Frustration and fluctuations in diamond antiferromagnetic spinels

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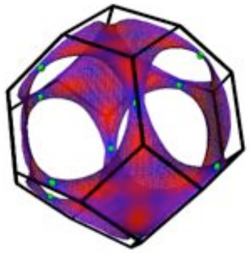
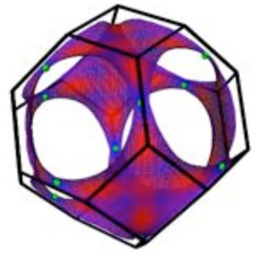
Degeneracy and Frustration



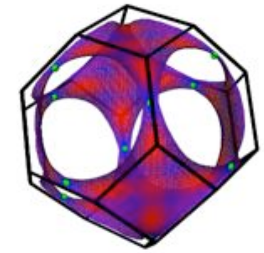
- Classical frustrated models often exhibit "accidental" degeneracy
- The degree of (classical) degeneracy varies widely, and is often viewed as a measure of frustration
- E.g. Frustrated Heisenberg models in 3d have spiral ground states with a wavevector **q** that can vary
  - FCC lattice: **q** forms lines
  - Pyrochlore lattice: **q** can be arbitrary
  - Diamond lattice $J_2>|J_1|/8$: **q** forms surface

Accidental Degeneracy is Fragile

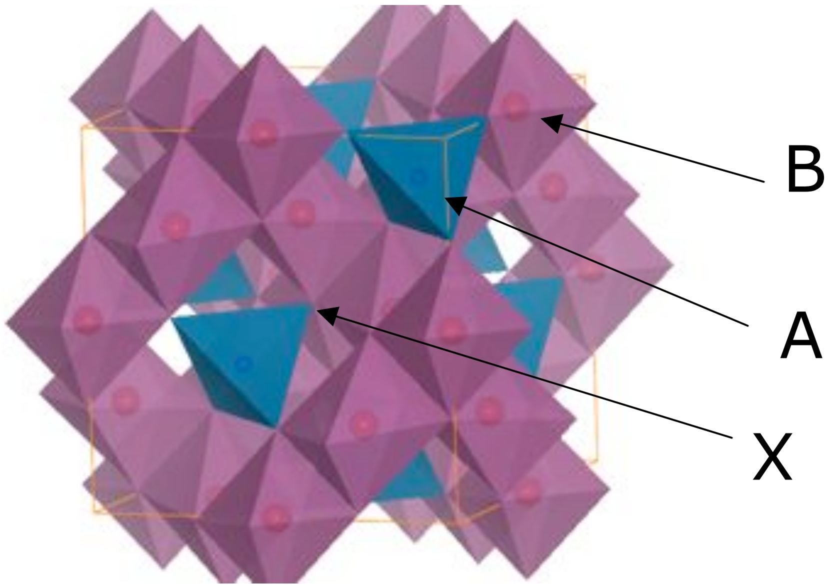


- Diverse effects can lift the degeneracy
  - Thermal fluctuations F=E-TS
  - Quantum fluctuations $E=E_{cl}+E_{sw}+\ldots$
  - Perturbations:
    - Further exchange
    - Spin-orbit (DM) interaction
    - Spin-lattice coupling
    - Impurities
- Questions:
  - What states result?
  - Can one have a “spin liquid”?
  - What are the important physical mechanisms in a given class of materials?
  - Does the frustration lead to any simplicity or just complication? Perhaps something useful?

Spinel Magnets



- Normal spinel structure: AB_2X_4 .

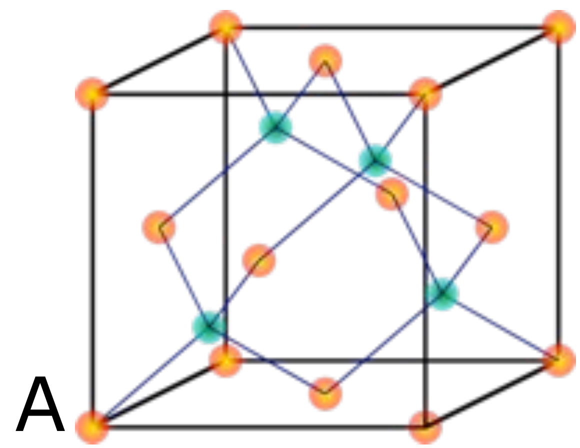


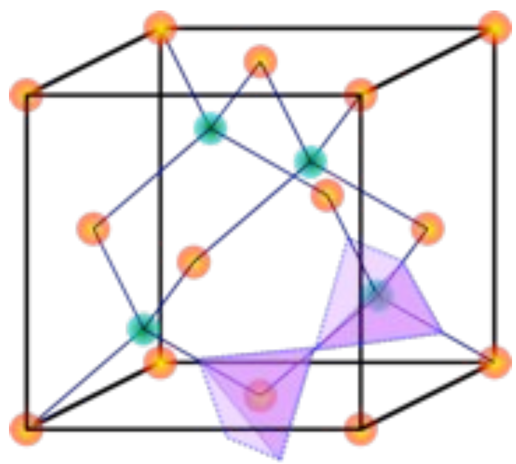
cubic $Fd\bar{3}m$

- Consider chalcogenide X^{2-}=O,S,Se
  - Valence: $Q_A+2Q_B = 8$
- A, B or both can be magnetic.

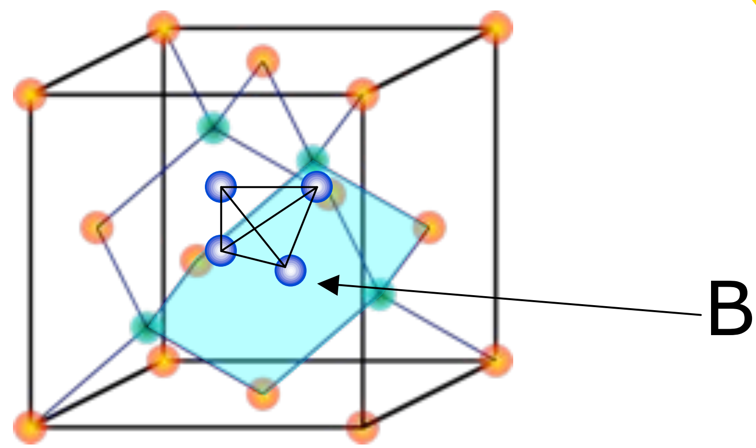
Deconstructing the spinel

- A atoms: diamond lattice
  - Bipartite: not *geometrically* frustrated
- B atoms: pyrochlore lattice
  - Two ways to make it:



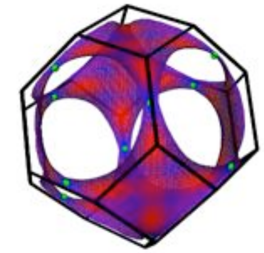


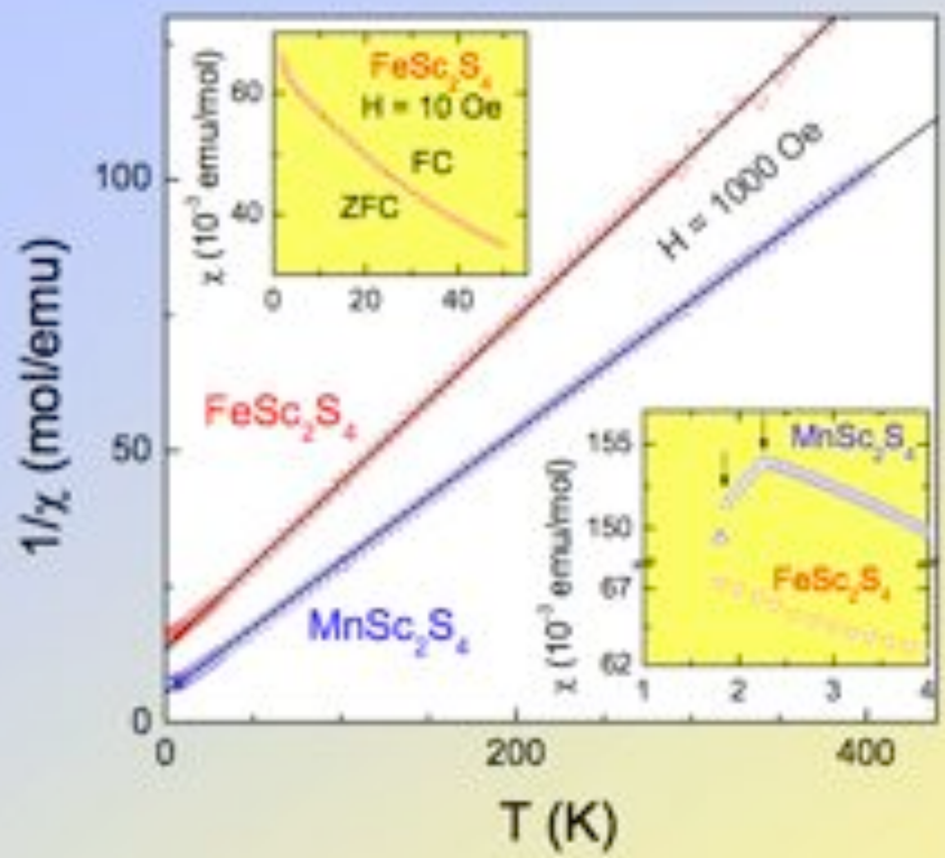
Decorate bonds



Decorate plaquettes

Frustrated diamond spinels





$FeSc_2S_4$: $\theta_{CW} = 50$ K

T > 30 mK:

no long-range magnetic order

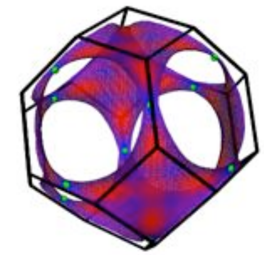
no spin-glass

$MnSc_2S_4$: $\theta_{CW} = 25$ K

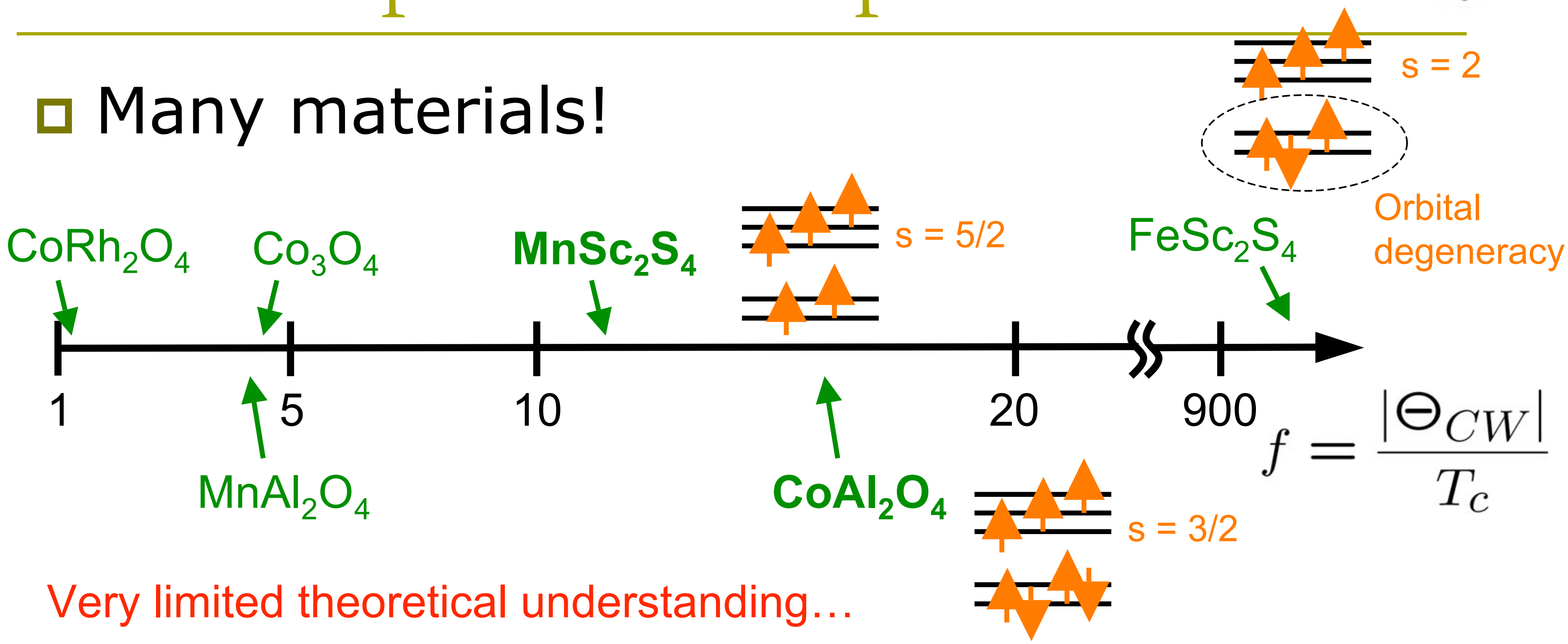
AFM transition @ 2 K

Fritsch *et al.*, PRL **92**, 116401, 2004

Road map to A-site spinels



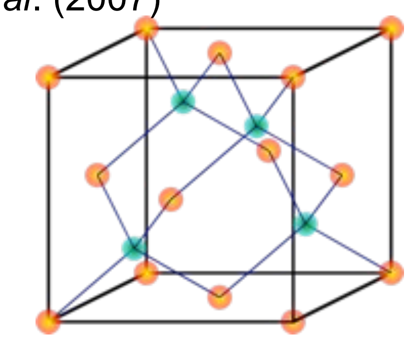
- Many materials!



Very limited theoretical understanding…

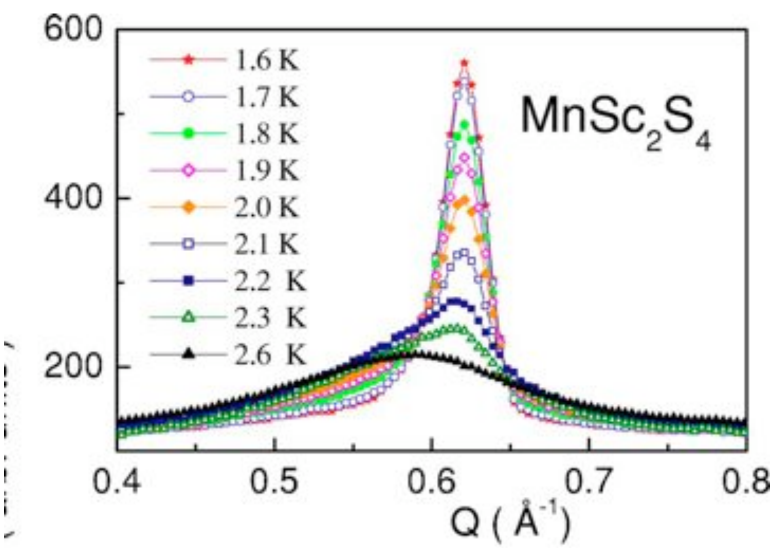
V. Fritsch et al. (2004); N. Tristan et al. (2005); T. Suzuki *et al*. (2007)

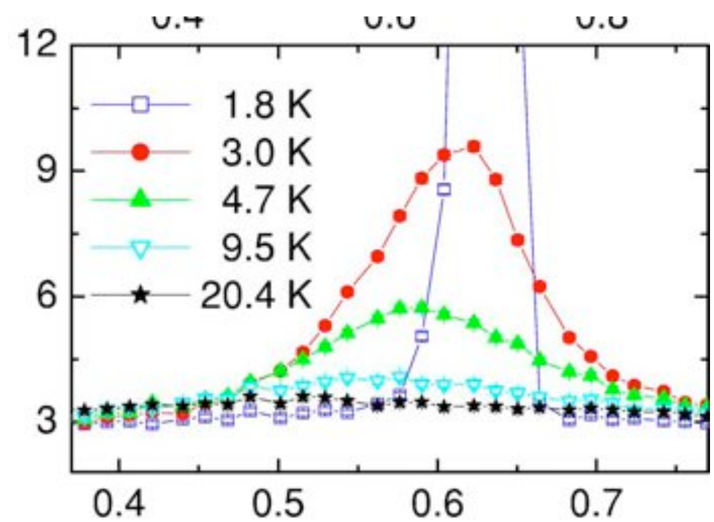
- Naïvely unfrustrated



Major experimental features

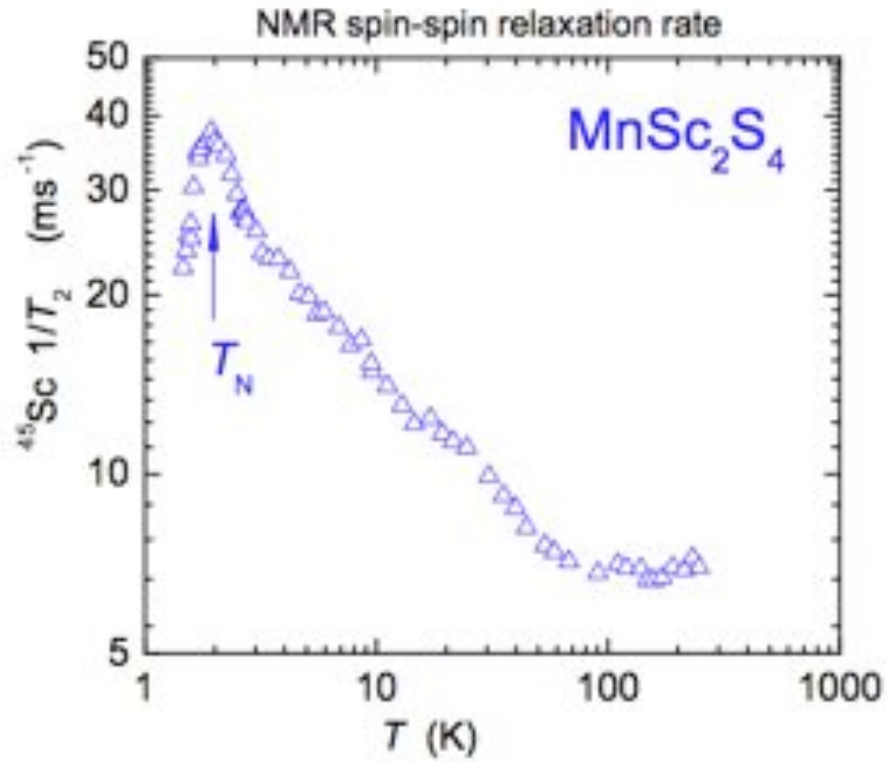
- Significant diffuse scattering which is temperature dependent for $T \gg T_N = 2.3K$
  - Correlations developing in spin liquid regime



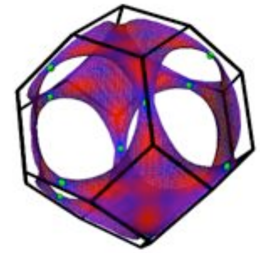


Major Experimental Features

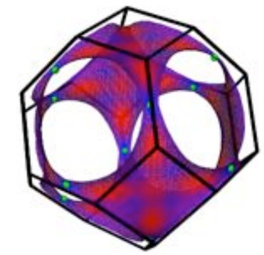
- Correlations visible in NMR



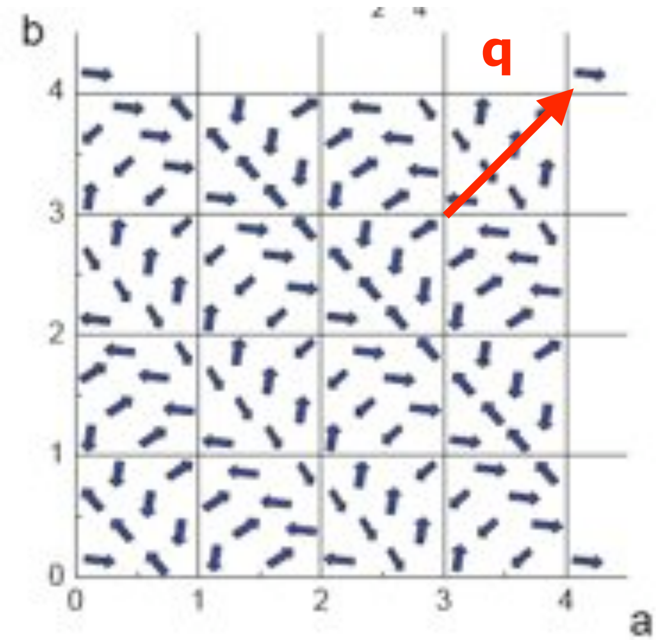
Loidl group, unpublished



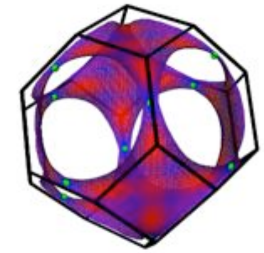
Major Experimental Features



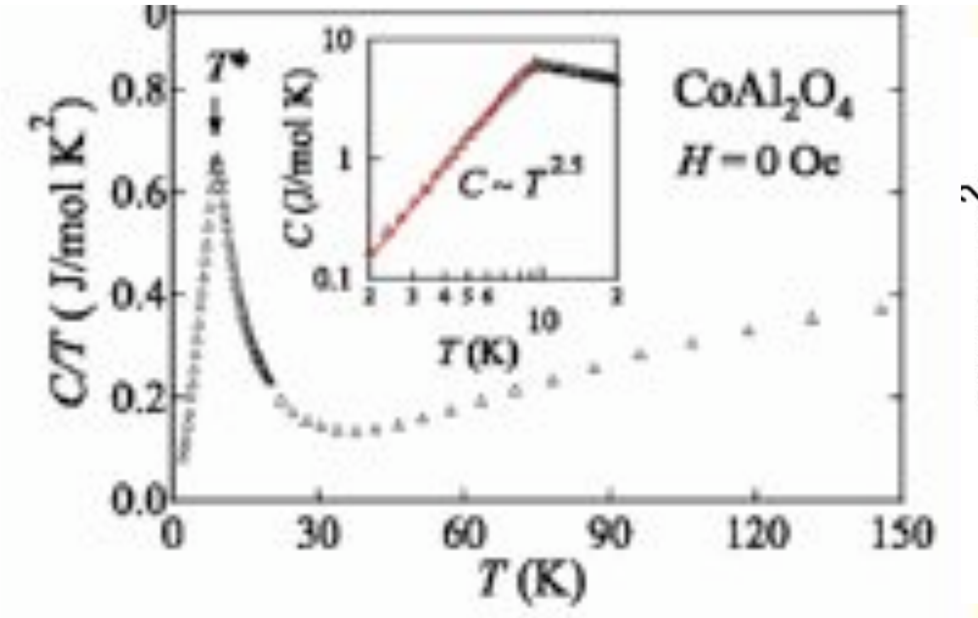
- Long range order in $MnSc_2S_4$:
  - T_N=2.3K
  - Spiral **q**=(q,q,0)
  - Spins in (100) plane
  - Lock-in to q=3¼/2 for T<1.9K
  - Reduced moment (80%) at T=1.5K



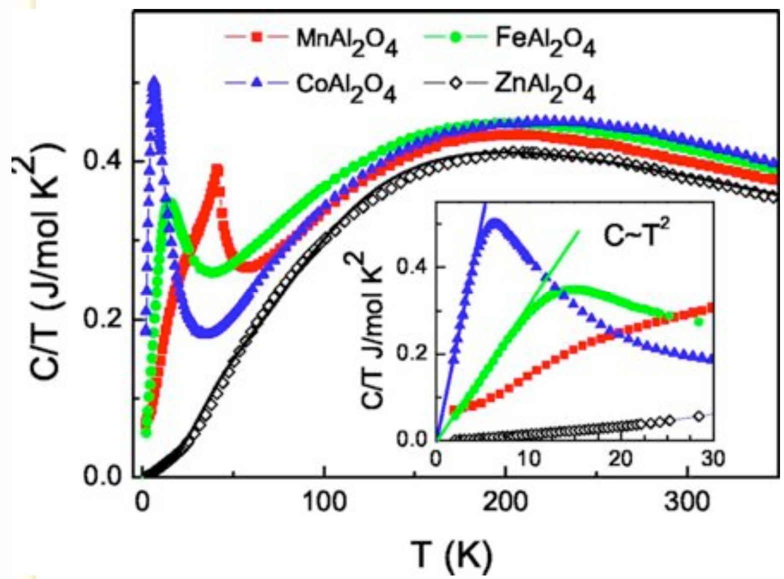
Major experimental features



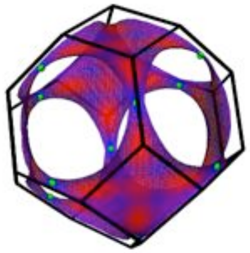
- Anomalous low temperature specific heat



$$C \sim T^{2.5}$$

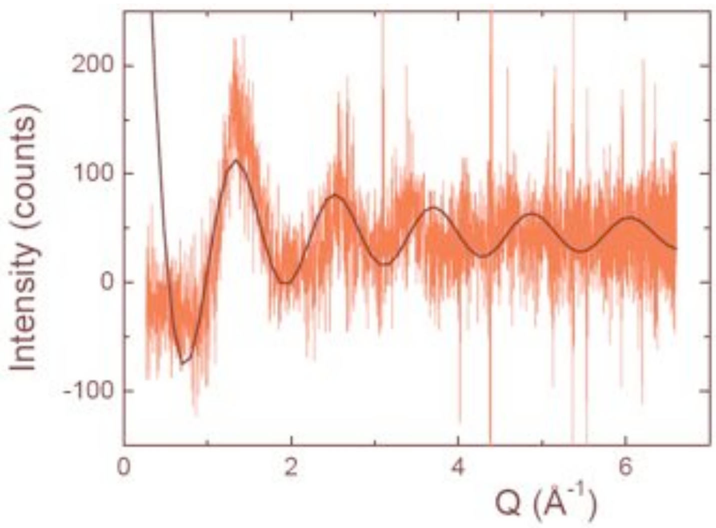


$$C \sim T^2$$

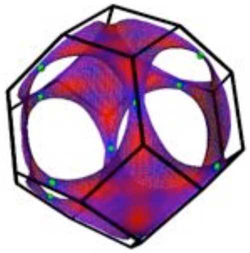


Major Experimental Features

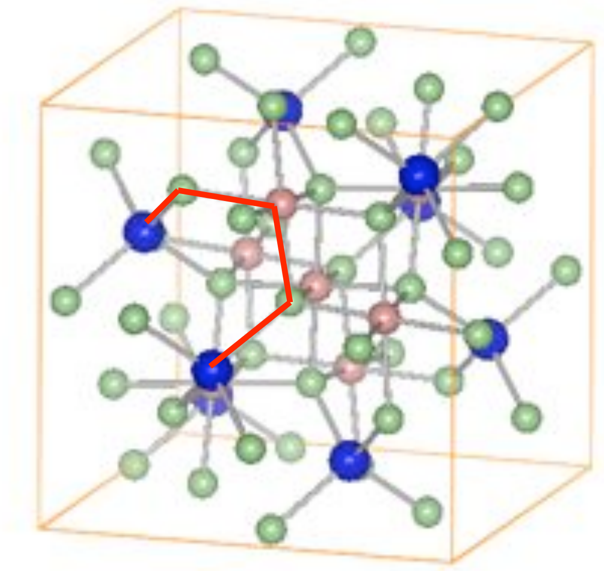
- “Liquid” structure factor at *low* temperature in $CoAl_2O_4$:
  - No long range order



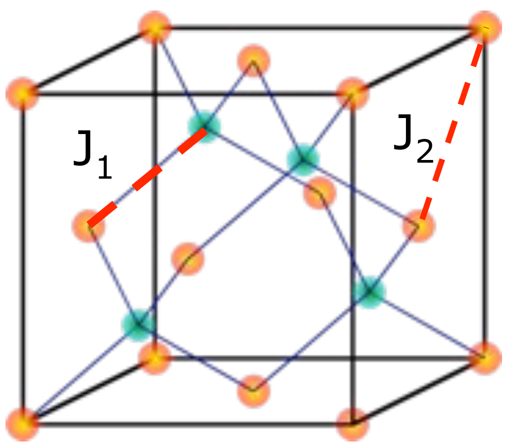
Frustration



- Roth, 1964: 2nd and 3rd neighbor interactions not necessarily small
  - Exchange paths A-X-B-X-A

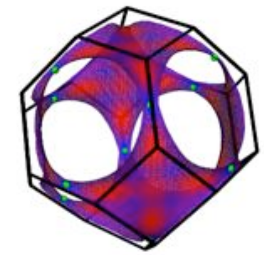


- Minimal theory:
  - Classical J_1-J_2 model

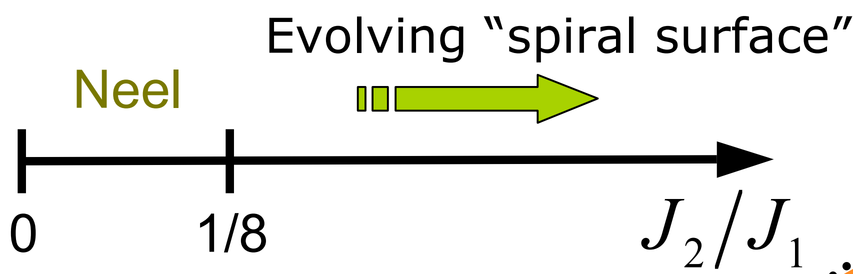


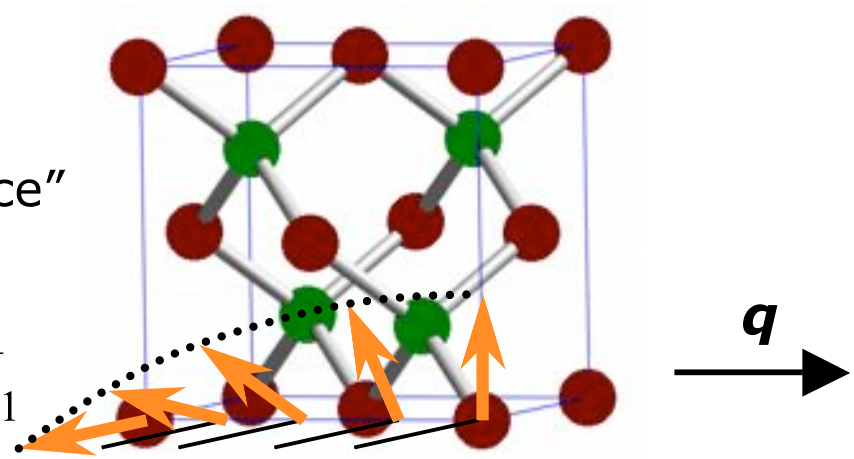
- Néel state unstable for $J_2>|J_1|/8$

Ground state evolution

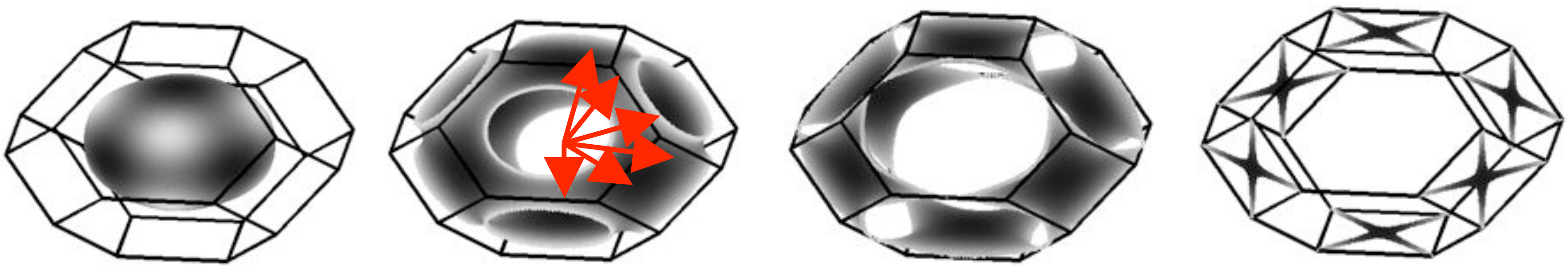


- Coplanar spirals



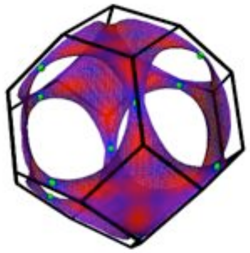


- Spiral surfaces:



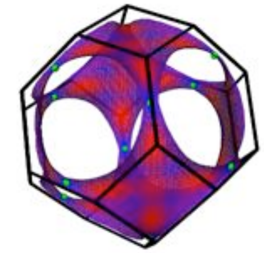
$J_2/J_1 = 0.2$ $J_2/J_1 = 0.4$ $J_2/J_1 = 0.85$ $J_2/J_1 = 20$

Effects of Degeneracy: Questions



- Does it order?
  - Pyrochlore: no order (**k** arbitrary)
  - FCC: order by (thermal) disorder (**k** on lines)
- If it orders, how?
  - And at what temperature? Is f large?
- Is there a spin liquid regime, and if so, what are its properties?
- Does this lead to enhanced quantum fluctuations?

Low Temperature: Stabilization

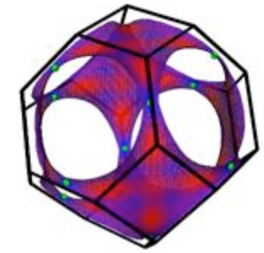


- There is a branch of normal modes with zero frequency for any wavevector on the surface (i.e. vanishing stiffness)
  - Naïve equipartion gives infinite fluctuations

$$\langle(\delta S_i)^2\rangle \sim \int d^3q \frac{T}{\omega_0^2(q)} \sim \int d\Omega \int d\delta q \frac{Tq(\Omega)^2}{(v\delta q)^2} = \infty$$

- Fluctuations and anharmonic effects induce a finite stiffness at T>0
  - Fluctuations small but $\gg$ T: $\langle(\delta S_i)^2\rangle \sim T^{1/3}$
  - Leads to non-analyticities $c_v \sim a + bT^{1/3}$

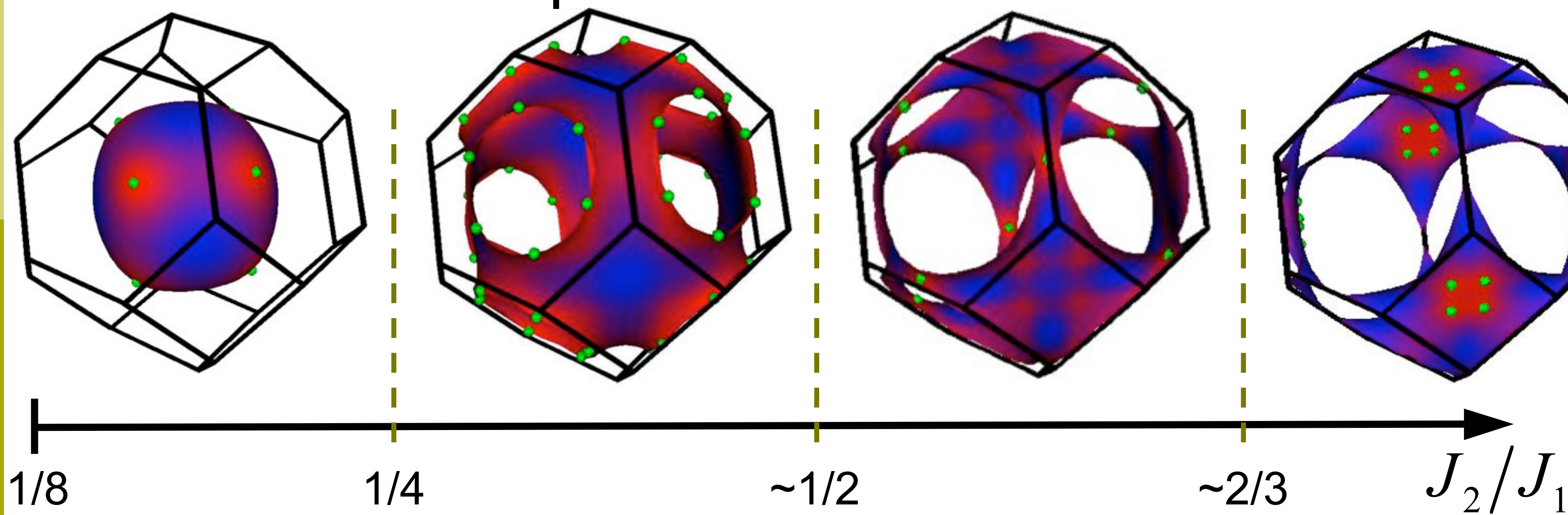
Low Temperature: Selection



- *Which state* is stabilized?
  - "Conventional" order-by-disorder
    - Need free energy on entire surface F(**q**)=E-T S(**q**)

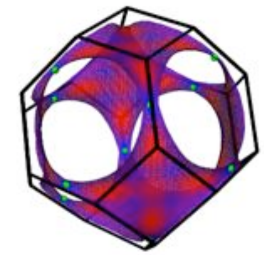
Normal mode contribution (→ S(**q**))

- Results: complex evolution!

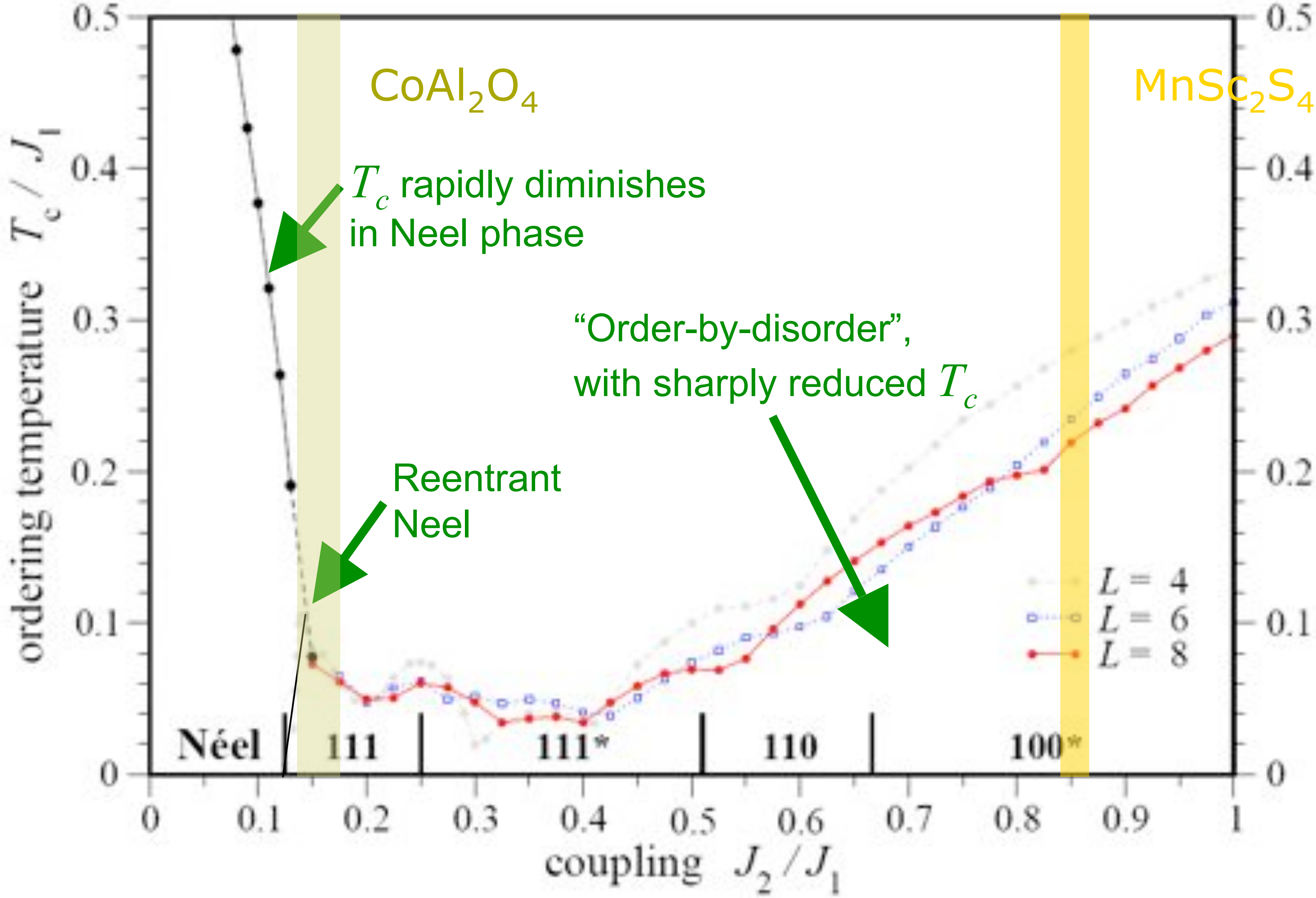


Green = Free energy minima, red = low, blue = high

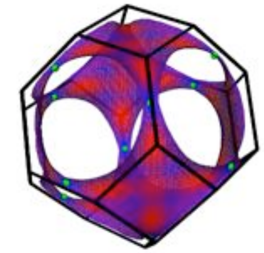
T_c: Monte Carlo



- Parallel Tempering Scheme (Trebst, Gull)



Spin Liquid: Structure Factor

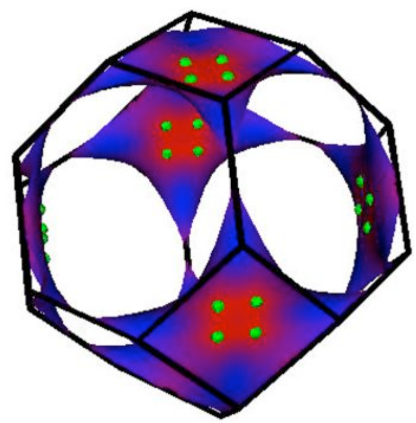


- Intensity S(q,t=0) images spiral surface

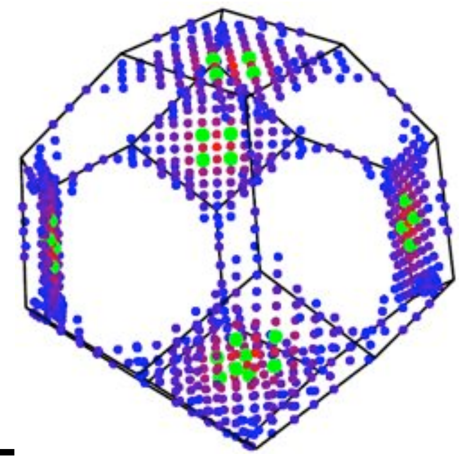
$J_2/J_1 = 0.85$

$MnSc_2S_4$

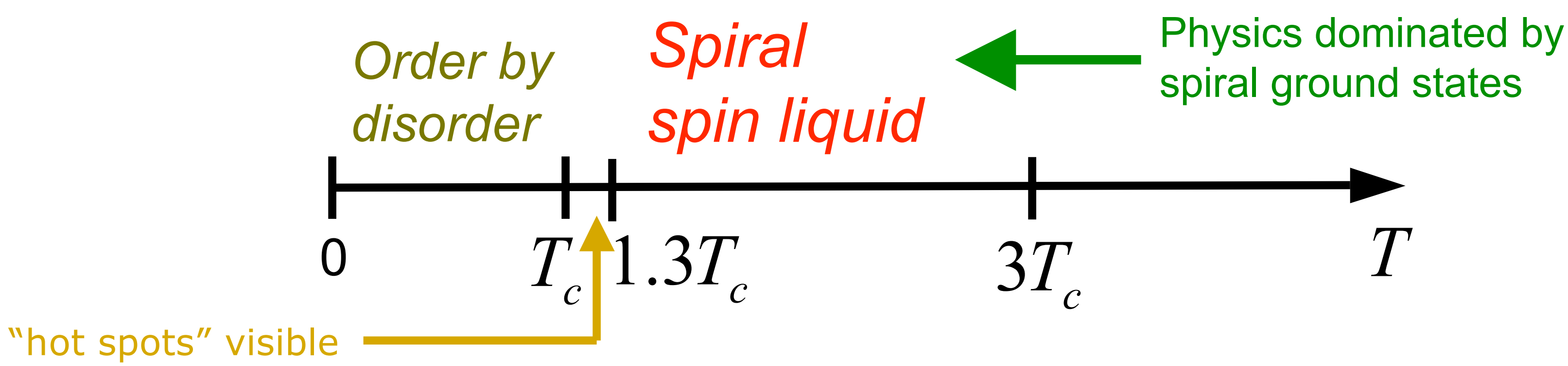
Analytic free energy



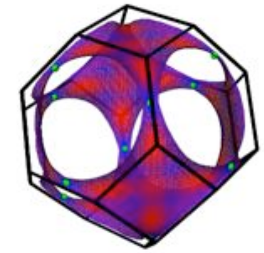
Numerical structure factor



- Spiral spin liquid: $1.3T_c<T<3T_c$



Capturing Correlations



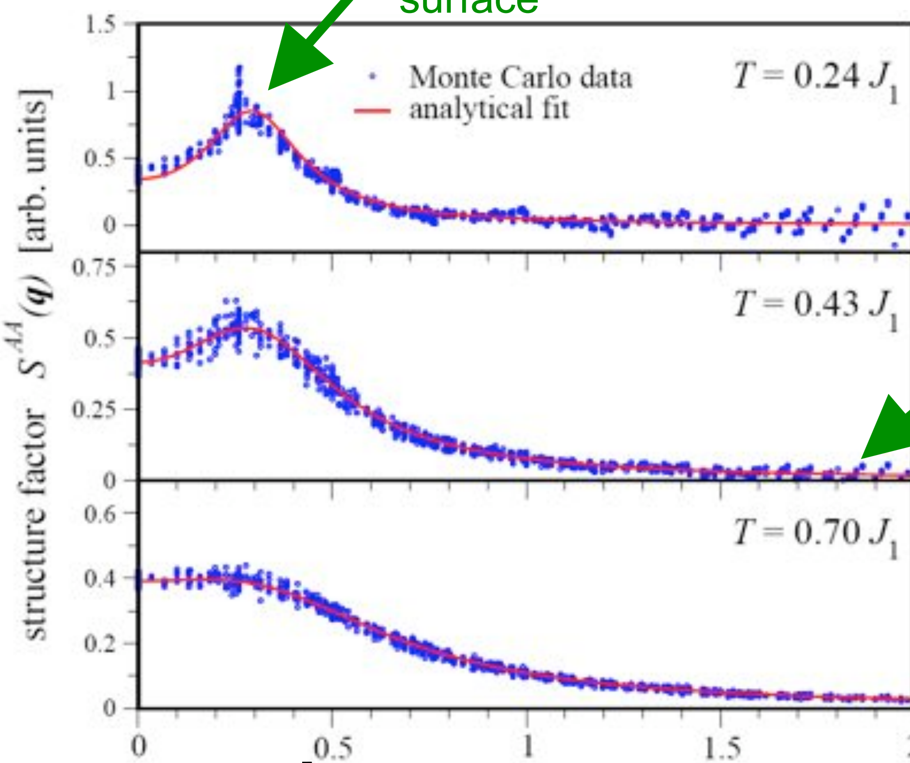
- Spherical model $|\vec{S}_i|^2 = 1 \rightarrow \sum_i |\vec{S}_i|^2 = N$
  - Predicts data collapse

$J_2/J_1 = 0.85$

$MnSc_2S_4$

Peaked near surface

Structure factor for one FCC sublattice

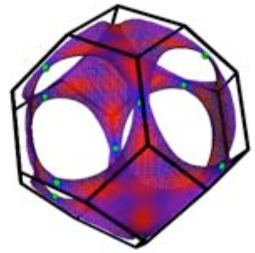


$$\Lambda(\mathbf{q}) = 2\left[\cos^2\frac{q_x}{4}\cos^2\frac{q_y}{4}\cos^2\frac{q_z}{4} + \sin^2\frac{q_x}{4}\sin^2\frac{q_y}{4}\sin^2\frac{q_z}{4}\right]^{1/2}$$

Quantitative agreement! (except very near T_c)

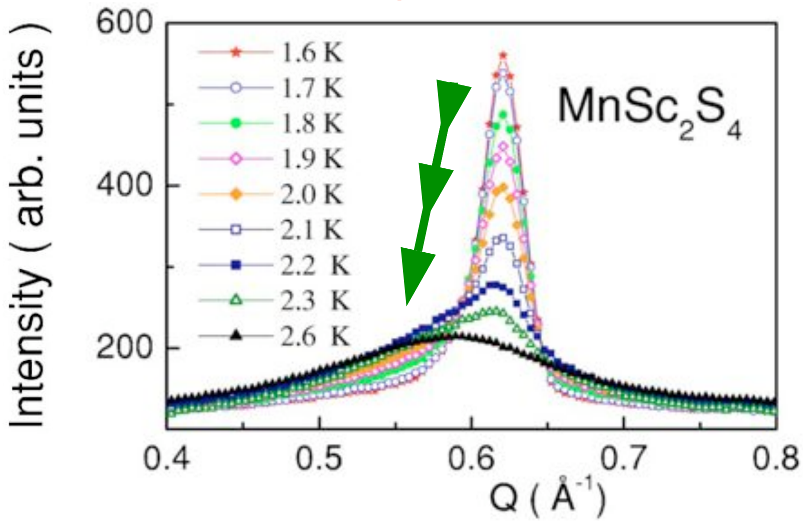
Nontrivial experimental test, but need single crystals…

Comparison to $MnSc_2S_4$

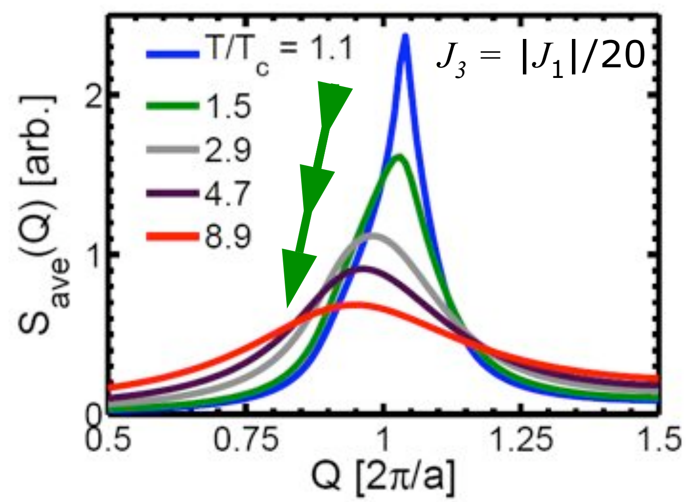


- Structure factor reveals intensity shift from full surface to ordering wavevector

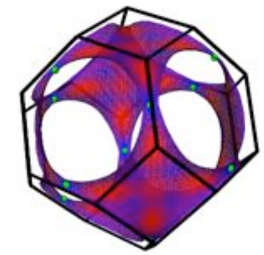
Experiment



Theory

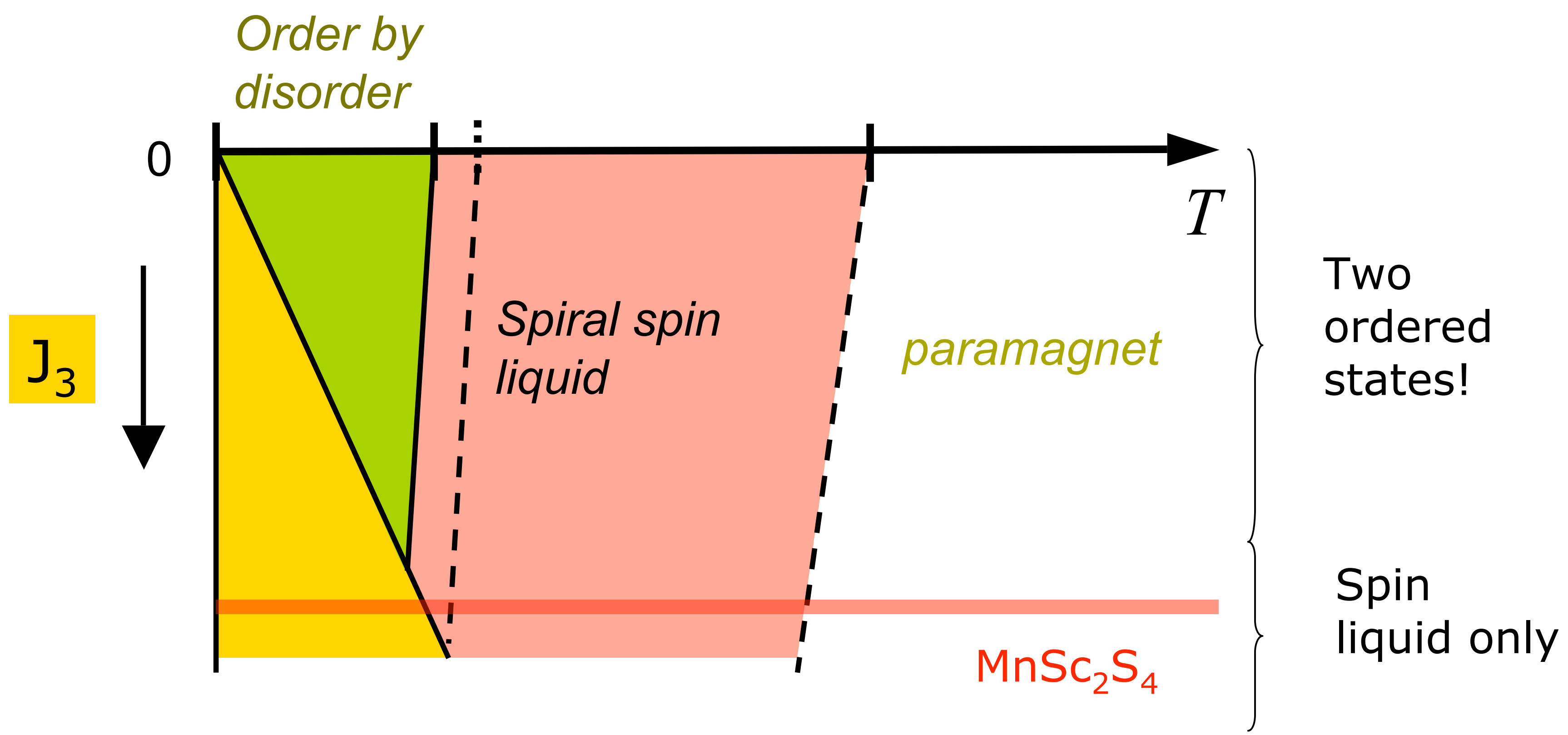


A. Krimmel et al. PRB **73**, 014413 (2006); M. Mucksch *et al*. (2007)

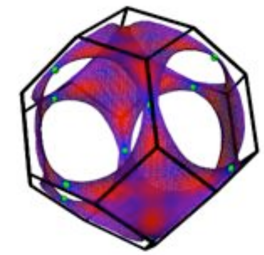


Degeneracy Breaking

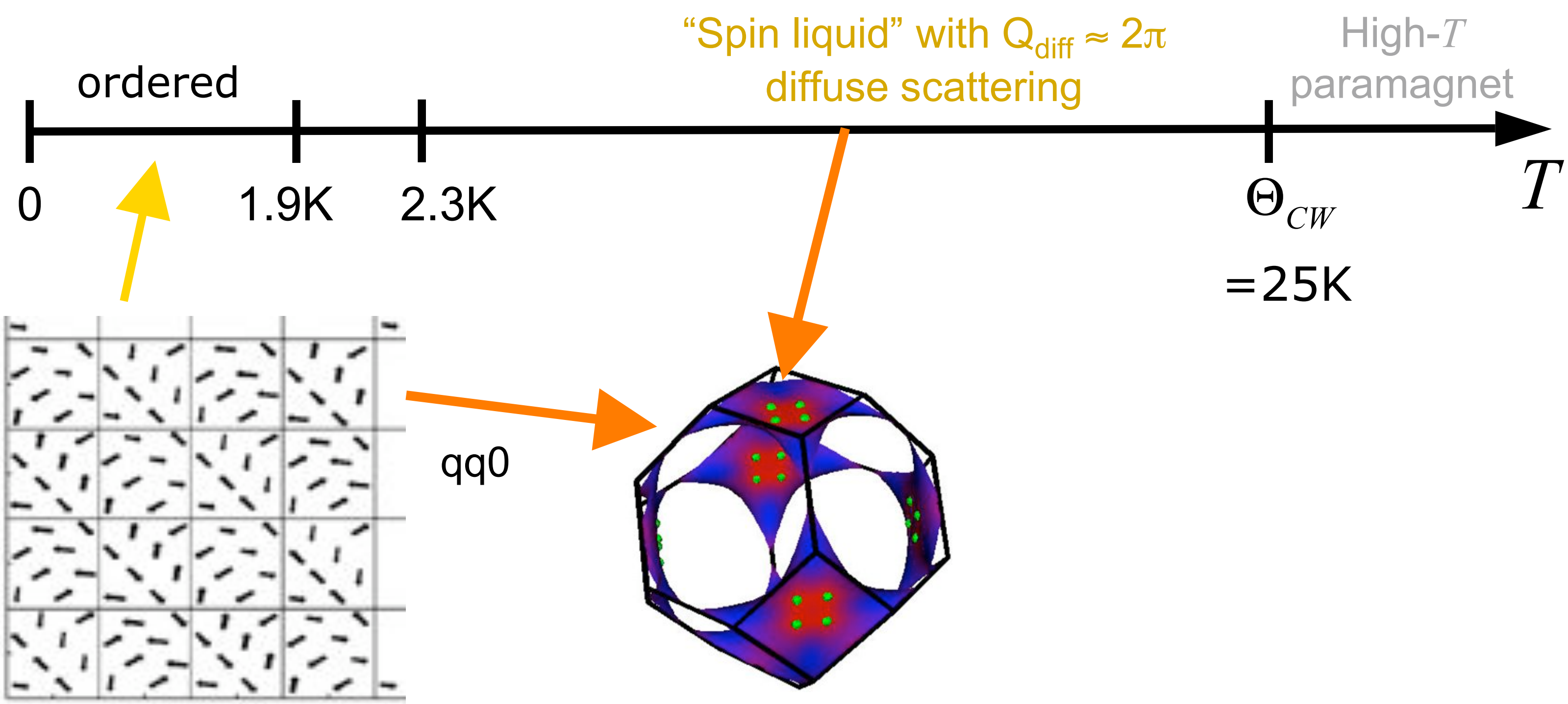
- Additional interactions (e.g. J_3) break degeneracy at low T



Comparison to $MnSc_2S_4$



- Ordered state $\mathbf{q}=2\pi(3/4,3/4,0)$ explained by *FM* J_1 and weak AF J_3



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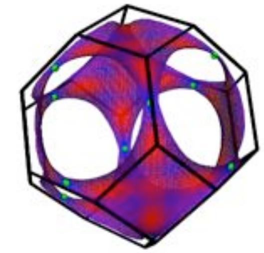
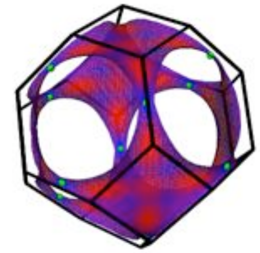


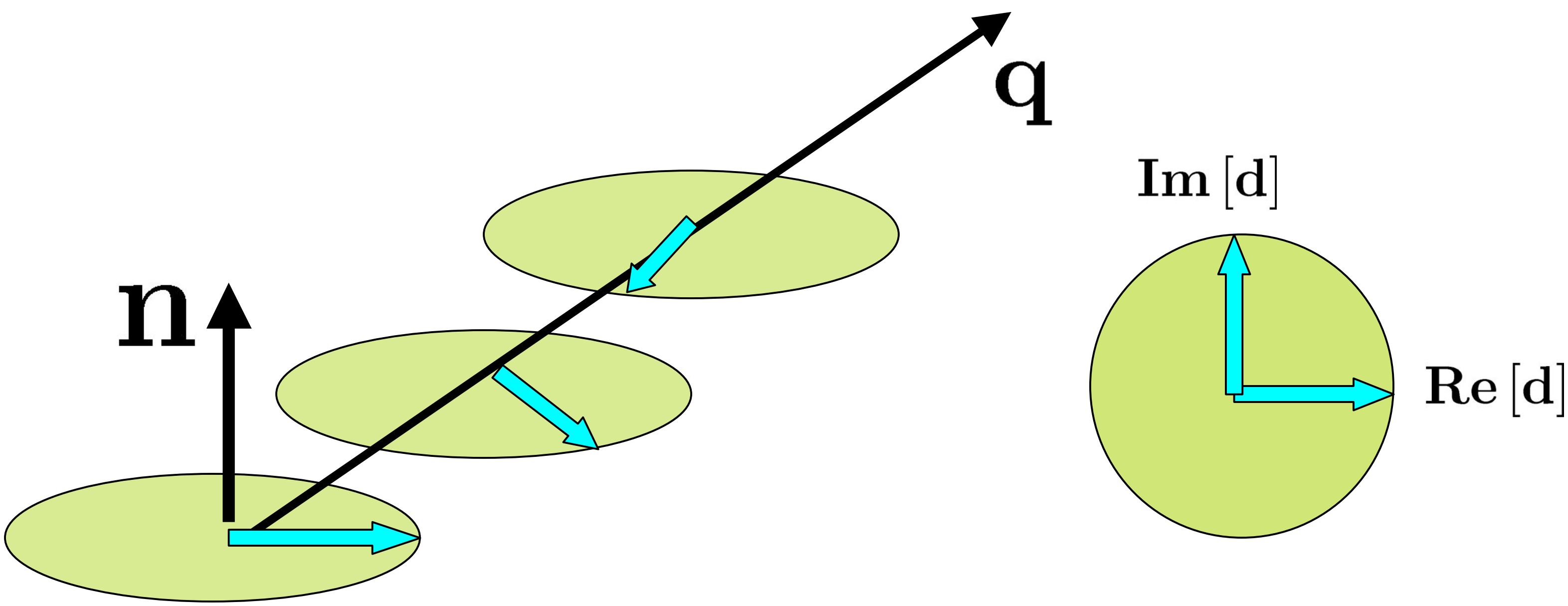
Magnetic anisotropy

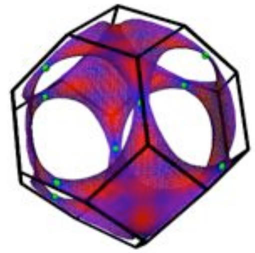
- Details of $MnSc_2S_4$ cannot be described by Heisenberg model
  - Spins in <100> plane
    - *Not* parallel to wavevector **q**=(q,q,0): ferroelectric polarization?
  - Wavevector "locks" to commensurate q=3¼/2

Landau theory



- Order parameter $\mathbf{S} = \mathrm{Re}\left[\mathbf{d}e^{i\mathbf{q}\cdot\mathbf{r}}\right]$
- Coplanar state $\mathbf{d}\cdot\mathbf{d} = 0 \qquad \mathbf{d}^*\cdot\mathbf{d} = 2$
- Spin plane $\mathbf{n} = i\mathbf{d}\times\mathbf{d}^*$

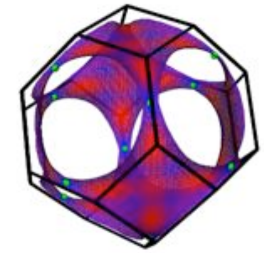




Order of energy scales

J_1, J_2	Spiral surface formed
J_3	Specific **q** selected
?	Spin spiral plane chosen
?	Lock-in

- Require symmetry under subgroup of space group preserving **q** =(q,q,0)

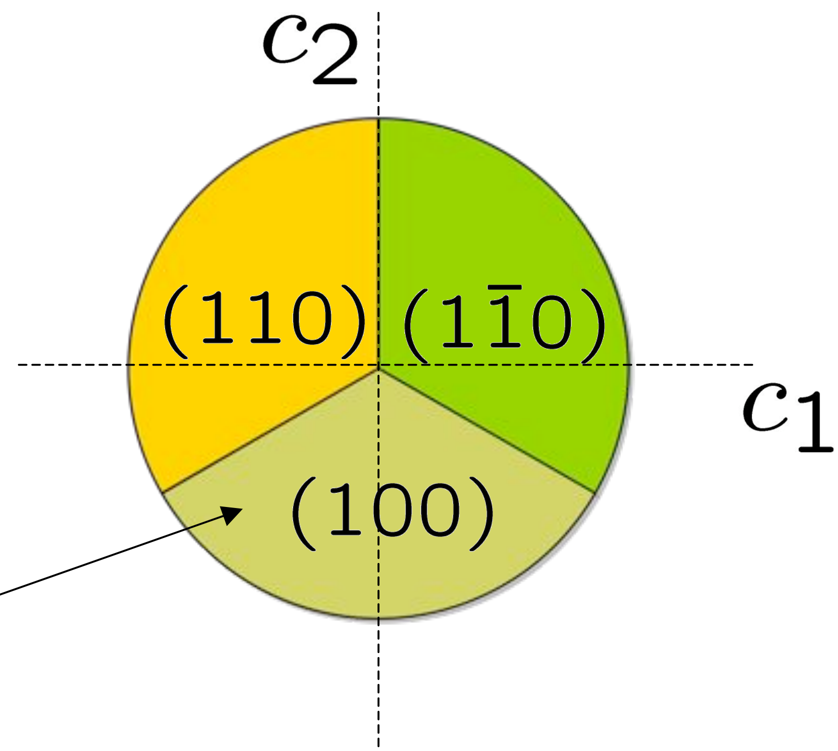


Landau Theory

- Free energy (**q**=(q,q,0))

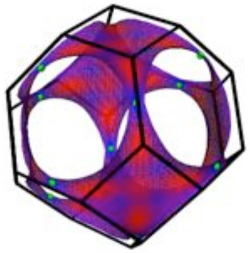
$$F_a = -c_1 \left[d_x^* d_y + d_y^* d_x \right] - c_2 d_z^* d_z$$

- Phase diagram
  - Direction of **n**



Observed spin order in $MnSc_2S_4$

Mechanisms?

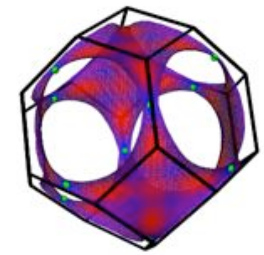


- Dipolar interactions

$$H_d = \lambda \sum_{ij} \left[\frac{\mathbf{S}_i \cdot \mathbf{S}_j}{r_{ij}^3} - \frac{\mathbf{S}_i \cdot \mathbf{r}_{ij} \mathbf{S}_j \cdot \mathbf{r}_{ij}}{r_{ij}^5} \right]$$

  - Effect favors **n**=(110)
  - Very robust to covalency corrections and fluctuations
    - Quantum fluctuations reduce moment by 20% but do not change dipole favored order
- Dzyaloshinskii-Moriya interactions
  - Ineffective due to inversion center
- Exchange anisotropy
  - Depending upon significance of first and second neighbor contributions, this can stabilize **n**=(100) order

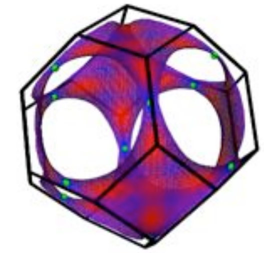
Predictions related to anisotropy



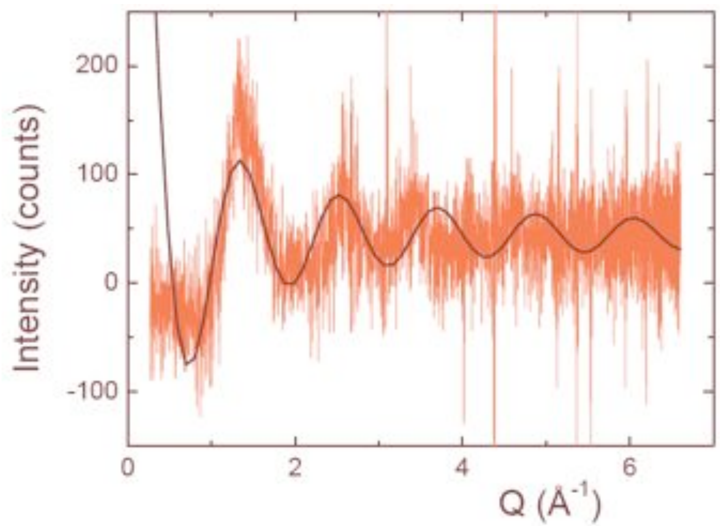
- Lock-in occurs as observed
- Spin flop observable in magnetic field not along (100) axis
  - Observed at B=1T field (Loidl group, private communication)
- Order accompanied by electric polarization, tunable by field

$$\mathbf{P} \sim \mathbf{q} \times \mathbf{n}$$

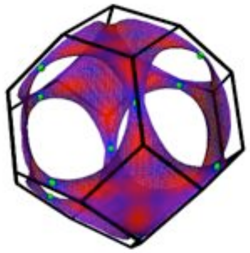
Impurity Effects



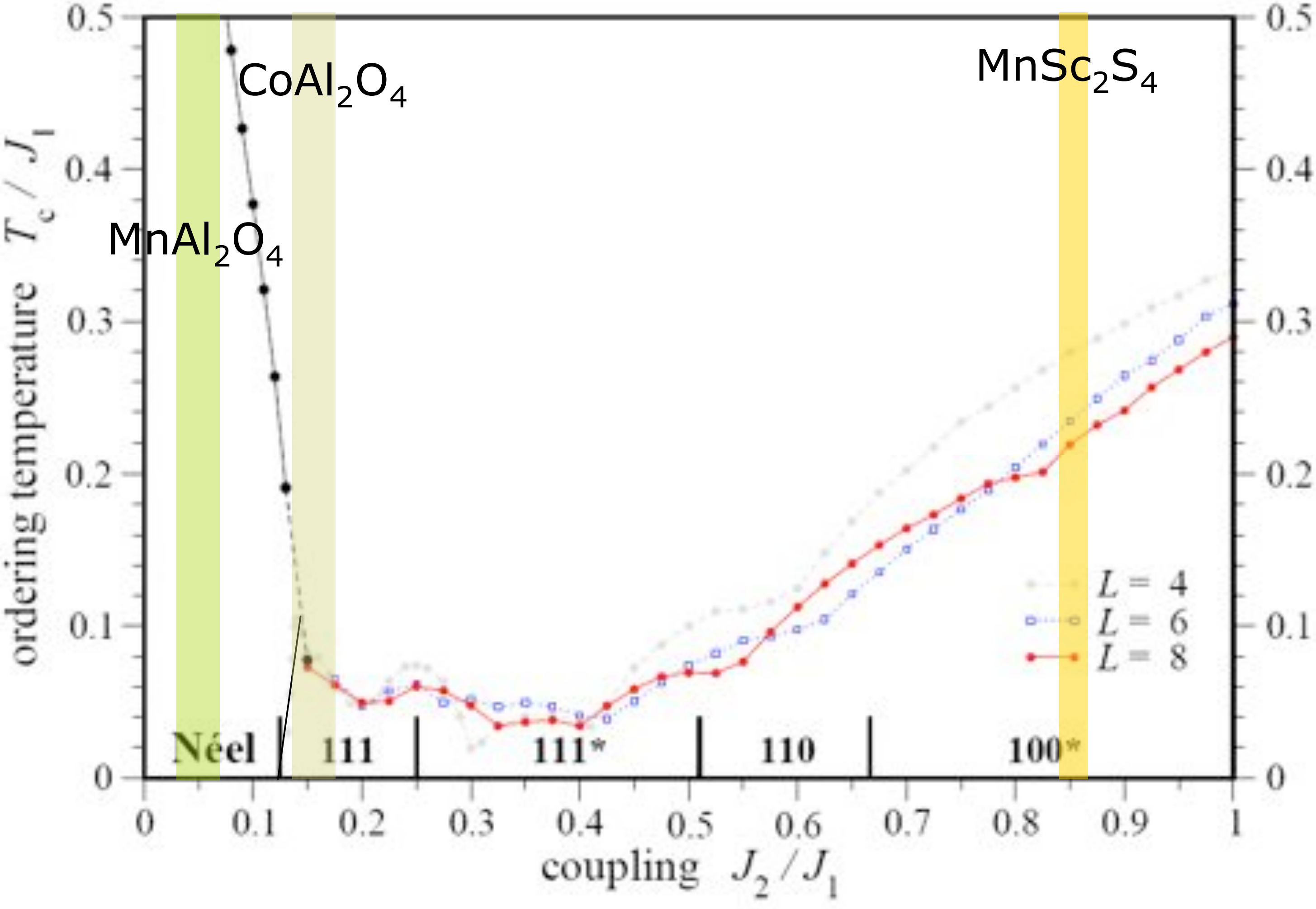
- Common feature in spinels
  - "inversion": exchange of A and B atoms
  - Believed to occur with fraction x ~ 5% in most of these materials
- Related to "glassy" structure factor seen in $CoAl_2O_4$?
  - But: why not in $MnAl_2O_4$, $CoRh_2O_4$, $MnSc_2S_4$?



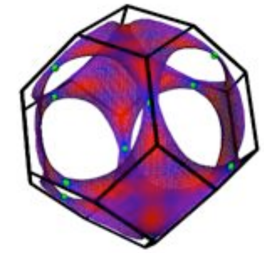
Impurity Effects: theory



- A hint: recall phase diagram



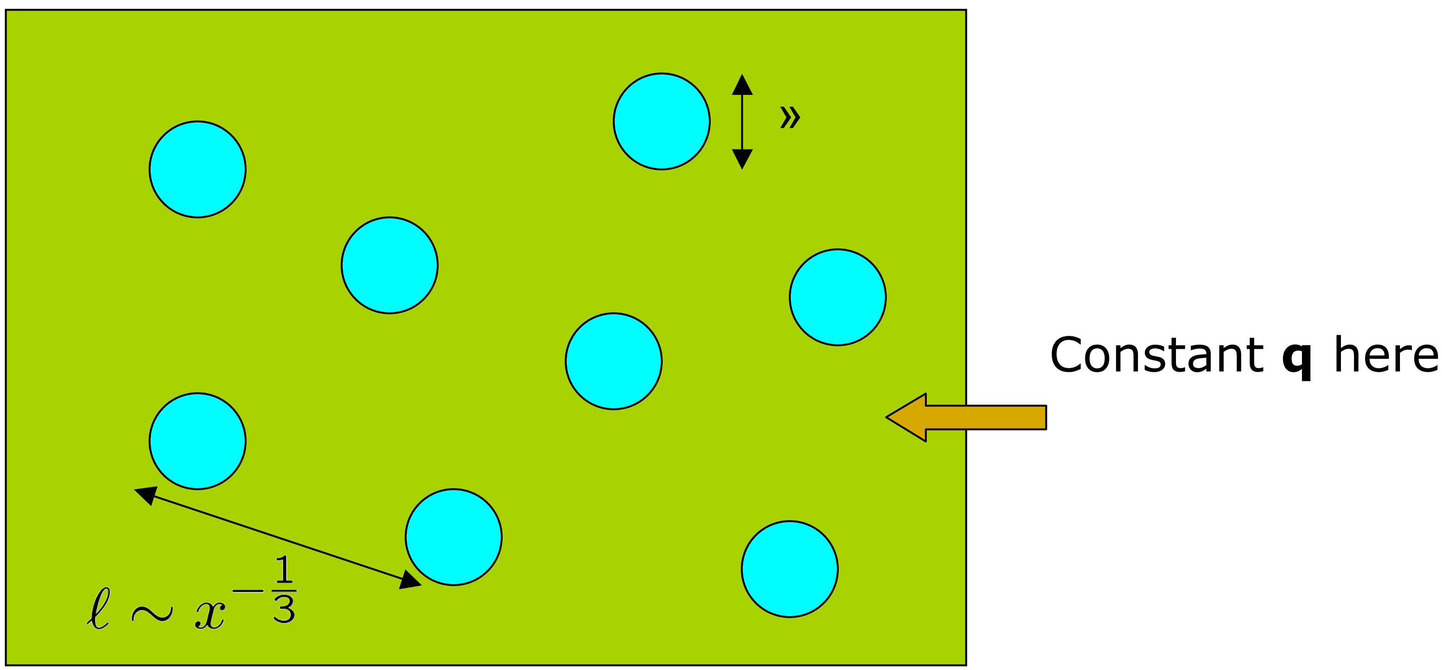
Sensitivity to impurities

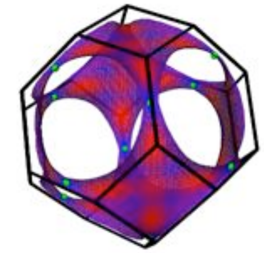


- Seems likely that $CoAl_2O_4$ is more sensitive to impurities because it lies near "Lifshitz point"
- What about spiral degeneracy for $J_2>J_1/8$?
- Competing effects:
  - Impurities break "accidental" spiral degeneracy: favors *order*
  - Different impurities prefer different wavevectors: favors *disorder*
- Subtle problem in disordered "elastic media"

Swiss Cheese Picture

- A single impurity effects spin state only out to some characteristic distance » & ¸
  - Stiffness energy $\int d^3x\, \rho(\nabla \cdot \mathbf{q})^2$





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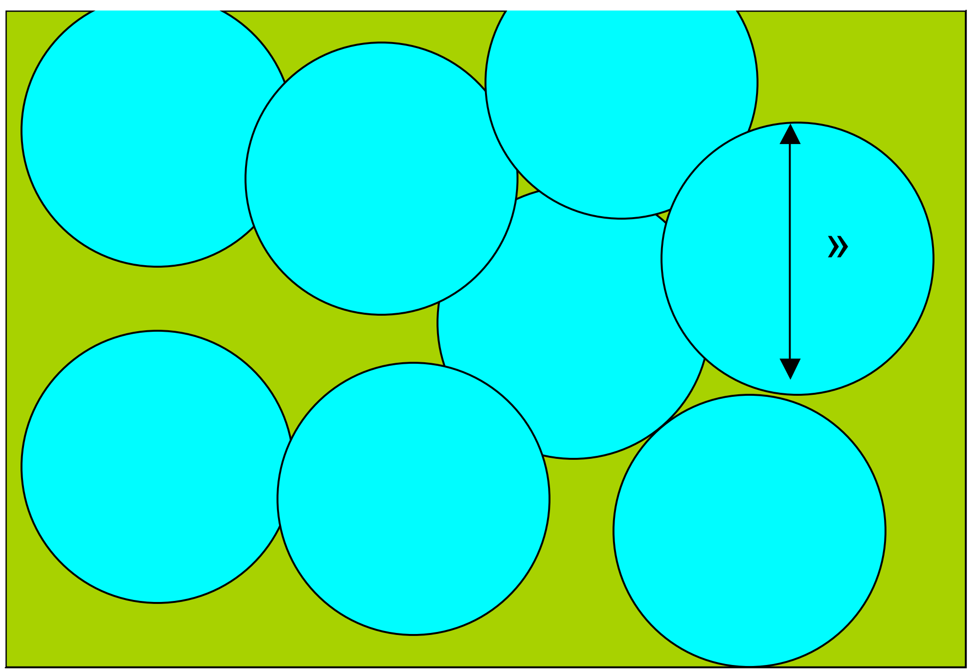
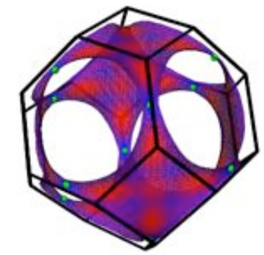


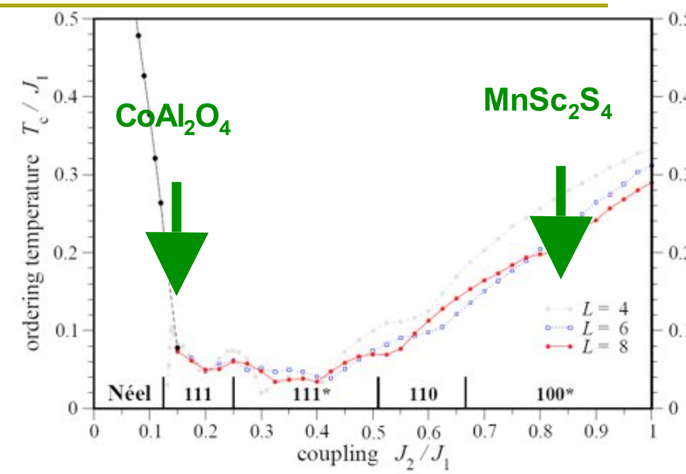
$$\xi \sim \ell$$

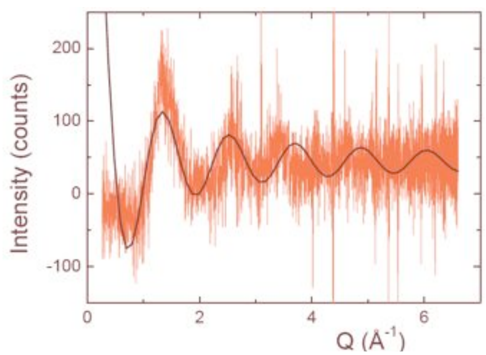
- local patches of different **q**



Comparison to $CoAl_2O_4$

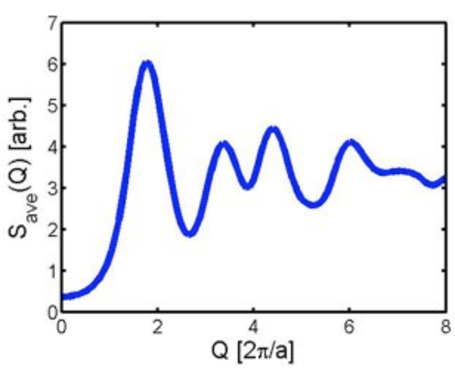
- Close to $J_2/J_1=1/8$
  - $|\mathbf{q}| \to 0$: ¸ $\to \infty$: large »
- "Theory":





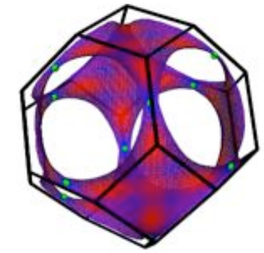
Experiment

T. Suzuki *et al*, 2007



"Theory":
average over
spherical surface

Outlook



- Combine understanding of A+B site spinels to those with *both*
  - Many interesting materials of this sort exhibiting ferrimagnetism, multiferroic behavior…
- Take the next step and study materials like $FeSc_2S_4$ with spin *and orbital* frustration
- Identification of systems with important quantum fluctuations?