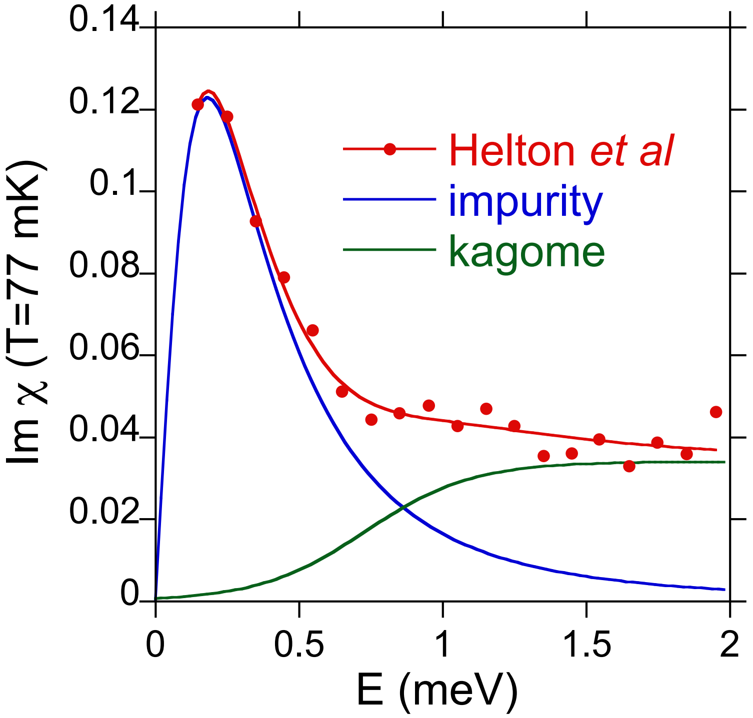


Han et. al. PRB **94** 160409

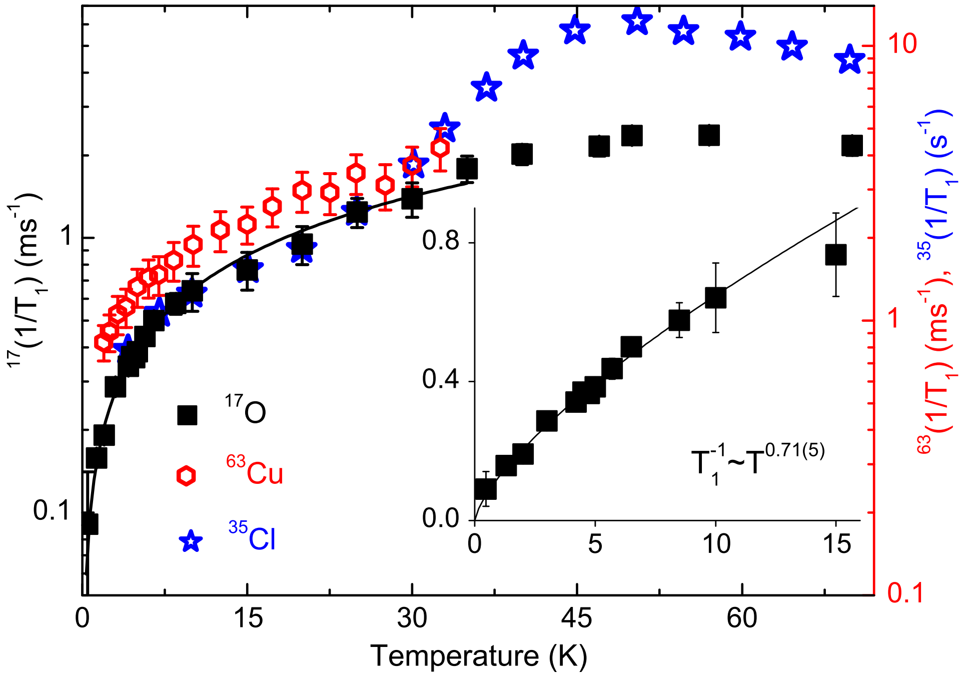
Antiferromagnetic coupling between interplane sites causes low-energy response.

Herbertsmithite: summary

1. Unclear whether spin gap is present or not - given large DM perturbation, expect gap to at least partially close.



Han et. al. PRB **94** 160409

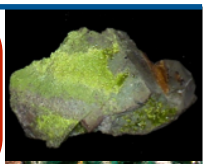
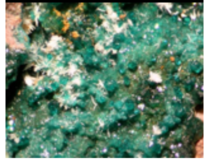


Olariu et. al. PRL **100** 087202

2. If gap is present, VBG or Z_2 QSL? Entirely depends on how many defects are present on the kagome lattice

What other states can be realised in kagome minerals?

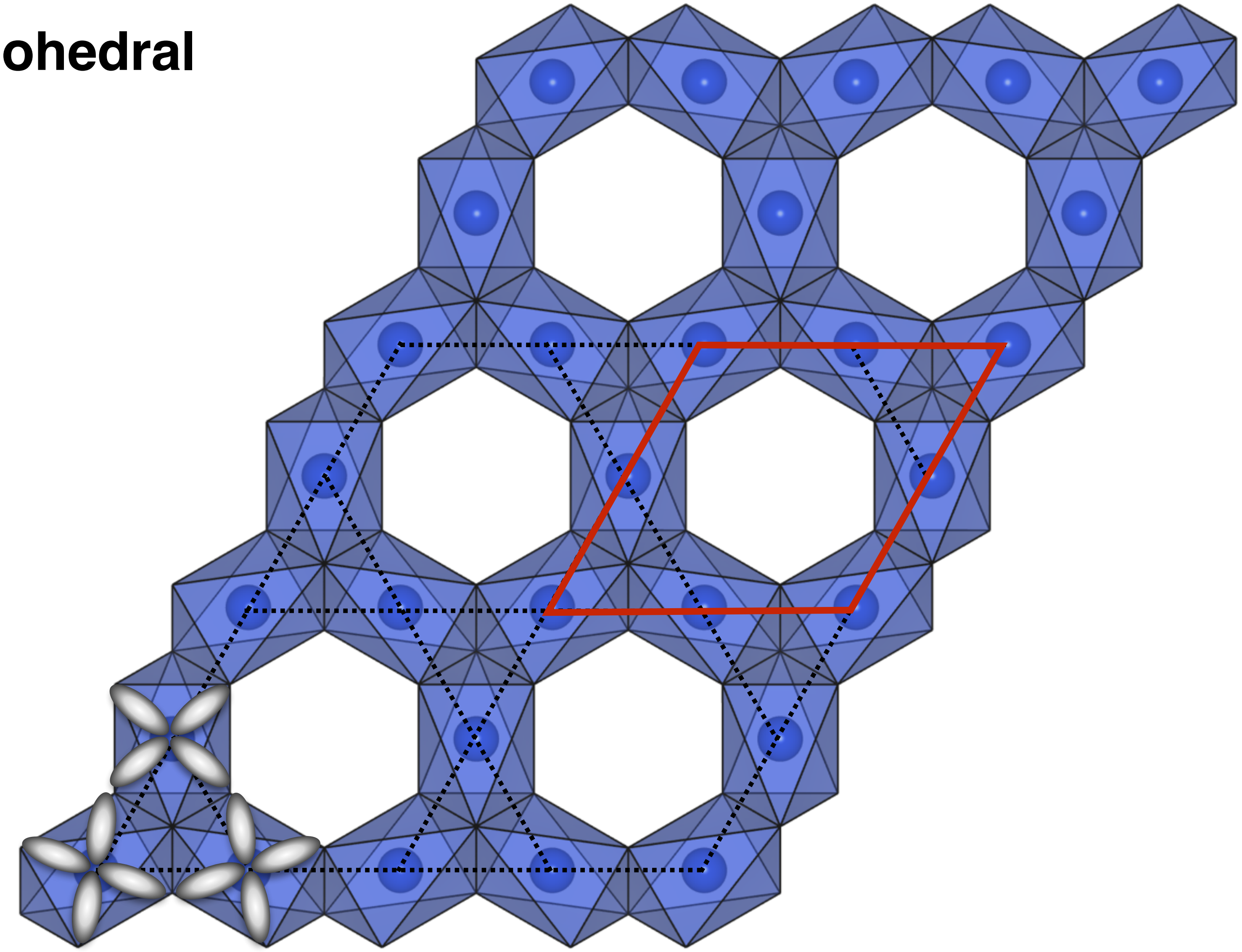
Kagome lattice materials

Material	SG	θ	Order	Reference(s)	
Volborthite $Cu_3V_2O_7(OH)_2.2H_2O$	$C2/m$	-115 K	1 K	Z. Hiroi *et. al.,* JPSJ **70**, 3377 M. Yoshida *et. al.,* PRL **103**, 077207 G. J. Nilsen *et. al.,* PRB **84**, 172401	
Herbertsmithite β-$Cu_3Zn(OH)_6Cl_2$	$R\bar{3}m$	-240 K	< 50 mK	M. P. Shores *et. al.* JACS **127**, 13462 de Vries *et. al.* PRL **103**, 237201 T. Han *et. al.* Nature **492**, 406	
$KCu_3As_2O_7(OD)_3$	$C2/m$	+13.4 K	7 K	Y. Okamoto *et. al.* JPSJ **81**, 033707	
Bayldonite $PbCu_3(AsO_4)_2(OH)_2$	$C2/c$	+49 K	< 2 K ?	Unpublished (H. Ishikawa, Y. Okamoto)	
Vesignieite $BaCu_3(VO_4)_2(OH)_2$	$C2/m$	-59 K	7 K	Y. Okamoto *et. al.,* JPSJ **78**, 033701 M. Yoshida *et. al.,* JPSJ **82**, 013702	
Edwardsite $Cu_3Cd_2(SO_4)_2(OH)_6.4H_2O$	$P2_1/c$	- 50 K	4.3 K	H. Ishikawa et. al. JPSJ **82**, 063710	
Kapellasite α-$Cu_3Zn(OH)_6Cl_2$	$R\bar{3}m$	0 K	< 50 mK	Colman *et al.*, Chem. Mater **20** 6897 Fåk *et. al.* PRL, **109** 137208	
$Cu_3Zn(OH)_6(SO_4)$	$P2_1/a$	- 79 K	< 50 mK	Y. Li et. al., cond-mat:1310.2795	

Kagome materials: Jahn-Teller

Cu^{2+} is strongly Jahn-Teller active. Orbital can be inferred from local geometry

Trigonal/rhombohedral



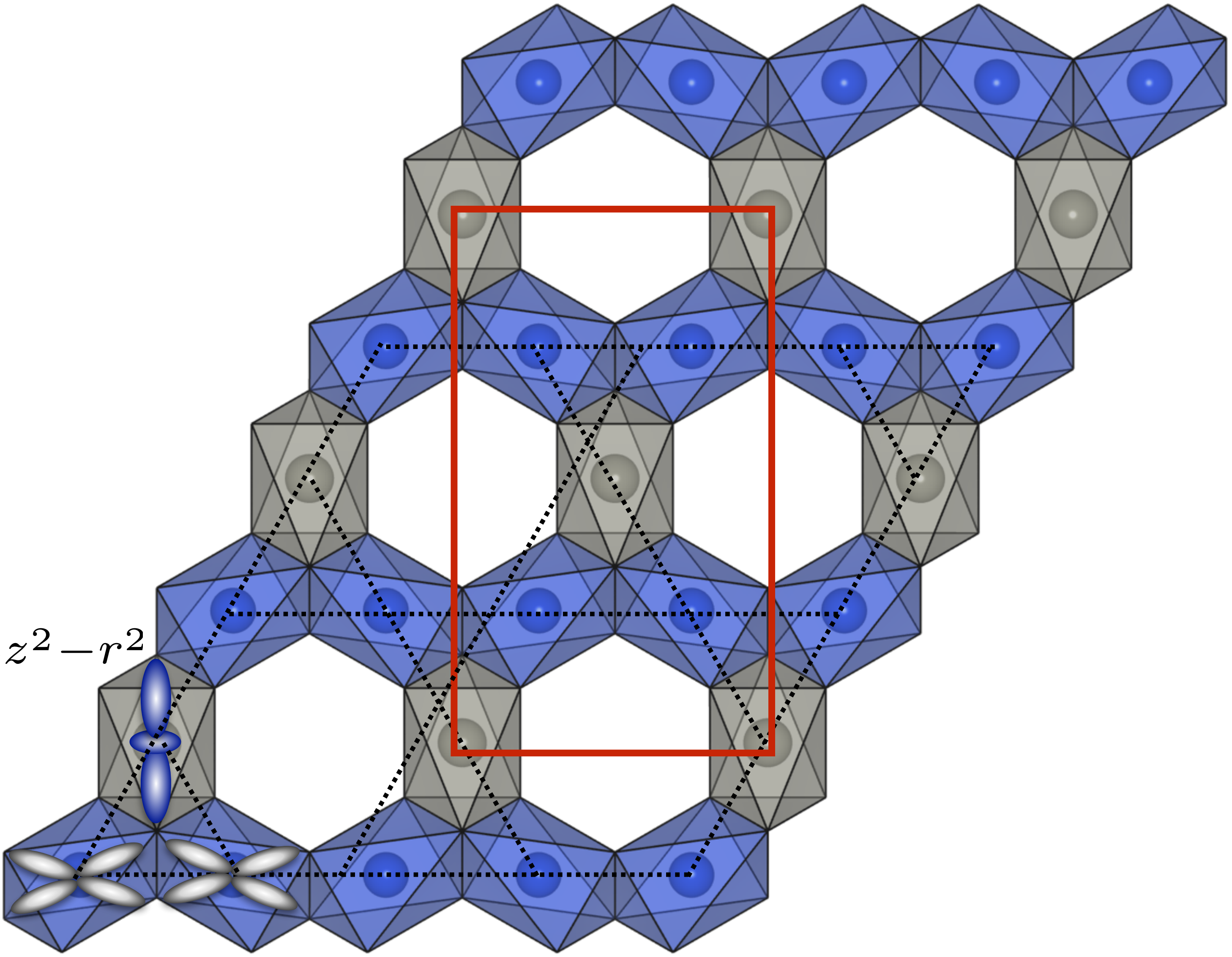
Uniform orbital order

$d_{x^2-y^2}$

Kagome materials: Jahn-Teller

Cu^{2+} is strongly Jahn-Teller active. Orbital can be inferred from local geometry

Monoclinic



$d_{3z^2-r^2}$

Alternating orbital order

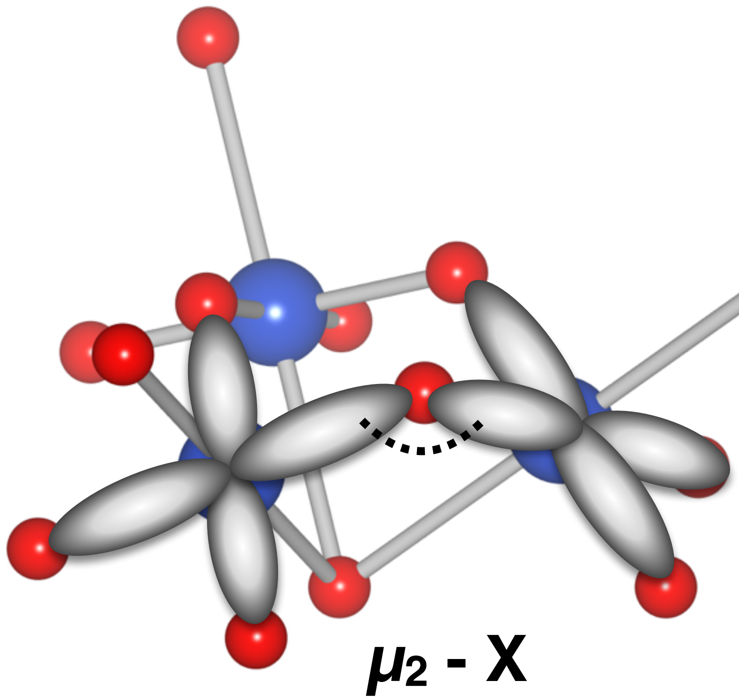
$d_{x^2-y^2}$

15 different combinations

Superexchange in Cu^{2+} minerals

The orbital order not only leads to an anisotropy in the nearest neighbour bond distances, but also to fundamentally different exchange pathways:

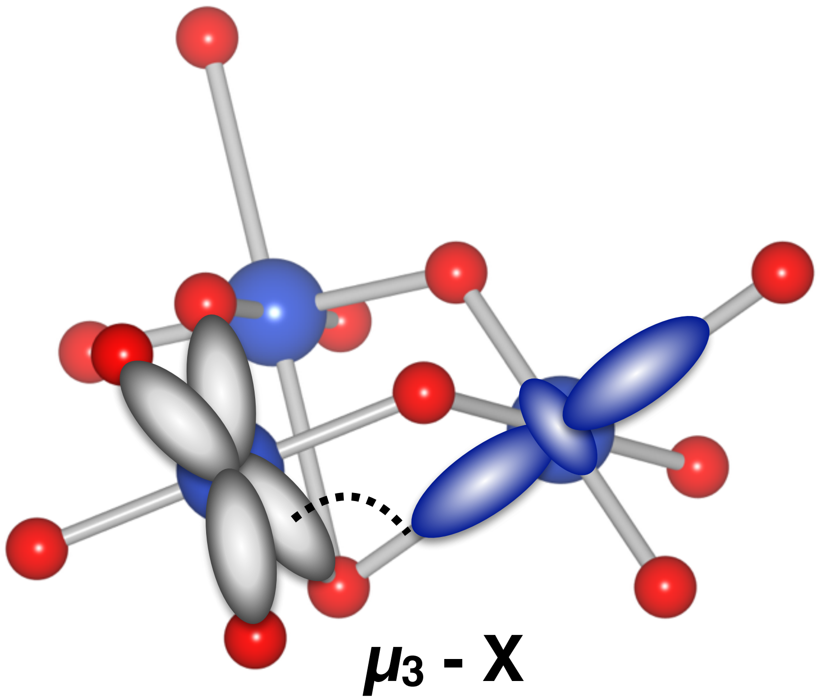
e. g. uniform



$\angle Cu^{2+}$ - X - Cu^{2+} ~ 120°

Antiferromagnetic

e.g. alternating



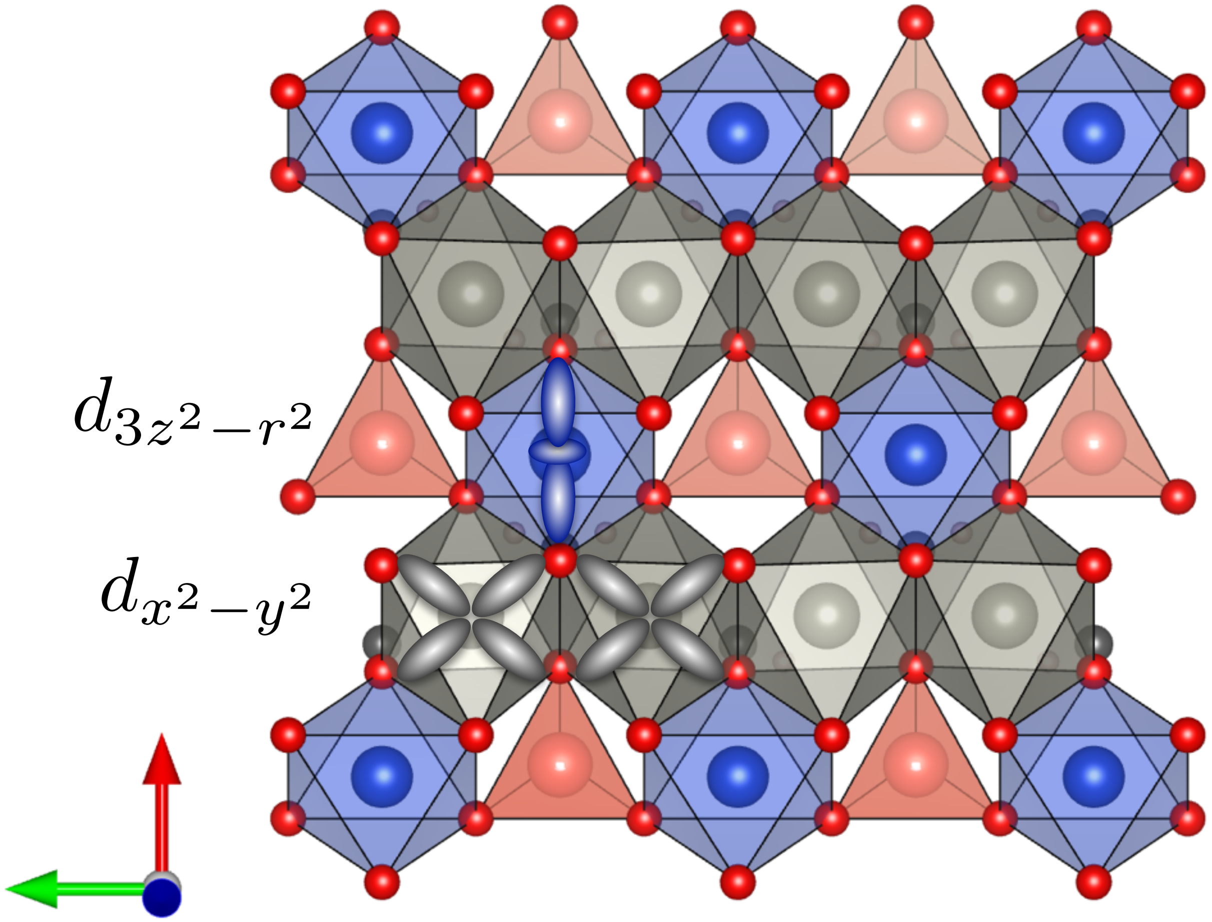
$\angle Cu^{2+}$ - X - Cu^{2+} ~ 90-105°

Can be ferromagnetic

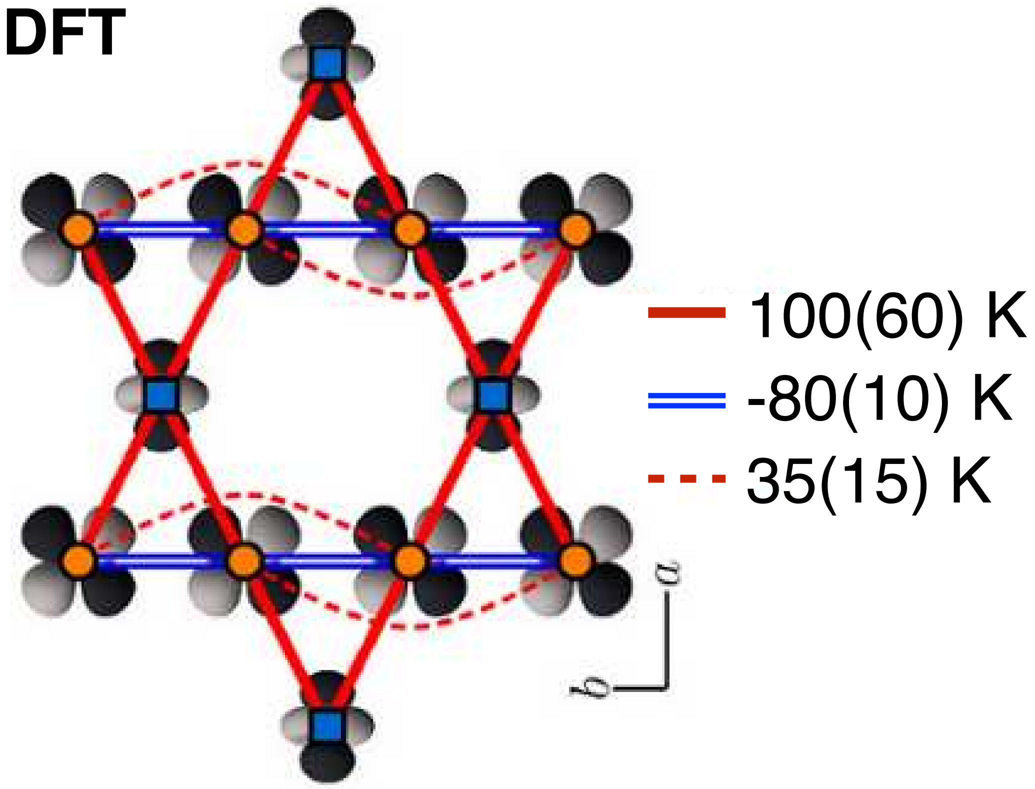
Yoon et. al. Inorg. Chem **44** 8076

Volborthite: $Cu_3V_2O_7(OH)_2.2H_2O$

C2/m, θ = -115 K , orbital order



Hiroi et. al. JSPJ **70** 3377

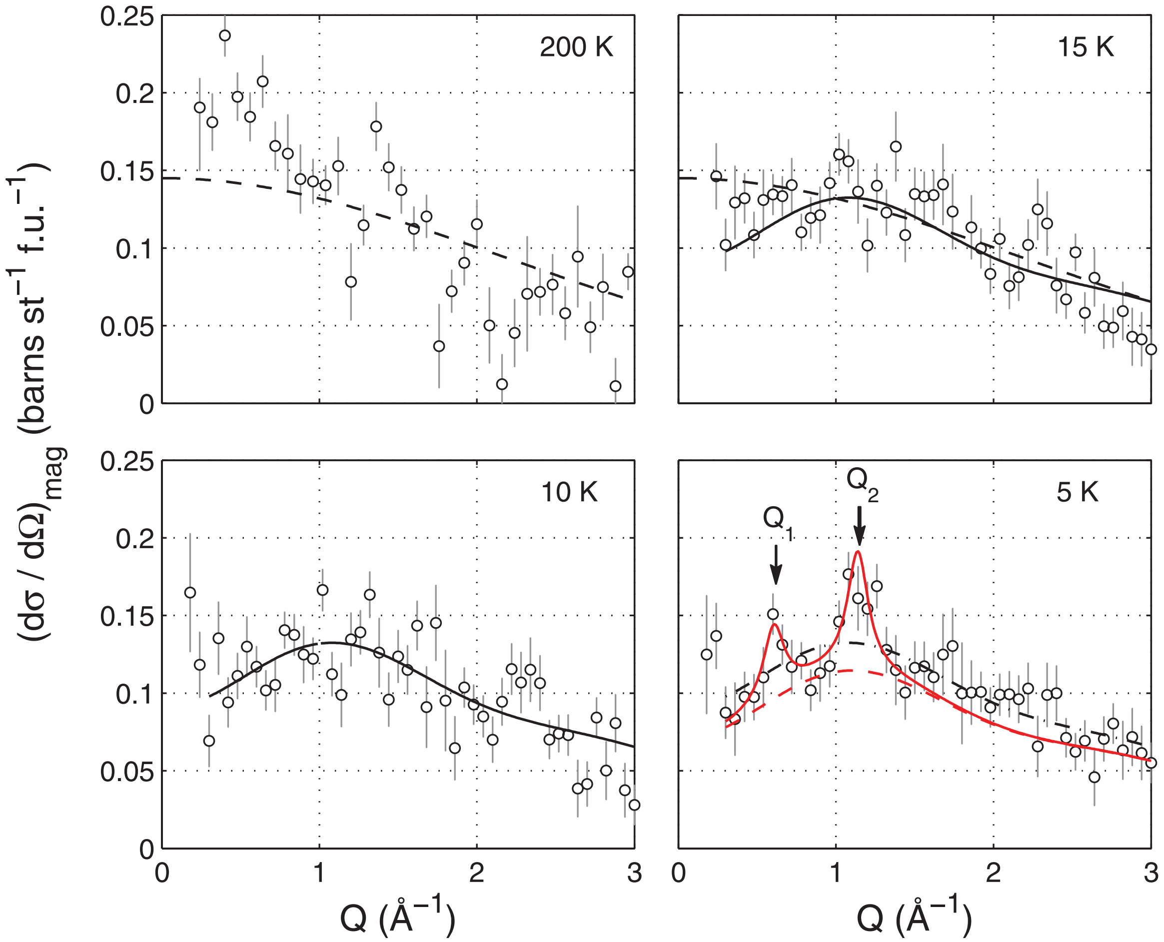


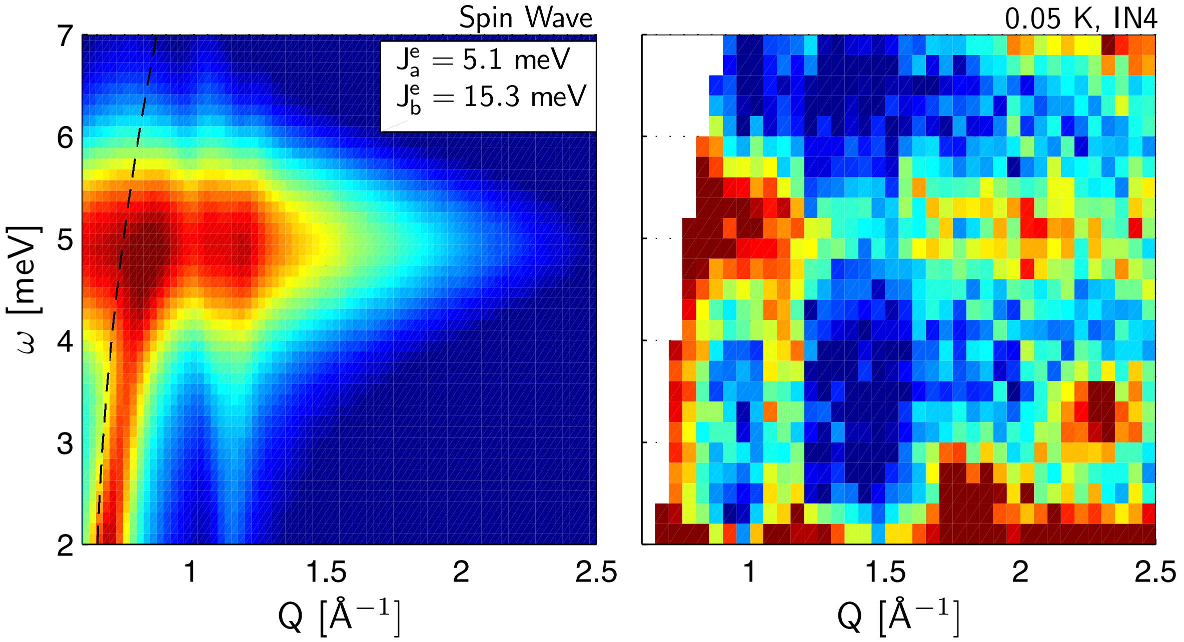
Janson et. al. PRB **82** 134434

DFT calculations consistent with naive assumptions from coordination of Cu^{2+}: looks like volborthite can be described as coupled spin chains…

Volborthite: powder

… however, despite being far away from the ideal kagome lattice antiferromagnet, volborthite shows no order down to low T





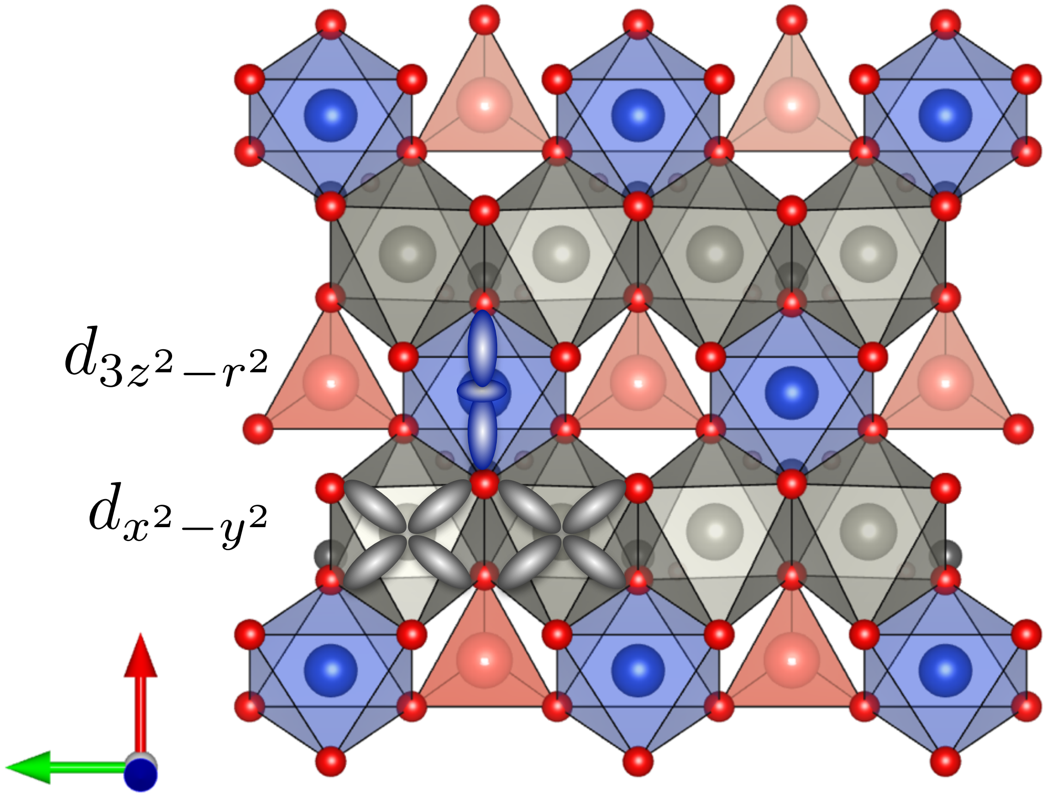
GJN et. al. PRB **84** 172401

Only weak short-range order associated with incommensurate positions Q_1 and Q_2, spin-wave-like spectrum at 50 mK. Order not captured by chain model.

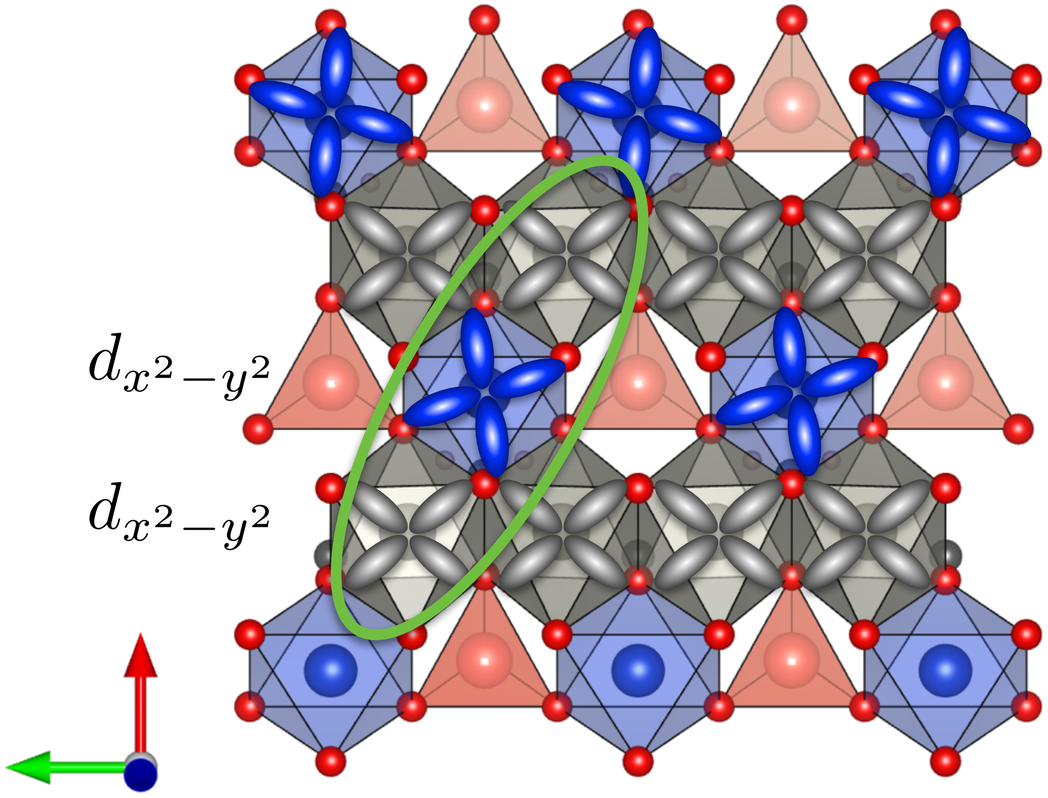
Volborthite: orbital order

A twist in the tale: high-quality powders and single crystals show an additional structural transition near room temperature:

T > 310 K C2/m



T < 310 K C2/c

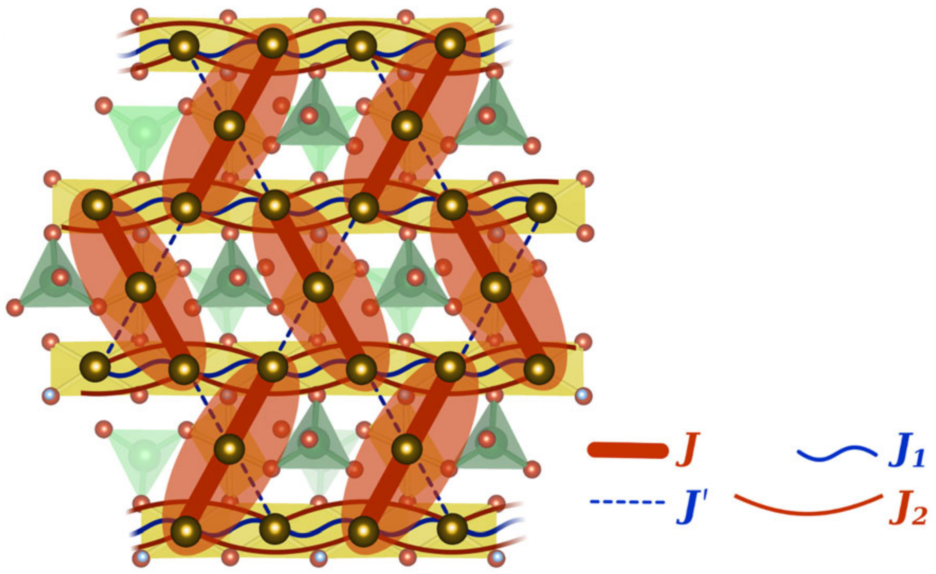


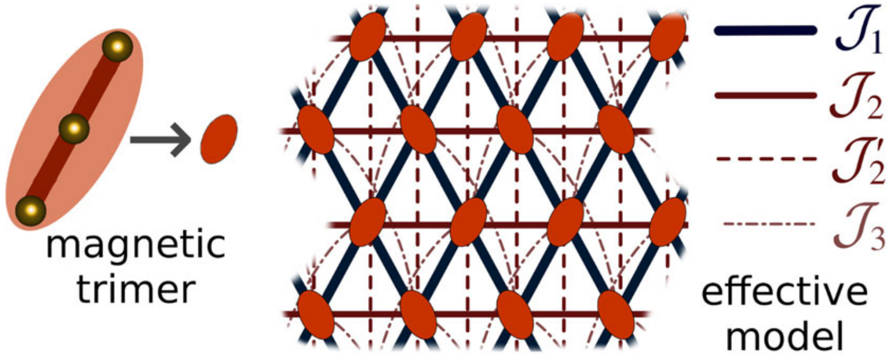
This transition is an “orbital switching” — a very rare case for Cu^{2+} in an inorganic material, where such transitions usually occur at high T.

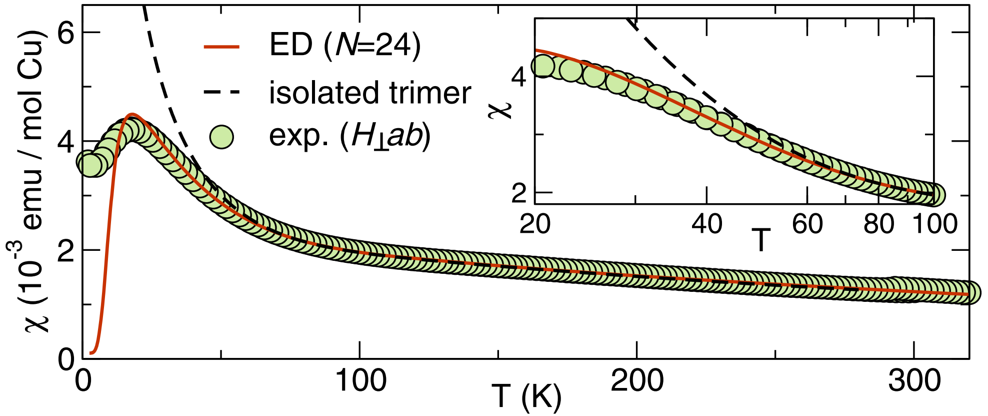
Yoshida, GJN et. al. Nature Comms. **3** 860

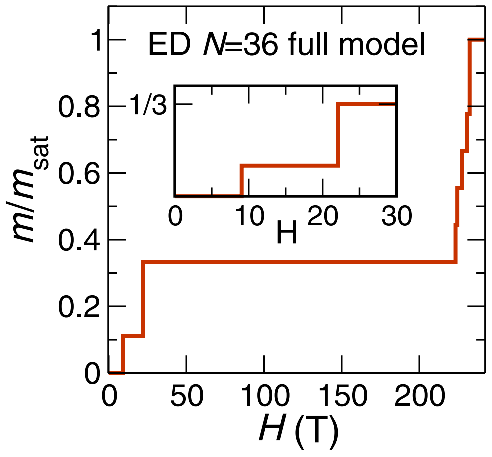
Volborthite: current status

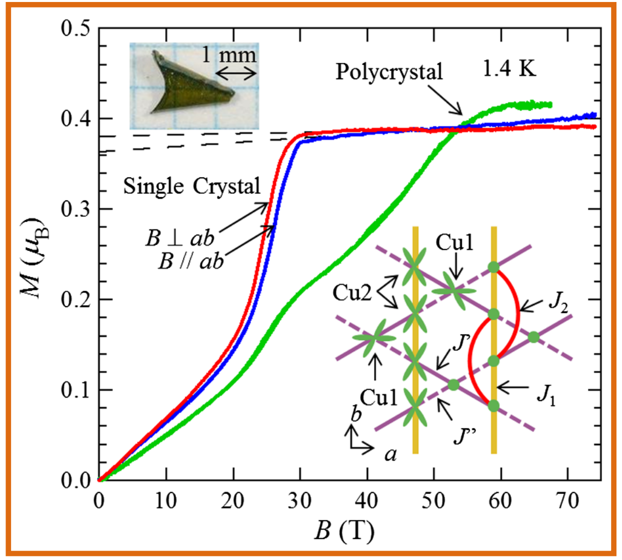
Interactions within trimers formed by orbital order dominate, resulting in effective triangular lattice system









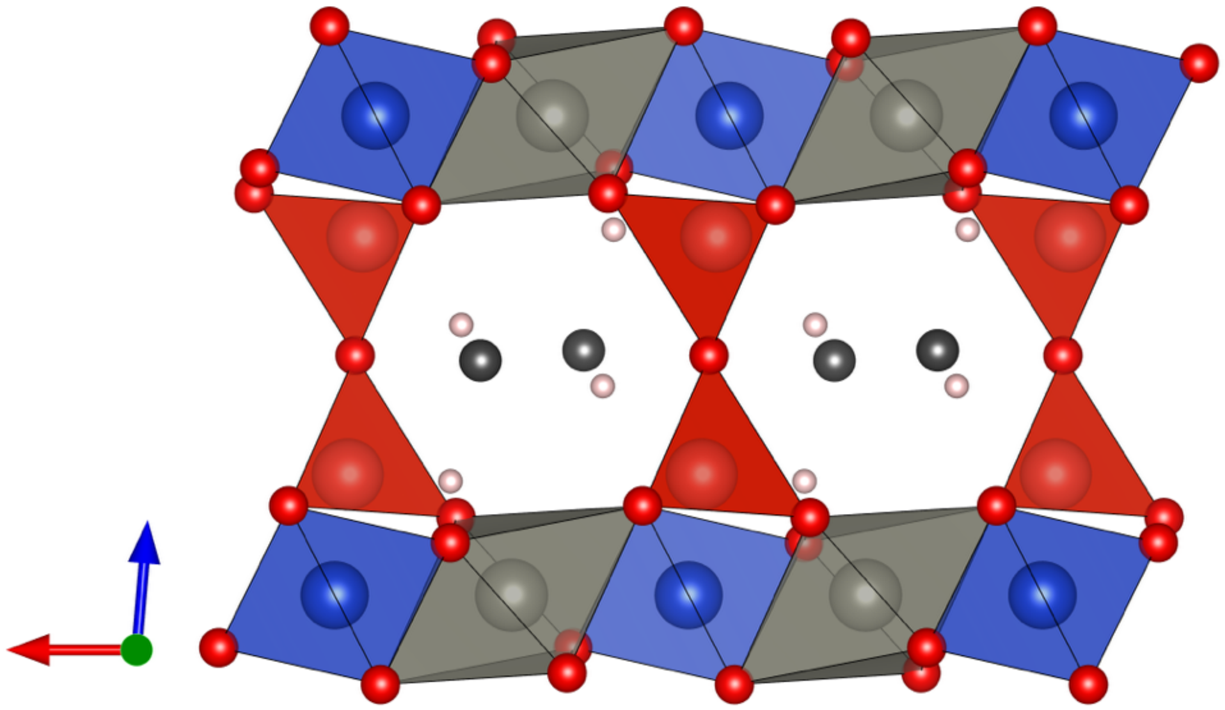


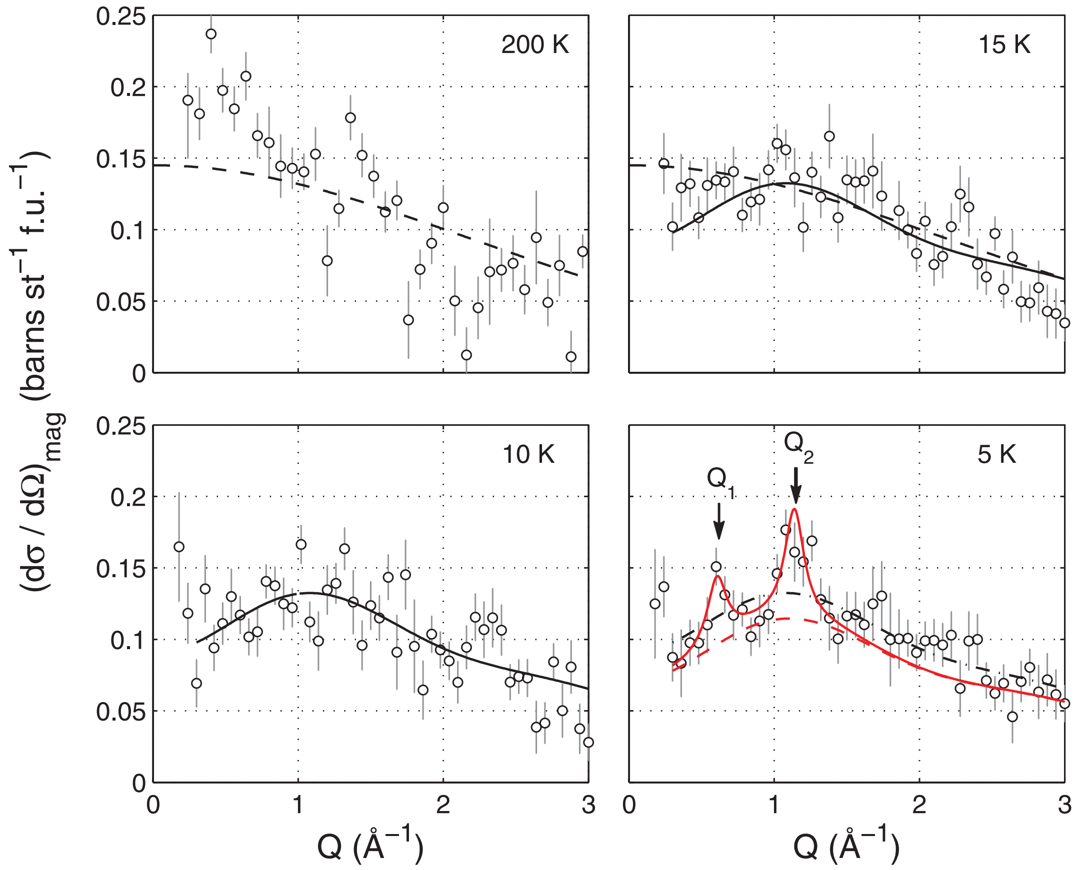
Janson et. al. PRL **117**, 037206

Interesting bond nematic phase formed from condensation of two-magnon bound states at low H…

Revisiting powder data:

Powders do no undergo “orbital switching” because of disorder (possibly related to disorder of interplane H_2O)



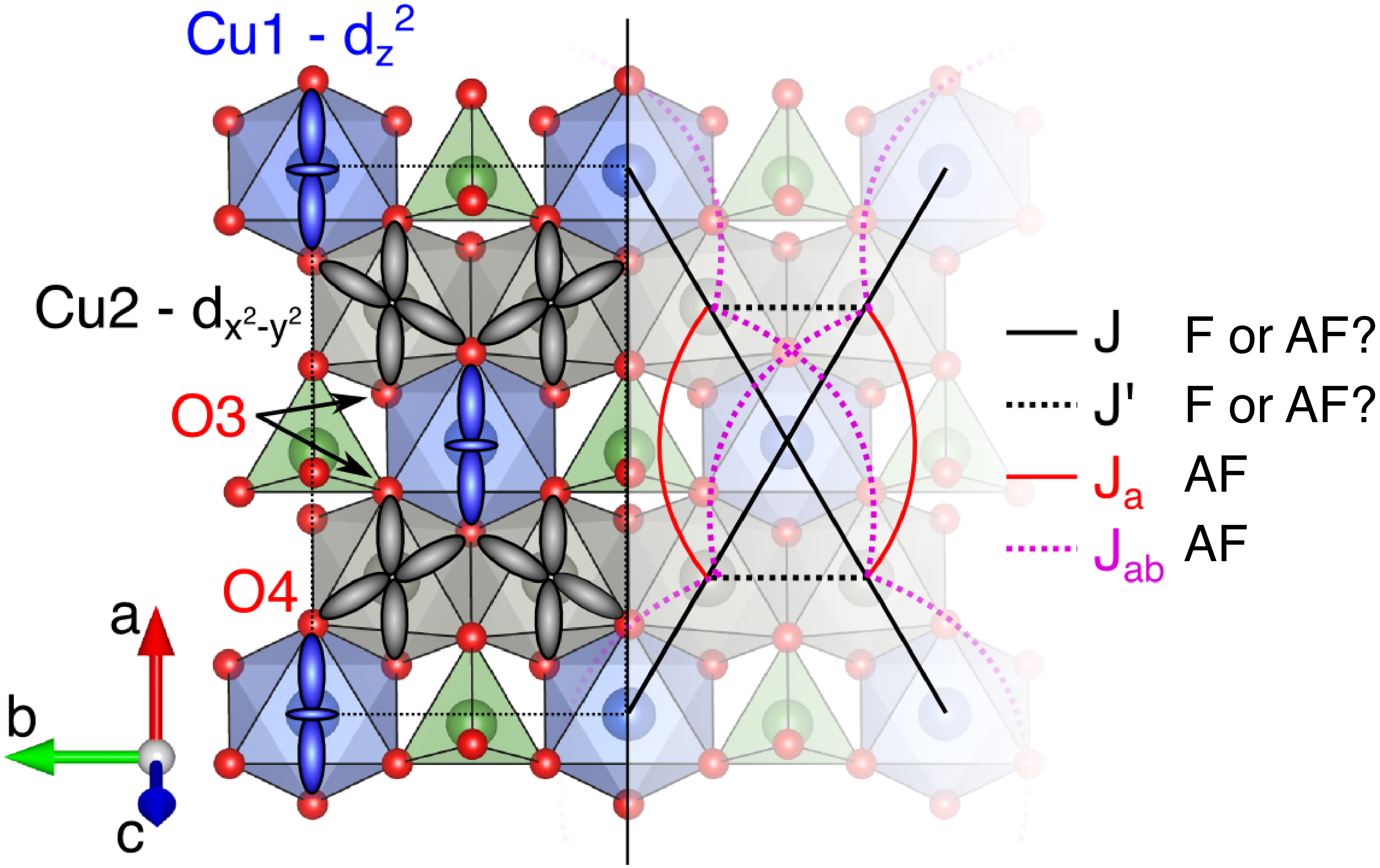


Diffuse scattering can thus be interpreted as small clusters (mostly dimers) + short-range magnetic order…

$KCu_3As_2O_7(OD)_3$ (KCAO)

Similar orbital order to volborthite, but different orbital orientations:

C2/m, θ = +14 K, T_N = 7.1 K

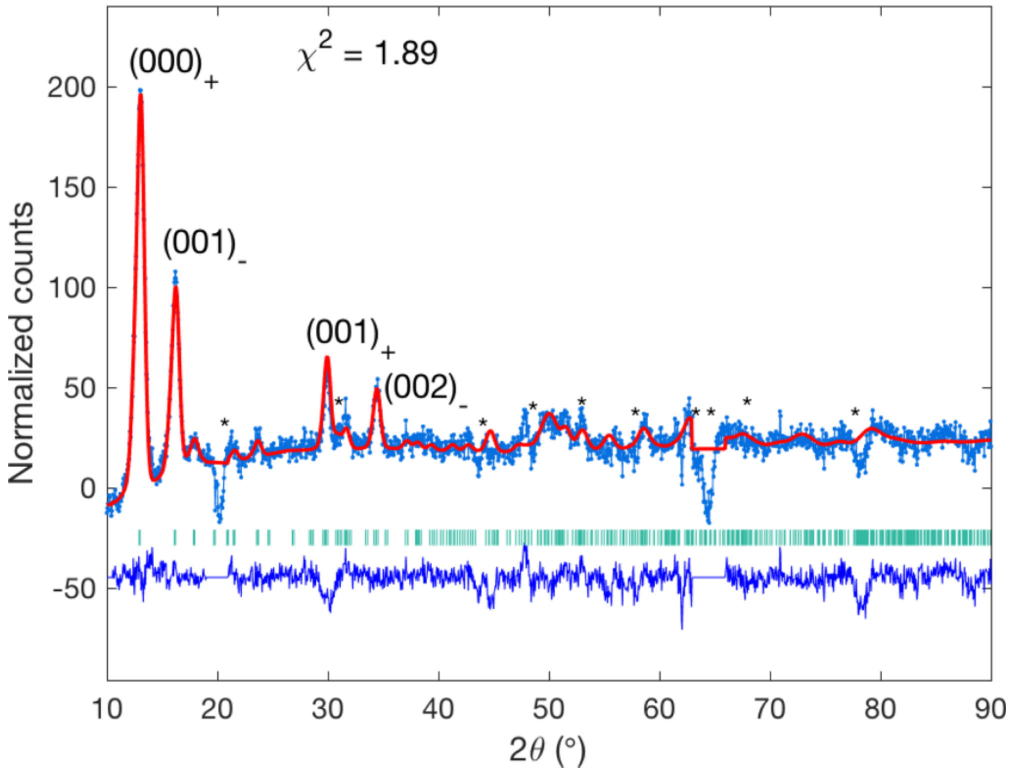


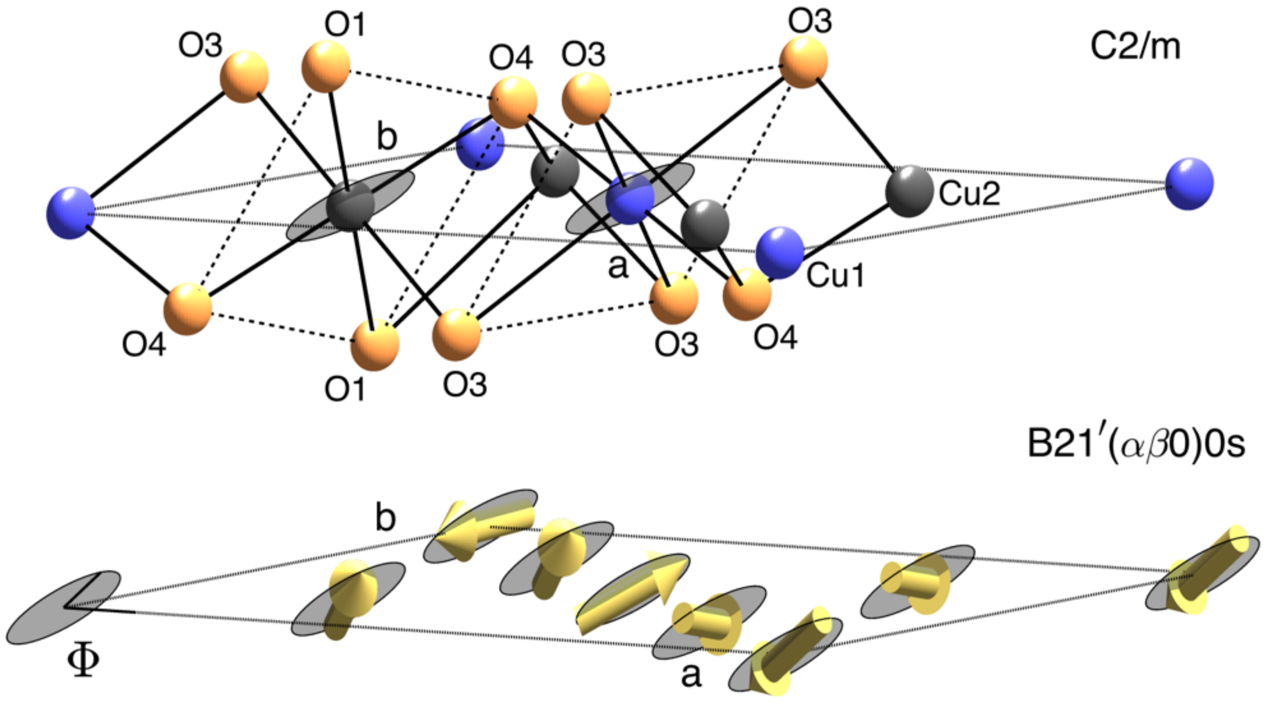
Okamoto GJN et. al. JPSJ **81**, 033707

Magnetic structure

Unlike volborthite, magnetic order at T ~ θ/2 in a helical magnetic structure with propagation vector **k** = (k_x 0 k_z) - there must be some frustration!

D20, 1.8 K

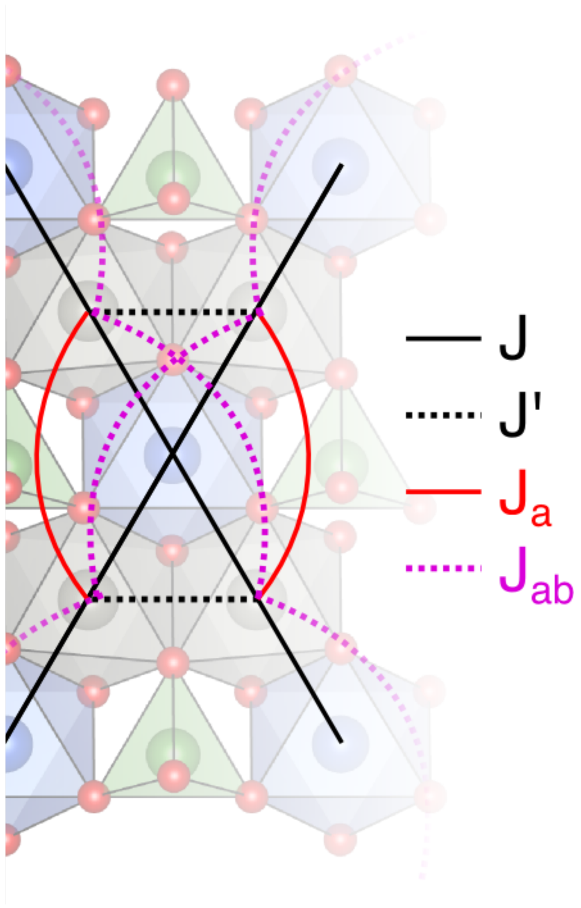




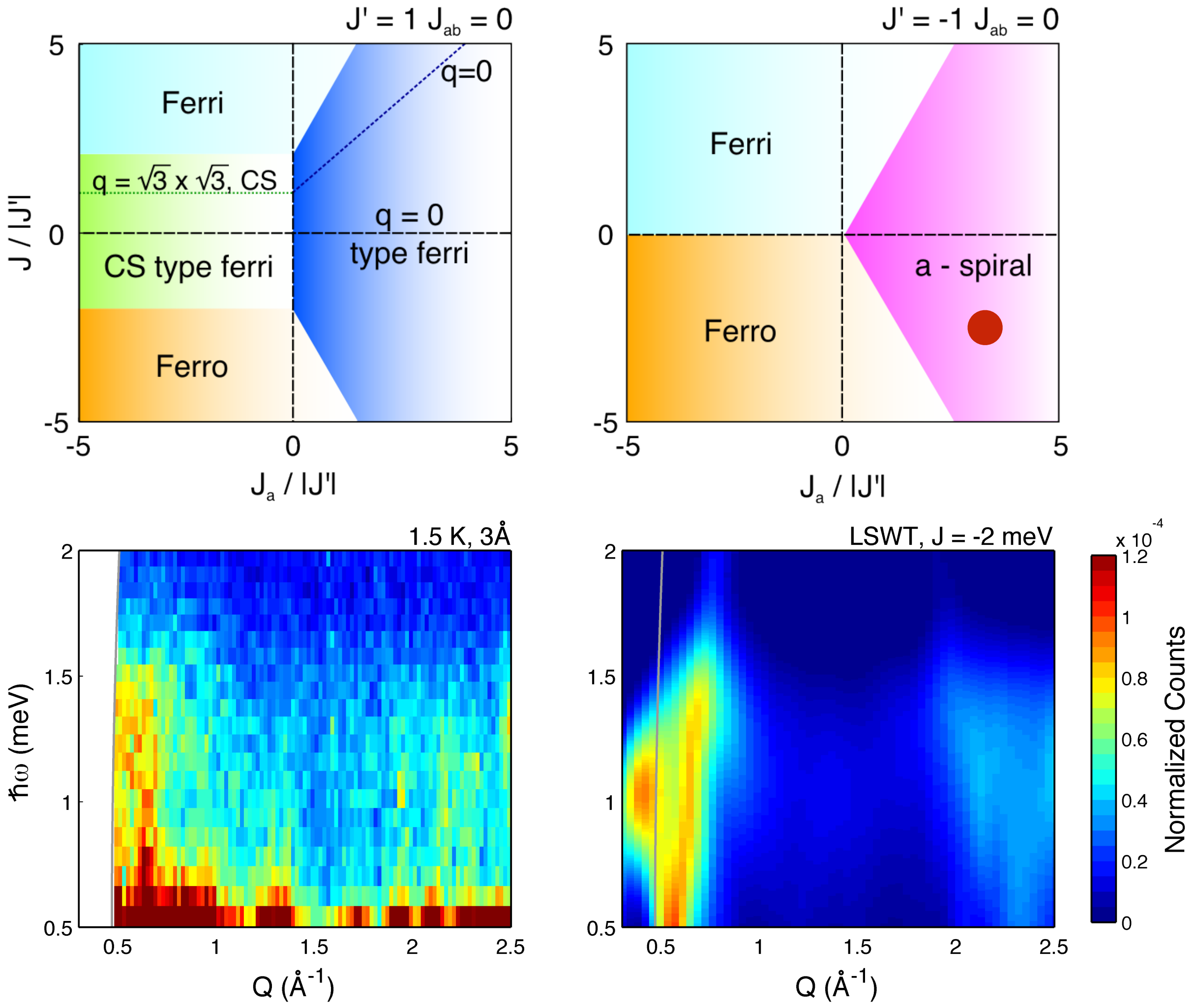
GJN et. al. PRB **89** 140412 (R)

$KCu_3As_2O_7(OD)_3$ Hamiltonian

Unlike volborthite, magnetic order at T ~ θ/2 in a helical magnetic structure with propagation vector **k** = (k_x 0 k_z) - there must be some frustration!



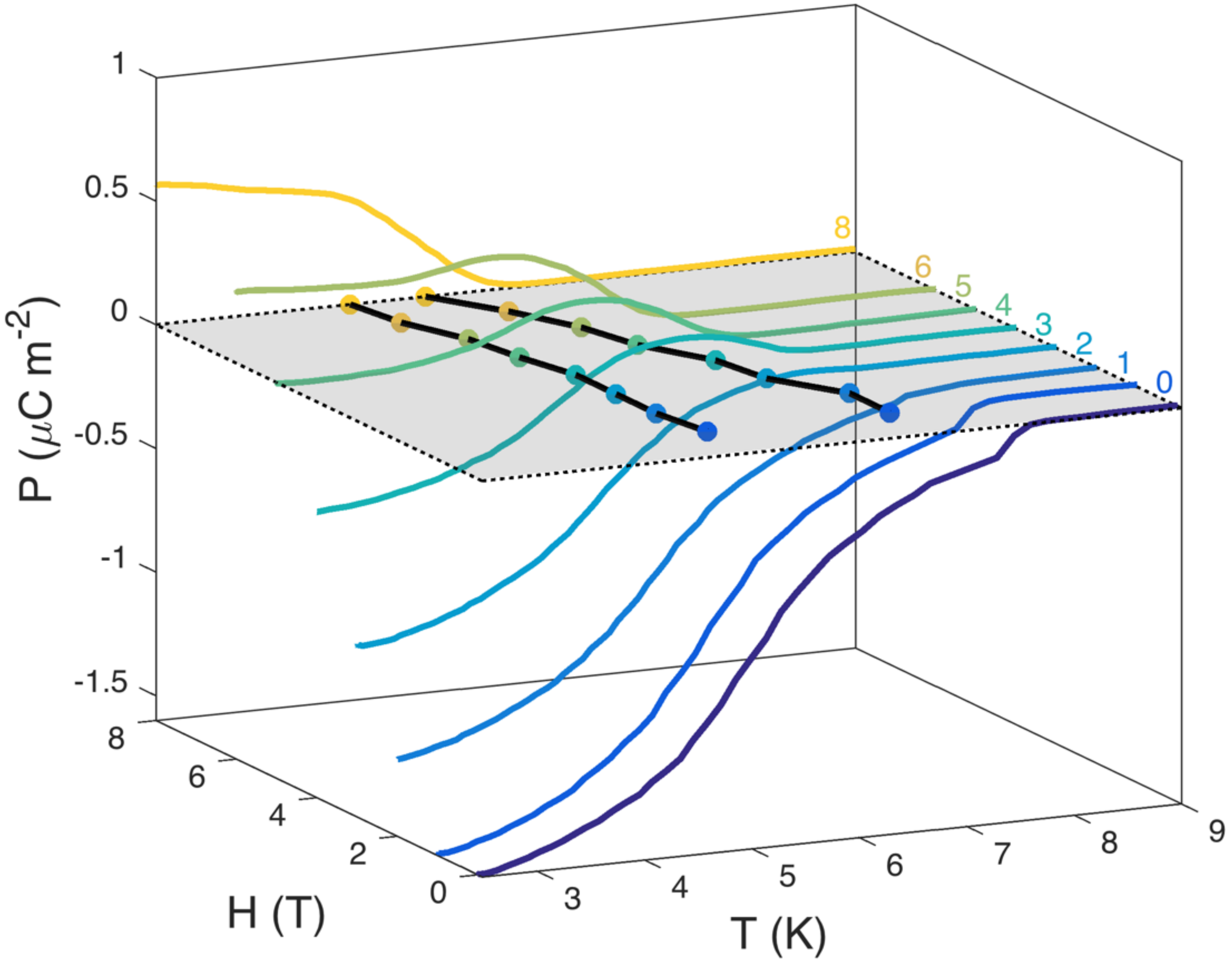
GJN et. al. PRB **89** 140412



Both nearest neighbour interactions ferromagnetic! Frustration from antiferromagnetic further neighbour couplings.

Multiferroicity

The polar point group (21′) of the magnetic structure permits a ferroelectric polarization:



GJN et. al. PRB **95**, 214415

Conclusions

- The kagome lattice antiferromagnet is the premier magnetic model for new quantum many-body states
- Most kagome lattice materials studied so far have been Cu^{2+} minerals, which allow for several perturbations beyond the nearest neighbour coupling
- Among these:
  - Herbertsmithite is very close to the ideal kagome lattice antiferromagnet
  - Volborthite shows orbital reorientation and trimerization
  - $KCu_3As_2O_7(OD)_3$ is far away from QSL, but still frustrated and multiferroic
- These large differences in behaviour can be traced back to the orbital occupation and consequent superexchange pathways
- Despite the difficulty realising a QSL in kagome minerals, new frustrated behaviours often result because of the topology of the kagome lattice
- Future work: other candidates, charge doping…

We’re not at the top yet, but at least now
we can enjoy the view

Collaborators

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Hiroyuki Yoshida…

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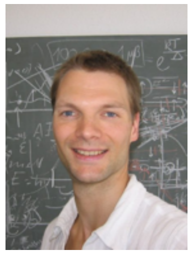
Virginie Simonet
Claire Colin



Henrik Rønnow

… and thank you for your attention!