Exotic Orders from Geometrical Frustration

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With:

Fa Wang (UC Berkeley)

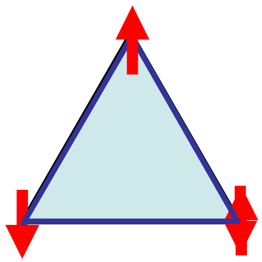
1. **Quantum and Classical Spins on the Spatially Distorted kagome Lattice: Applications to Volborthite**
   Fa Wang, AV, **Y. B. Kim**, *Phys. Rev.B. 76, 094421 (2007).*

2. **Spin phonon induced colinear order and magnetization plateaus in triangular and kagome antiferromagnets**
   Fa Wang and AV, arXiv:0709.3546

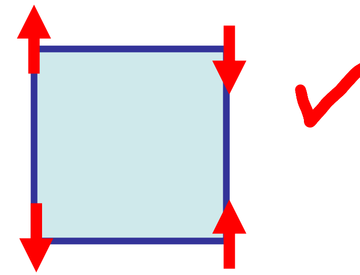
$$: *Sloan Fellowship, Hellman Fund, DOE-LBNL (Quantum Materials), DARPA, NSF- Career.*

Geometric Frustration

- Frustration ~ unable to simultaneously optimize all energetic requirements.

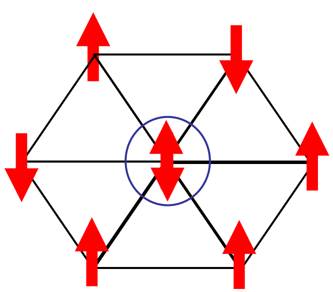


$$E = J \sum_{i,j\,\mathbf{neighbors}} S_i S_j$$

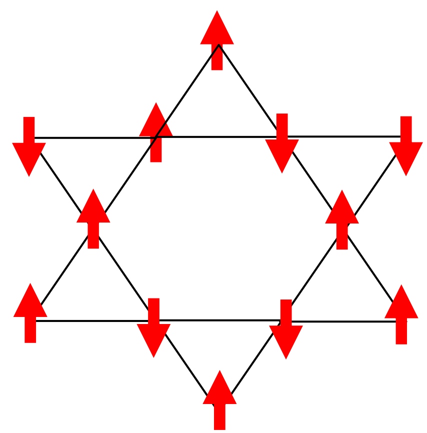


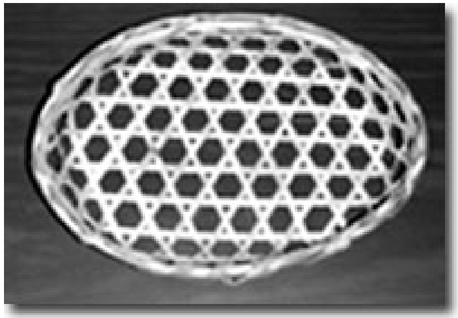
$$J > 0, S_i = \pm 1$$ (Classical Spin)

Triangular Lattice:
#of ground states= $e^{0.323\mathbf{N}}$
(N sites)



Kagome Lattice: $e^{0.502\mathbf{N}}$





Frustration leads to (classical) Degeneracy.

Geometrical Frustration in ICE

[Contribution from the Chemical Laboratory of the University of California]

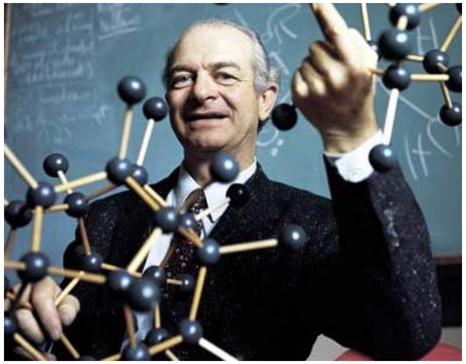
The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K.

By W. F. Giauque and J. W. Stout

Residual Entropy of Ice (1936): $S_0 = 0.82 \pm 0.05\,\mathbf{cal/mol\ ^oK}$

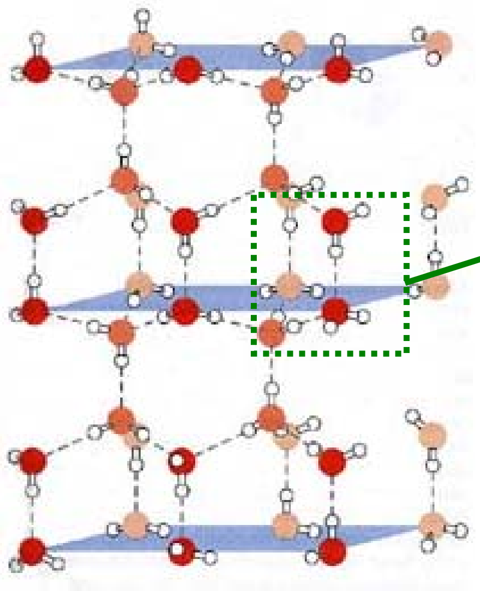
Would have expected that as T→0, unique ground state, Entropy → 0.

Geometrical Frustration in Ice
Pauling's Solution:

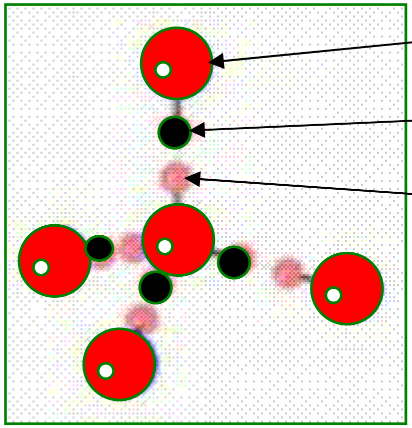


$S_0 = 0.82 \pm 0.05\,\mathbf{cal/mol\ ^oK}$

Structure:



Bernal Fowler Rules – 2 **H** near, 2 **H** far.



Allows 6 out of 2x2x2x2=16 possible **H** configurations.

Idea: **Hydrogens** remain disordered giving entropy

Pauling's estimate (N H_2O): $\Omega = 2^{2\mathbf{N}} \times \left(\frac{6}{16}\right)^{\mathbf{N}}$

$$S = \left(\frac{R}{\mathbf{N}}\right)\log\Omega$$

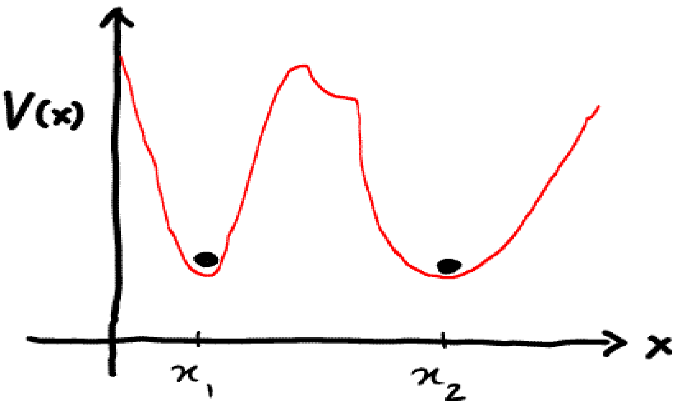
$S_{Pauling} = 0.806\ \mathbf{cal/mol\ ^oK}$

(In other Ice structures, **H** orders.)

Geometric Frustration & Relief

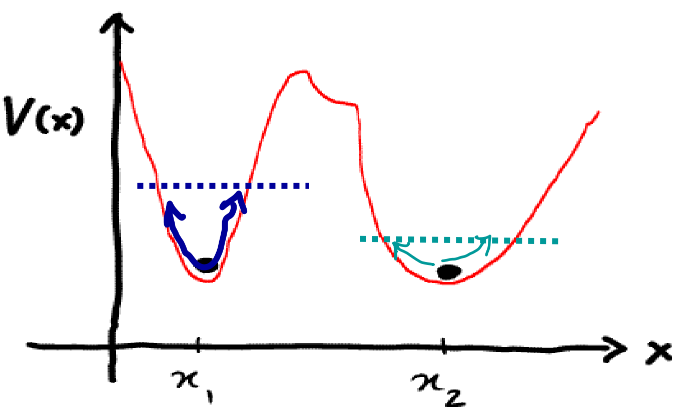
Outline

1. Frustration relief by residual interactions
   - *eg.* complex orders from lattice couplings
   - applications? (multi-ferroics)
   - *Here* – $CuFeO_2$



Classically degenerate

2. Selection by quantum/thermal fluctuations
   - *eg.* supersolid order
   - *Here* – distorted Kagome: Volborthite



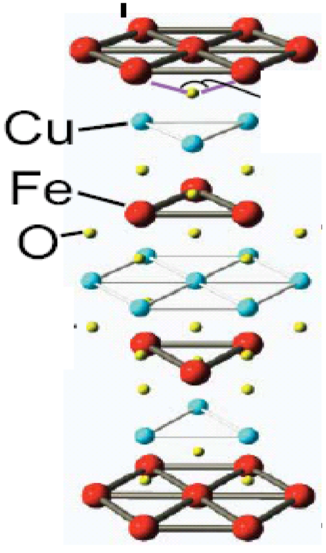
3. Quantum spin-orbital liquids.
   - *Here* – new slave particle theory

Strong tunneling

$CuFeO_2$:An unusual triangular AFM

<u>Delafossite Structure</u> $R\bar{3}m$

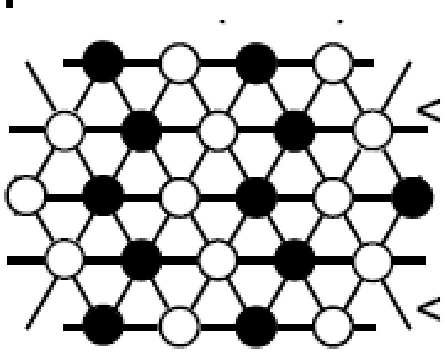
- Triangular layers of magnetic Fe^{3+} ions; S=5/2, L=0.
- Non-magnetic Cu^{+}

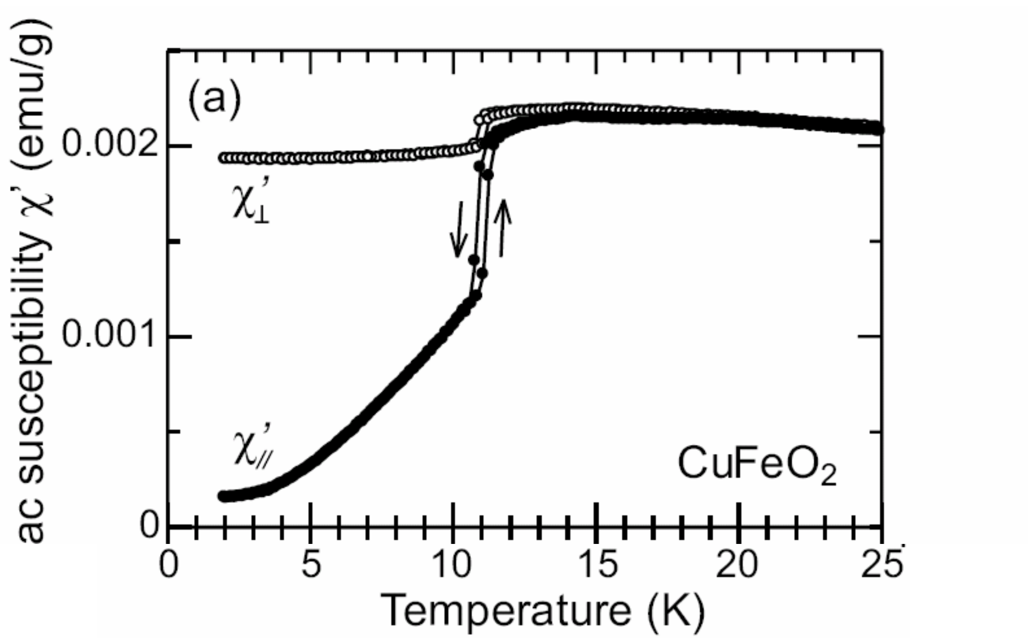


Isotropic magnetic susceptibility (expect 120^{o} state):

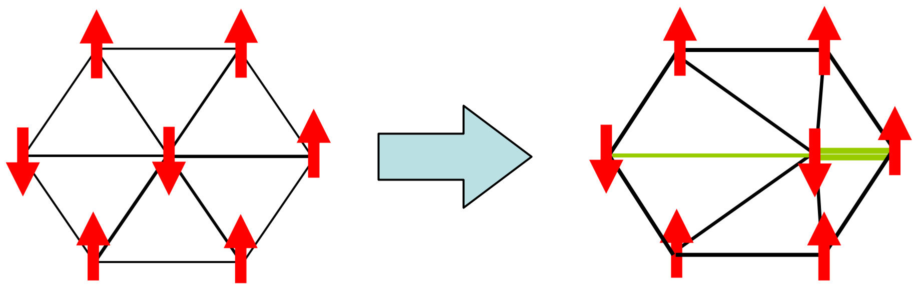
BUT

Colinear ground state with zig-zag pattern below 11K





Frustration and Relief - Lattice coupling



$$E = \sum_{i,j\,\mathbf{nbrs}} (J + \partial_r J \cdot [\delta r_i - \delta r_j]) S_i S_j + K \sum_i \delta r_i^2$$

Restoring force

Change in J

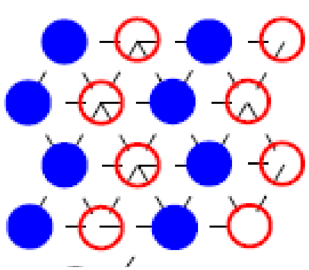
Tchernyshyov et al., Penc et al., Bergmann et al. for pyrochlore

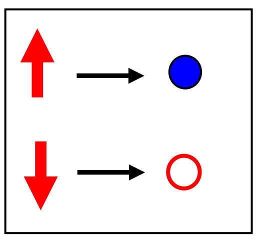
Ising antiferromagnet on the triangular lattice

More realistic Heisenberg spin model:

$$S_i S_j \rightarrow \vec{\mathbf{S}}_\mathbf{i} \cdot \vec{\mathbf{S}}_\mathbf{j}$$

Optimal Configuration?





Z state

Zigzag stripes

Integrating out phonons:

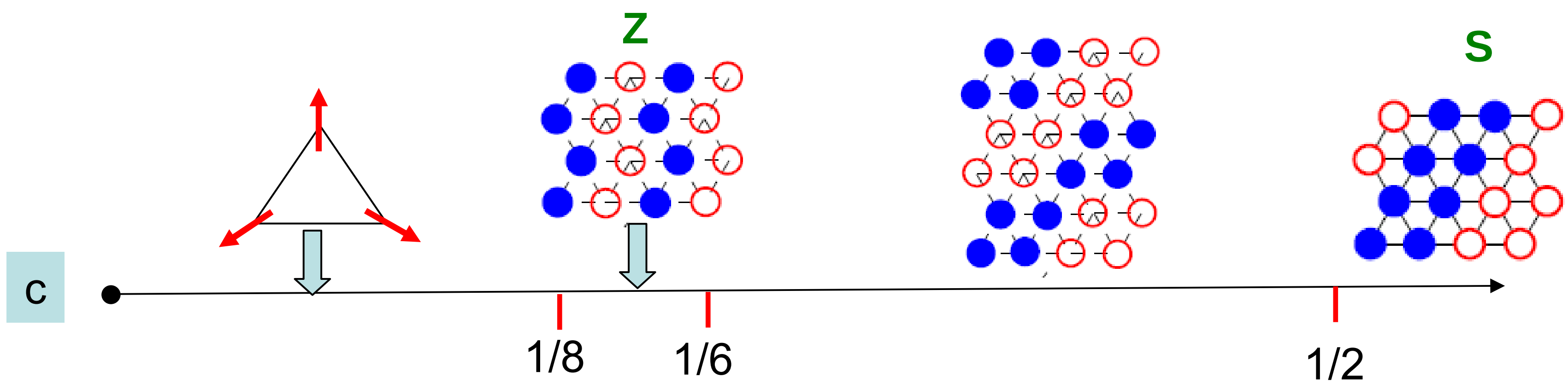
$$H = J\left[\sum_{<ij>} \vec{\mathbf{S}}_\mathbf{i} \cdot \vec{\mathbf{S}}_\mathbf{j} - c \sum_i \vec{\mathbf{F}}_\mathbf{i}^2\right]$$

$$\vec{\mathbf{F}}_\mathbf{i} = \sum_{<j>} \hat{\mathbf{e}}_\mathbf{ij} \vec{\mathbf{S}}_\mathbf{i} \cdot \vec{\mathbf{S}}_\mathbf{j} \qquad c = \frac{\alpha^2 J S^2}{2K}$$

Generates $(\vec{\mathbf{S}}_\mathbf{i} \cdot \vec{\mathbf{S}}_\mathbf{j})(\vec{\mathbf{S}}_\mathbf{j} \cdot \vec{\mathbf{S}}_\mathbf{k})$ terms

Fa Wang and AV, preprint ‘07.

Spin-Phonon model phase diagram



- Ground state of classical model obtained using simulated annealing upto 10x10 system size.
- Coupling to phonons induces frustration (colinear order) *and* resolves it.

- For CuFeO2: **c~0.1** [α=7; J=13Kelvin; K=10,000Kelvin].
- Lattice displacement ~5%. Large!
- Structural change observed $T<T_c$. [Ye et al., Terada et al.]

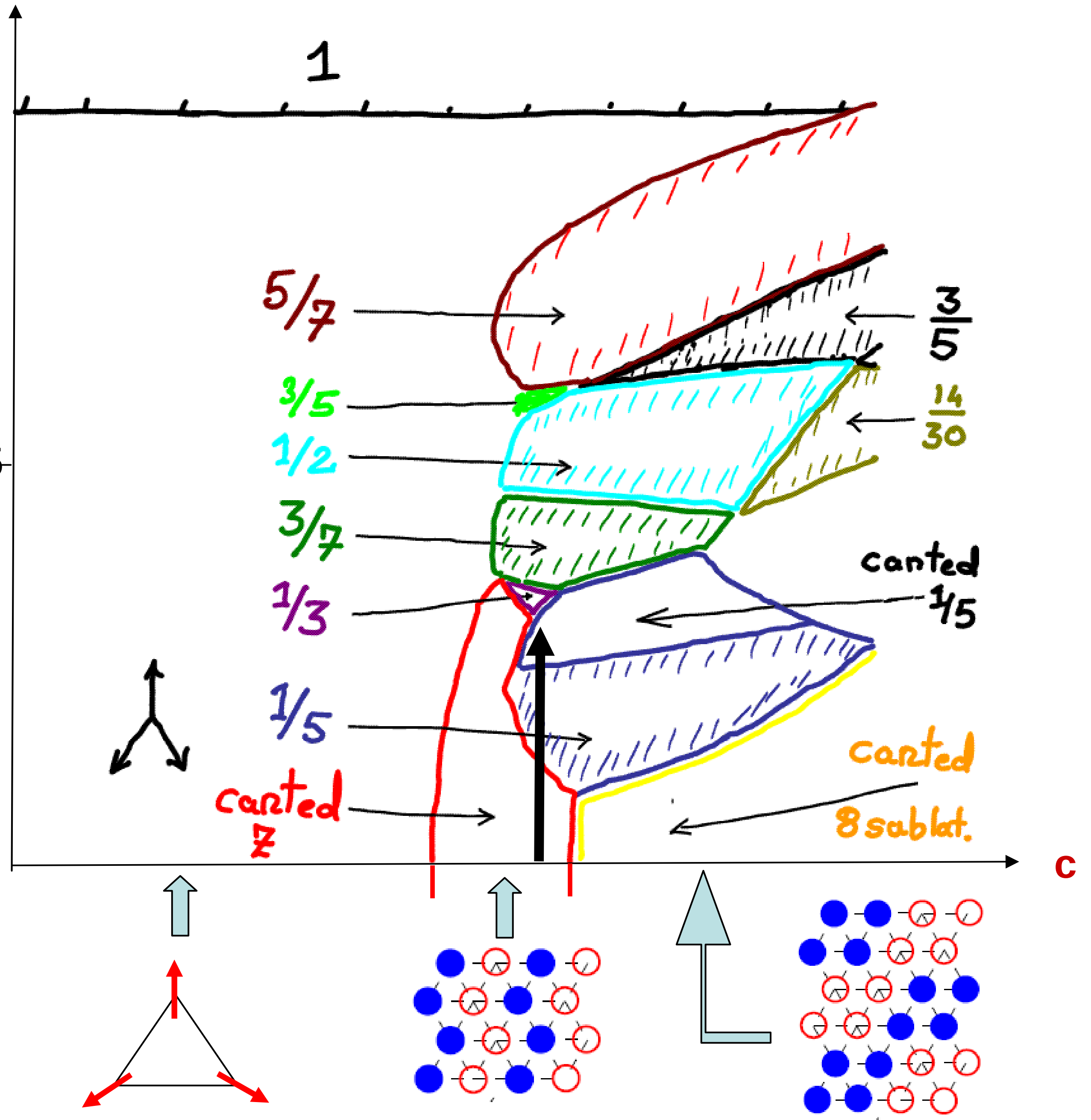
- **S** state observed α-$NaFeO_2$ and $MnBr_2$

Magnetization Plateaus in a Field

In a magnetic field **h**:

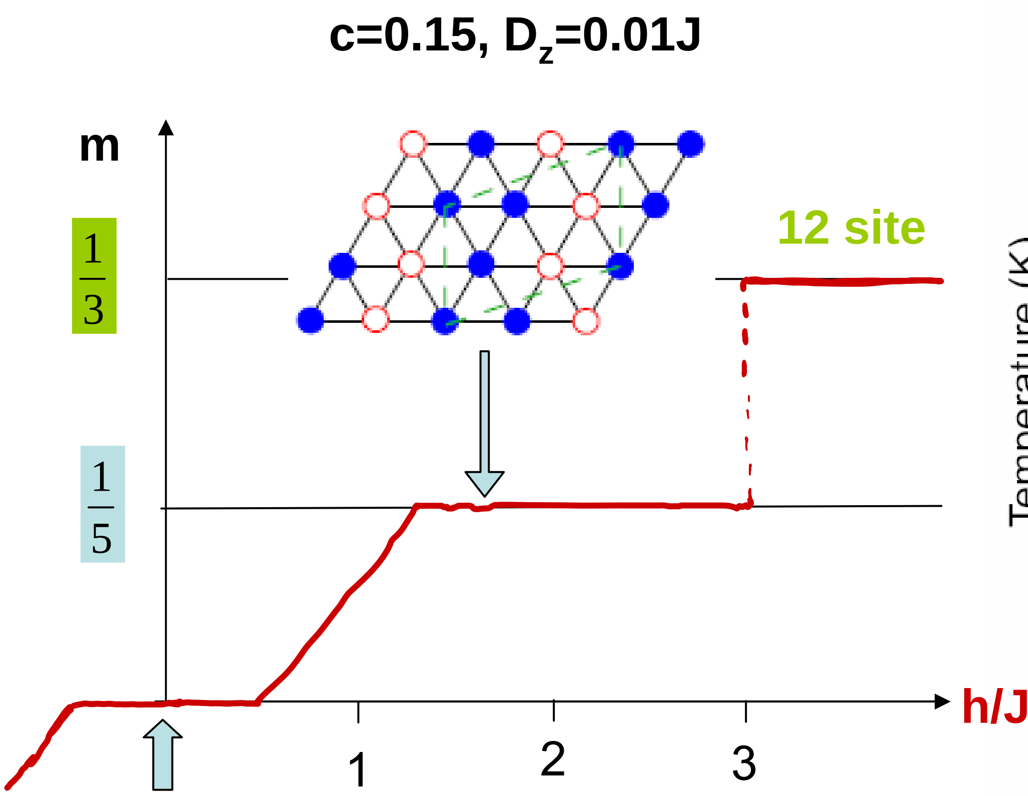
<u>**Magnetization plateaus**</u>

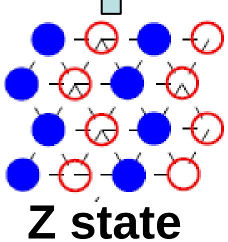
(*shaded*)



Fa Wang and AV, preprint '07.

Magnetization Plateaus and $CuFeO_2$

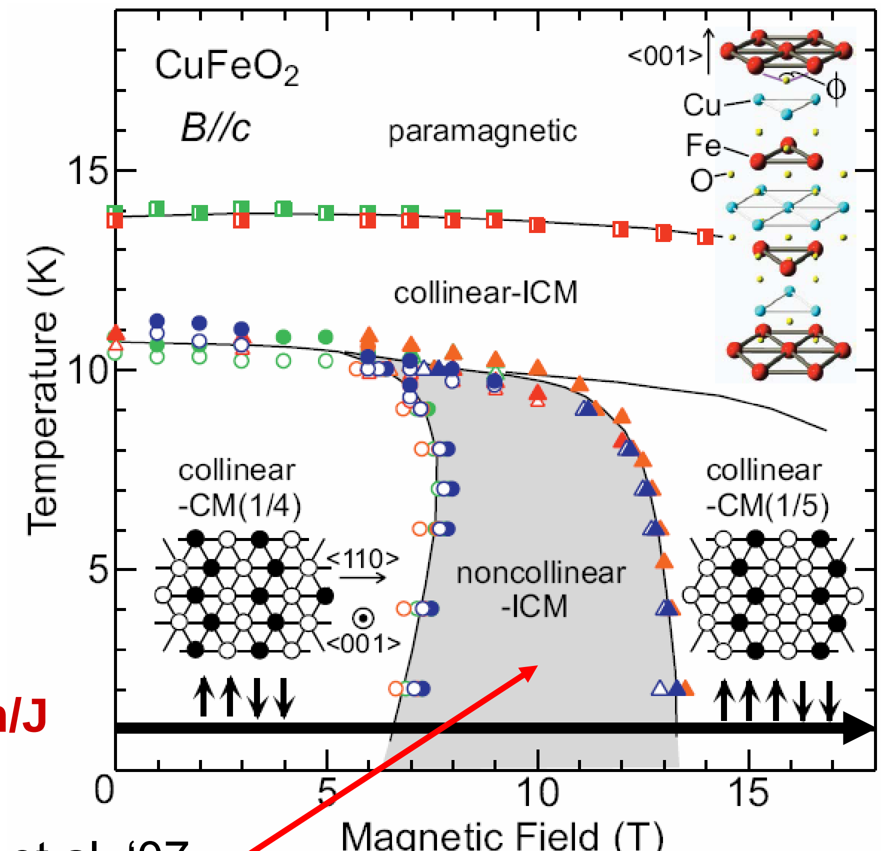




1/3 plateau observed Terada et al. ‘07

Phases of Triangular magnet $CuFeO_2$

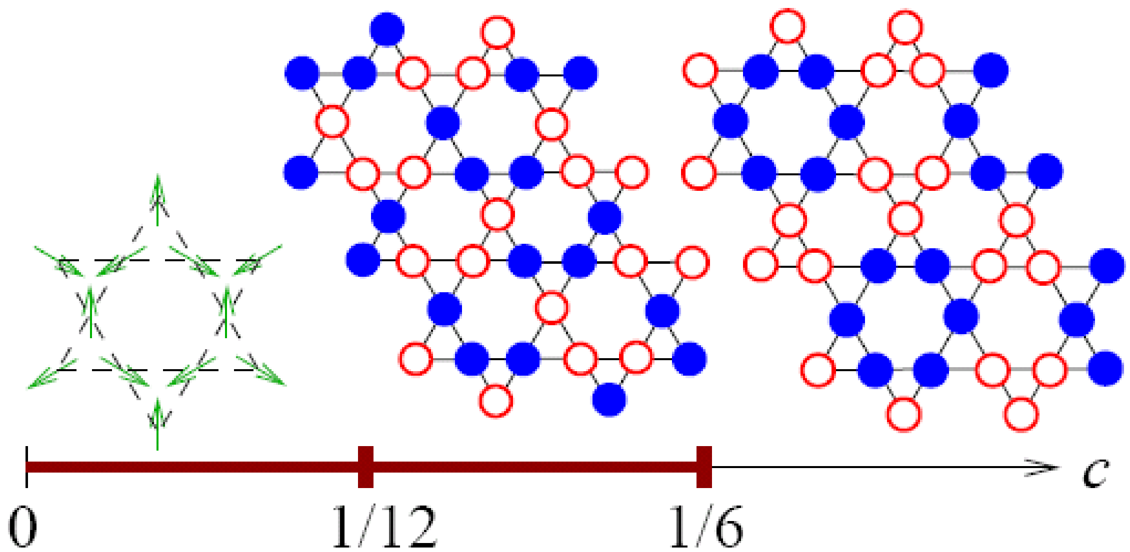
Lashley, Kimura, Ramirez



Also Ferroelectric: **P**

(Multi-ferroic – “cooperating orders”)

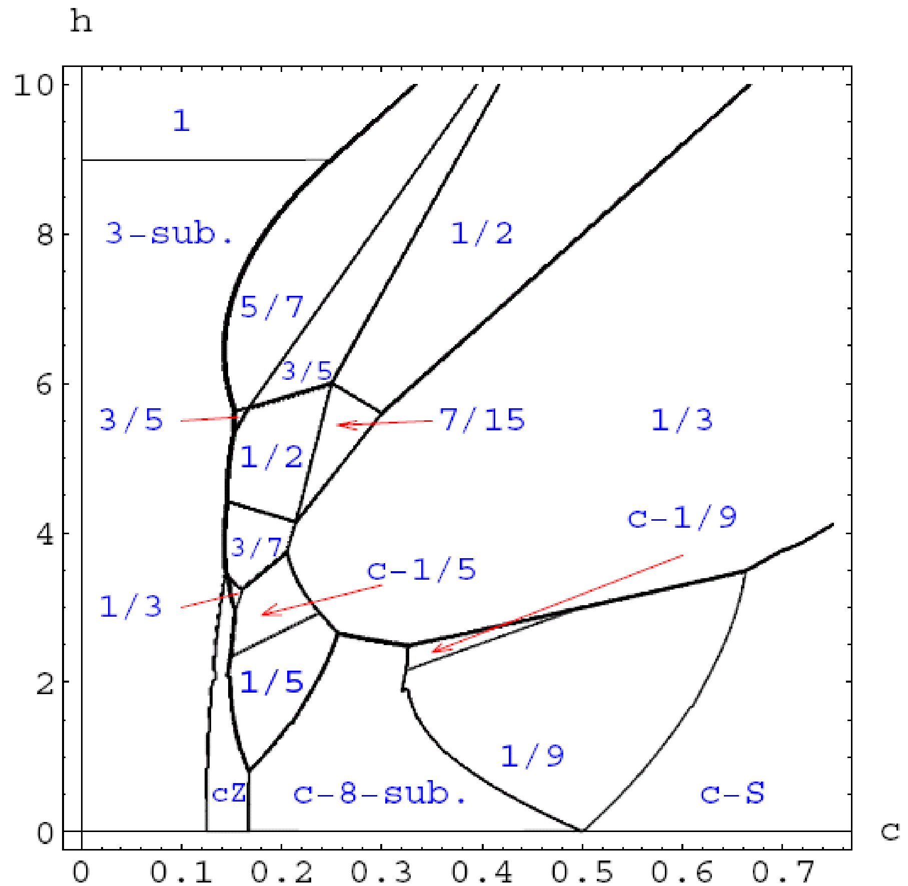
Spin Phonon Coupling on the Kagome



- Colinear order established at c=1/12, but extensive degeneracy remains. Ensemble is a subset of Ising ground state ensemble.
- 1/9 plateaus expected immediately 1/12<c<1/6.
- Quantum fluctuations? Candidate $Mn_3V_2O_8$?

Conclusions Part 1

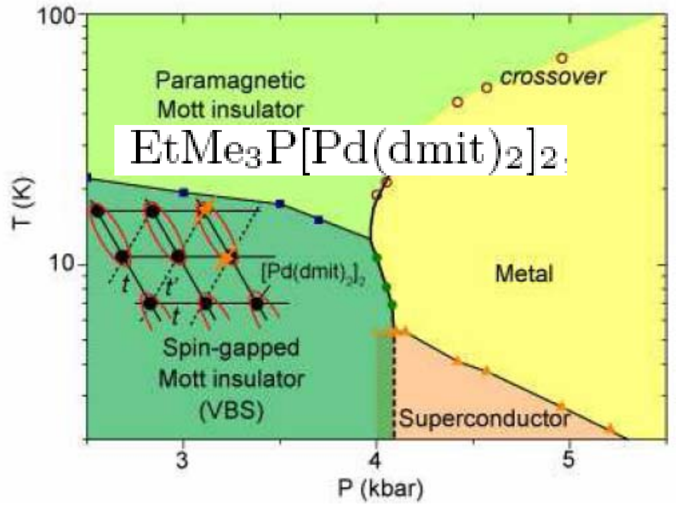
- Spin-phonon couplings of moderate strength => rich phase diagram of colinear states on the triangular and kagome lattices



- **Future directions:**

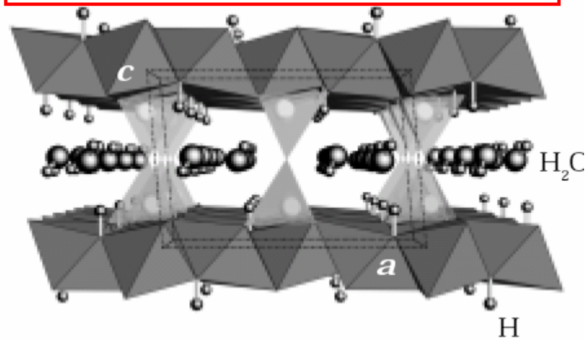
Quantum limit (S=1/2) – disordered colinear states => dimer order (VBS).

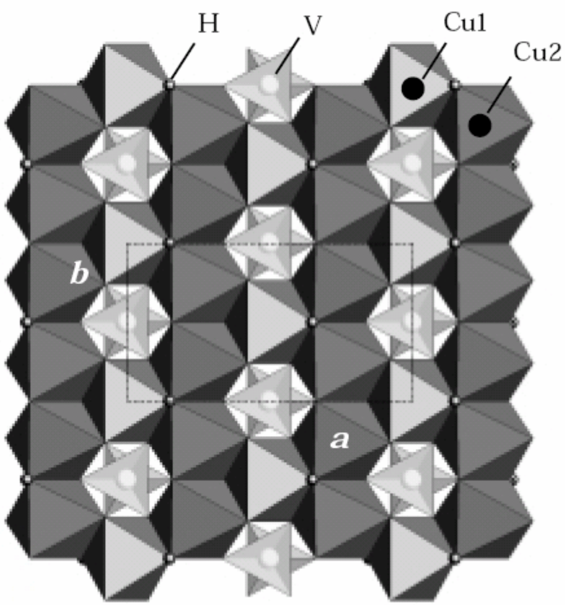
(eg. Y. Shimizu et al. 06)



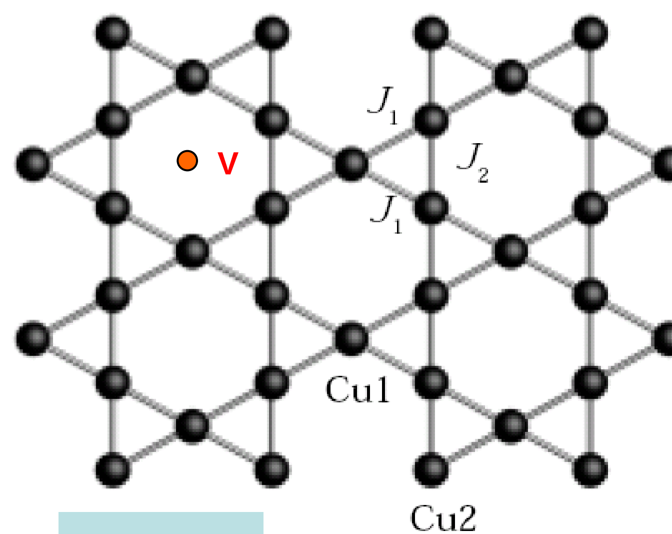
2. Quantum spins on a distorted kagome lattice

$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$





Volborthite:
Alexander von Volborth (1800-1876),

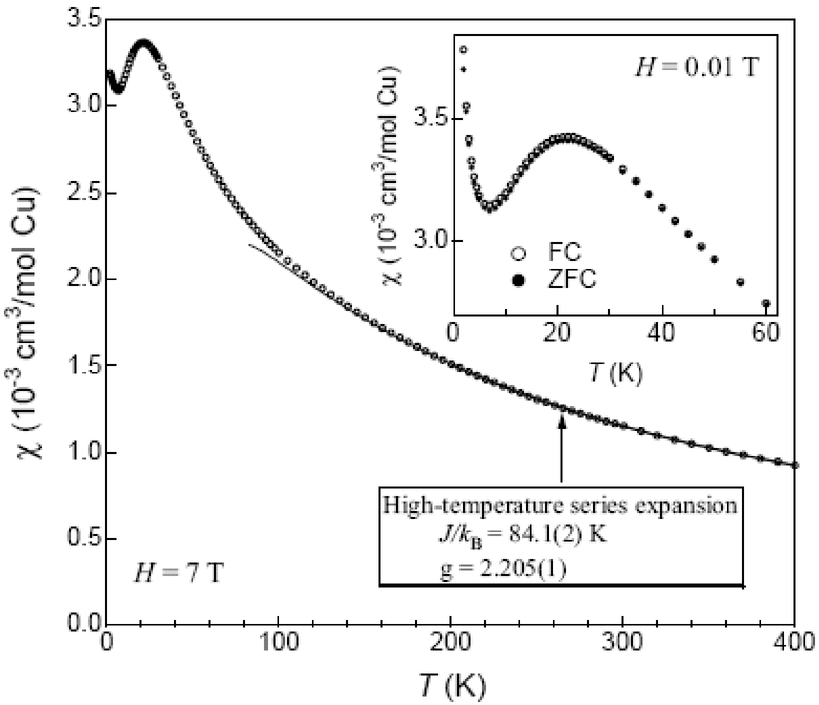


$J_1 \neq J_2$

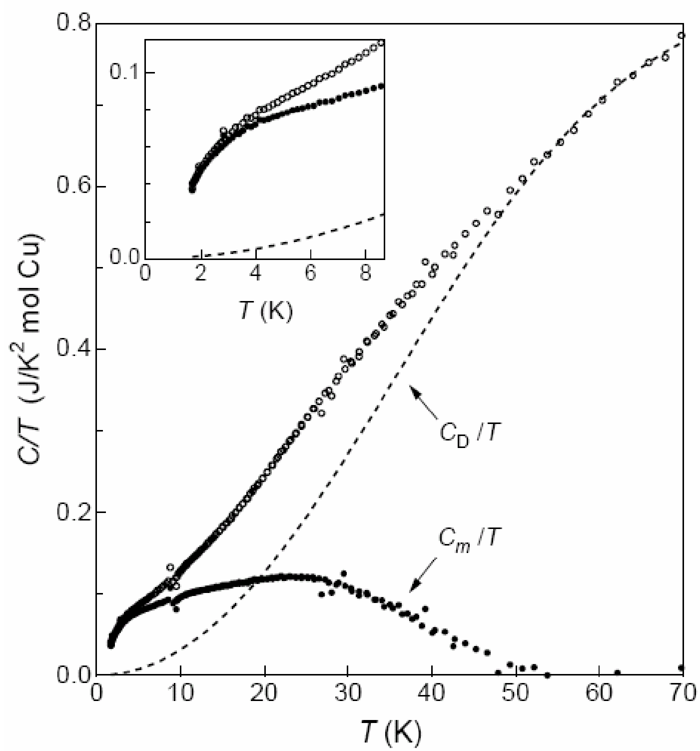
- Volborthite – spin ½ on slightly distorted Kagome lattice (Hiroi et al. 2001)

Volborthite Properties I

- Exchange constant J=85Kelvin.
- No order down to 1.8Kelvin, finite magnetic susceptibility.
- Low energy excitations visible in specific heat.



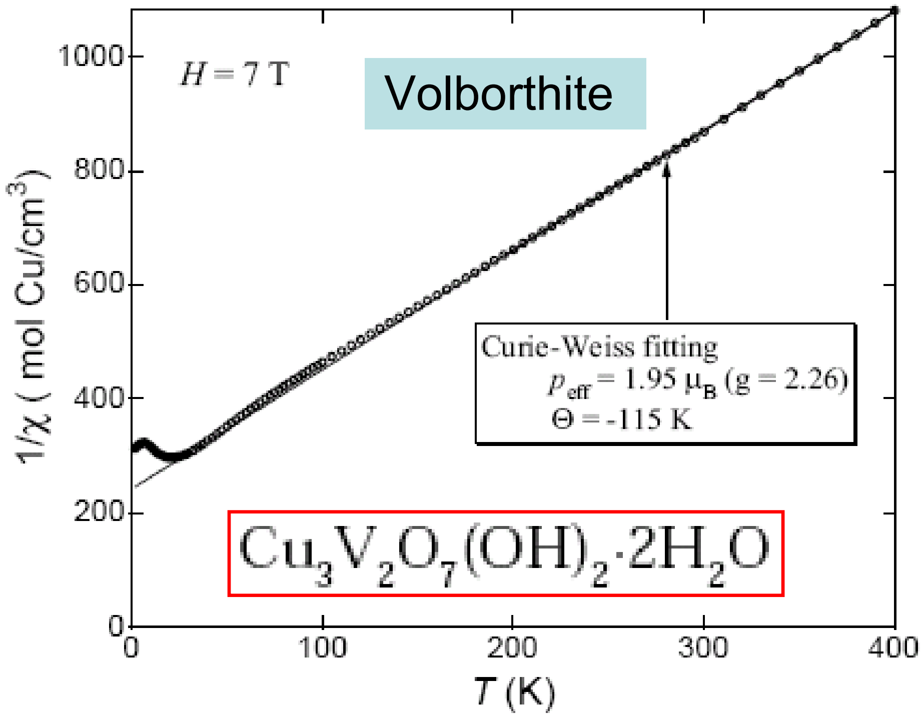
•magnetic susceptibility

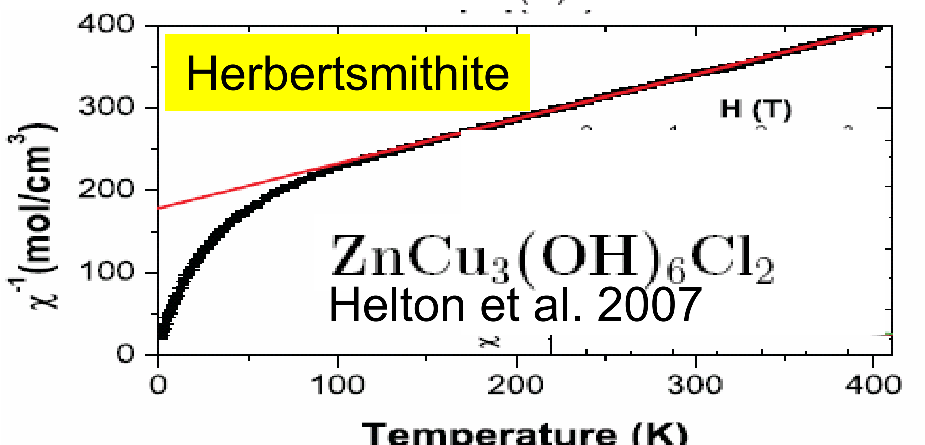


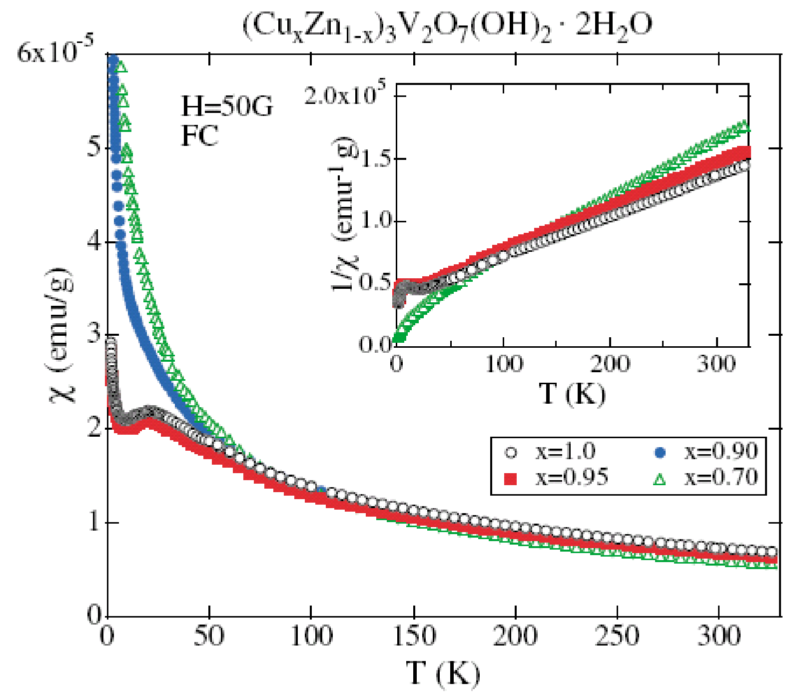
specific heat

Volborthite Properties I

- Comparison with herbertsmithite (isotropic kagome)



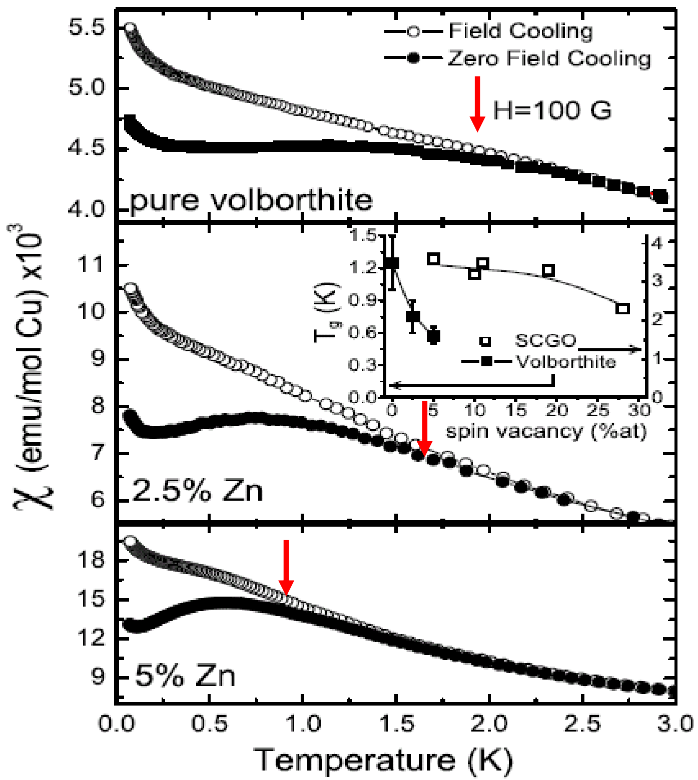




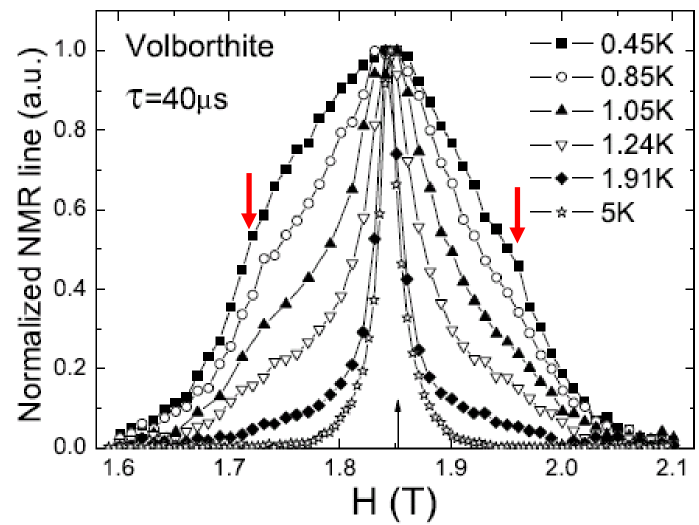
Diluted volborthite – Fukaya et al. PRL 03

Volborthite Properties II

- Spin freezing (glass) observed below 1.6Kelvin.
  (F. Bert et al. PRL '05)



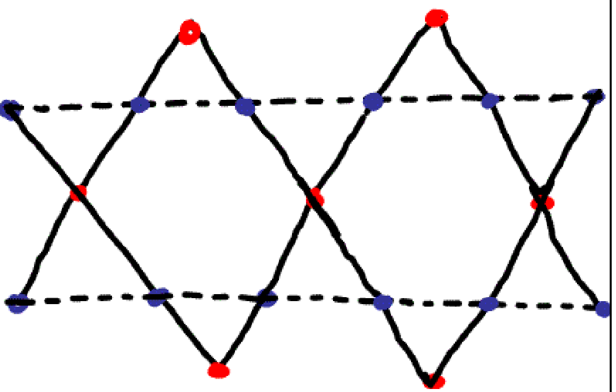
Hysterisis in magnetic susceptibility and dilution dependence of freezing temperature



Two static magnetic fields observed in ^{51}V NMR below T_g. Large field 20%, small field 80%.

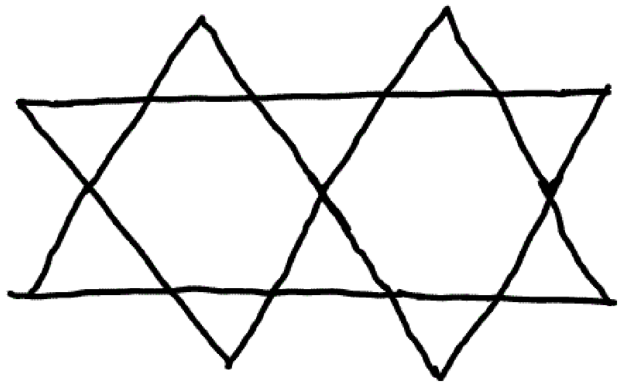
Classical spins on the distorted kagome

$\alpha < 1/2$ **(unfrustrated)**

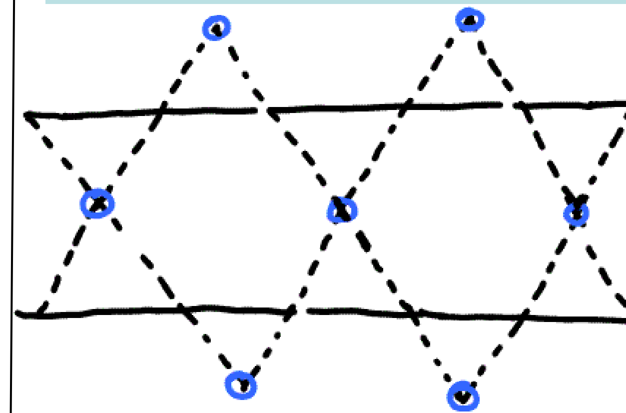


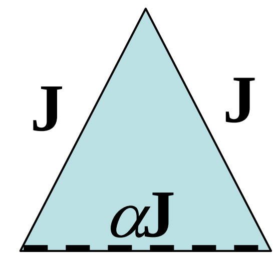
•Colinear ferrimagnet with m=1/3

$\alpha = 1$ **(kagome)**

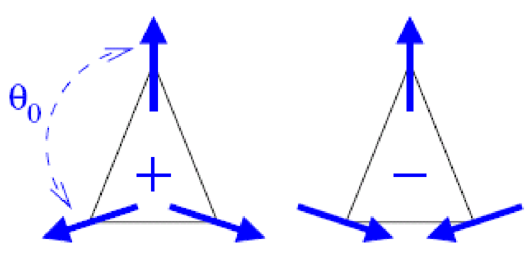


$\alpha >> 1$ **(1D + decoupled spins)**





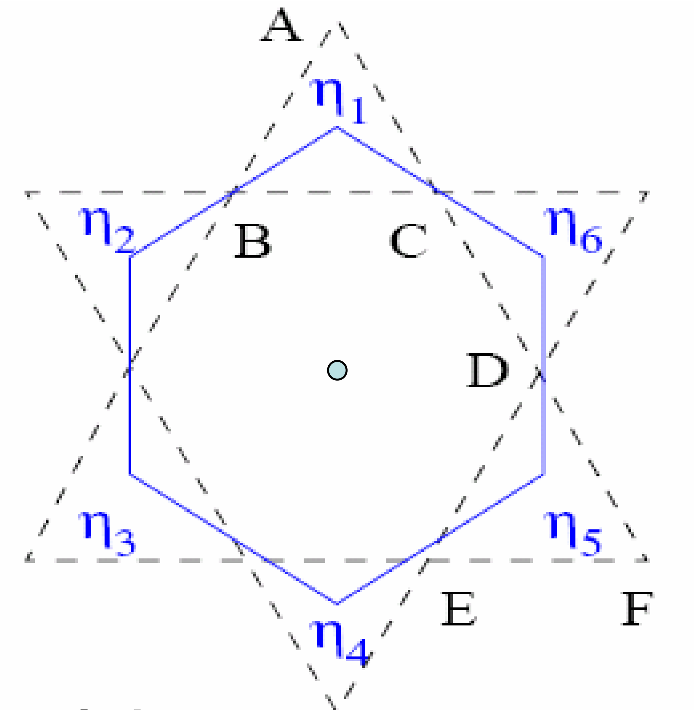
- For α>1/2, coplanar configuration on a triangle with Θ=arccos[- 1/2α].
- Coplanar configurations – still labeled by chirality.



Classical Degeneracy

- For α=1, extensive coplanar ground state degeneracy ~$e^{\#N}$
- For α>1/2, (α≠1) large but sub-extensive $e^{\#\sqrt{N}}$ degeneracy

$$\sum_{i=1}^{6}\eta_i = \begin{matrix} \pm 6 & \textbf{or} \\ 0 & \&(\eta_1+\eta_4=0) \end{matrix}$$



In this ensemble, exchange field at central site:

$25\% \sqrt{3}H_0$ *and* $75\%\ 0H_0$ **Connection to NMR result?**

Splitting the Degeneracy

- To quadratic order (harmonic spin waves), all coplanar ground states remain degenerate since energy density pattern is *identical*.
- Flat band at zero energy expected.

$$H = \frac{\alpha}{2} \sum_{\text{triangles}} \left[(1/\alpha)\mathbf{S}_{\mathrm{A}} + \mathbf{S}_{\mathrm{B}} + \mathbf{S}_{\mathrm{C}}\right]^2$$

Energy density

$$H_2 = \sum_{\langle ij \rangle} J_{ij} \cos\theta_{ij} \, \delta S_i' \, \delta S_j'$$

Chirality

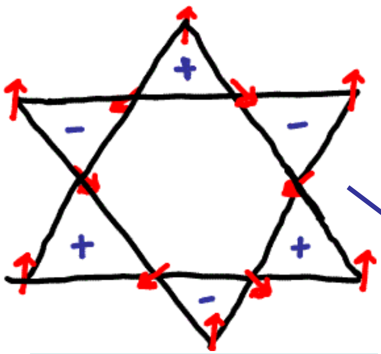
$$H_3 = \sum_{\langle ij \rangle} J_{ij} \sin\theta_{ij} \, \delta S \, \delta S \, \delta S$$

•Integrate out spin waves to get effective chirality Hamiltonian (Henley)

•Done here for classical spins in a low T expansion.

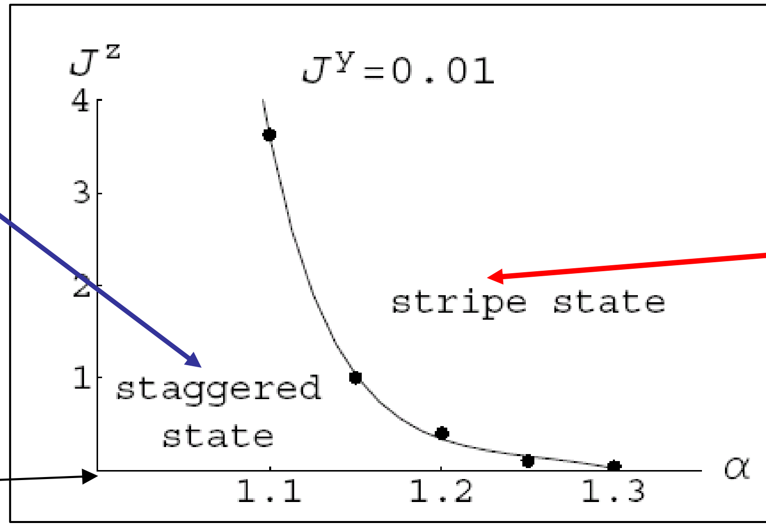
•Need anisotropy J_z,J_y to regulate spin waves

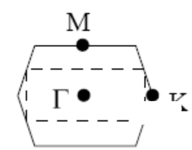
Splitting the Degeneracy

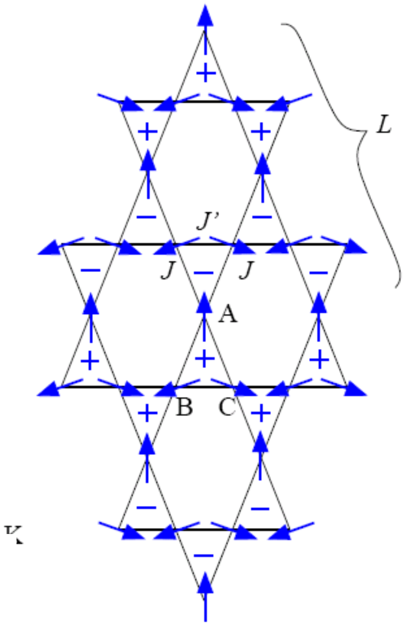


$\sqrt{3}\times\sqrt{3}$ **state**

Kagome







Chirality stripe state

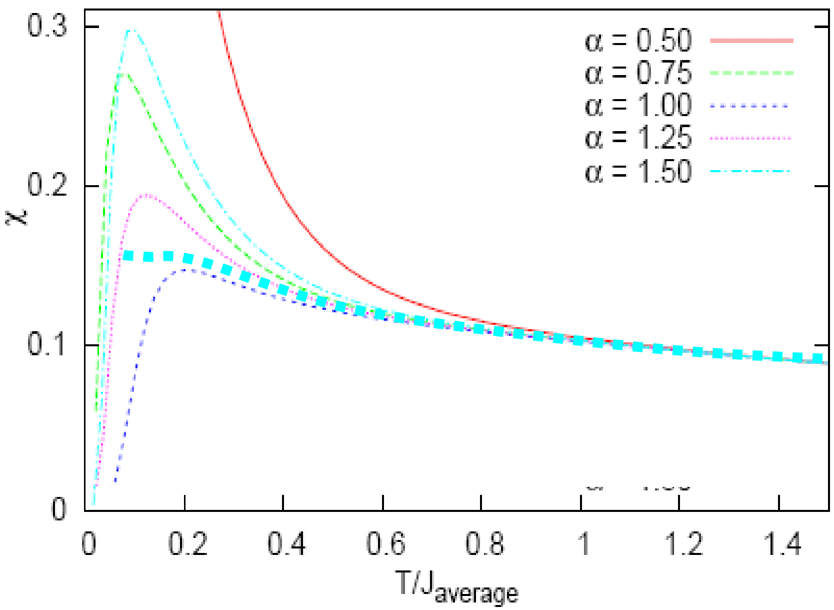
Chirality stripe state realized for α>1.

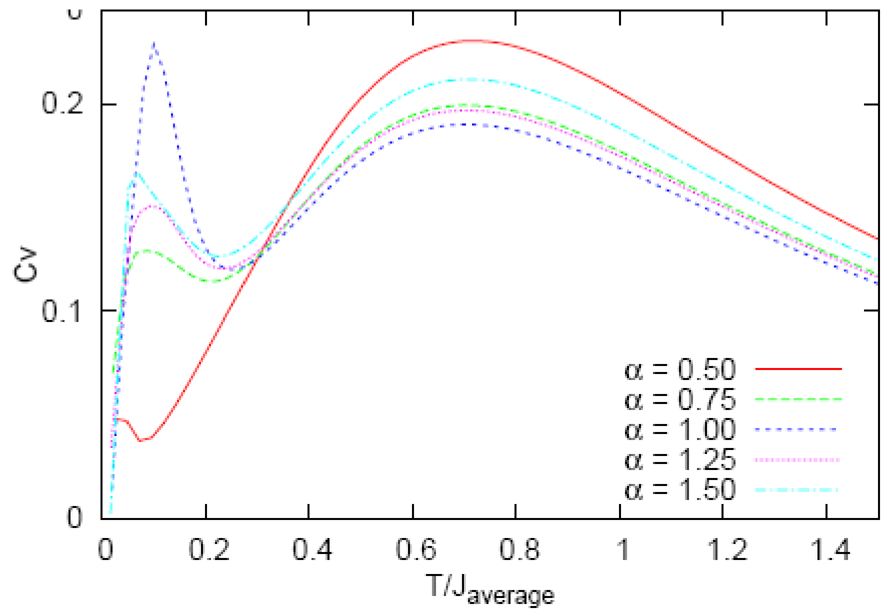
•Order at the **M** point

•Ferrimagnetic

Also appears in a high T expansion.

Exact Diagonalization- Thermodynamics



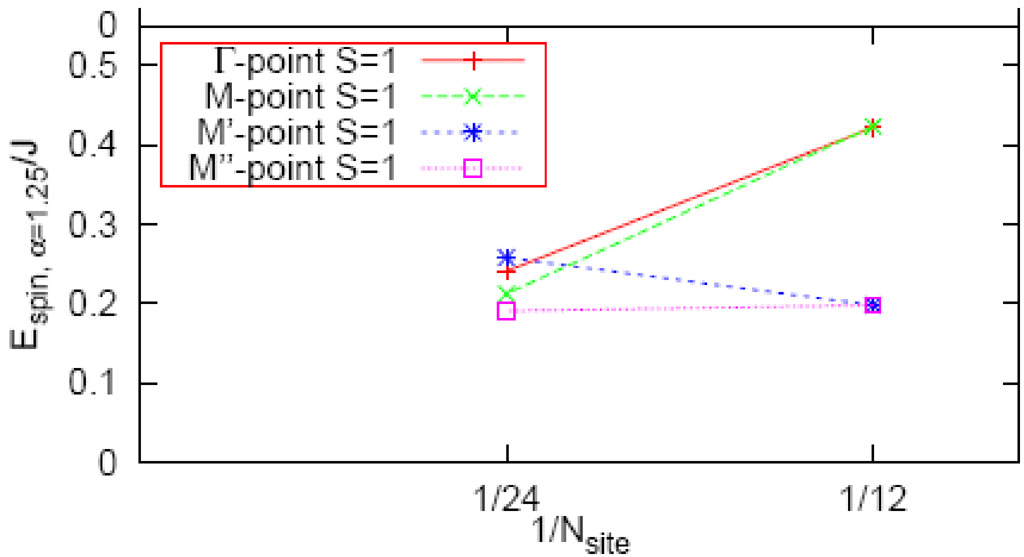


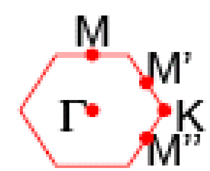
- Compare exact diagonalization on small clusters with experiments – does Heisenberg model work well? If so, what is the anisotropy parameter?
- [here: 12 spin cluster, P. Sindzingre: 24 spins]

Exact Diagonalization- Low energy excitations

- <u>For α<1/2</u>: Classically expect 1/3 magnetized ferrimagnet. Verified in ED

  S=2 ground state for 12 spins, S=3 for 18 spins at α=0.5. No renormalization of critical α!





- <u>For α>1</u>: Semi-classically expect M point ordered ferri-magnet.
  - BUT, ground state singlet.
  - Lowest spin excitations at M'
  - Finite size effects? Extrapolation indicates decrease in M point and Γ point gap

Conclusions - Part 2

- Spatially anisotropic Kagome retains significant degree of frustration.
- In the semi-classical limit – an M point ordered ferrimagnetic state (chirality stripe state) is favored for $\alpha>1$.
- More experiments and ab-initio modeling of Volborthite needed.

3. Spin Orbital Liquids

- Experimental motivation – $FeSc_2S_4$. f=1,000. and $LiNiO_2$.
- Theoretical motivation – more quantum fluctuations than spin systems alone.

- Consider here 1 electron in an *e* orbital.
  - Four state system on each site.
  - Typically symmetry is SU(2)xDiscrete. Assume SU(4) symmetry to begin (Mila, Zhang, Penc,…).

$$H = \frac{J}{4} \sum_{<ij>} (1 + \vec{\sigma}_i \cdot \vec{\sigma}_j)(1 + \vec{\tau}_i \cdot \vec{\tau}_j)$$

  - Describing a spin orbital liquid? *New* slave theory (Wang and A.V. in prep.)