Jan. 2015
Winter Theory School
Tallahassee, FL

# Experimental Pyrochlore Systems

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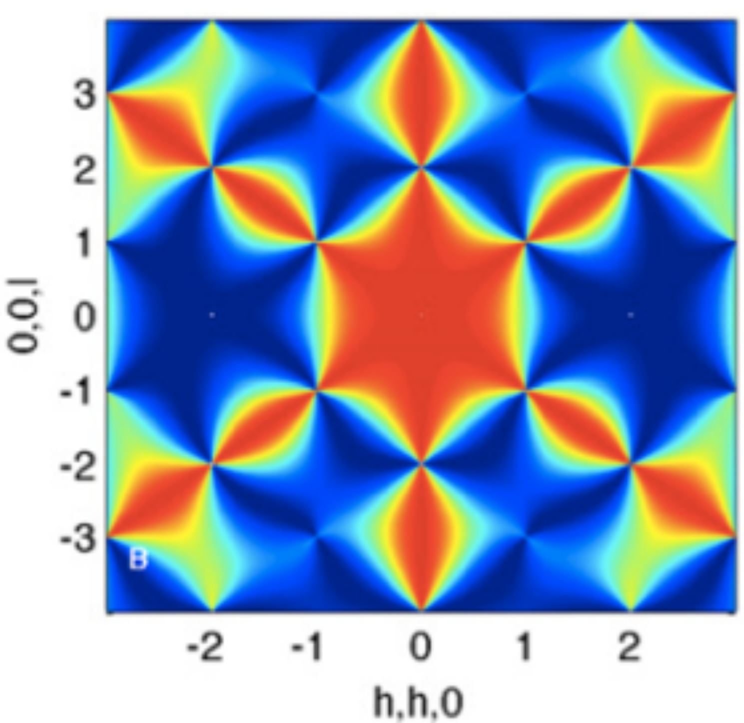
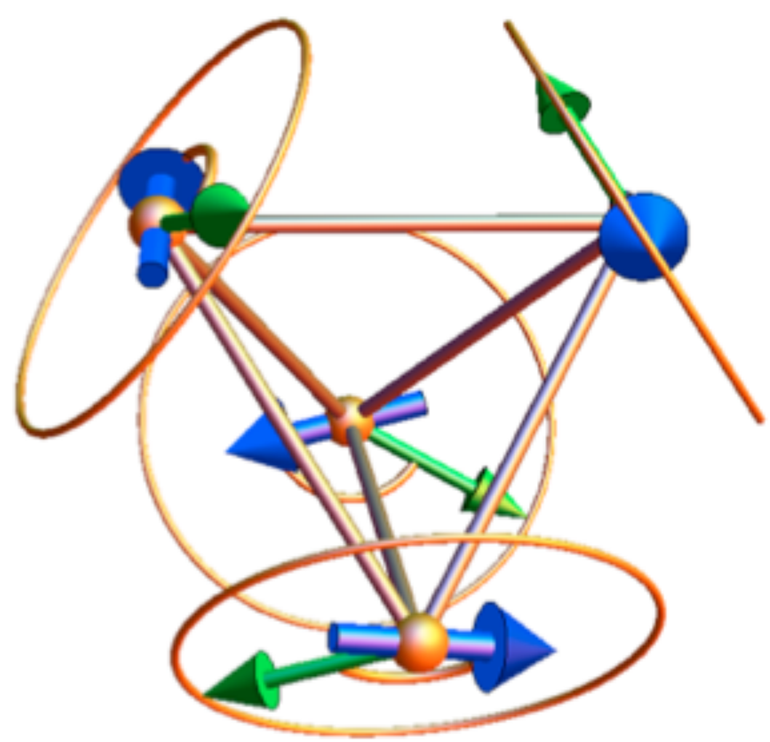
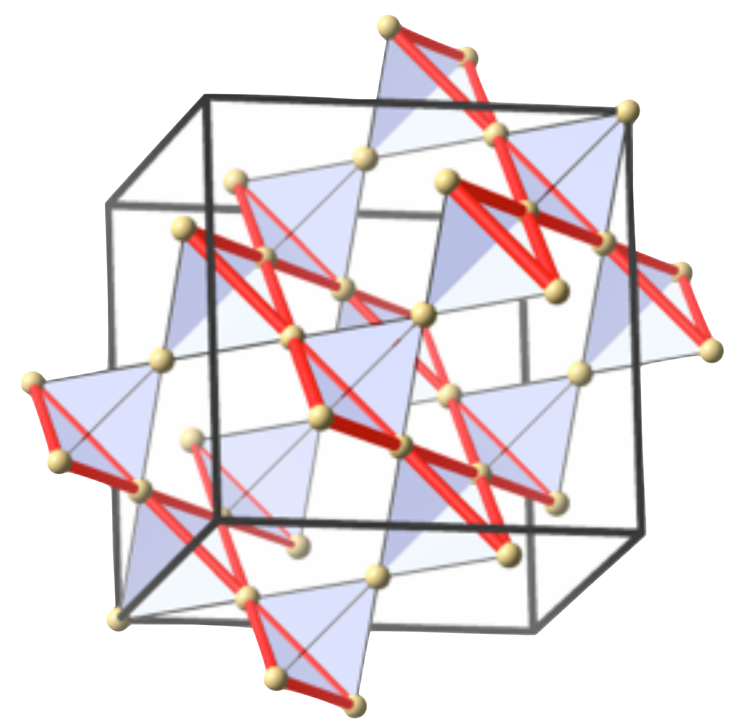
Colorado State University





# Colorado State University

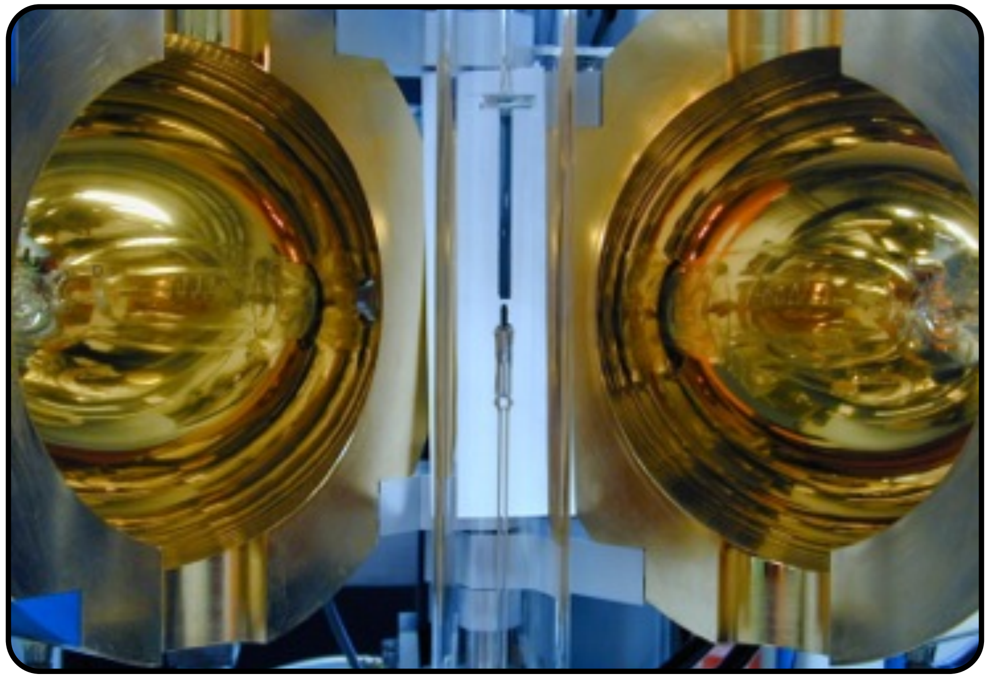
**<u>Located in Fort Collins, CO</u>**
~1 hour drive north of Denver, up against the Rocky Mountains

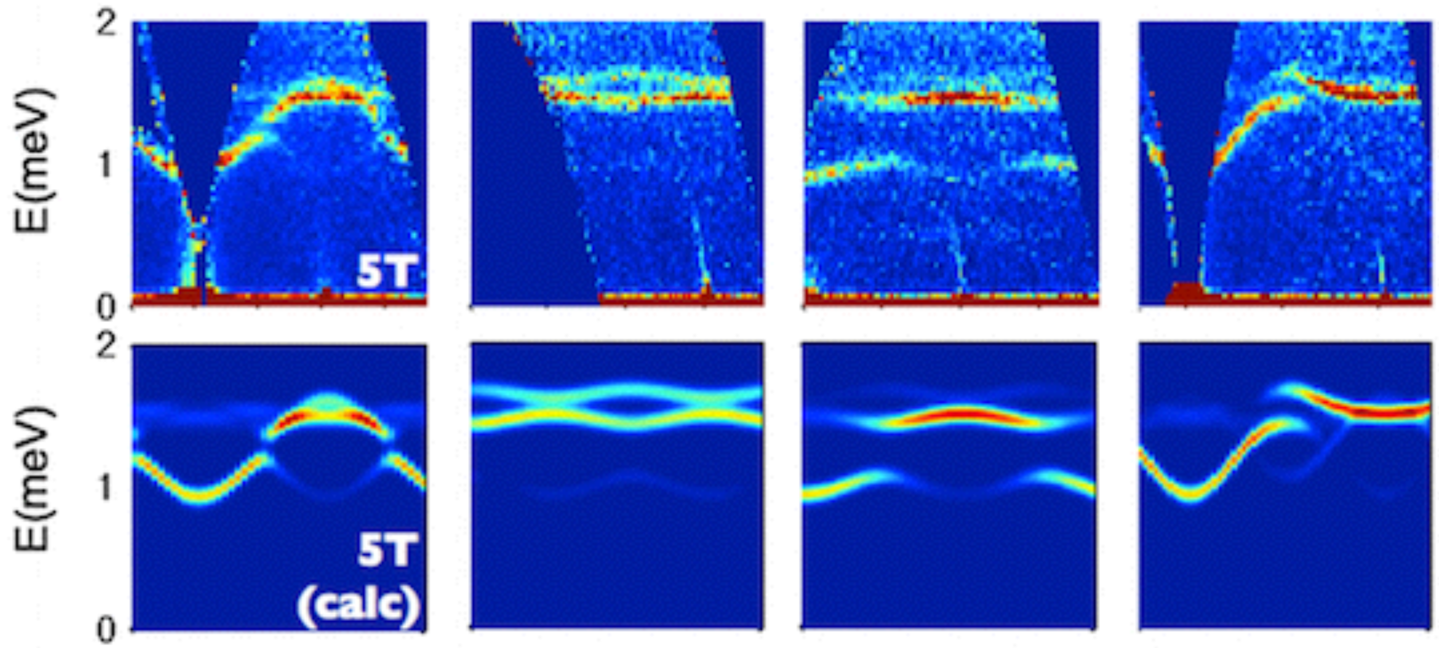
# Ross Lab: Quantum Magnetism and Neutron Scattering

- Frustrated Magnetism
- Quantum Spin Liquids
- Quantum Phase Transitions
- Crystal Growth

- Strong collaborations with theory and Chemistry groups

http://www.physics.colostate.edu/our-people/kate-ross/





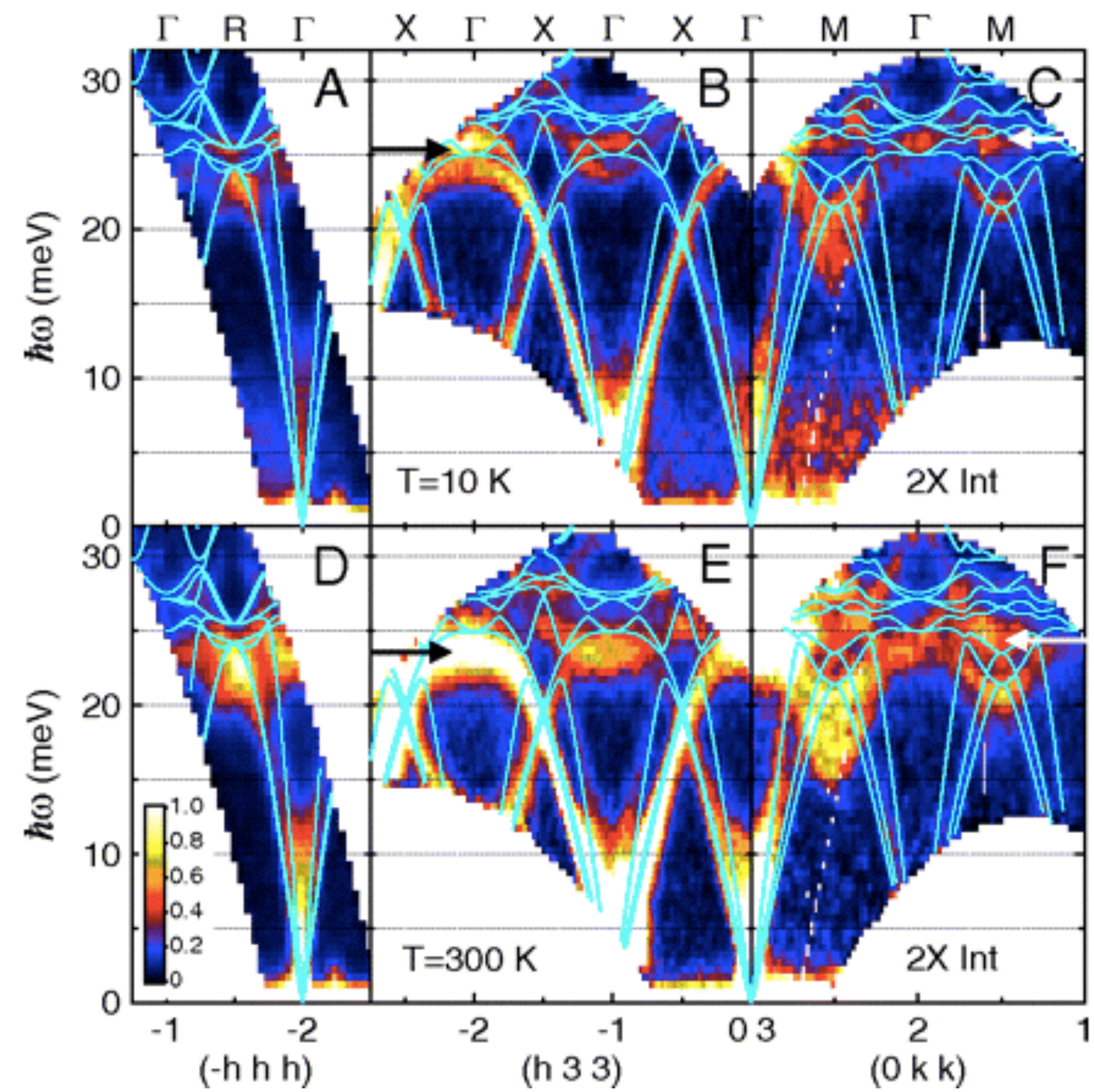
# Overview

- Very short primer on neutron scattering
- Overview of Pyrochlore Materials
- Spin Ice
- Quantum Spin Ice
- Order By Disorder in XY pyrochlore

**At the end of each section I will list some useful references**

# Neutron Scattering

- Neutrons are waves, and we can use them for diffraction ($\lambda = 2\, d \sin(\theta)$, $E = h^2/2m\lambda^2$ )
- for thermal neutrons, $\lambda \sim 2$Å, E ~ 20 meV
- Well suited to probe lattice structure *and* dynamics in condensed matter
- Neutrons have a magnetic dipole moment: Magnetic diffraction possible




Phonons from FeSi
ARCS instrument at SNS
O. Delaire, et al PNAS **108** 4725 (2013)

# Neutron Scattering

- Neutrons take the **Fourier transform** in space and time of pairwise correlations

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int\int G(\mathbf{r},t)e^{i\mathbf{Q}\cdot\mathbf{r}}e^{-i\omega t}d^3r dt$$

G(**r**,t) = Pairwise Correlations in Space and Time

$$\mathcal{S}^{\alpha\beta}(\mathbf{Q},\omega) \equiv \frac{1}{2\pi\hbar}\int dt e^{-i\omega t}\frac{1}{N}\sum_{ll'} e^{i\mathbf{Q}\cdot(\mathbf{r}_l-\mathbf{r}_{l'})}\left\langle S_l^{\alpha}(0)S_{l'}^{\beta}(t)\right\rangle$$

e.g. Spin-Spin correlations

# Fluctuation Dissipation Theorem

General linear response susceptibility:

$$\chi(Q,\omega) = \chi'(Q,\omega) + \chi''(Q,\omega)$$

Energy absorbing response

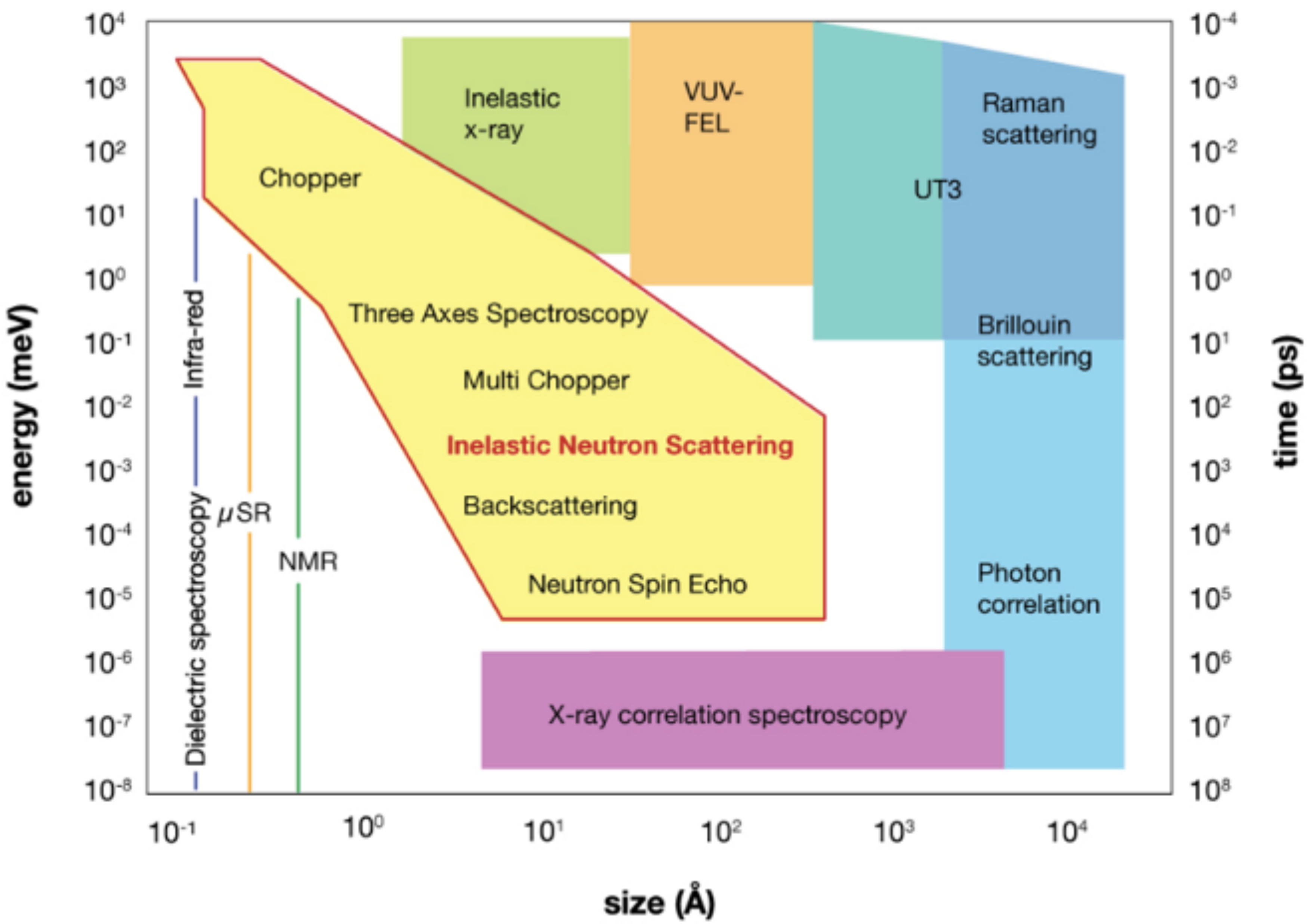
**Fluctuation Dissipation Theorem**

$$S(Q,\omega) = \frac{1}{1-e^{-\beta\hbar\omega}} \frac{\chi''(Q,\omega)}{\pi(g\mu_B)^2}$$

With inelastic neutron scattering,
we are measuring the imaginary part of the susceptibility

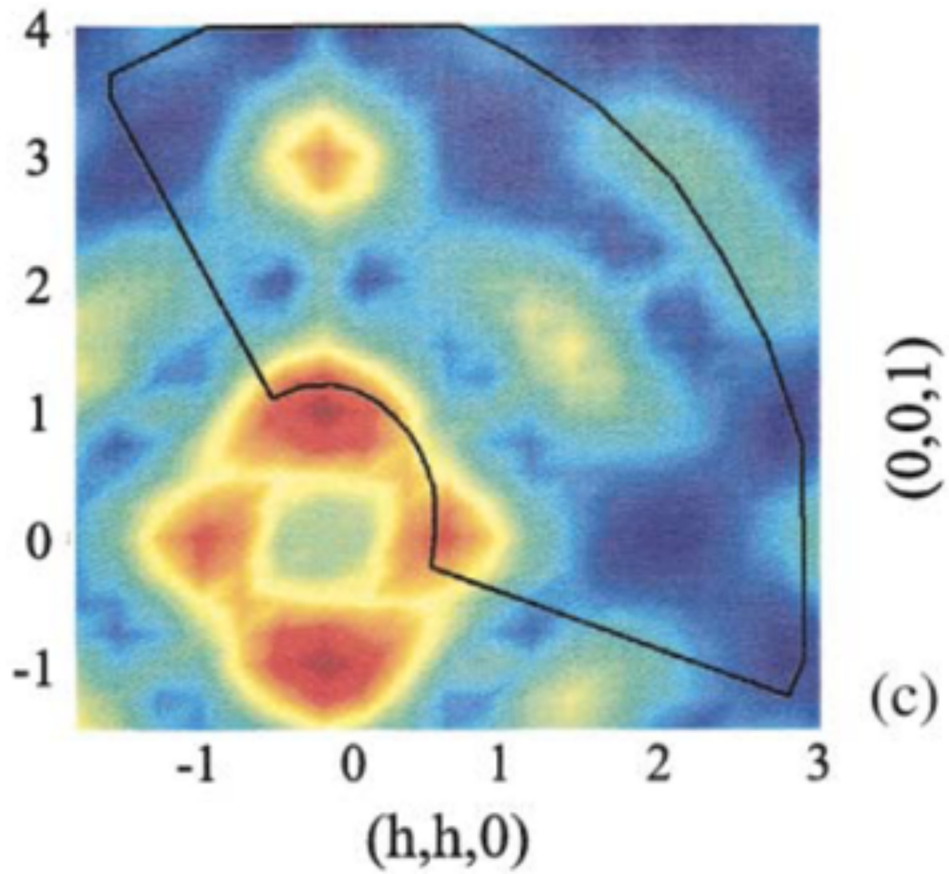
# Time and Length Scales probed by Neutron Scattering

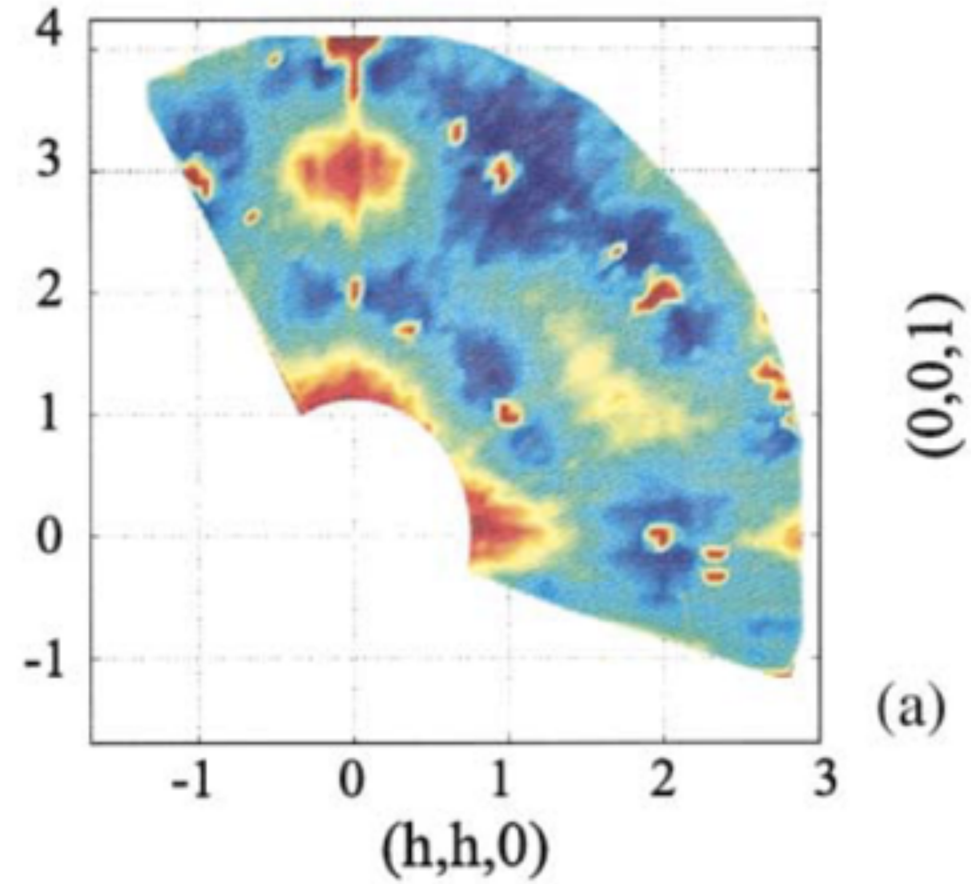
http://www.mlz-garching.de/englisch/neutron-research/experimental-methods/inelastic-scattering.html




- Huge dynamic range available
- ~5 eV down to 5e-6 eV (5 fs to 500 ns) accessible by combining techniques
- ~0.1 Å to 500 Å (60 $Å^{-1}$ to 0.01 $Å^{-1}$)

# Elastic Scattering Maps



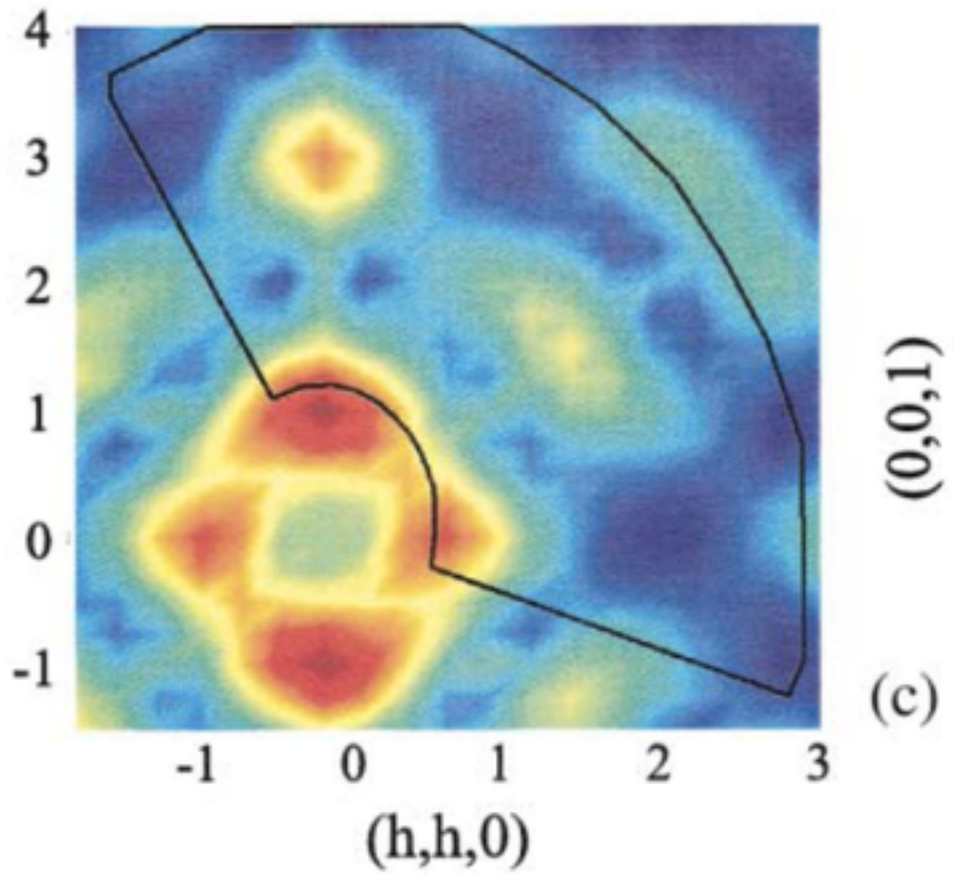



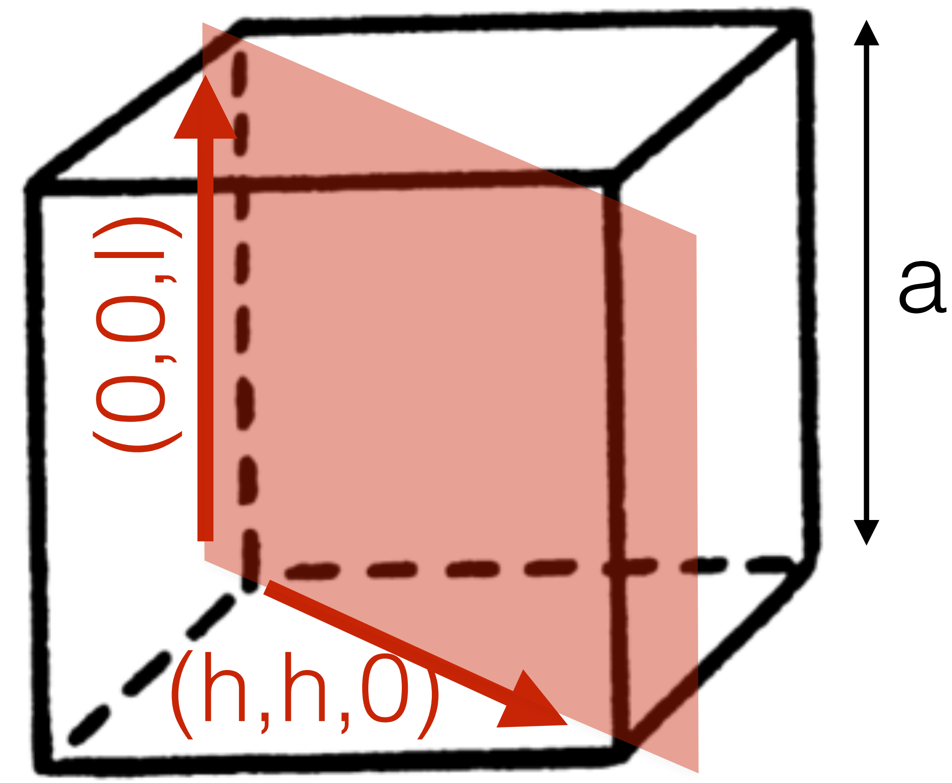

S.T. Bramwell et al, PRL **87** (2001)

**Common Questions**

1) What do the axes mean, and what units are they in?
2) Why does it have the weird seashell shape?
3) What do the colors mean?

# Elastic Scattering Maps




e.g. h = $Q_x$ / (2π/$a$)

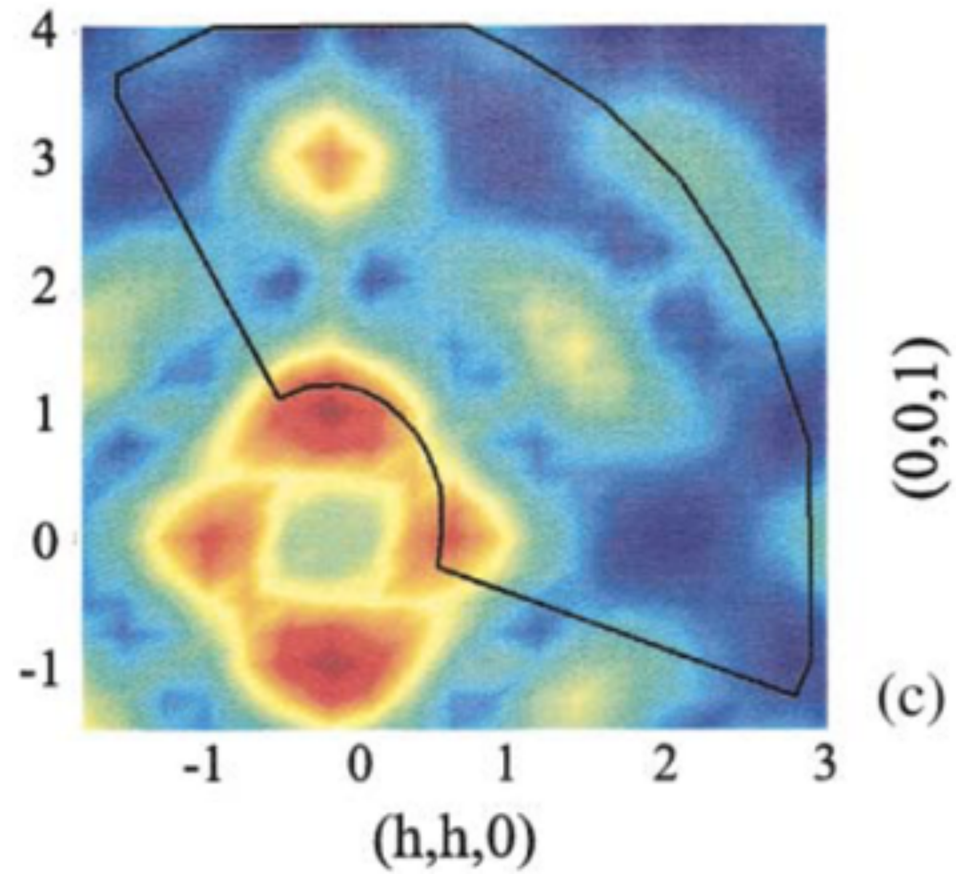
**Common Questions**

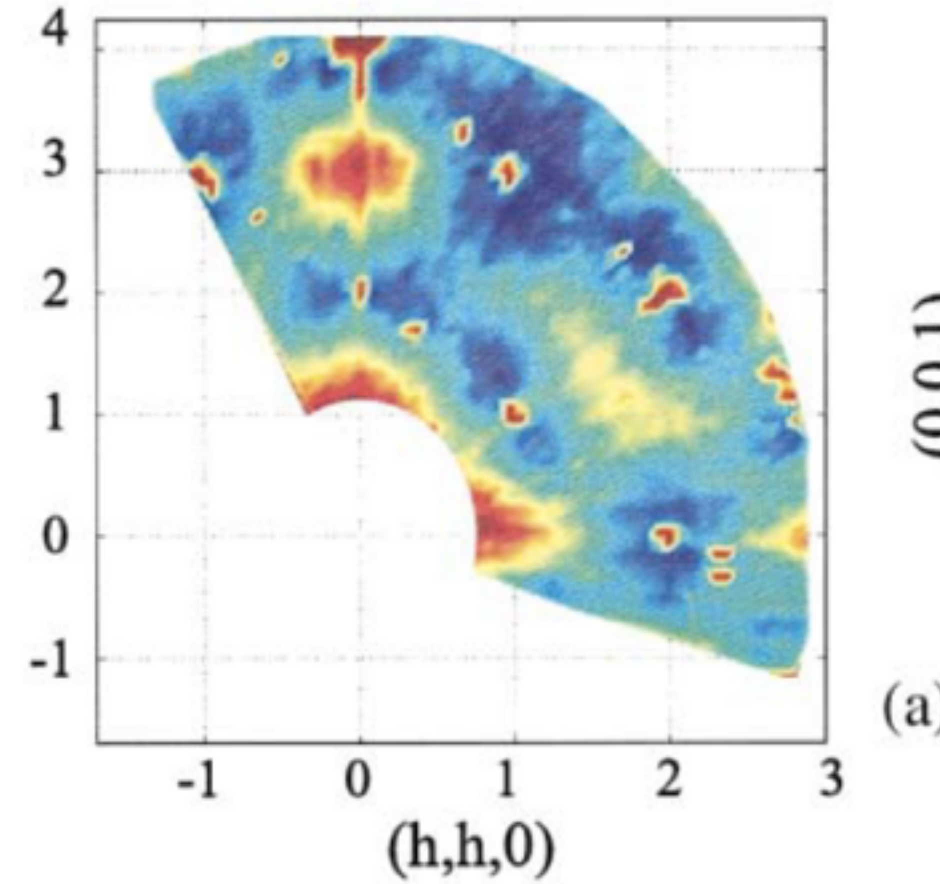
1) What do the axes mean, and what units are they in?

**Answer**

Momentum directions in reciprocal space. (h,h,0) means a vector along the [110] direction, (0,0,l) is along the [001] direction. Units are "reciprocal lattice units" (r.l.u.)

# Elastic Scattering Maps




- λ = 4π Q sin(θ)

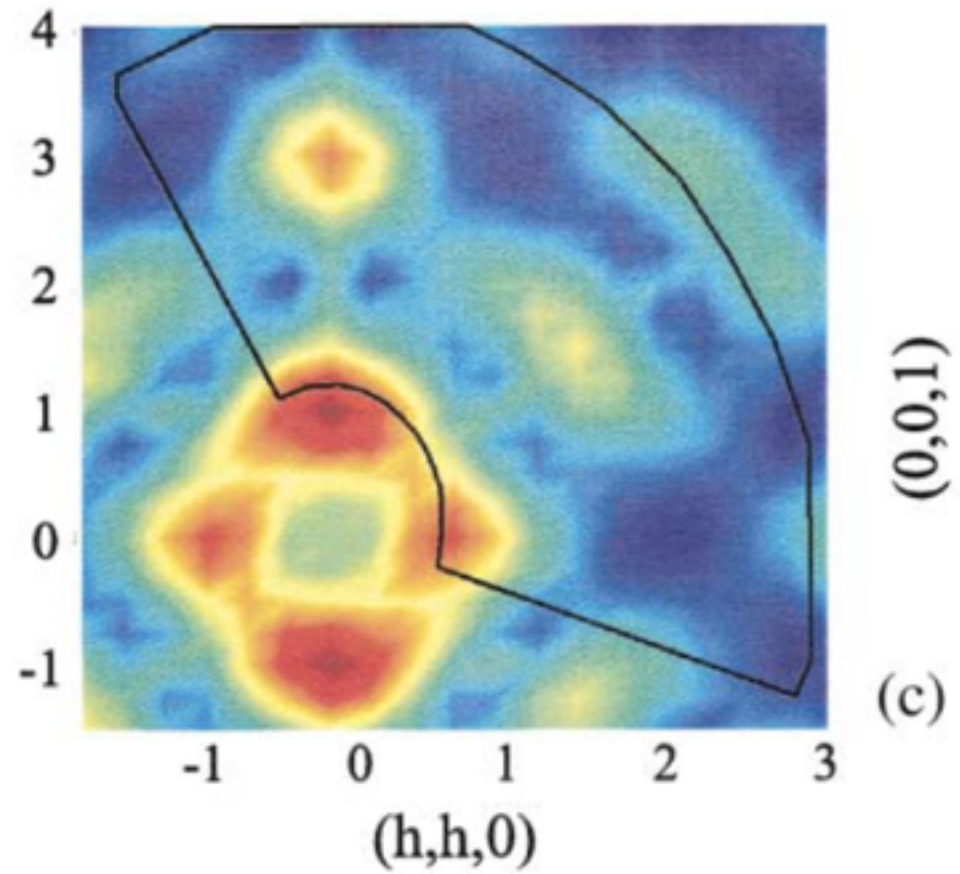
**Common Questions**

2) Why does it have the weird seashell shape?

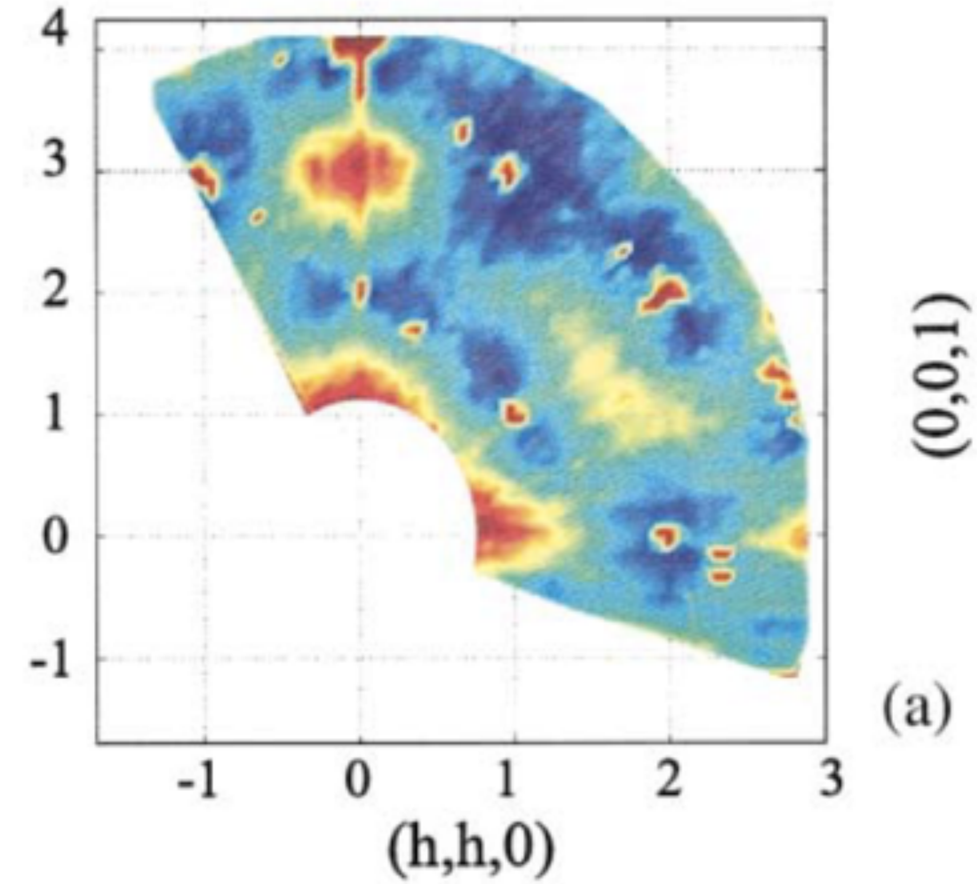
**Answer**

We measure momentum transfer by varying instrumental angles (Bragg's Law). The shape represents the angular limits of the instrument.

# Elastic Scattering Maps




(c)




(a)

**Common Questions**

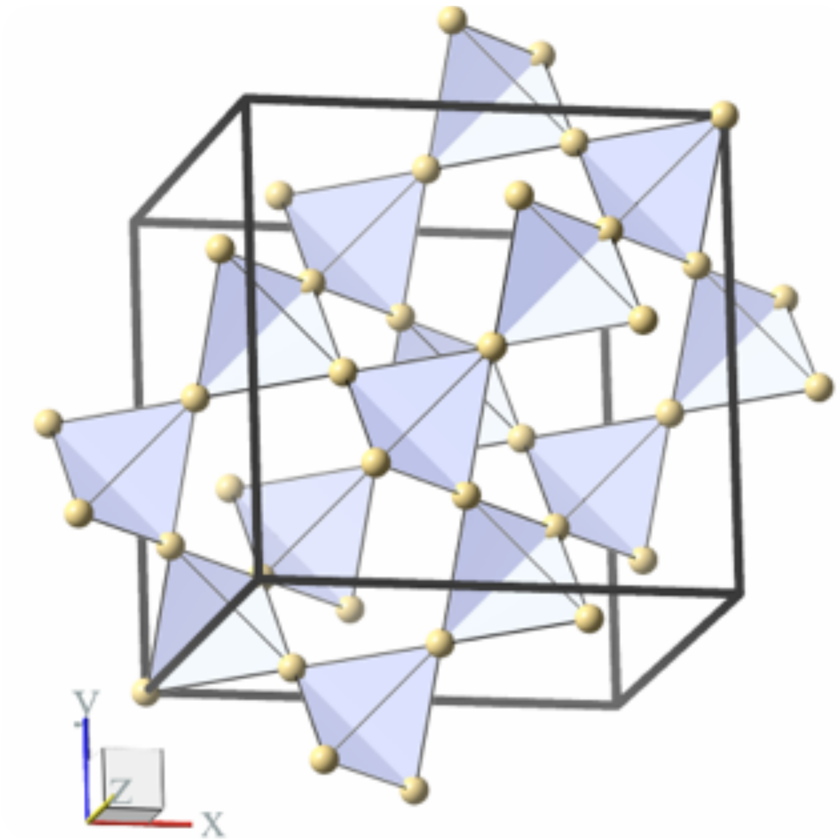
1) What do the colors mean?

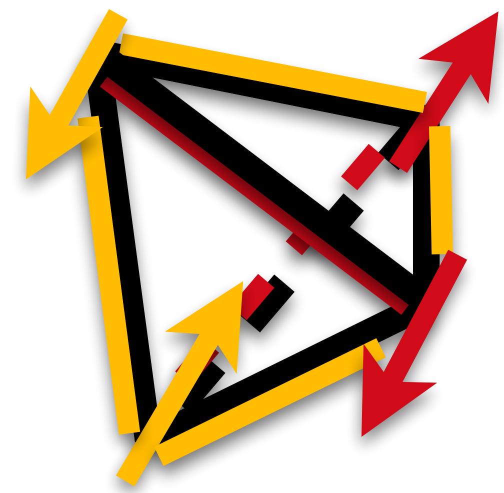
**Answer**

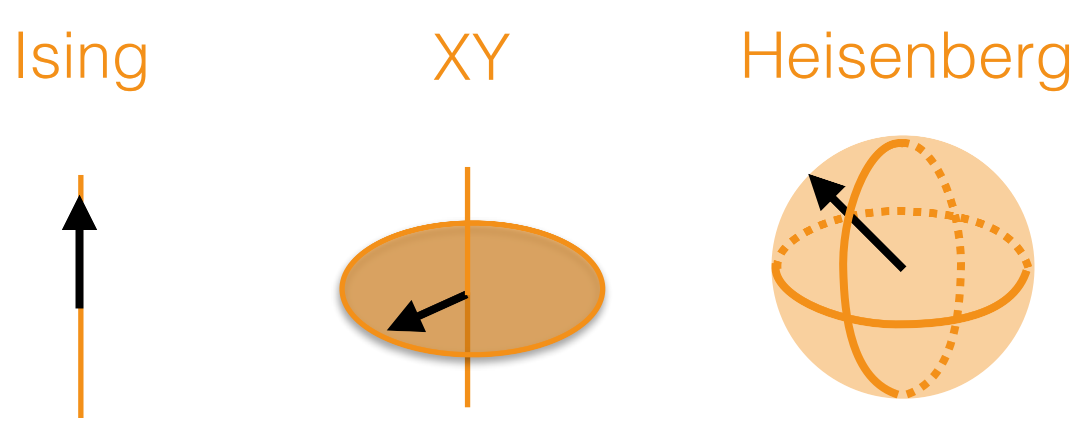
The number of neutrons counted corresponding to that momentum transfer (usually in arb. units). This is the strength of S(**Q**, 0).

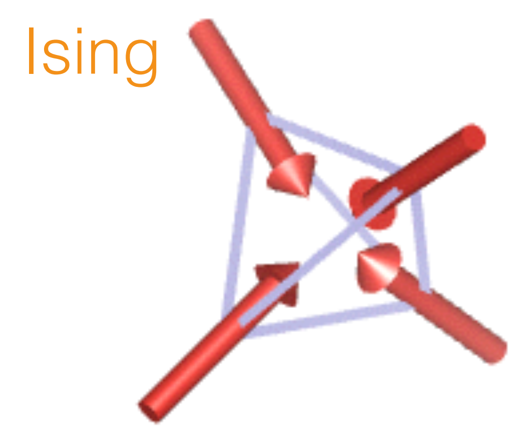
# Magnetic Pyrochlore Lattice

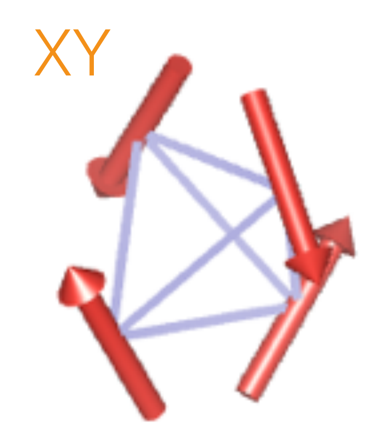
- Tetrahedra — frustration in 3D
- corner linked
- LOCAL anisotropy axes



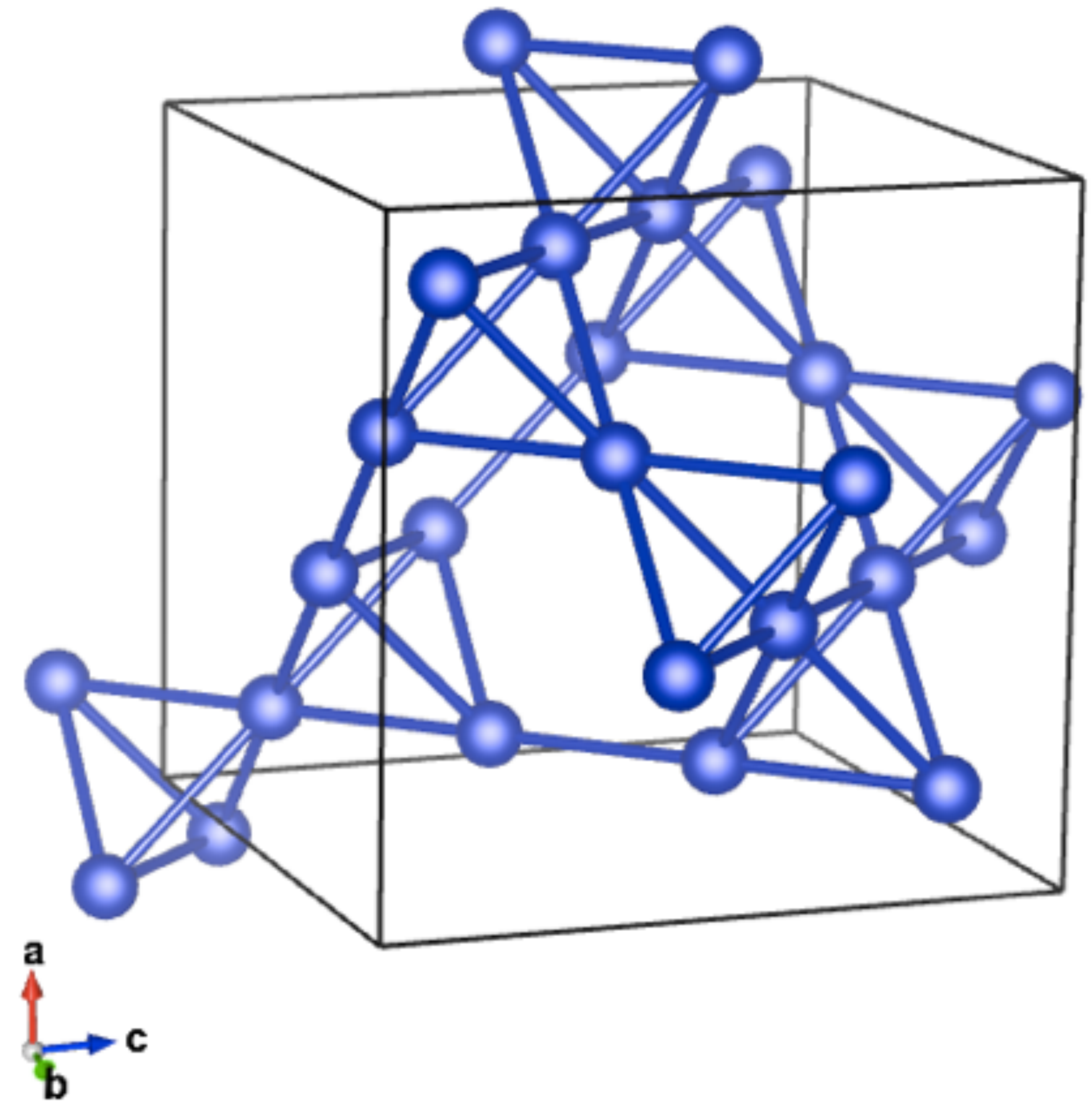


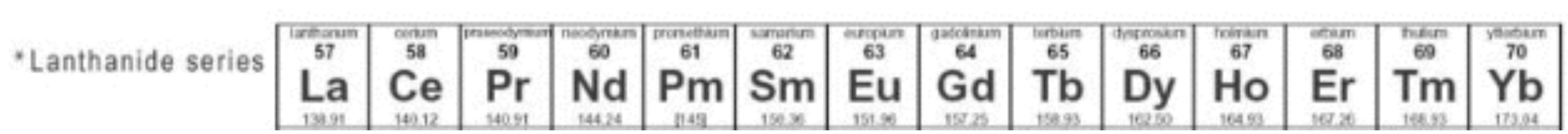



# Pyrochlore Materials

B-site

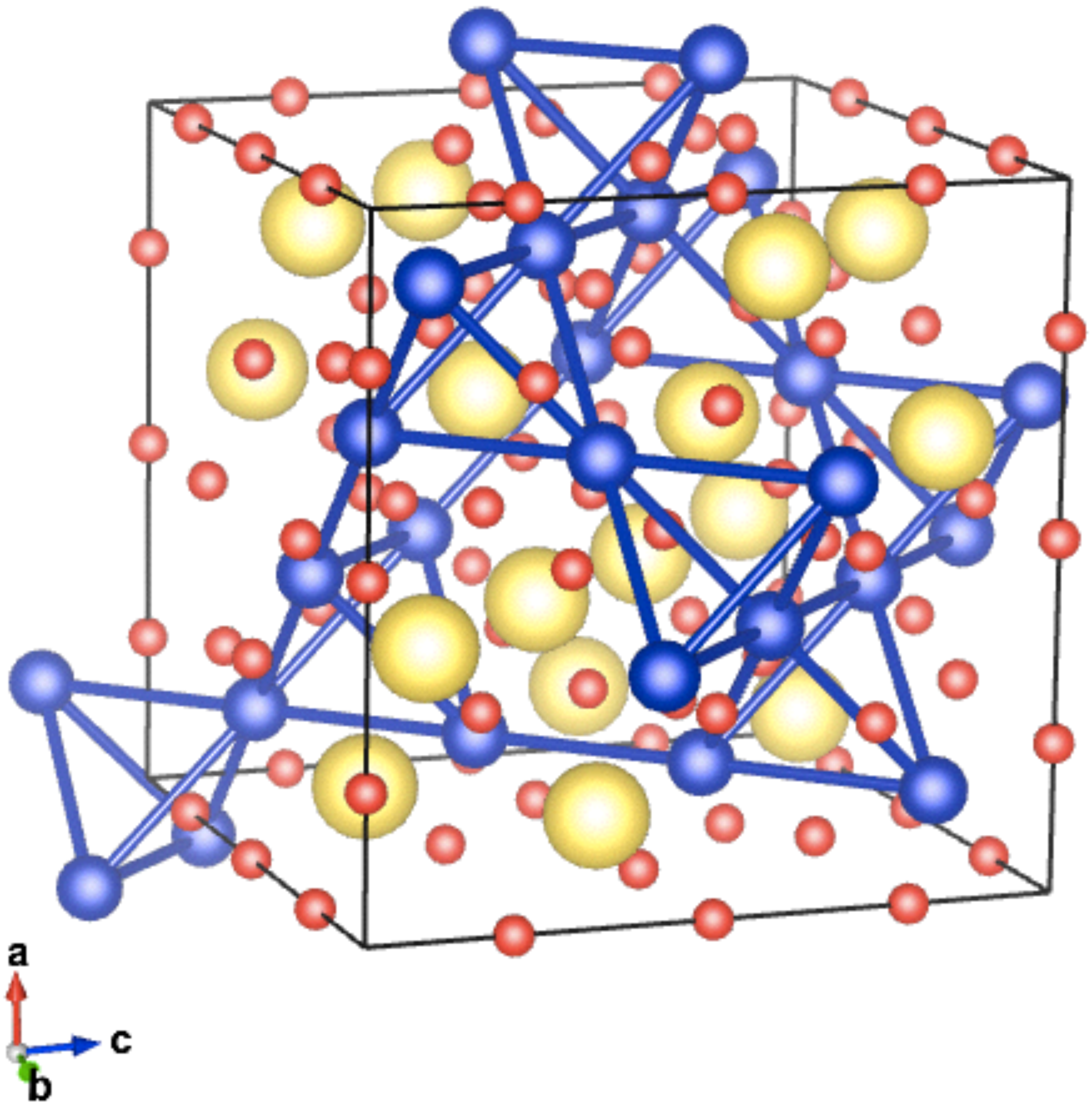



- $A_2B_2X_7$
  - *A* and *B* are cations (positive charge)
  - *X* is anion (like $O^{2-}$, $F^-$)
  - typical, rare earth titanates ($\boldsymbol{R_2Ti_2O_7}$)

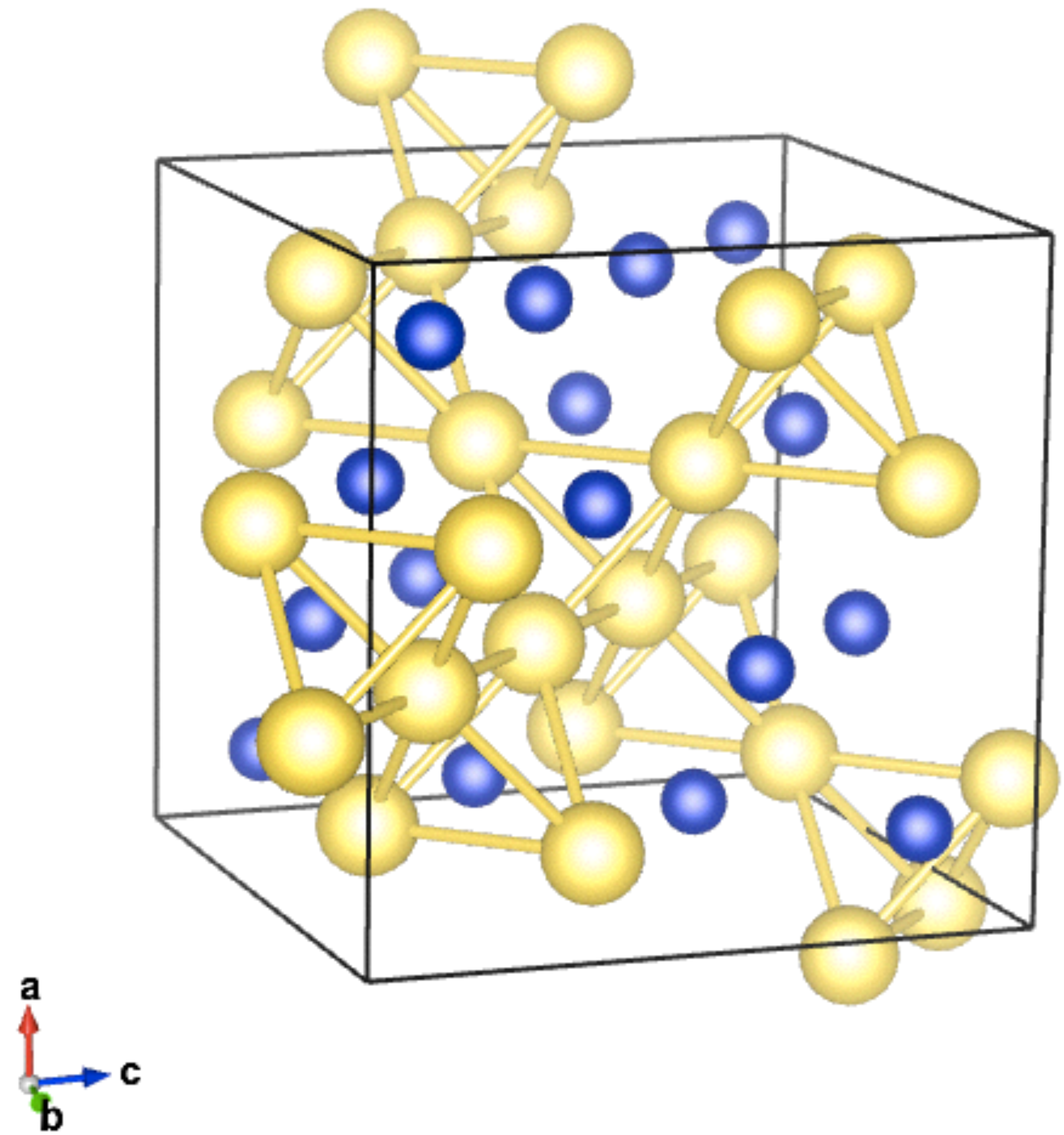


# Pyrochlore Materials

All sites




A-site



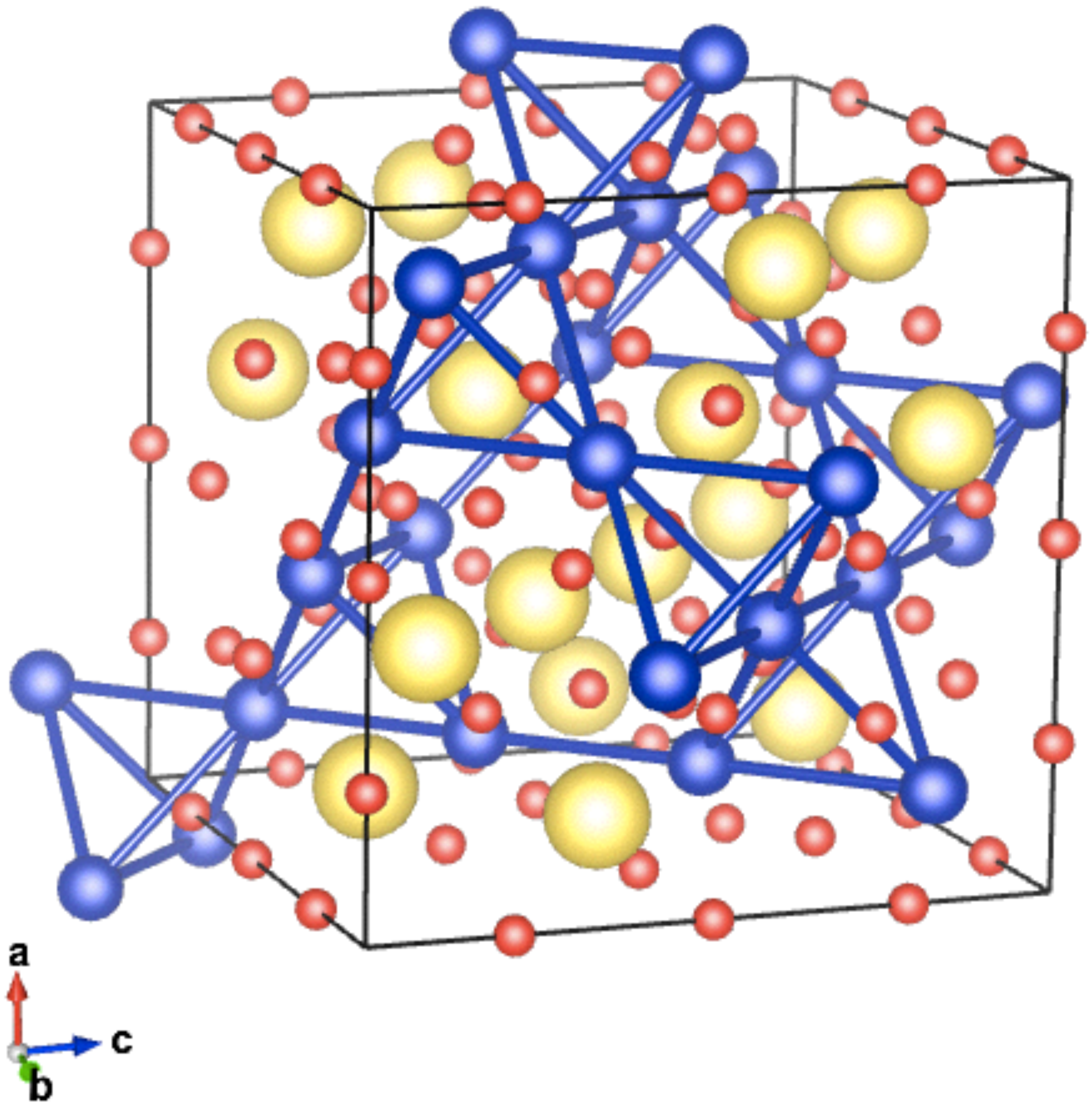

two interpenetrating pyrochlore lattices

*Lanthanide series

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| lanthanum | cerium | praseodymium | neodymium | promethium | samarium | europium | gadolinium | terbium | dysprosium | holmium | erbium | thulium | ytterbium |
| 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 |
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
| 138.91 | 140.12 | 140.91 | 144.24 | [145] | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 |

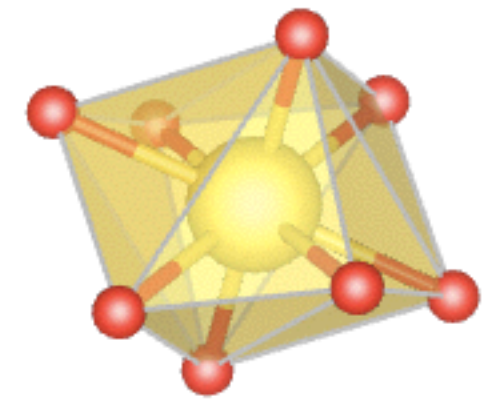
# Pyrochlore Materials

*Fd-3m* (227)



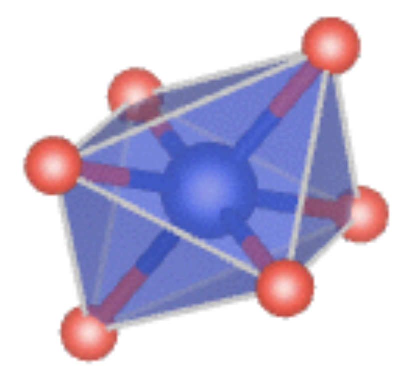

Cation Site Symmetries: $D_{3d}$

A-site



8-fold coordinated

B-site



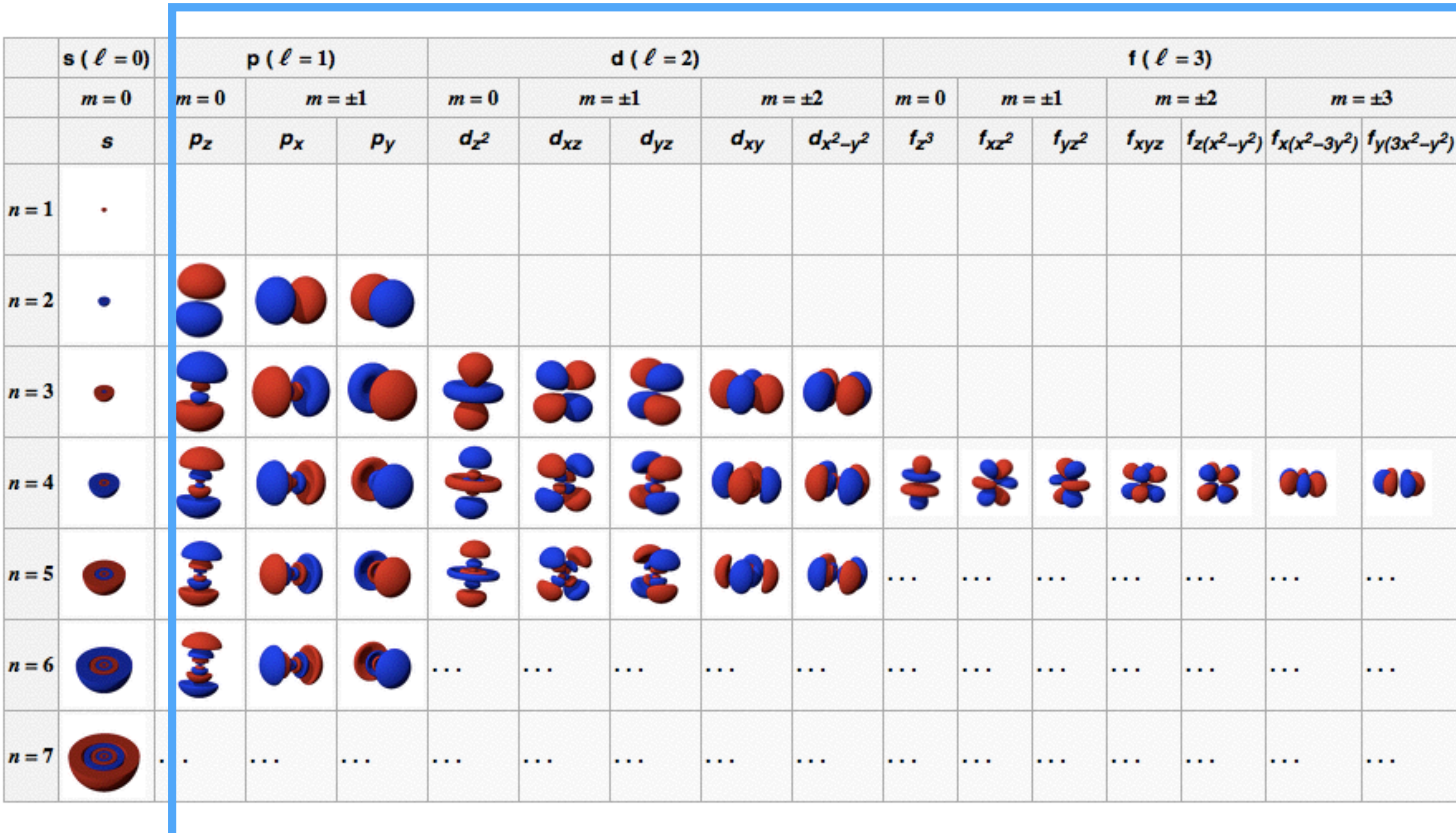
6-fold coordinated

*Lanthanide series

| lanthanum | cerium | praseodymium | neodymium | promethium | samarium | europium | gadolinium | terbium | dysprosium | holmium | erbium | thulium | ytterbium |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 |
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
| 138.91 | 140.12 | 140.91 | 144.24 | [145] | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 |

# Anisotropy from Orbital Contributions

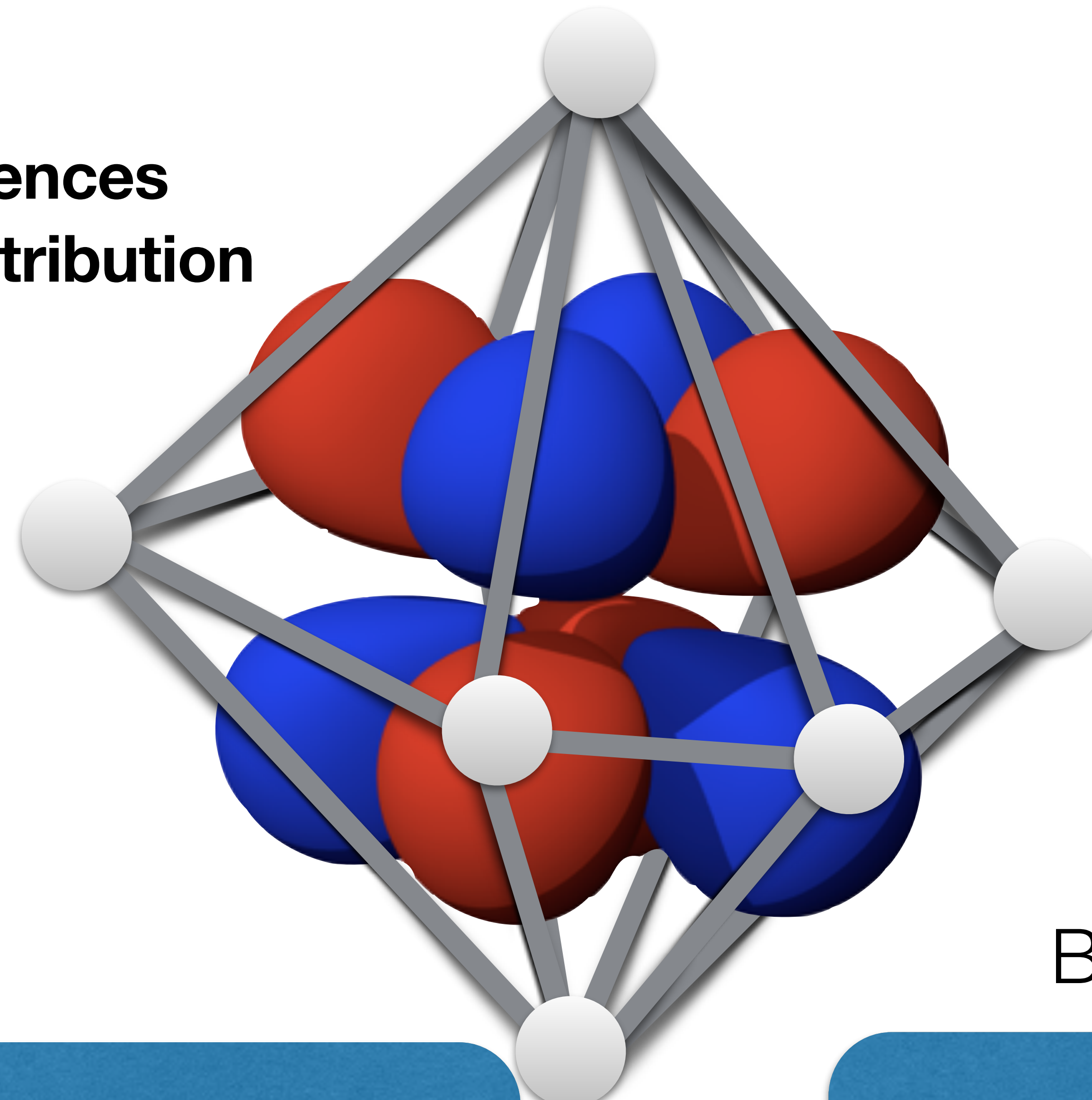
**Anisotropic**




http://en.wikipedia.org/wiki/Atomic_orbital

# LS coupling

**"Crystal Electric Field" influences Charge (and hence spin) distribution**



**__4*d*, 5*d*, 4*f* etc. ions:__**

Spin Orbit Coupling is strong

$$H = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + \lambda \sum_i \vec{S}_i \cdot \vec{L}$$

Basis

$$|J, J_z\rangle$$

$$\vec{J} = \vec{L} + \vec{S}$$

The full ***J*** multiplet is split by crystal field - **anisotropies possible!**

# "Effective Spins" at low energies

## $Yb_2Ti_2O_7$

Malkin et al, PHYSICAL REVIEW B **70**, 075112 (2004)

680K

$g_{||} = 1.78$
$g_{\perp} = 4.28$

## $Er_2Ti_2O_7$

Dasgupta *et al,* Solid State Communications 139 (2006) 424–429

76K

$g_{||} = 2.32$
$g_{\perp} = 6.80$

## $Ho_2Ti_2O_7$

Malkin et al, PHYSICAL REVIEW B **70**, 075112 (2004)

240K

$g_{||} = 19.0$
$g_{\perp} = 0$

**Anisotropic pseudo-spin 1/2**

# "Effective Spins" at low energies

**$Yb_2Ti_2O_7$**

Malkin et al, PHYSICAL REVIEW B **70**, 075112 (2004)

680K

**$Er_2Ti_2O_7$**

Dasgupta *et al,* Solid State Communications 139 (2006) 424–429

**$Ho_2Ti_2O_7$**

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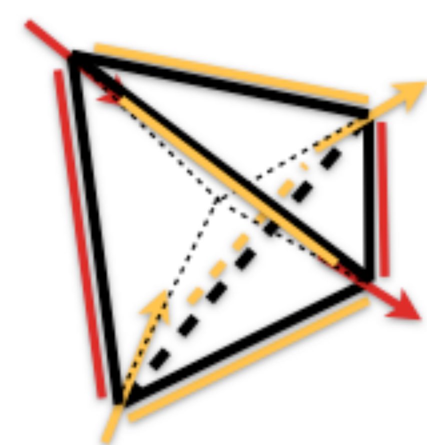
240K



**Anisotropic pseudo-spin 1/2**

# Survey of Electronic Behavior in Pyrochlores

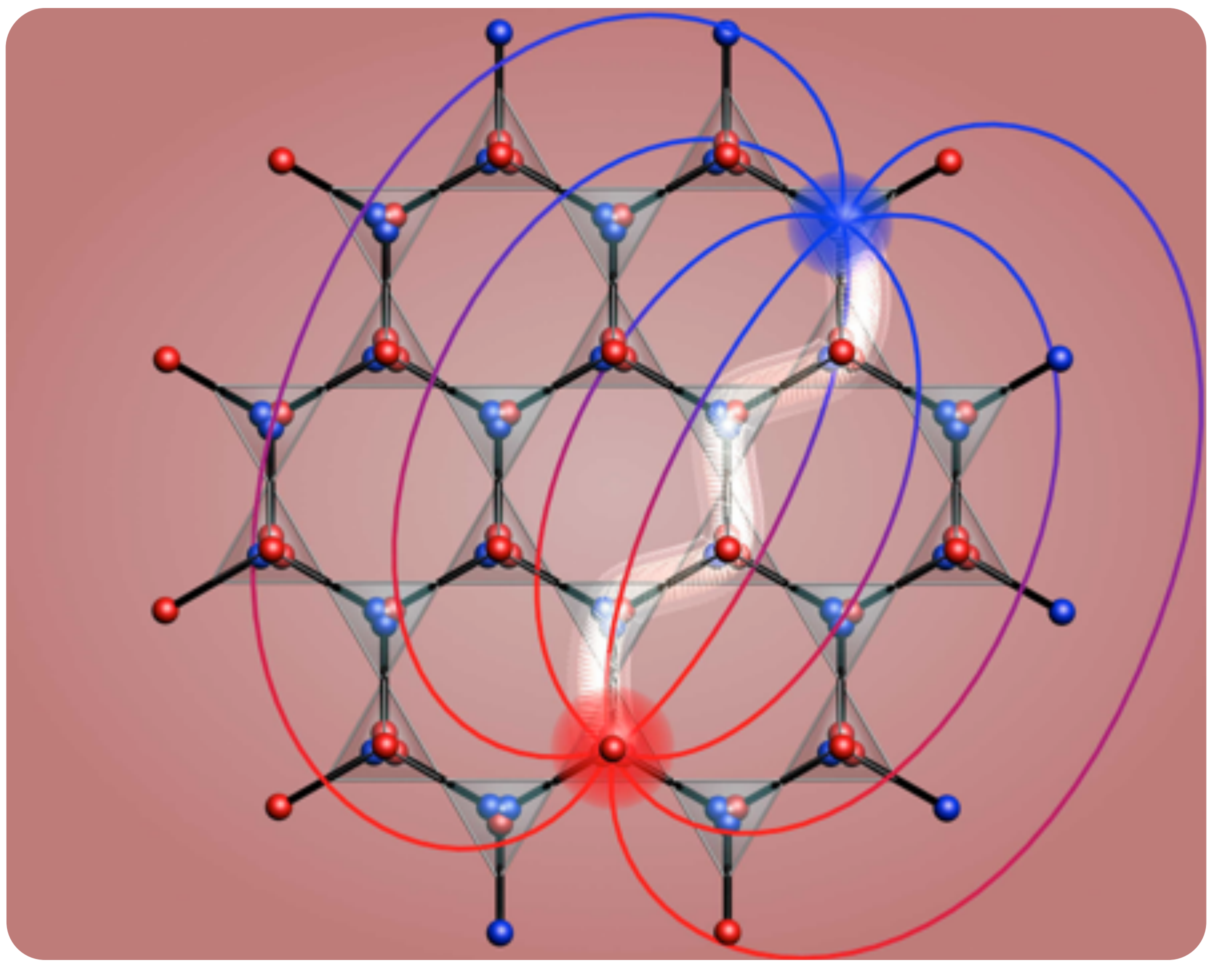
| | |
|---|---|
| • Spin Ice | $Dy_2Ti_2O_7$<br>$Ho_2Ti_2O_7$ |
| • Quantum Spin Ice | $Pr_2M_2O_7$ ($M$ = Ir,Sn,Zr)<br>$Yb_2M_2O_7$, $Tb_2M_2O_7$ ($M$ = Ti,Sn) |
| • Spin Liquid | $Tb_2Ti_2O_7$<br>$Yb_2Ti_2O_7$ , $Pr_2Ir_2O_7$ |
| • Ordered Phases | $Gd_2M_2O_7$ ($M$=Ti,Sn)<br>$Er_2Ti_2O_7$ |
| • Frozen / Spin Glass | $(NaCa)Co_2F_7$<br>$Y_2Mo_2O_7$, $R_2Mo_2O_7$ (R = Yb - Tb) |
| • Metallic | $R_2Ir_2O_7$<br>$R_2Mo_2O_7$ ($R$ = Gd - Nd) |
| • Superconducting | $AOs_2O_6$ ($A$ = Rb, Ca, K)<br>$Cd_2Re_2O_7$ |

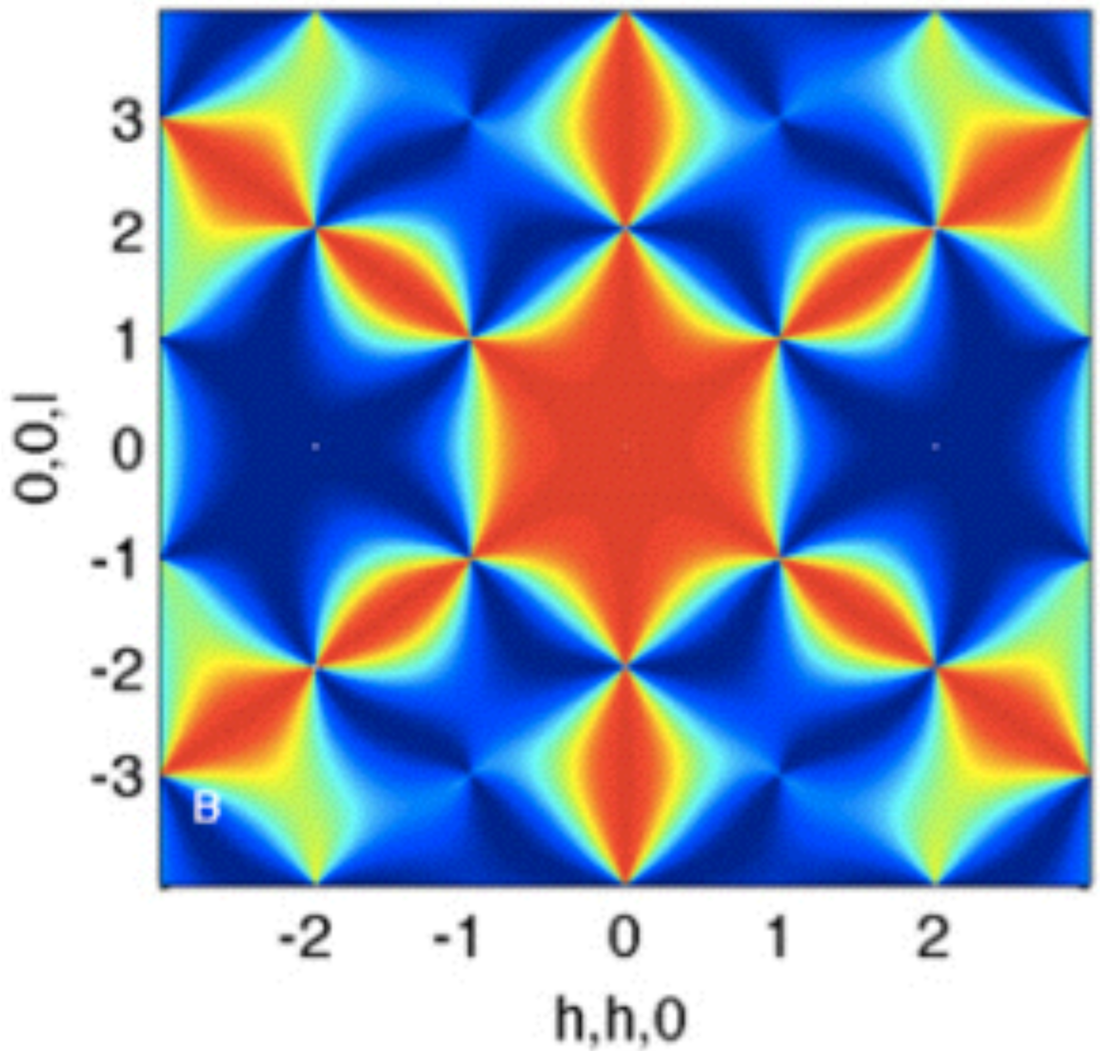
# References


- S. W. Lovesey. *Theory of Neutron Scattering from Condensed Matter,* The International Series of Monographs on Physics No. 72; Oxford University Press (1987)

- J.S. Gardner, M.J.P. Gingras, J. E. Greedan, *Magnetic Pyrochlore Oxides*. Rev. Mod. Phys., **82**, (2010)

# 1) Spin Ice

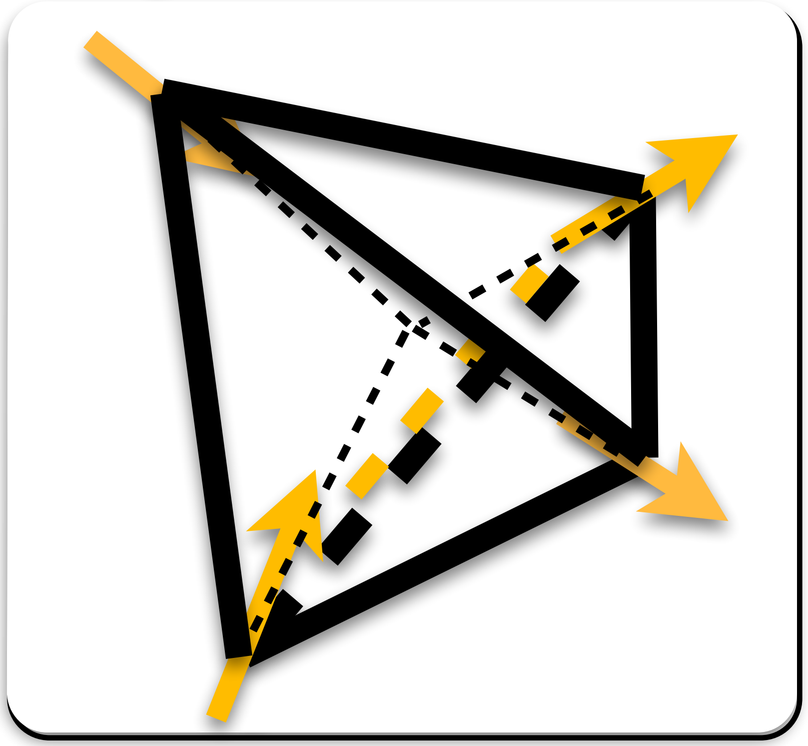




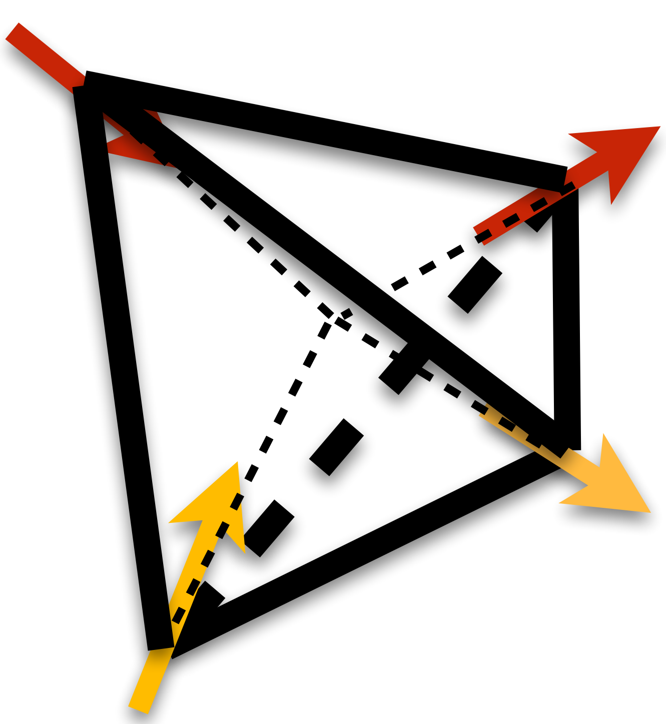
# Ising Pyrochlore

$$H = J \sum_{\langle ij \rangle} \vec{S}_{z_i} \cdot \vec{S}_{z_j}$$

e.g.
Ising exchange



Ferromagnetic Ising exchange on pyrochlore lattice:
“Ice Rules”: Two-in Two-out



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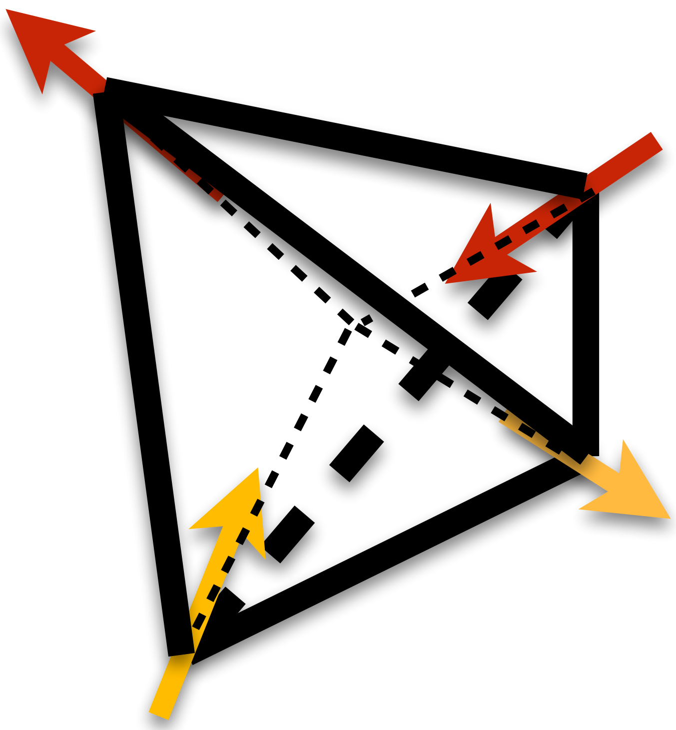
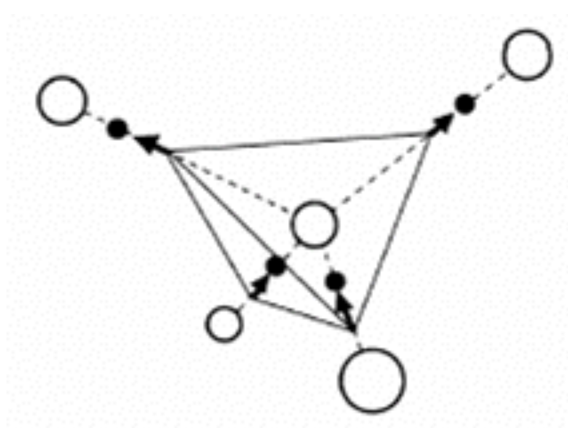


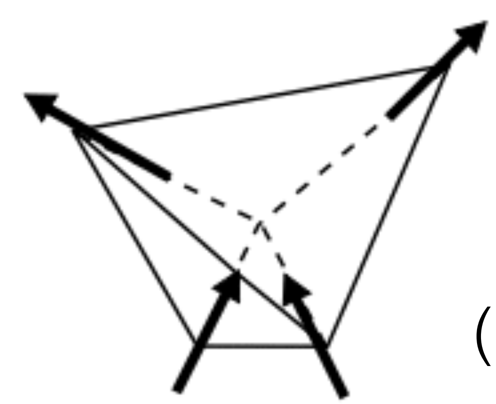
6 possible states per tetrahedra : macroscopic degeneracy

# Spin Ice

- "2 in 2 out": rule does not constrain entire lattice
- macroscopic degeneracy arises - residual entropy at T=0
- System ***freezes*** into one particular ice configuration (every tetrahedron obeys ice rules)



water ice
2 in 2 out
(hydrogen distances from oxygen)



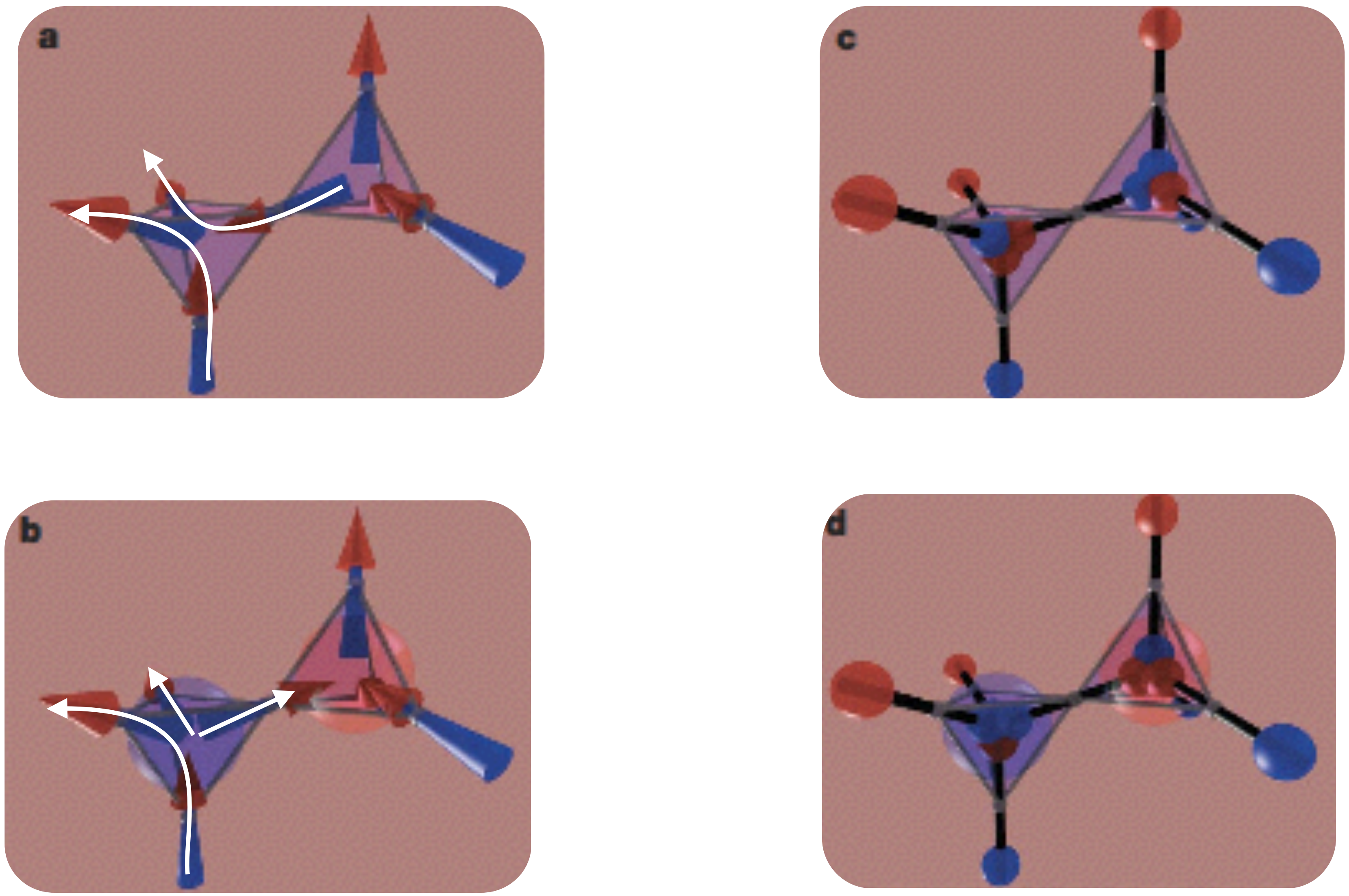
spin ice
2 in 2 out
(magnetic moments)

"Independent Tetrahedra":
Pauling Residual Entropy, $S_{\mathrm{p}} = 1/2\ R \ln(3/2)$

# Emergent Gauge Field in Spin Ice

Spin Language

“Dumbell” Language




Castelnovo, Moessner, Sondhi. Nature, 451 (2008)

2-in 2-out ground state

$$\vec{\nabla} \cdot \vec{B} = 0$$

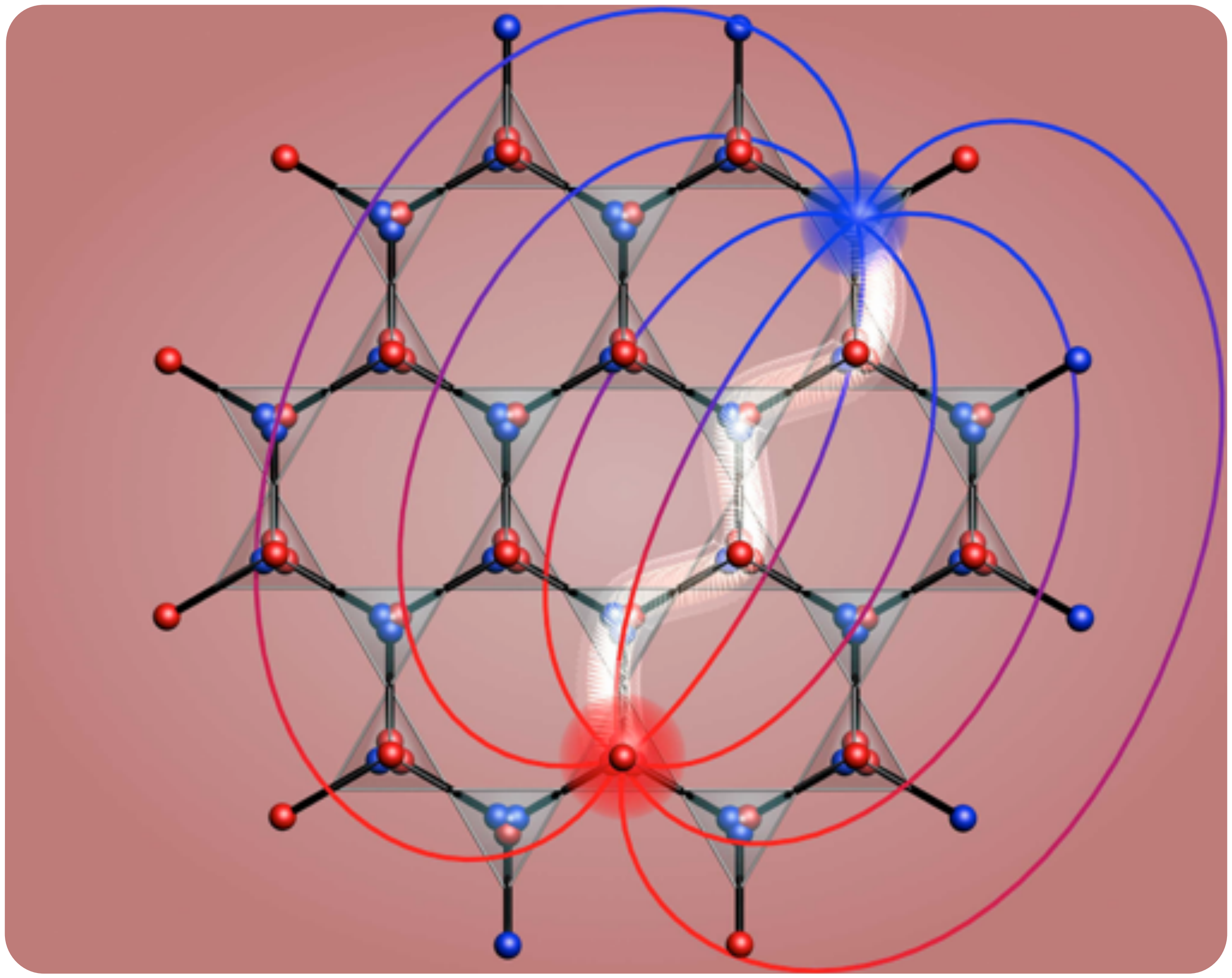
3-out 1-in excitation

$$\vec{\nabla} \cdot \vec{B} \neq 0$$

fundamental excitations (a spin flip) are analogous to magnetic monopoles

$$V(r_{\alpha\beta}) = \begin{cases} \frac{\mu_0}{4\pi} \frac{Q_\alpha Q_\beta}{r_{\alpha\beta}} & \alpha \neq \beta \\ \frac{1}{2} \upsilon_o Q_\alpha^2 & \alpha = \beta \end{cases}$$

# Monopoles in Spin Ice



Castelnovo, Moessner, Sondhi. Nature, 451 (2008)

- Coulomb interaction between monopole and anti-monopole
- *deconfined* - i.e. finite energy of separation

3-out 1-in excitation

$$\vec{\nabla} \cdot \vec{B} \neq 0$$

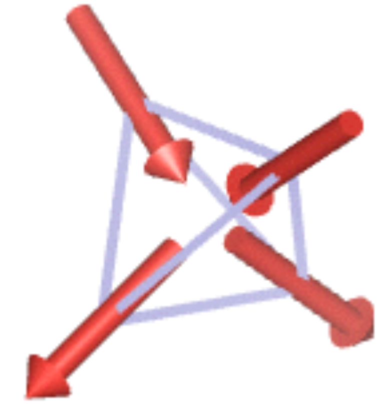
fundamental excitations (a spin flip) are analogous to magnetic monopoles

$$V(r_{\alpha\beta}) = \begin{cases} \frac{\mu_0}{4\pi} \frac{Q_\alpha Q_\beta}{r_{\alpha\beta}} & \alpha \neq \beta \\ \frac{1}{2} \upsilon_o Q_\alpha^2 & \alpha = \beta \end{cases}$$

# How to make a spin ice

- <u>Three main ingredients:</u>
  - Magnetic pyrochlore lattice
  - Ferromagnetic nearest neighbor interactions
  - Ising Anisotropy

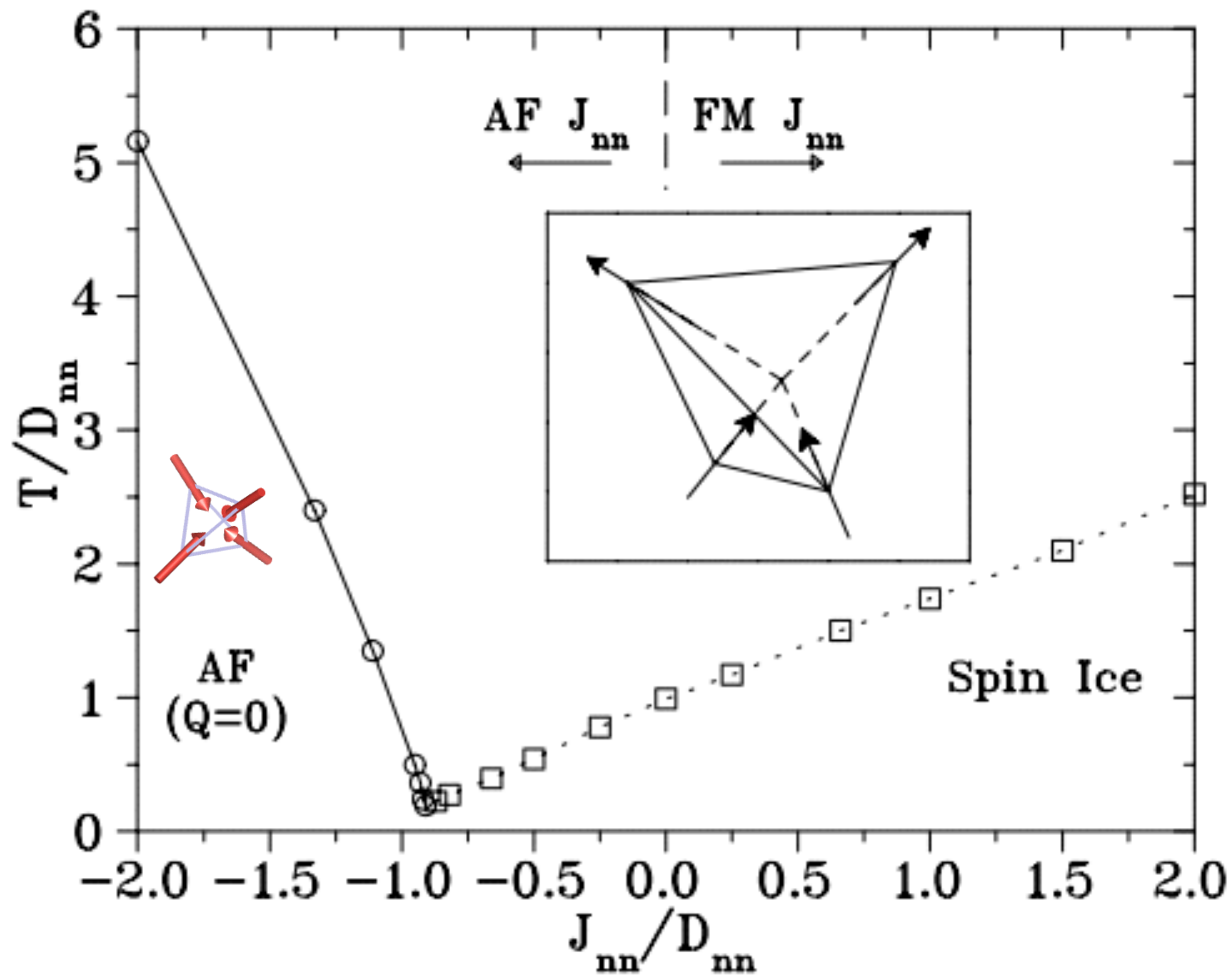
$$H = J \sum_{\langle ij \rangle} \vec{S}_{z_i} \cdot \vec{S}_{z_j}$$



# How to make a spin ice

Dipolar spin ice (i.e. $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$)

- Large moment ($\mu \sim 10\ \mu_B$) leads to large dipolar interaction
- $D_{nn} \propto \mu^2 / r_{nn}^3 \sim 2$ K
- Relatively small nearest neighbor *exchange interaction, J*
- Because of strong anisotropy and particular lattice symmetry, **dipolar interaction mimics nearest neighbor ferromagnetic exchange**




B. C. den Hertog et al, PRL **84**, 3430 (2000)

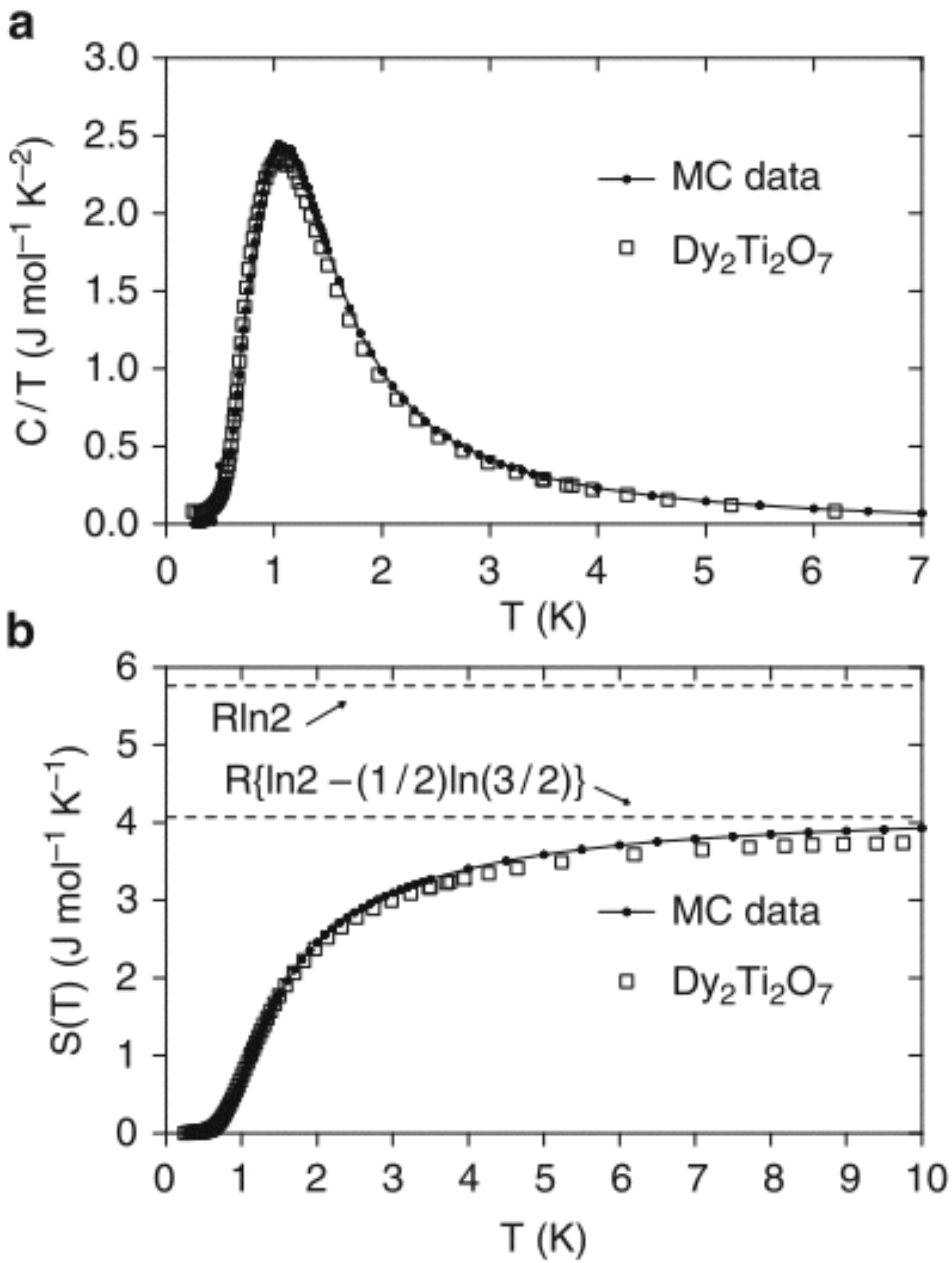
$$H = -J\sum_{\langle ij\rangle}\mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j} + Dr_{\rm nn}^3\sum_{j>i}\frac{\mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i}\cdot\mathbf{r}_{ij})(\mathbf{S}_j^{z_j}\cdot\mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

# Experimental Signatures of Classical Spin Ice

**“$Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$”**

- No long range order (no anomalies in thermodynamics)
- Residual Entropy [1/2 R ln (3/2)]: **FREEZING**
- Divergence of spin relaxation time: **FREEZING**
- Magnetization plateau for [111] field: **KAGOME ICE**
- Pinch Points in neutron scattering: **COULOMB PHASE**

# Residual Entropy



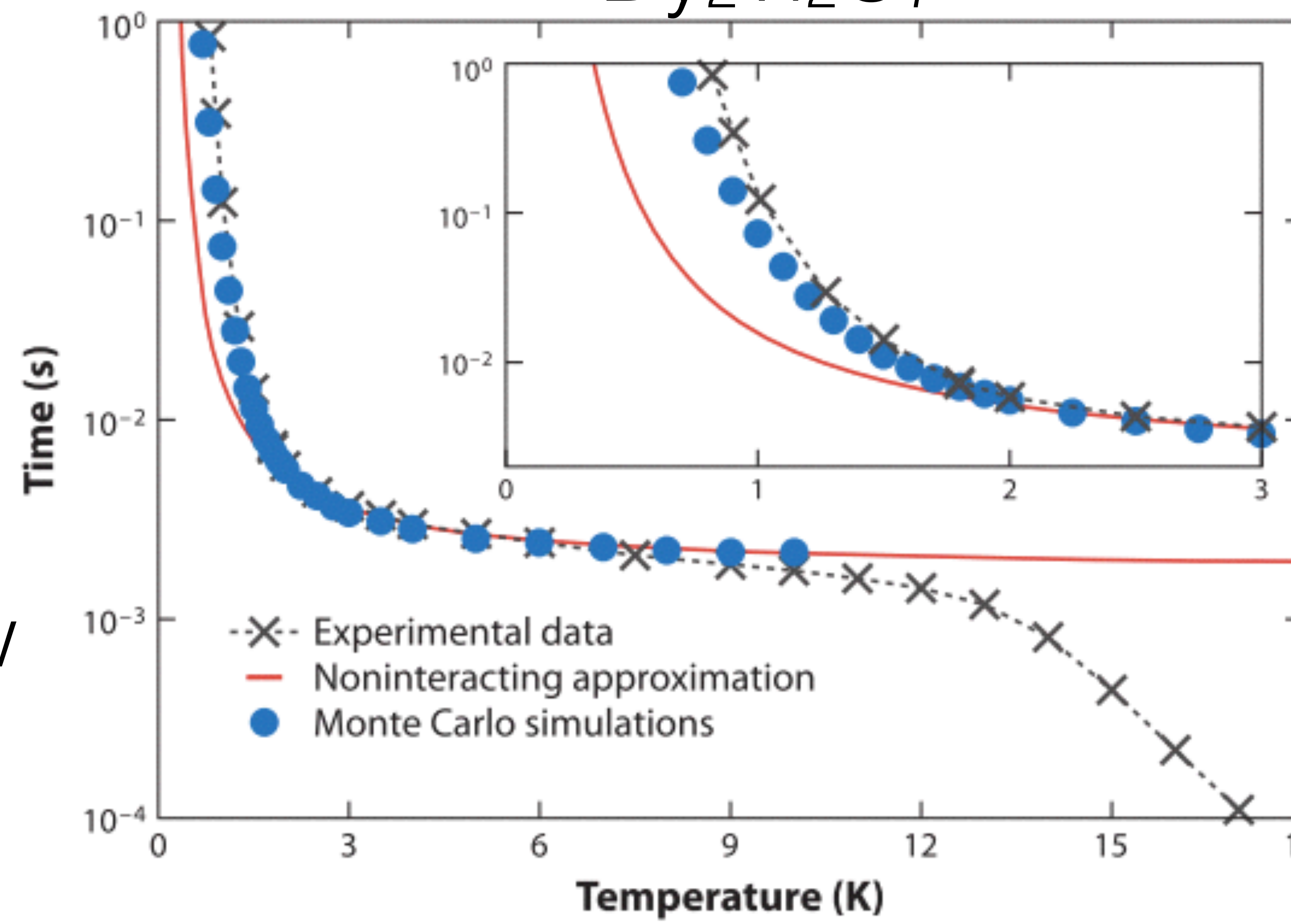

Magnetic Specific Heat of $Dy_2Ti_2O_7$

- two level system: R ln(2)
- spin ice: R ln(2) - $S_{pauling}$
- Zero point entropy? Violation of the 3rd law?

# Freezing

- $\tau$ from ac susceptibility measurements
- sharp upturn below 2K
- reaches ~1 second at low temperatures
- **Spin ice falls out of equilibrium**

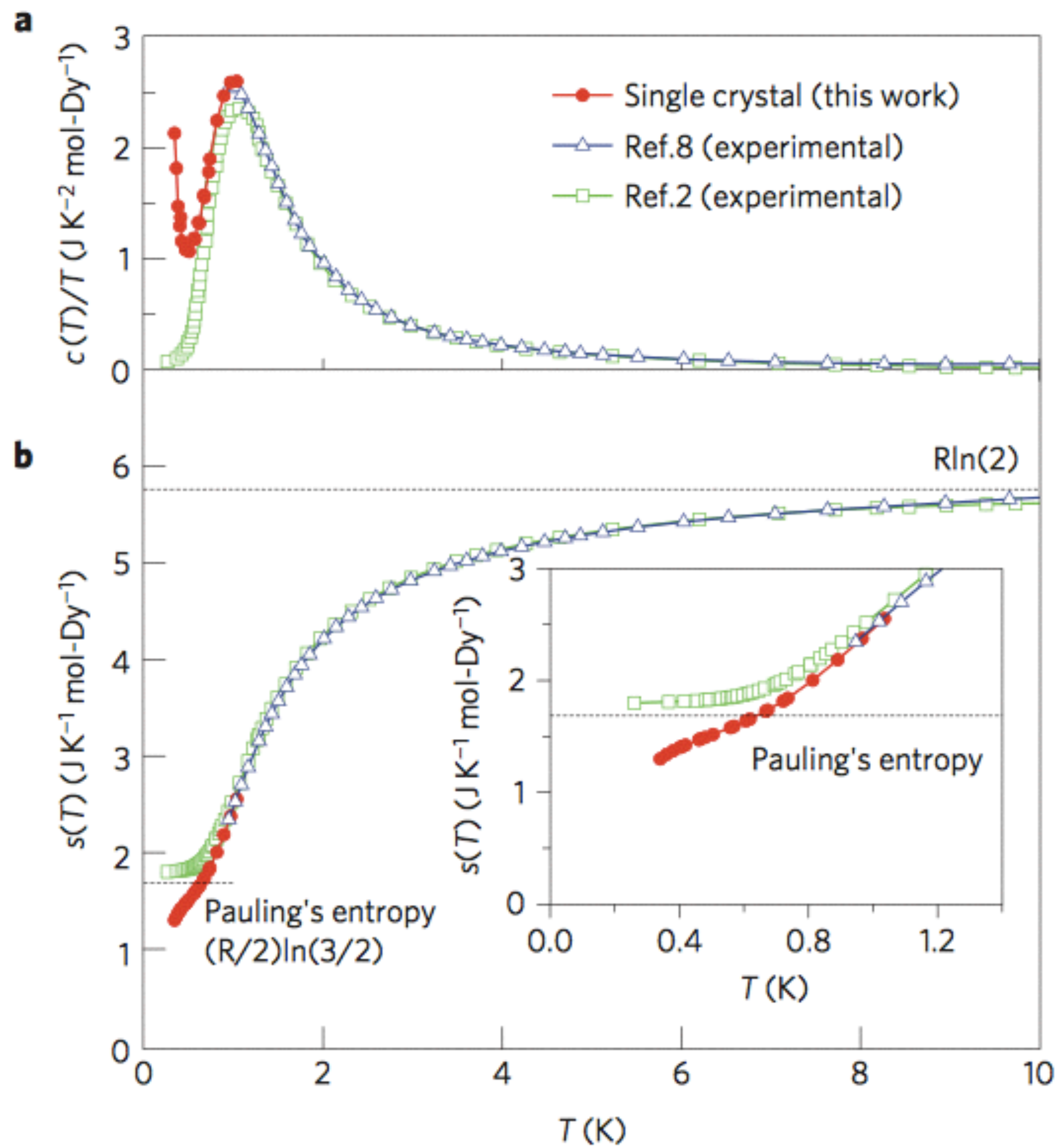
$Dy_2Ti_2O_7$

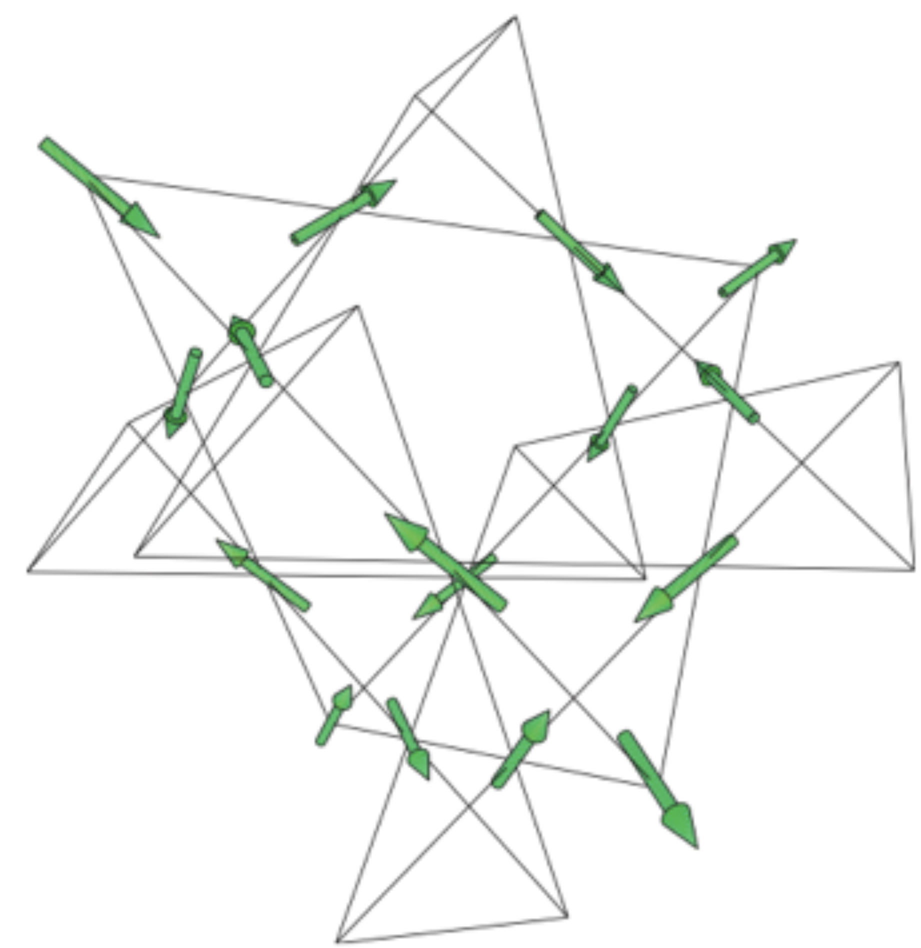



C. Castelnovo, R. Moessner, and S.L. Sondhi. Annu. Rev. Condens.Matter Phys. 2012. **3**:35–55

# Thermally Equilibrated Dy2Ti2O7

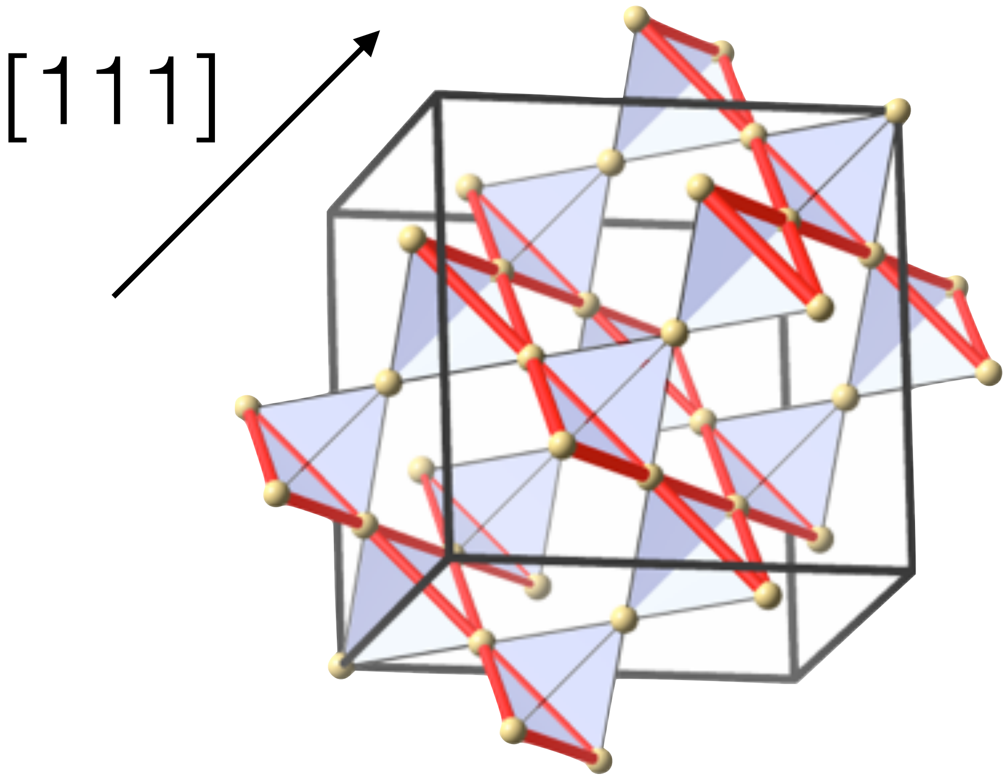
D. Pomaranski et al, *Absence of Pauling's residual entropy in thermally equilibrated Dy2Ti2O7.* Nature Phys. **9** 2013



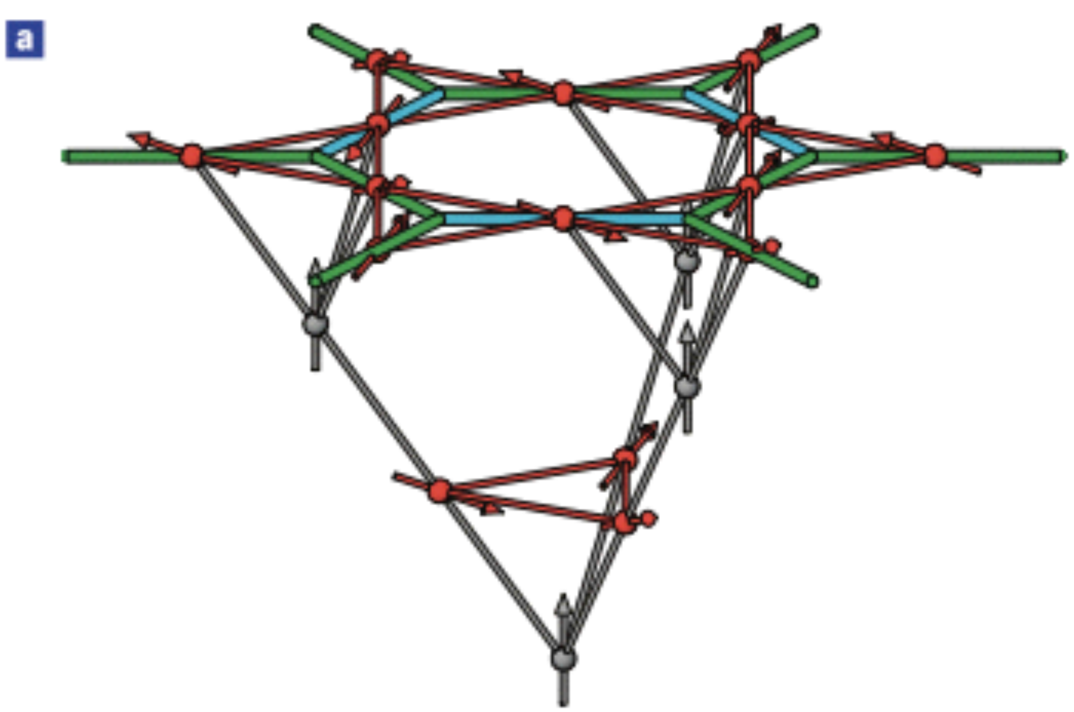



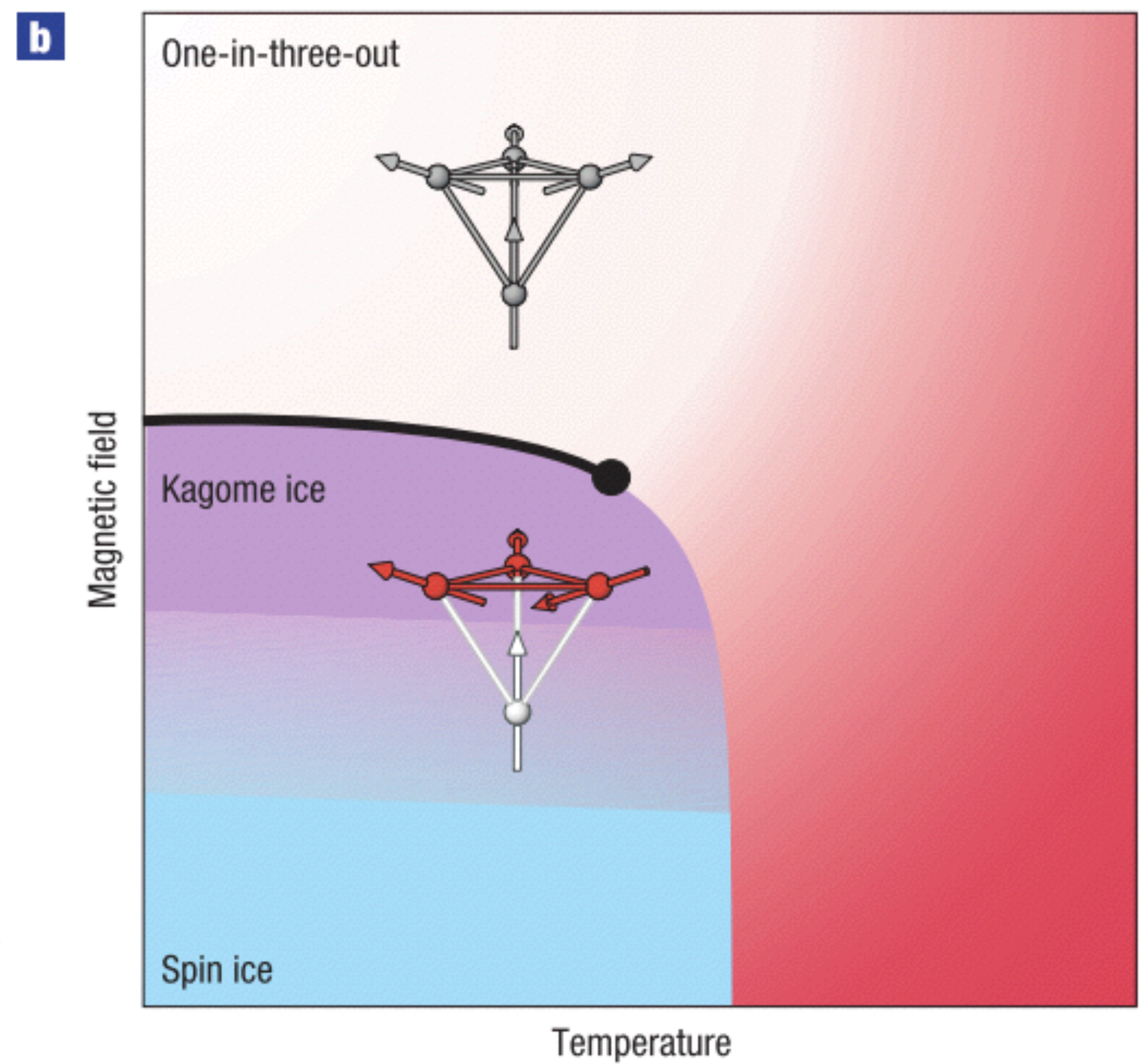
Ordered state predicted for dipolar spin ice

# Kagome Ice




Magnetic Field along [111]

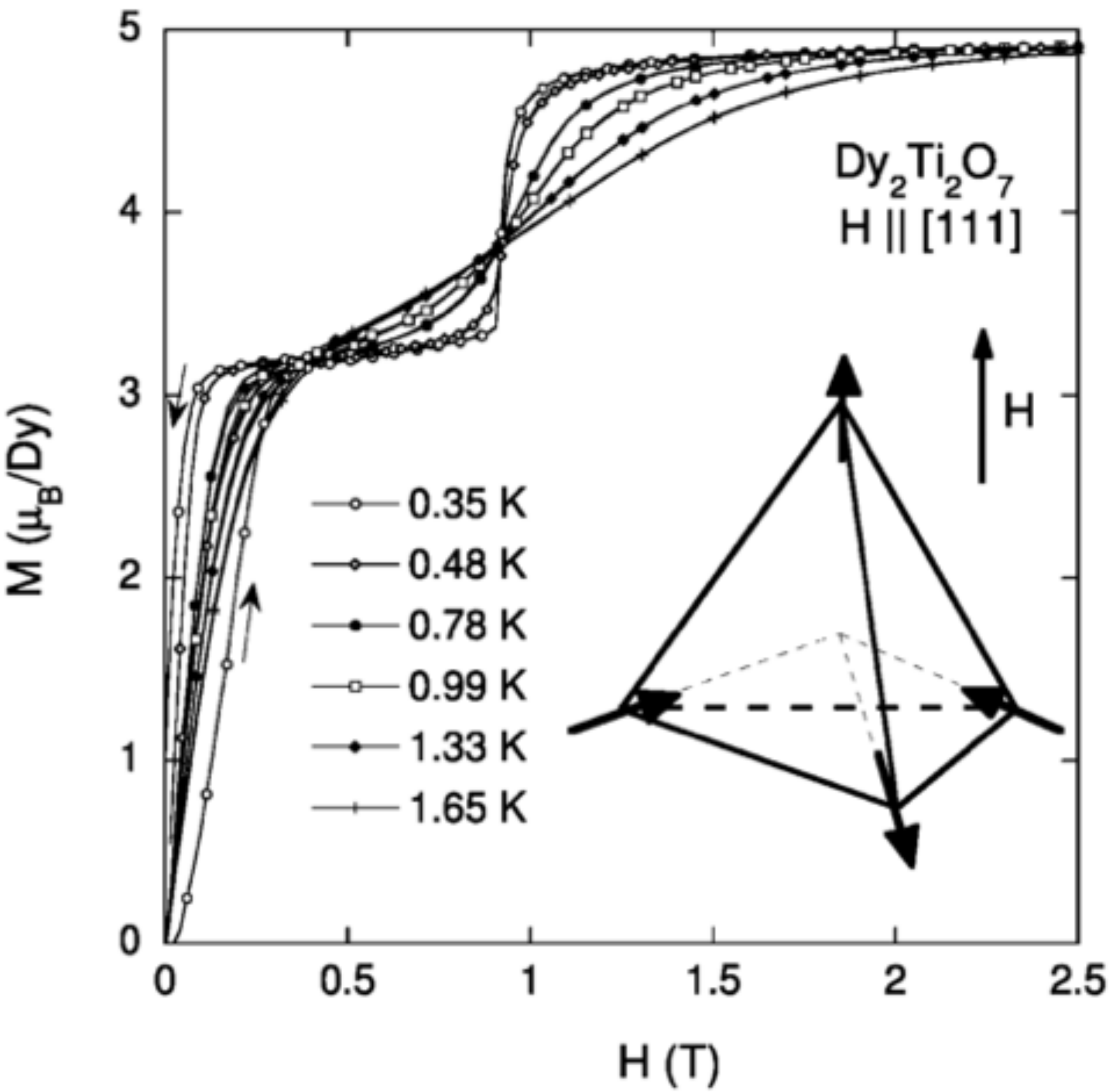


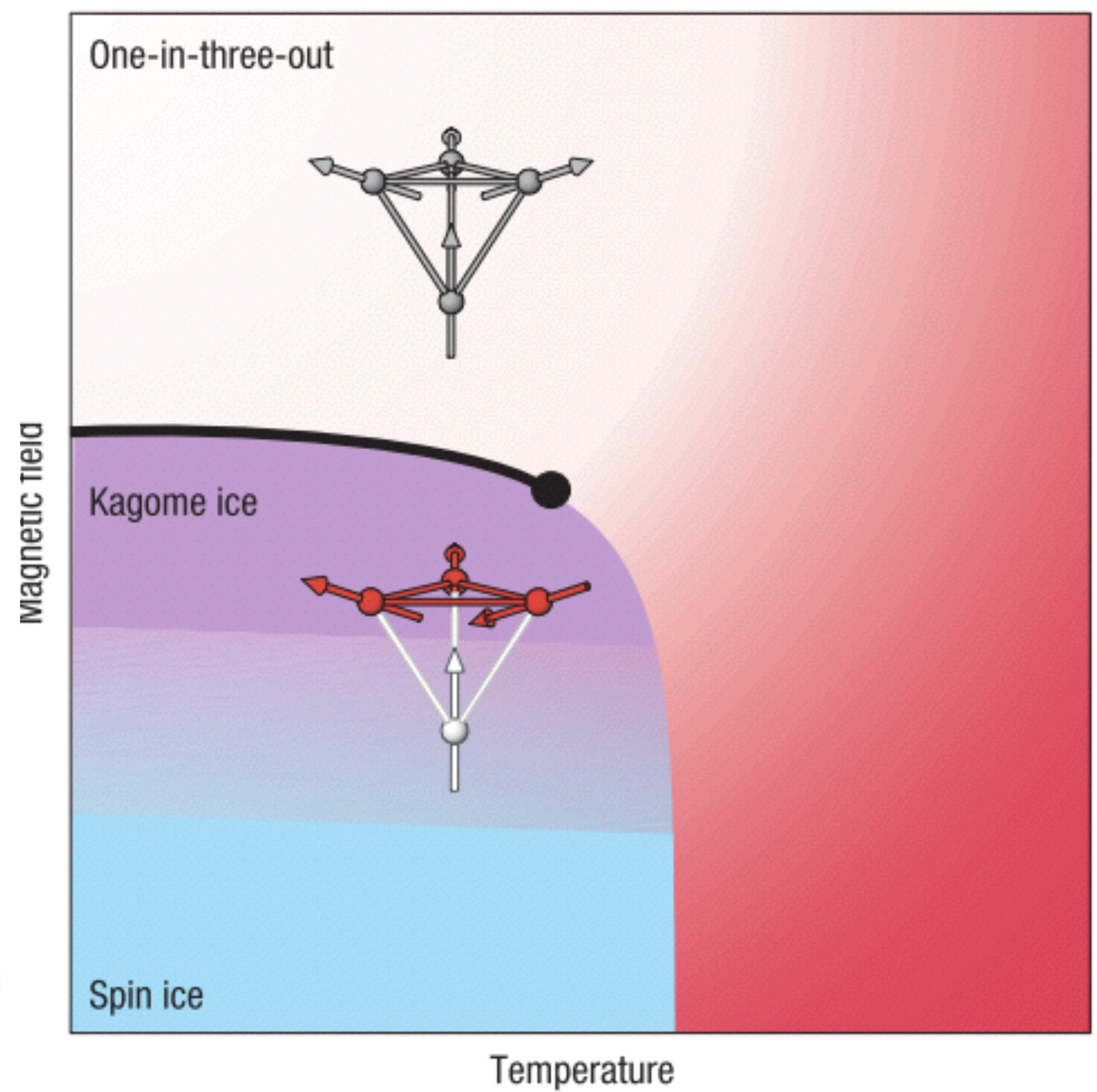



# Kagome Ice

[111]

Magnetic Field along [111]

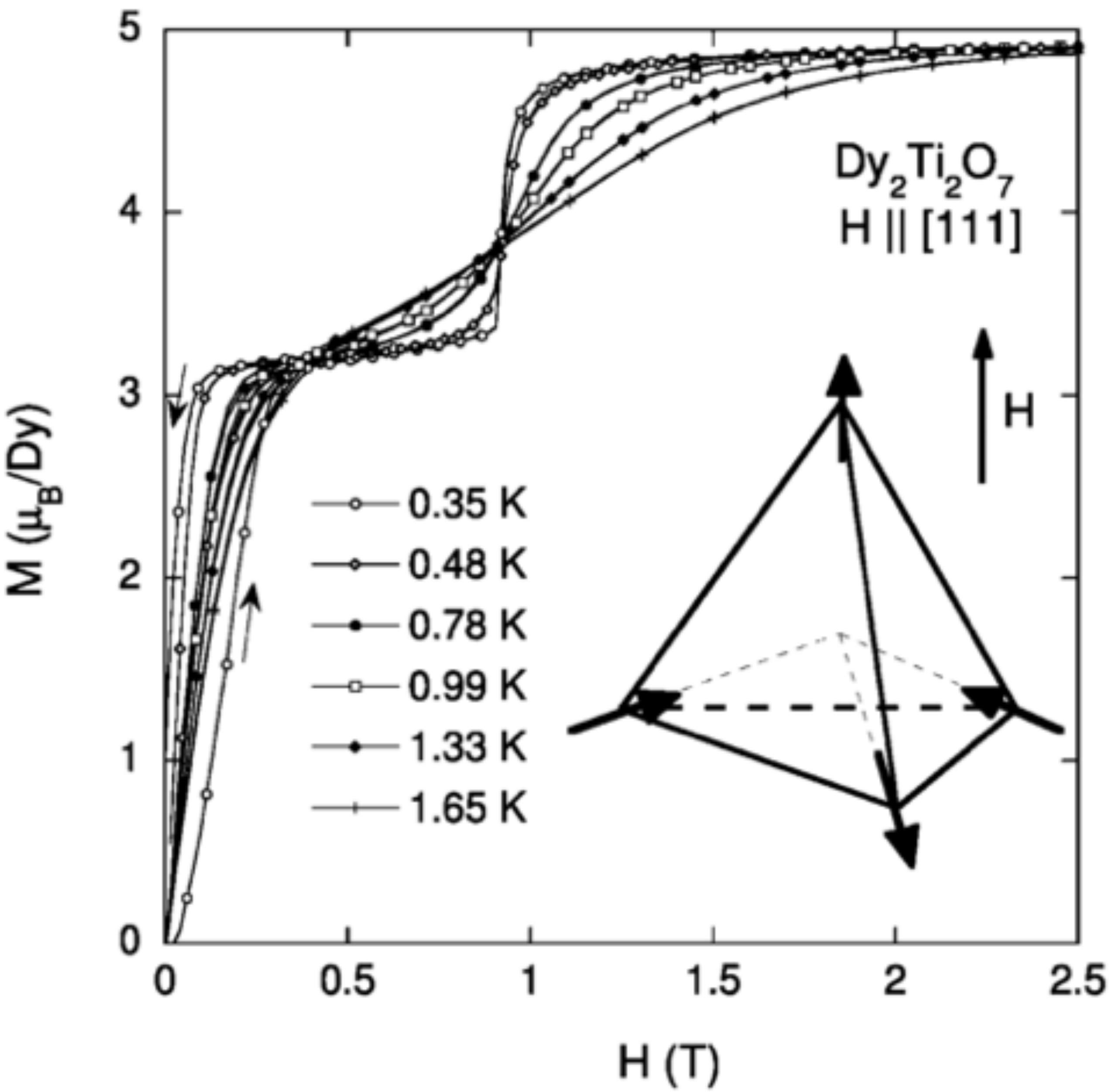


# [111] Plateau

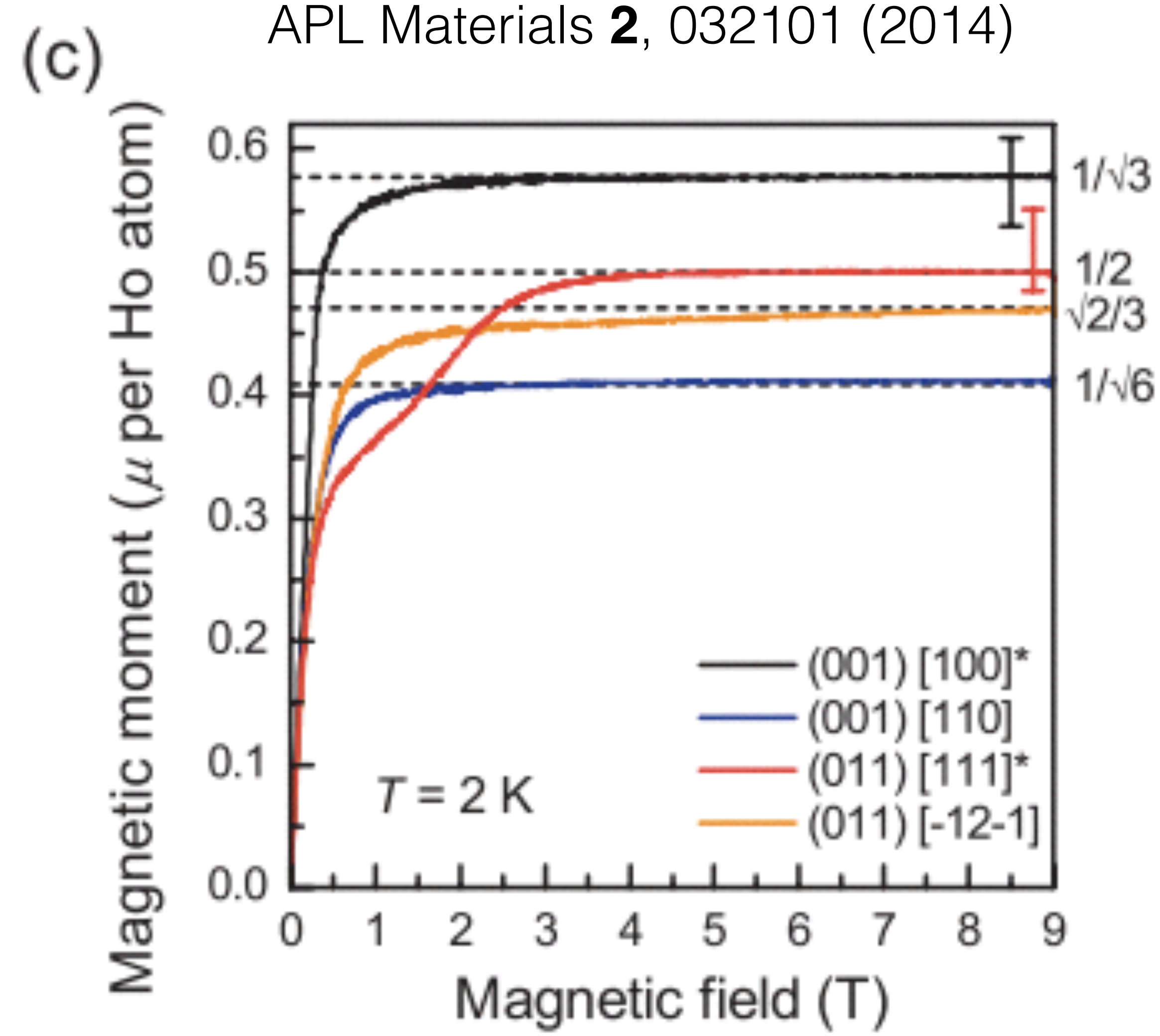
$Dy_2Ti_2O_7$

T. Sakakibara, PRL **90**, 207205 (2003)

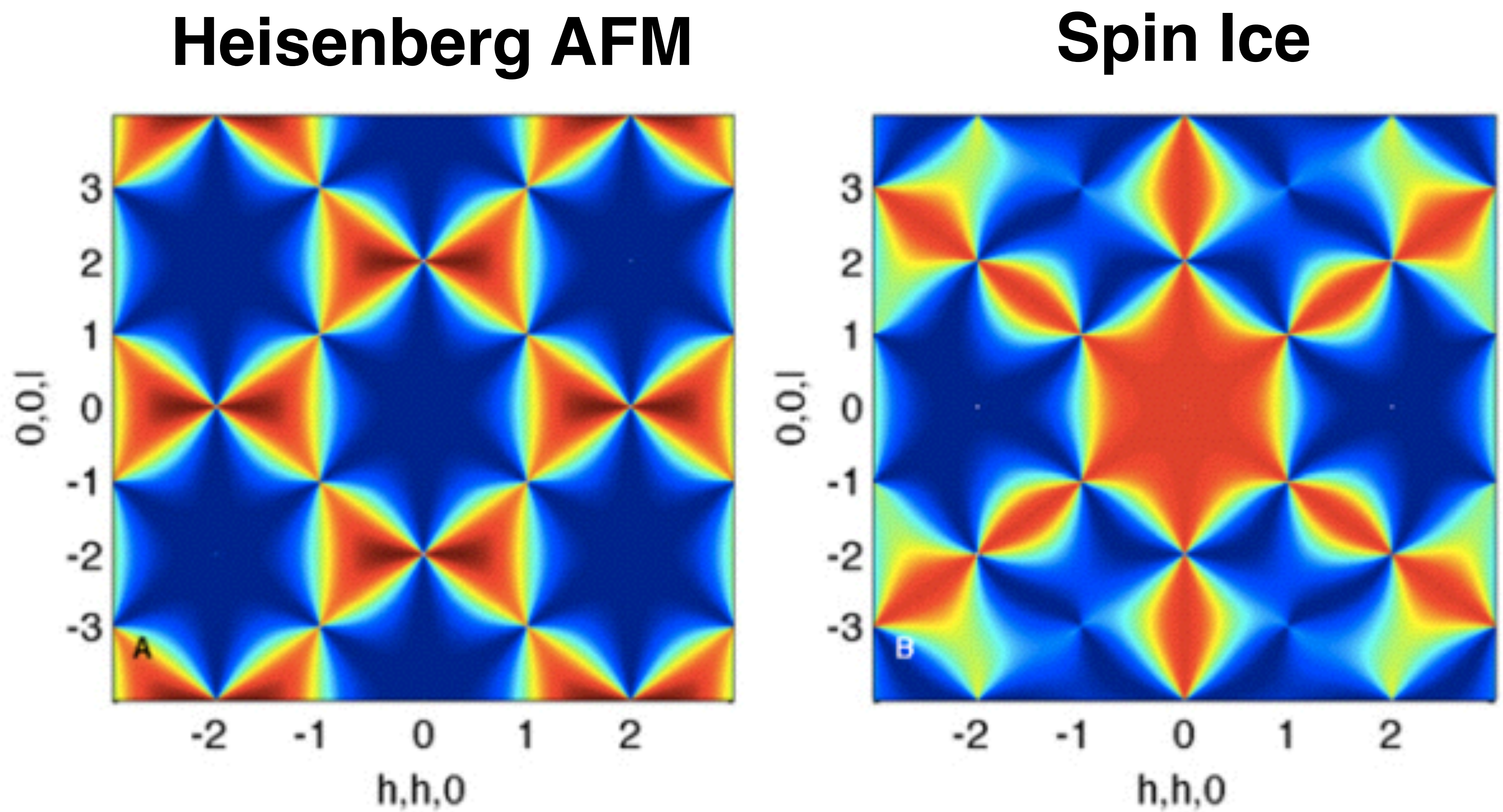



Thin Film $Ho_2Ti_2O_7$

Leusnik, D.P., *et al*,
APL Materials **2**, 032101 (2014)



# Pinch Points in Neutron Scattering

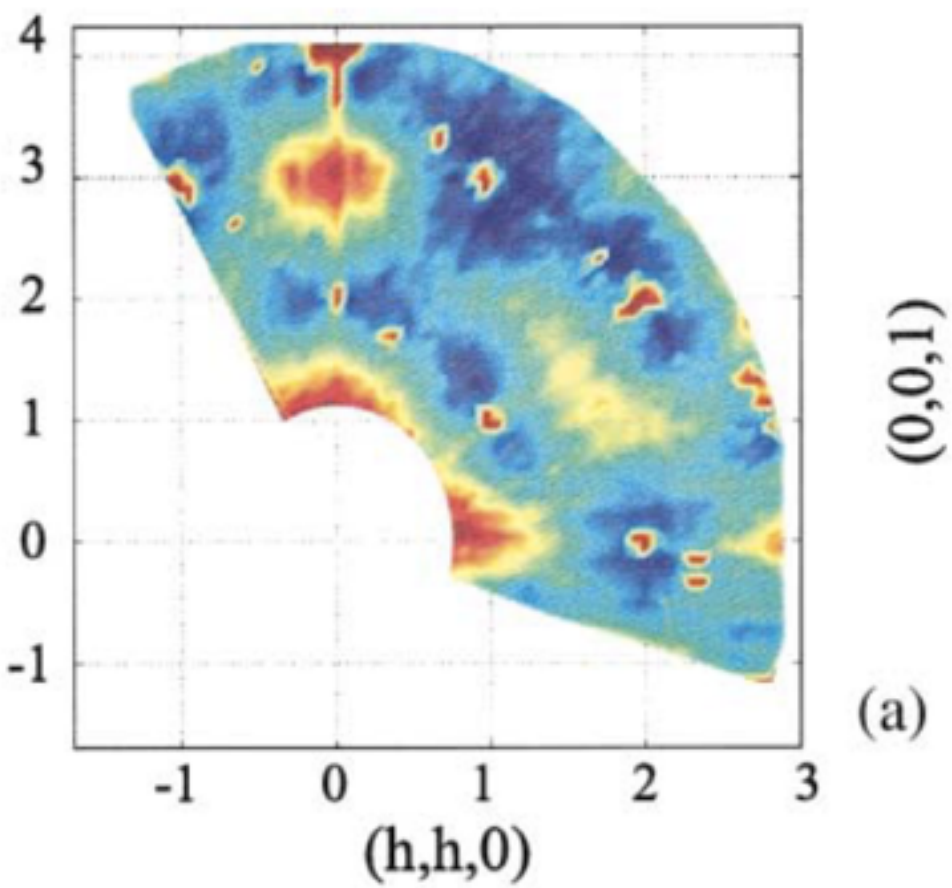



T. Fennell, *Collection SFN* **13**, 04001 (2014)

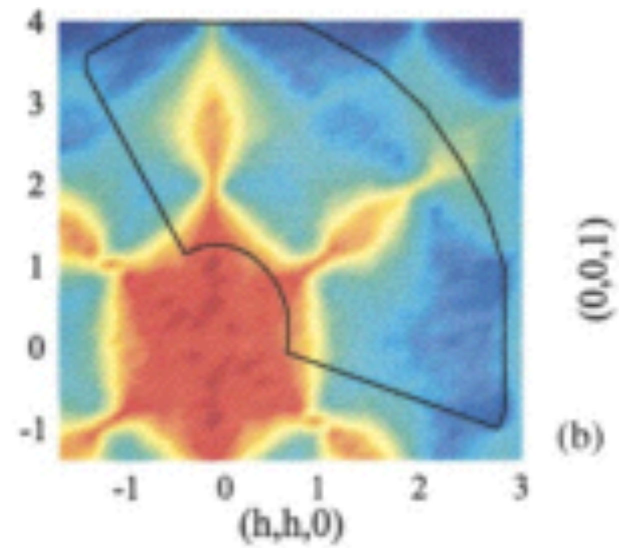
- Signature of emergent gauge field (**Divergence-free condition**)
- results from $1/r^3$ dependence of spin correlation function
- not unique to *spin ice* — present in any 3D Coulomb phase (models which have divergence-free flux)

# "Hidden Pinch Points" in Dipolar Spin Ice

Measured elastic neutron scattering $Ho_2Ti_2O_7$

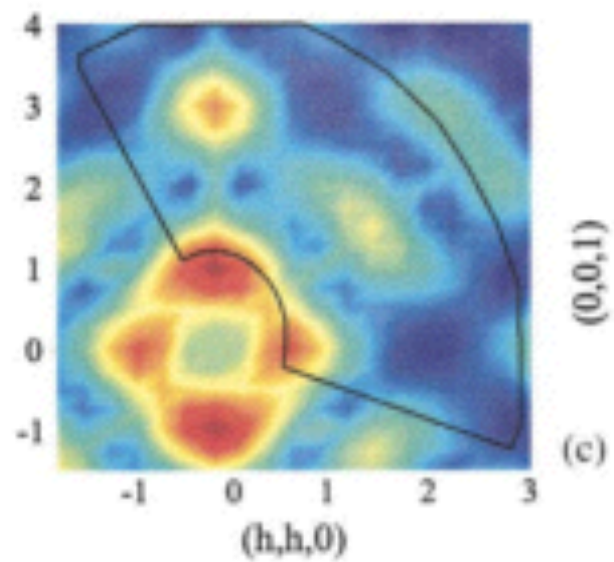



S.T. Bramwell et al,
PRL **87** (2001)




Predicted pattern for nearest neighbor spin ice

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}$$




Predicted pattern for **dipolar** spin ice

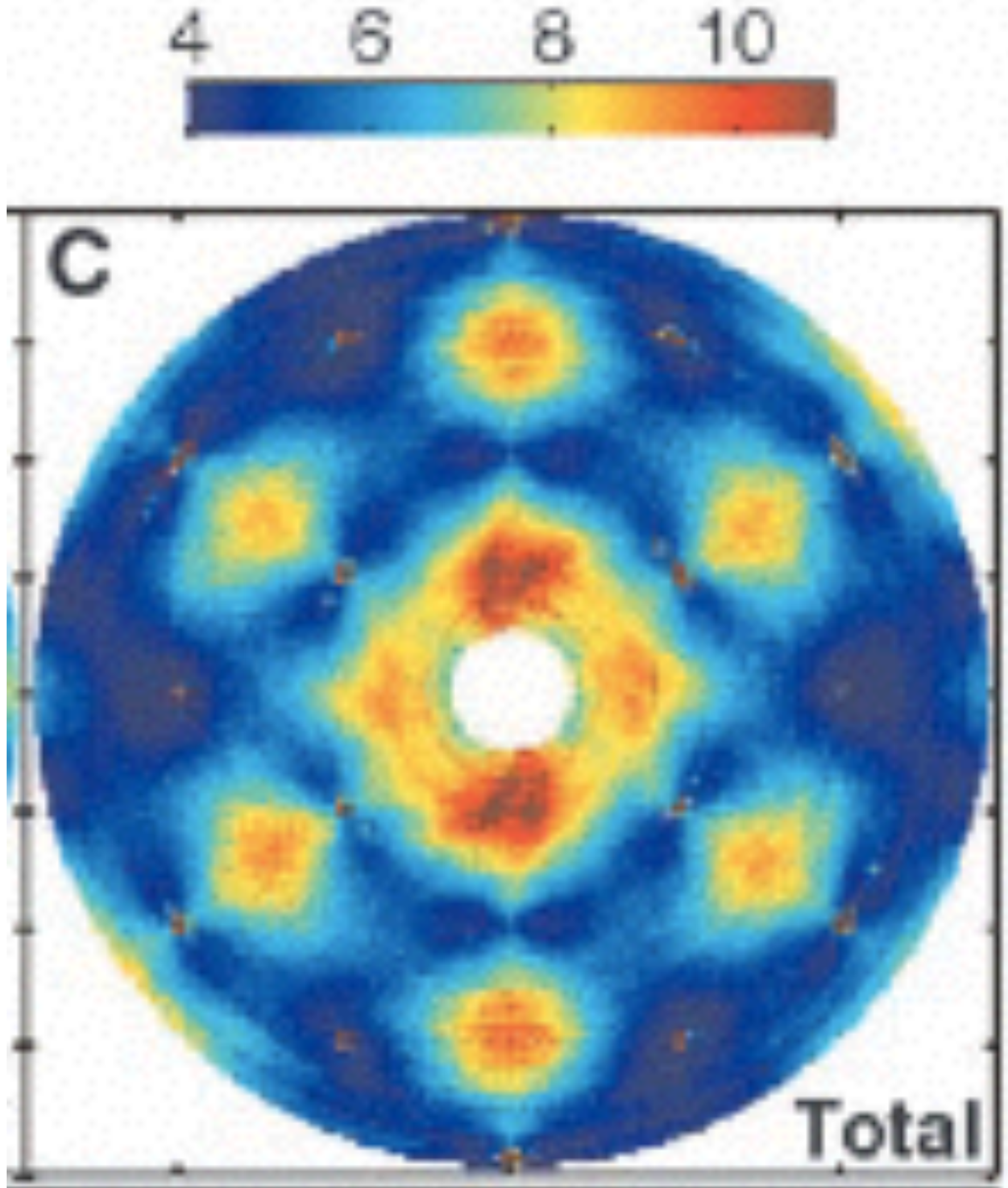
$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}$$

$$+ D r_{\rm nn}^3 \sum_{i>j} \frac{\mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{z_j} \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

# "Hidden Pinch Points" in Dipolar Spin Ice

T. Fennell, *et al*, Science,vol. **326**, p. 415, 2009

Unpolarized
vs.
Polarized
Neutron
Scattering



# “Hidden Pinch Points” in Dipolar Spin Ice

T. Fennell, *et al*, Science,vol. **326**, p. 415, 2009

Unpolarized vs. Polarized Neutron Scattering

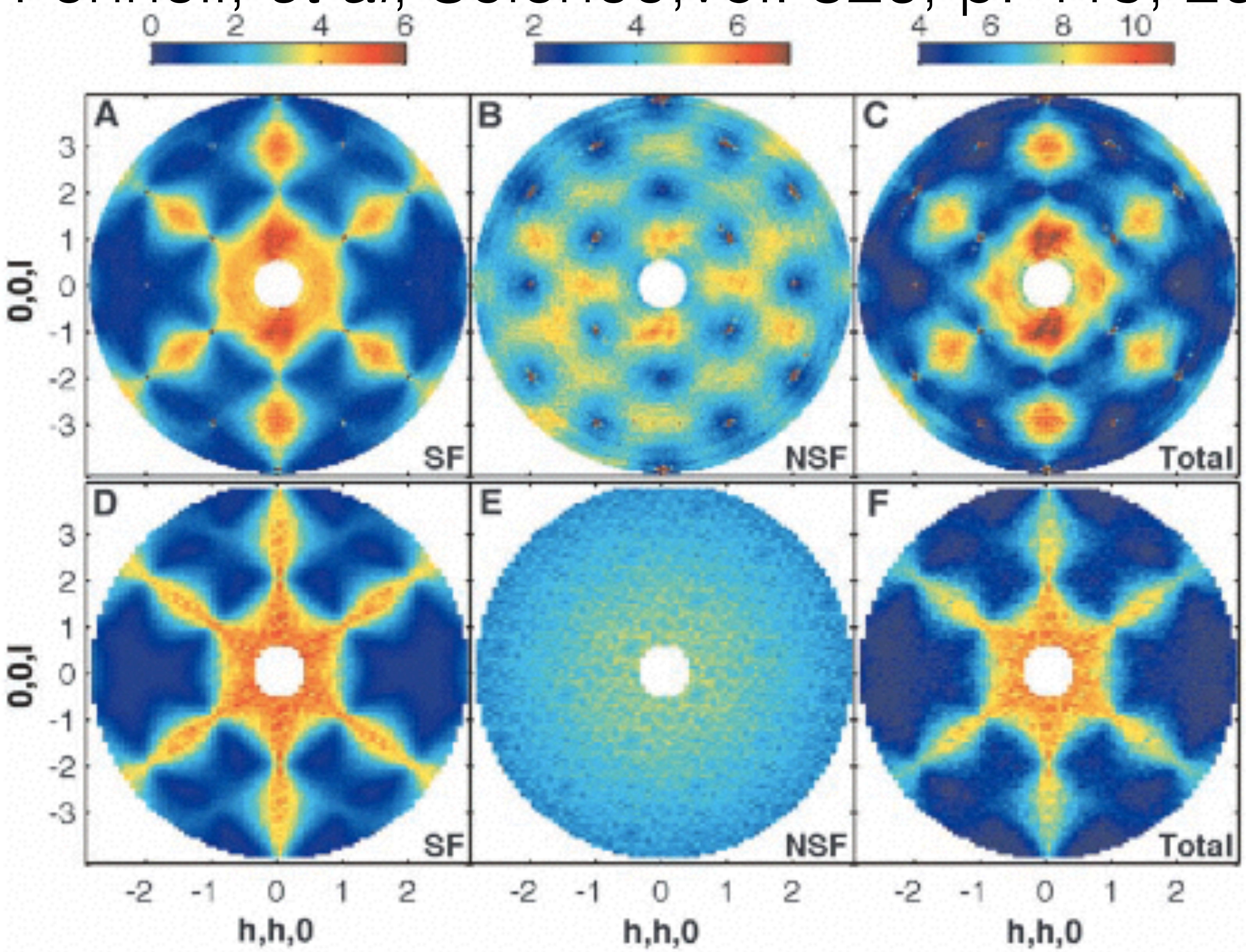



**Fig. 2.** Diffuse scattering maps from spin ice, $Ho_2Ti_2O_7$. Experiment [(**A**) to (**C**)] versus theory [(**D**) to (**F**)]. (A) Experimental SF scattering at $T = 1.7$ K with pinch points at (0, 0, 2), (1, 1, 1), (2, 2, 2), and so on. (B) The NSF scattering. (C) The sum, as would be observed in an unpolarized experiment (*20*, *22*). (D) The SF scattering obtained from Monte Carlo simulations of the near-neighbor model, scaled to match the experimental data. (E) The calculated NSF scattering. (F) The total scattering of the near-neighbor spin ice model.

# Selection of Spin Ice References

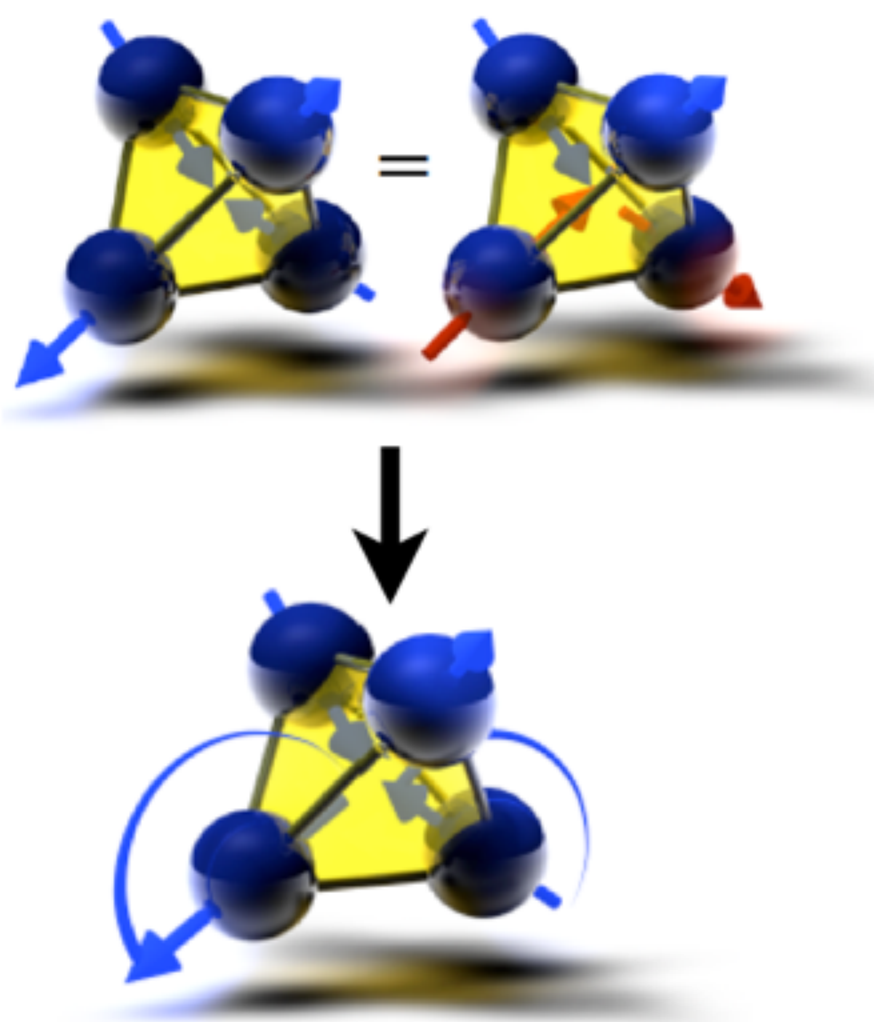

- B. C. den Hertog et al, *Dipolar Interactions and Origin of Spin Ice in Ising Pyrochlore Magnets*. PRL **84**, 3430 (2000)

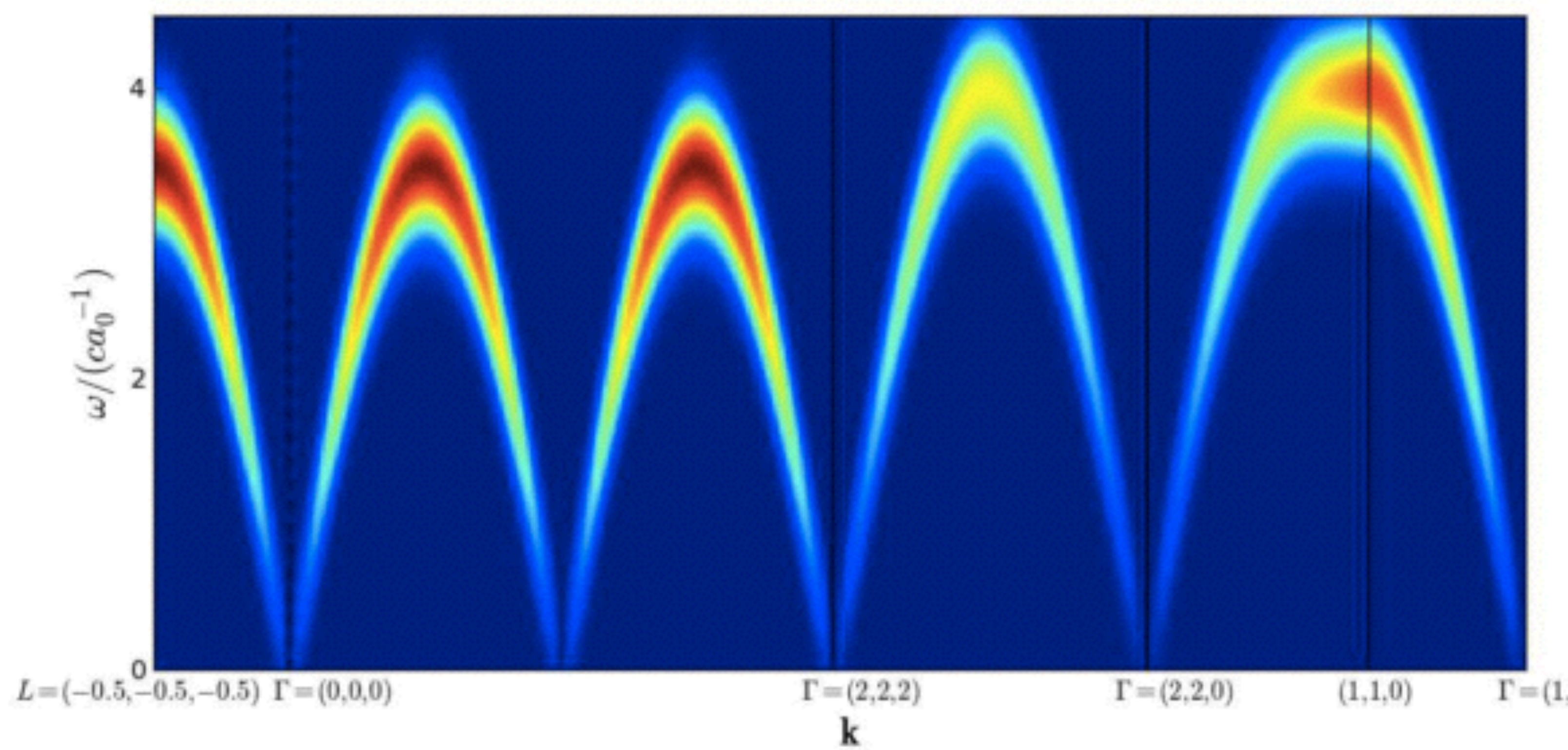
- T. Fennell, *et al*, *Magnetic Coulomb Phase in the Spin Ice* $Ho_2Ti_2O_7$*.* Science,vol. **326**, p. 415, 2009

- C. Castelnovo, R. Moessner, S.L. Sondhi, *Magnetic Monopoles in Spin Ice*. Nature **451**, 42-45 (2008)

- C. Castelnovo, R. Moessner, S.L. Sondhi, *Spin Ice, Fractionalization, and Topological Order.* Annu. Rev. Condens.Matter Phys. **3,** 35–55 (2012)

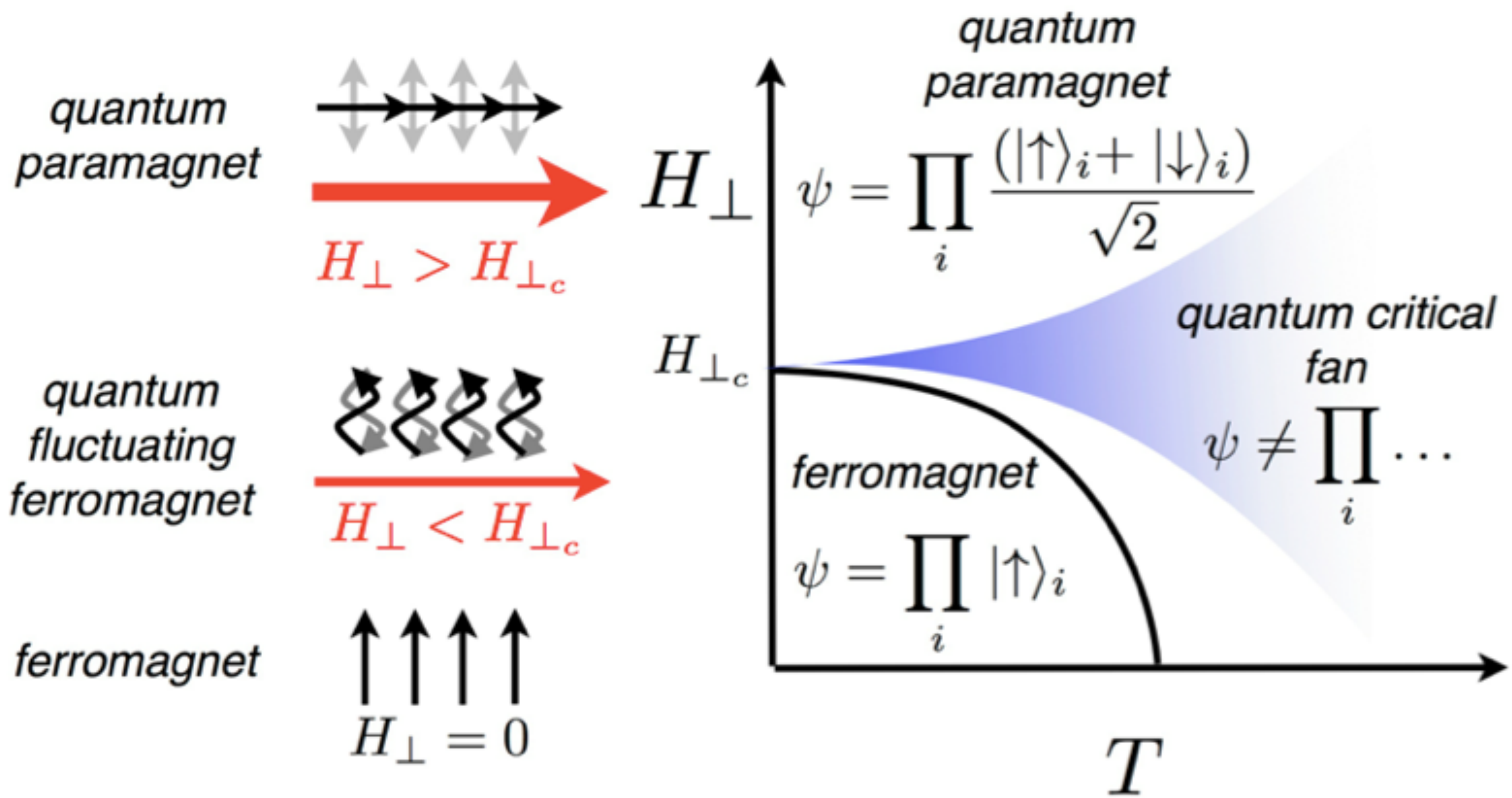
# 2) Quantum Spin Ice





# Quantum Fluctuations Example

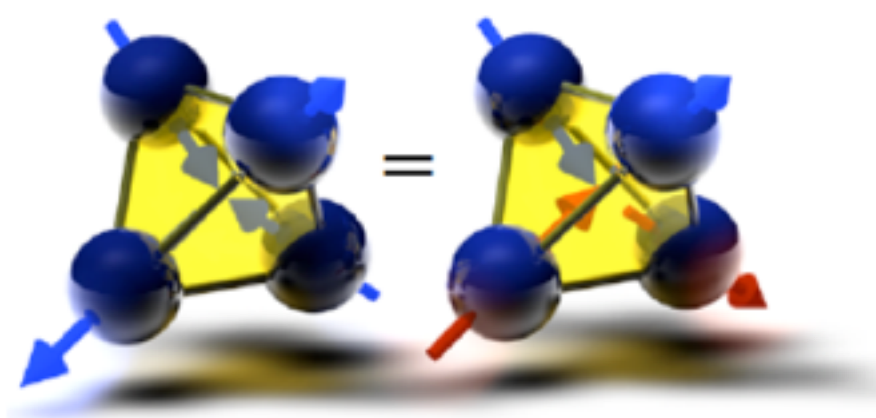
## e.g. Transverse Field Ising Model



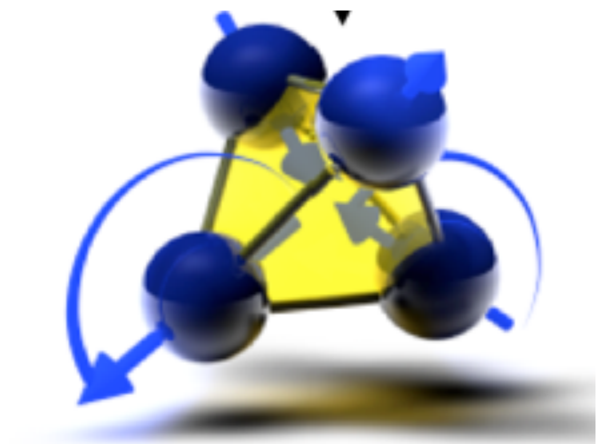

$$H = -J \sum_{ij} S_{i_z} S_{j_z} - H_\perp \sum_i S_{i_x}$$

# Adding Quantum Fluctuations to Spin Ice

$\boldsymbol{\psi}_1$ $\boldsymbol{\psi}_2$



$\boldsymbol{\psi}_1 + \boldsymbol{\psi}_2$



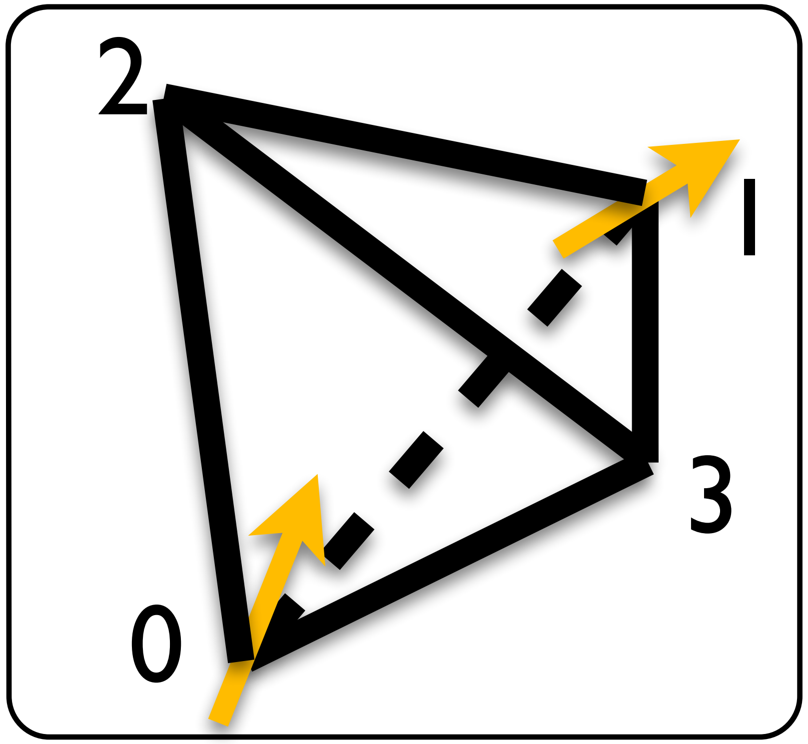
$$H = J \sum_{\langle ij \rangle} \vec{S}_{z_i} \cdot \vec{S}_{z_j} \quad + \quad \boxed{??}$$

- ?? = Additional terms that don't commute with Sz.Sz
- These terms mix together our previously stationary ice rule states

# General Anisotropic Exchange

$$H = \frac{1}{2}\sum_{ij} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu}$$

$$J_{01} = \begin{pmatrix} J_2 & J_4 & J_4 \\ -J_4 & J_1 & J_3 \\ -J_4 & J_3 & J_1 \end{pmatrix}$$




**4 symmetry-allowed exchange terms**


Hermele, M., Fisher, M. & Balents, L. Phys. Rev. B 69, 064404 (2004)

K.A. Ross,et al, Phys. Rev. X **1**, 021002 (2011)

# General Anisotropic Exchange

$$H = \frac{1}{2}\sum_{ij} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu}$$

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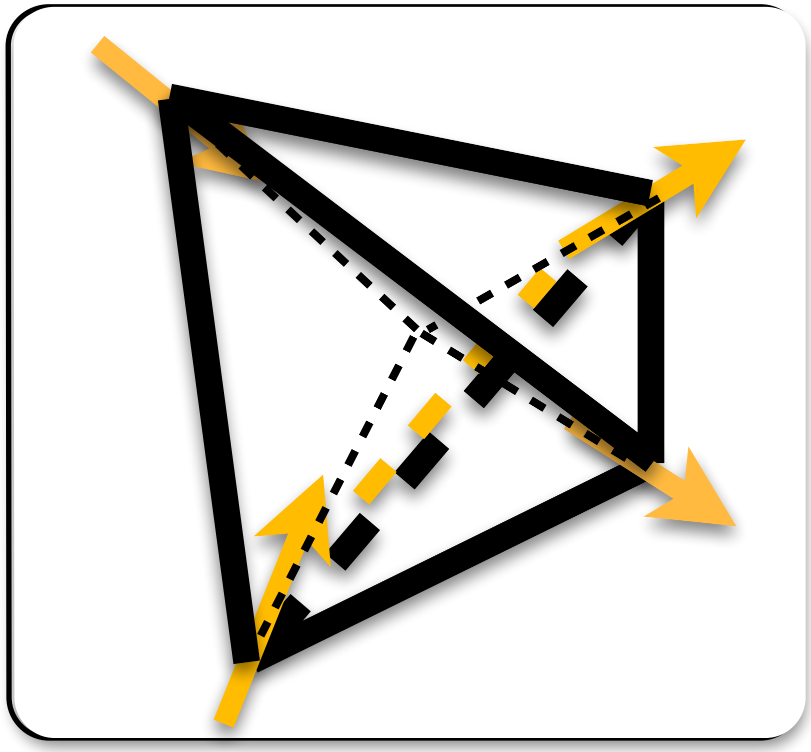


**4 symmetry-allowed exchange terms**

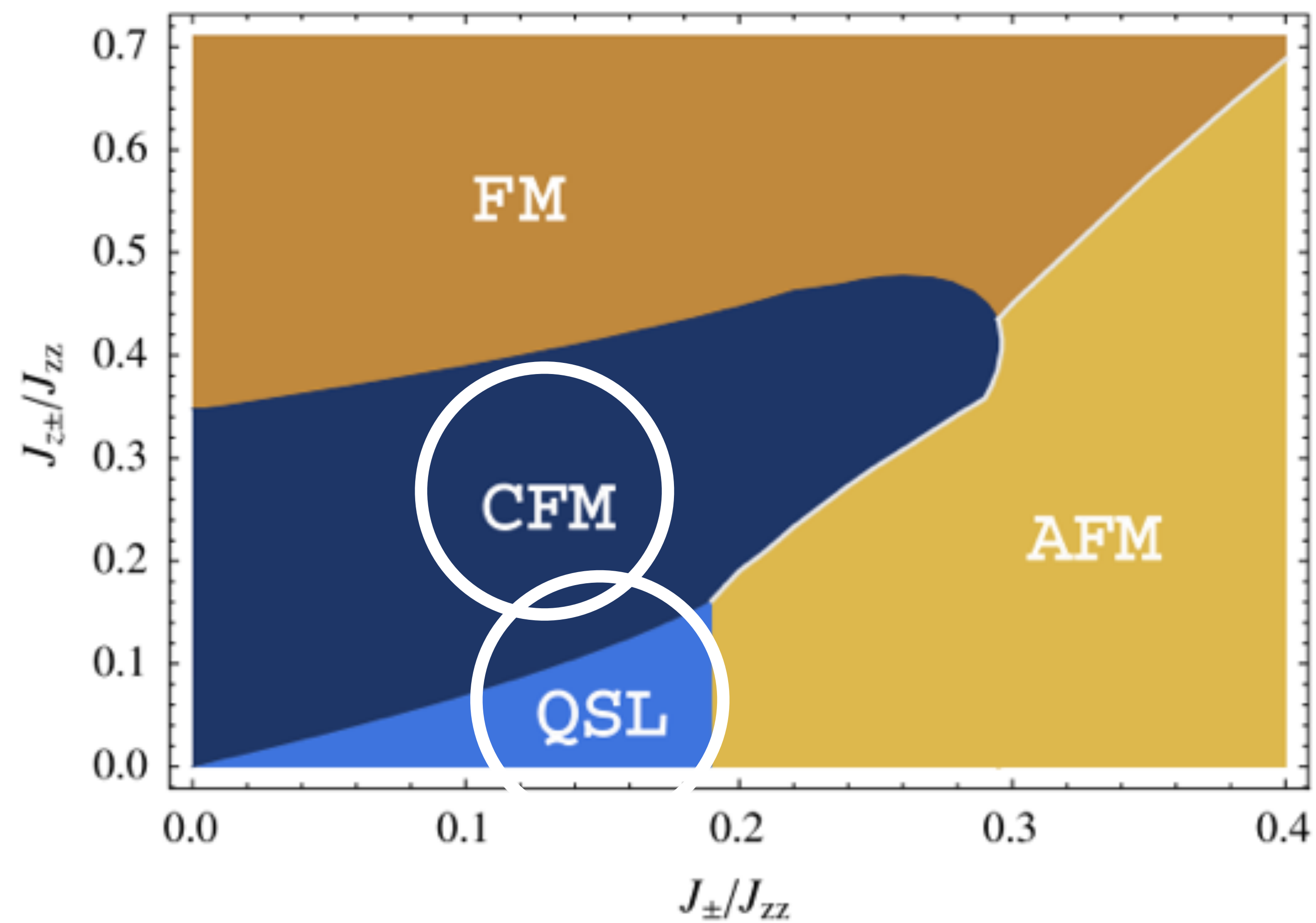
$$H = \sum_{\langle ij \rangle} \{ J_{zz} S_i^z S_j^z - J_{\pm}(S_i^+ S_j^- + S_i^- S_j^+) + J_{++}\left[\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-\right] + J_{z\pm}\left[S_i^z(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^-) + i \leftrightarrow j\right] \},$$

Hermele, M., Fisher, M. & Balents, L. Phys. Rev. B 69, 064404 (2004)

K.A. Ross, et al, Phys. Rev. X **1**, 021002 (2011)

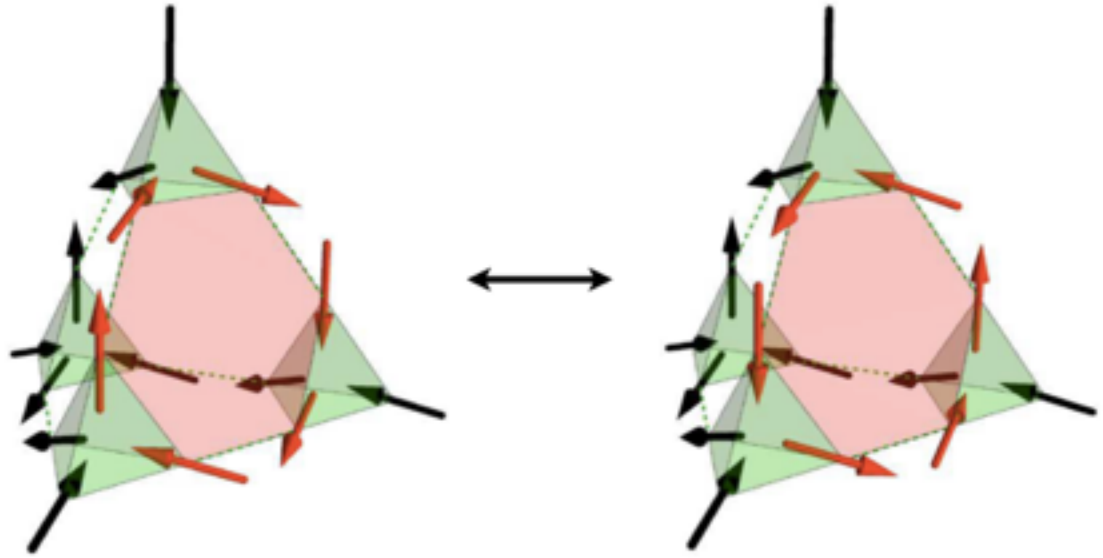
# Phase Diagram for J++ = 0

- From Gauge Mean Field Theory (gMFT)
- Coulomb phases exist
  - U(1) Quantum spin liquid (QSL)
  - Coulomb Ferromagnet (CFM) has same features as QSL but with partially polarized moment




Savary, Balents. PRL **108**, 037202 (2012)

# Emergent Electrodynamics in U(1) phase of Quantum Spin Ice



O. Benton et al, Phys. Rev. B **86**, 2002

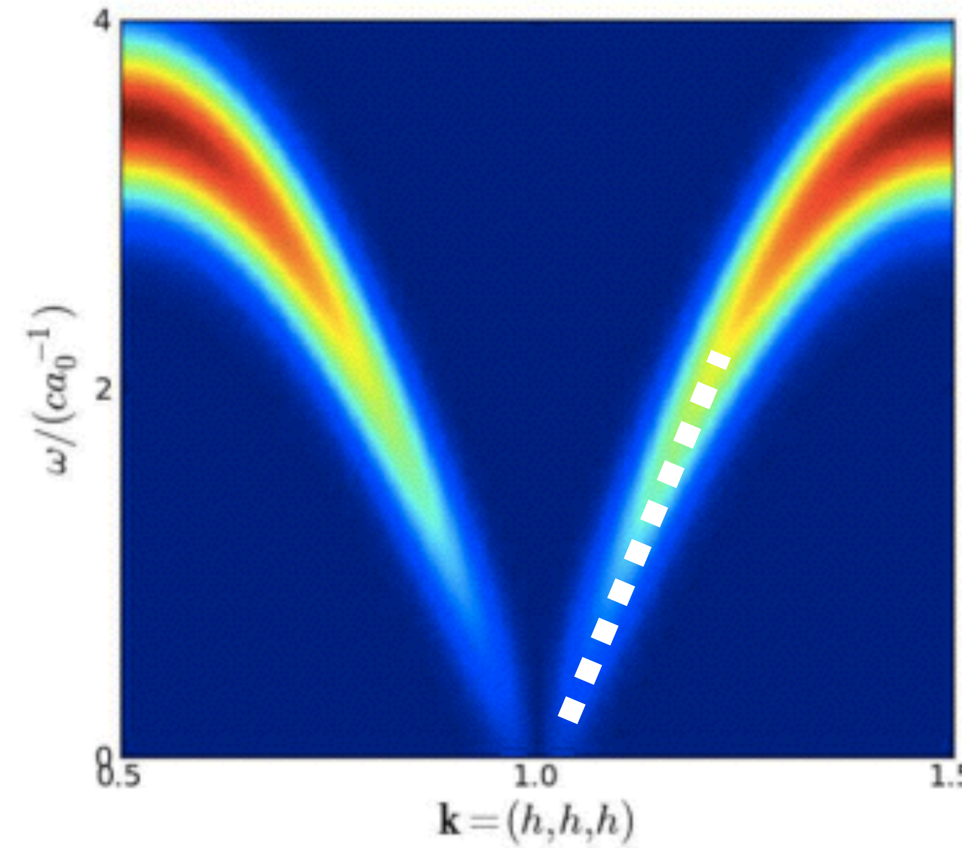
$$\vec{\nabla} \cdot \vec{B} = \rho_m$$
$$\vec{B} = \vec{\nabla} \times \vec{A}$$
$$\vec{E} = -\frac{\partial \vec{A}}{\partial t}$$

- Can tunnel between ice rules states
- Introduces *fluctuations* in the gauge field
  - **Electric monopoles —** coherent, propagating wavepacket of ice configurations
  - **Magnetic monopoles —** violate ice rules, i.e. 3-in 1-out
  - **Gauge photons —** transverse fluctuations of gauge field

# Photons in Quantum Spin Ice

- Ways to think of Photons:
  - Linearly dispersing $S_z = 0$ fluctuations
  - Transverse Fluctuations of gauge field
  - Local magnetization fluctuations that are transverse to propagation direction
  - **"Bloch waves"** of spin ice configurations which propagate through the lattice

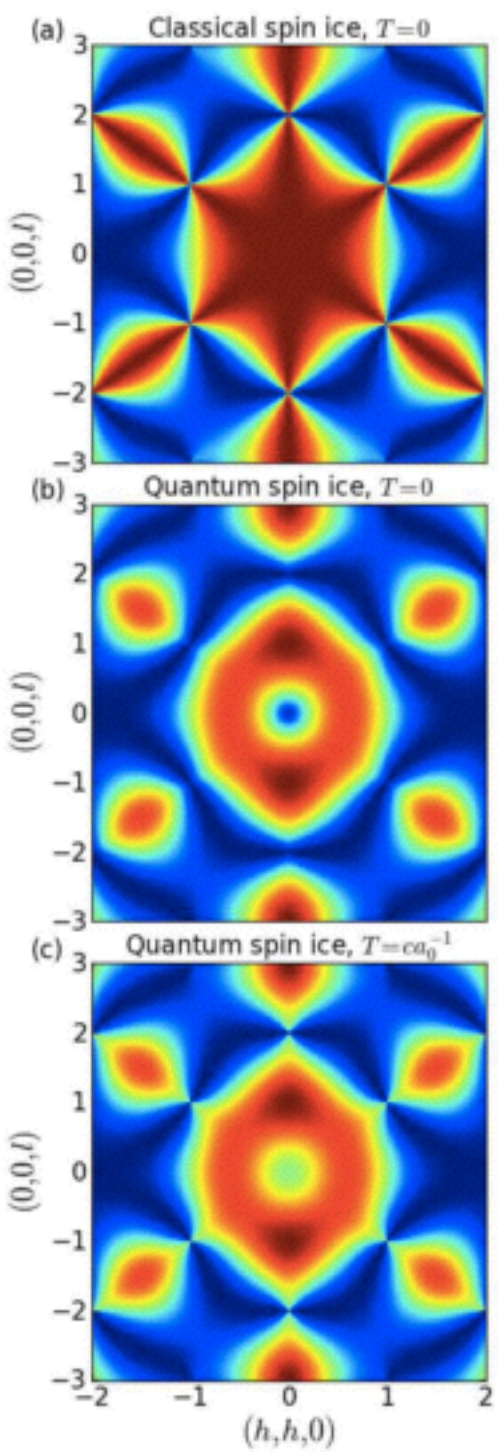
O. Benton et al, Phys. Rev. B **86**, 2002




Speed of light, *c*, depends on material parameters (J's)

# Pinch Points in U(1) phase of Quantum Spin Ice

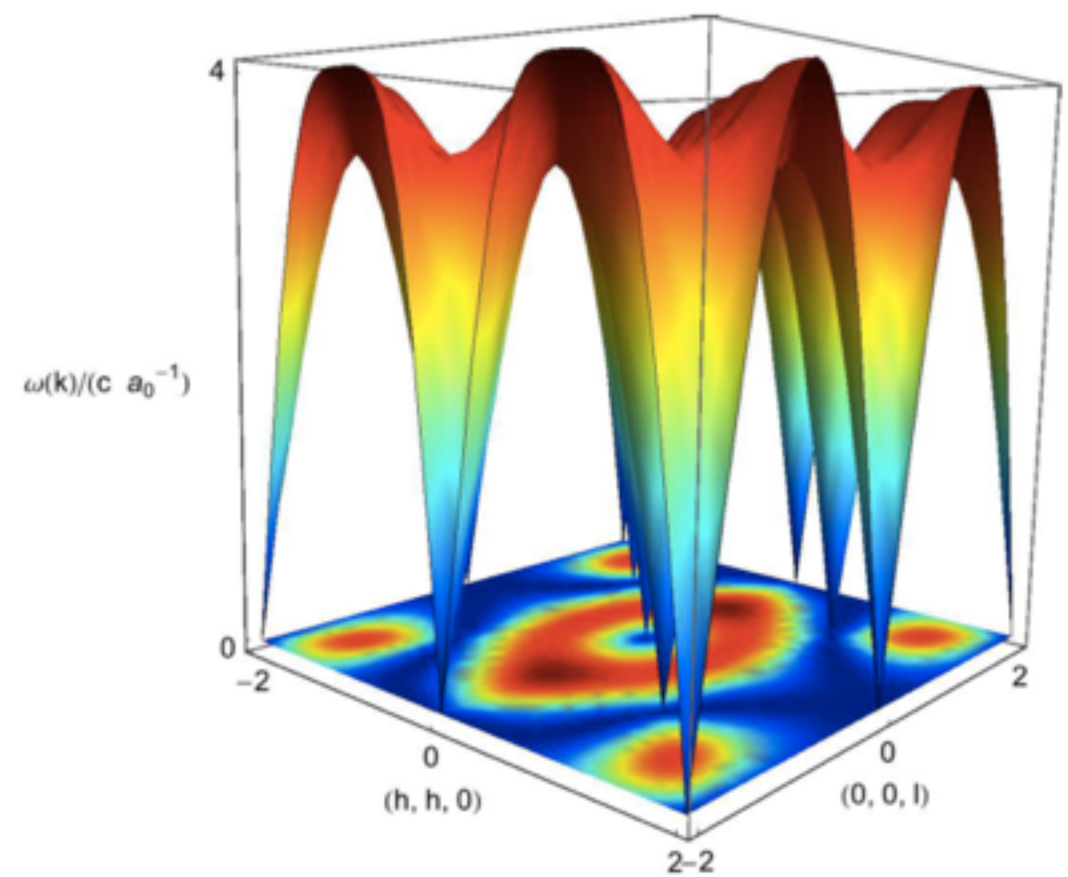
O. Benton et al, Phys. Rev. B **86**, 2002




Classical Spin Ice

"minimal" Quantum Spin Ice
at T=0
(J++, Jz+- = 0)

"minimal" Quantum Spin Ice
at T>0
(J++, Jz+- = 0)




Predicted S(Q,w) for photons vanishing spectral weight at pinch points near w=0

# Experimental Signatures of Photons

- Direct measurement via inelastic neutron scattering
    - vanishing spectral weight that goes as 1/w near pinch point positions
- Thermodynamics
    - Large $T^3$ contribution to specific heat, field dependent

# Experimental Signatures of *Quantum Spin Ice*

- Required
  - persistent spin dynamics (no freezing / ordering, or only *partial* freezing / ordering)
  - spin ice interactions:  <111> ferromagnetic effective exchange
- Optional
  - **possible phase transition** with thermodynamic anomaly
  - rounded <111> magnetization plateau
  - pinch points (or vestiges of pinch points)
  - **entropy plateau** near Pauling's entropy for spin ice
  - **Photon** modes: neutrons or thermodynamics

# Experimental Signatures of *Quantum Spin Ice*

- persistent spin dynamics: $Pr_2Zr_2O_7$, $Pr_2Sn_2O_7$, $Pr_2Ir_2O_7$, $Tb_2Ti_2O_7$, $Tb_2Sn_2O_7$, $Yb_2Sn_2O_7$, $Yb_2Ti_2O_7$

- spin ice interactions (111 ferromagnetic exchange): $Pr_2Zr_2O_7$, $Pr_2Sn_2O_7$, $Pr_2Ir_2O_7$, $Tb_2Ti_2O_7$, $Tb_2Sn_2O_7$, $Yb_2Sn_2O_7$, $Yb_2Ti_2O_7$

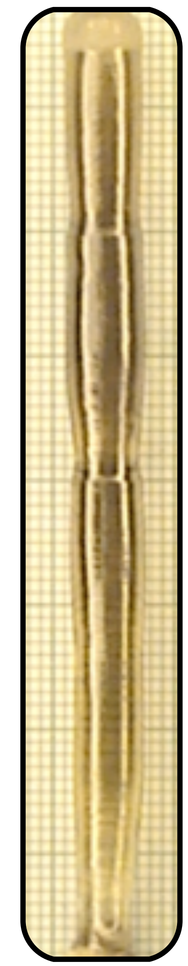
- rounded 111 magnetization plateau (need xtals to see): $Tb_2Ti_2O_7$(?), $Pr_2Ir_2O_7$, $Pr_2Zr_2O_7$

- pinch points (need xtals to see): $Pr_2Zr_2O_7$, $Yb_2Ti_2O_7$, $Tb_2Ti_2O_7$

- entropy related to Pauling… examples: $Pr_2Sn_2O_7$, $Yb_2Ti_2O_7$

# Example: $Yb_2Ti_2O_7$

- Best-known microscopic Hamiltonian of all QSI materials
- Ground state unusually sensitive to disorder
- Some evidence for ordering, but also unusual fluctuations persist
- Is it related to the CFM phase?



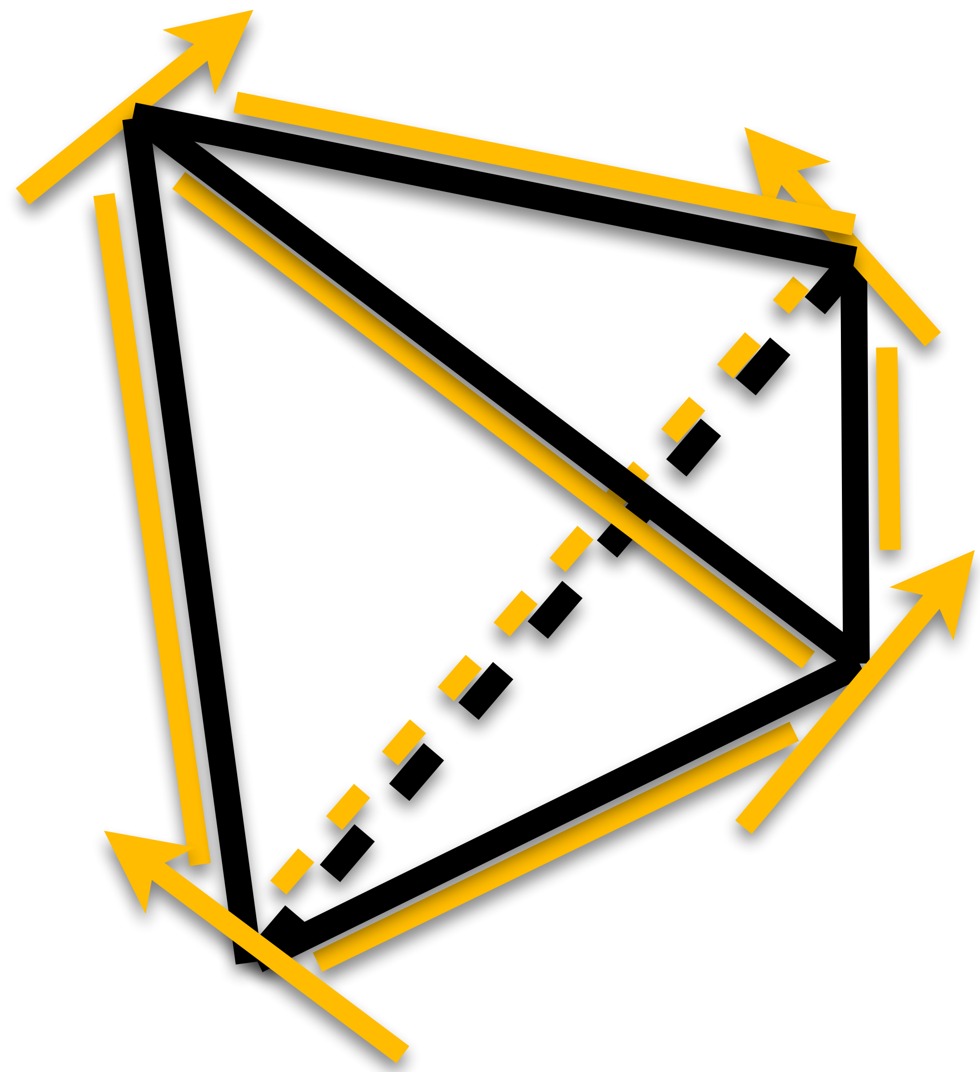
Single Crystal $Yb_2Ti_2O_7$

7.5 cm long

# $Yb_2Ti_2O_7$

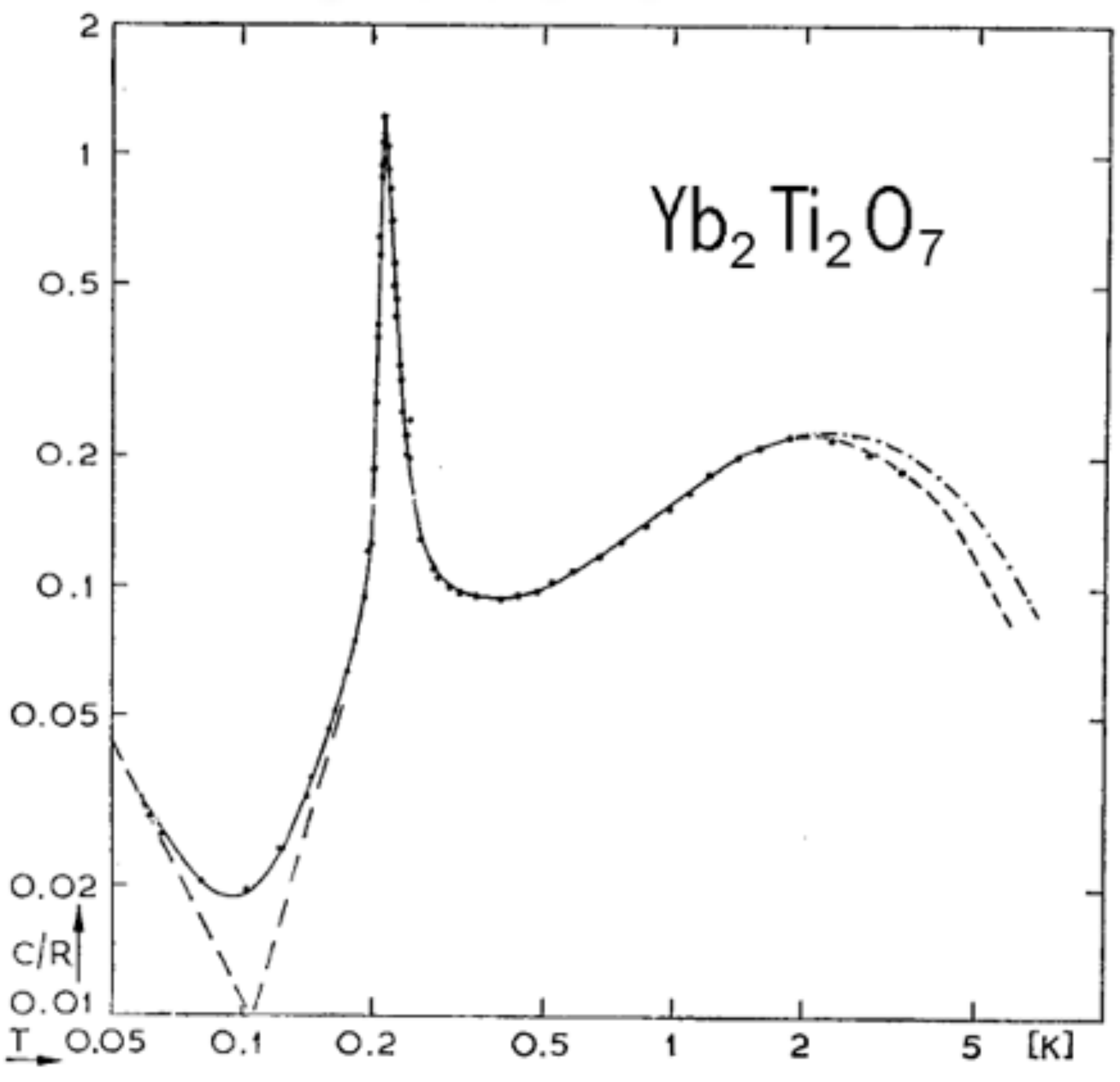
- **Unlike spin ice,** the single ion anisotropy is mostly XY-like
- $g_{xy}$ / $g_z$ ~ 2
- The overall exchange interactions are **ferromagnetic** ($\Theta_{cw}$~ 300 mK)
- The ferromagnetic XY pyrochlore is not frustrated so we expect a transition to LRO

Ferromagnetic
**Easy-Plane (XY) anisotropy**

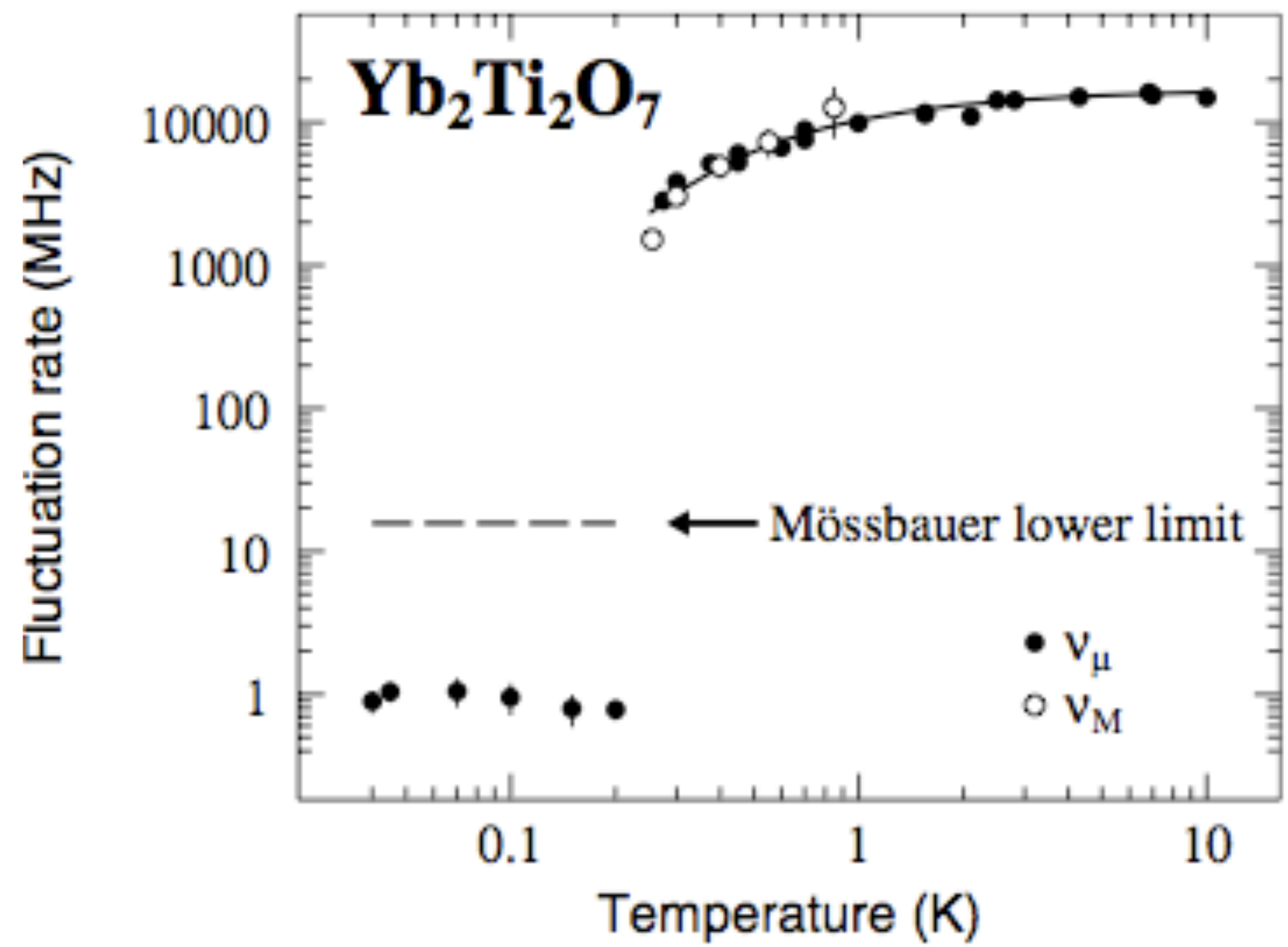


# Transition! But persistent dynamics?

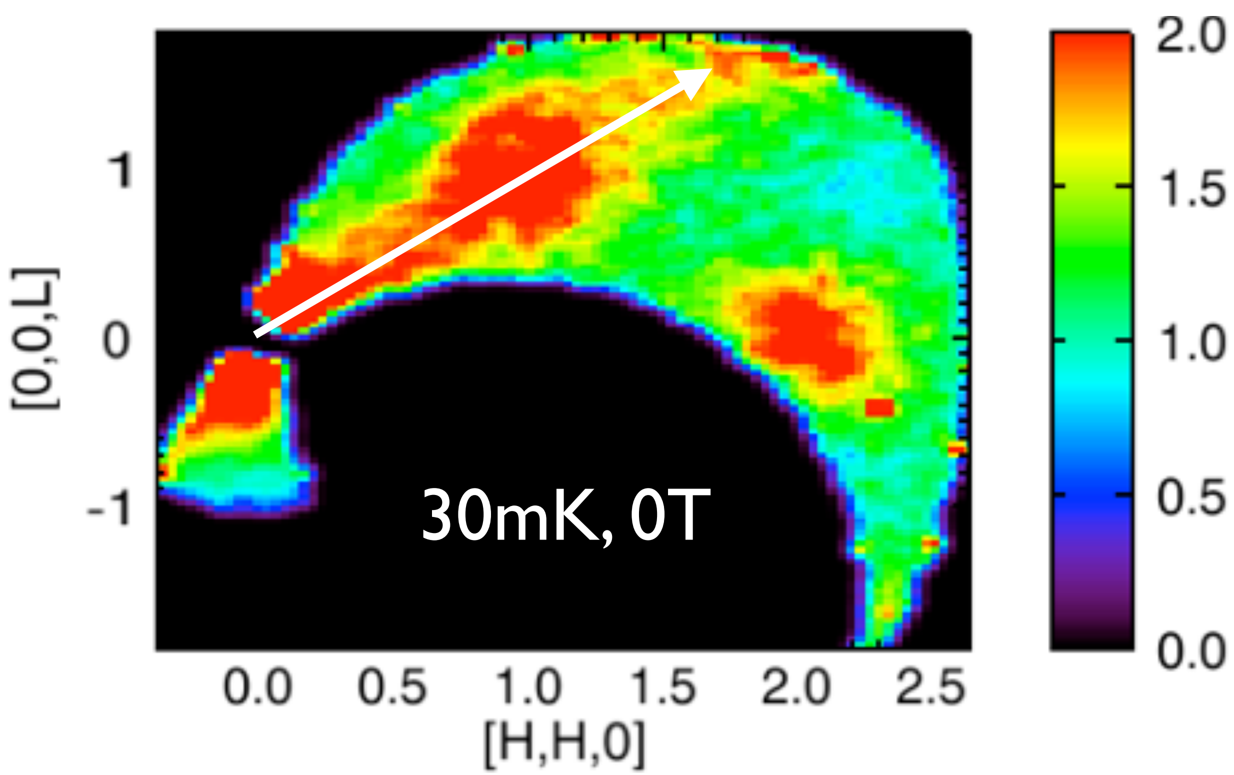
Blote et al,
Physica, **43**, 4 (1969)

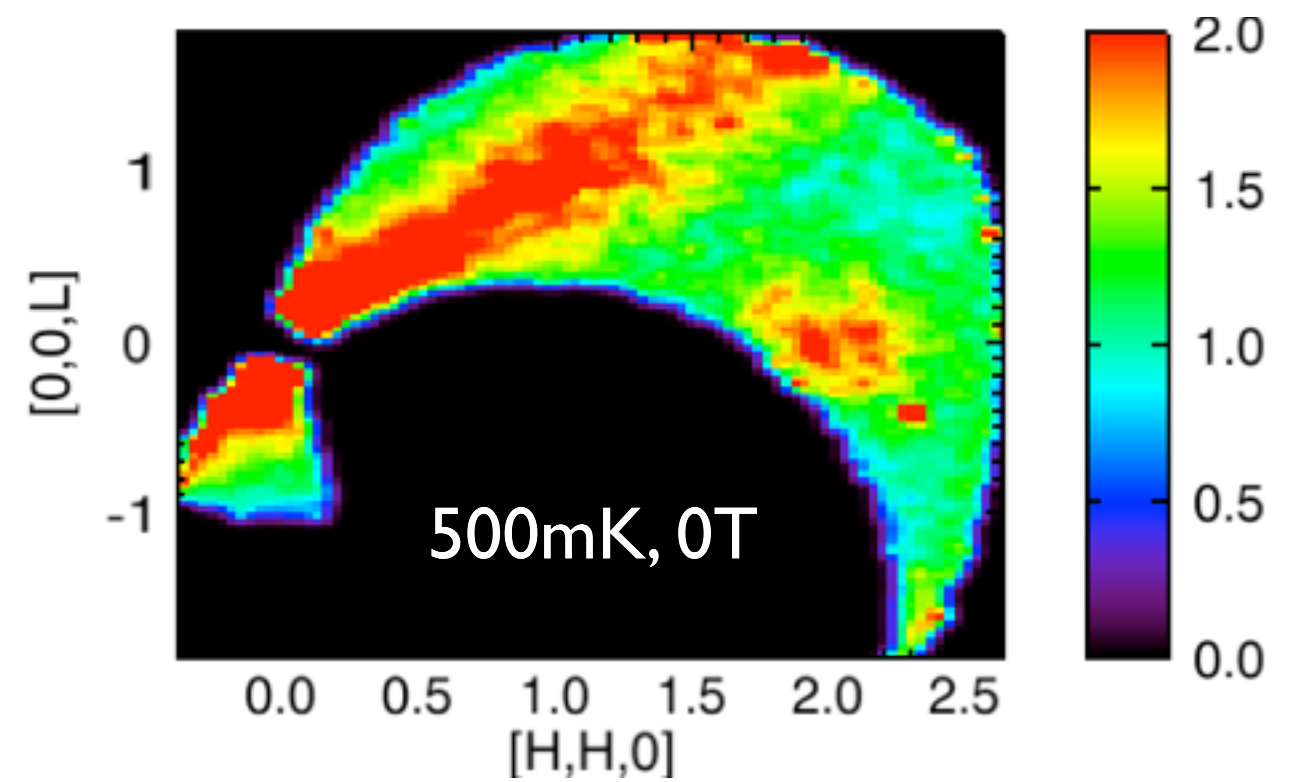


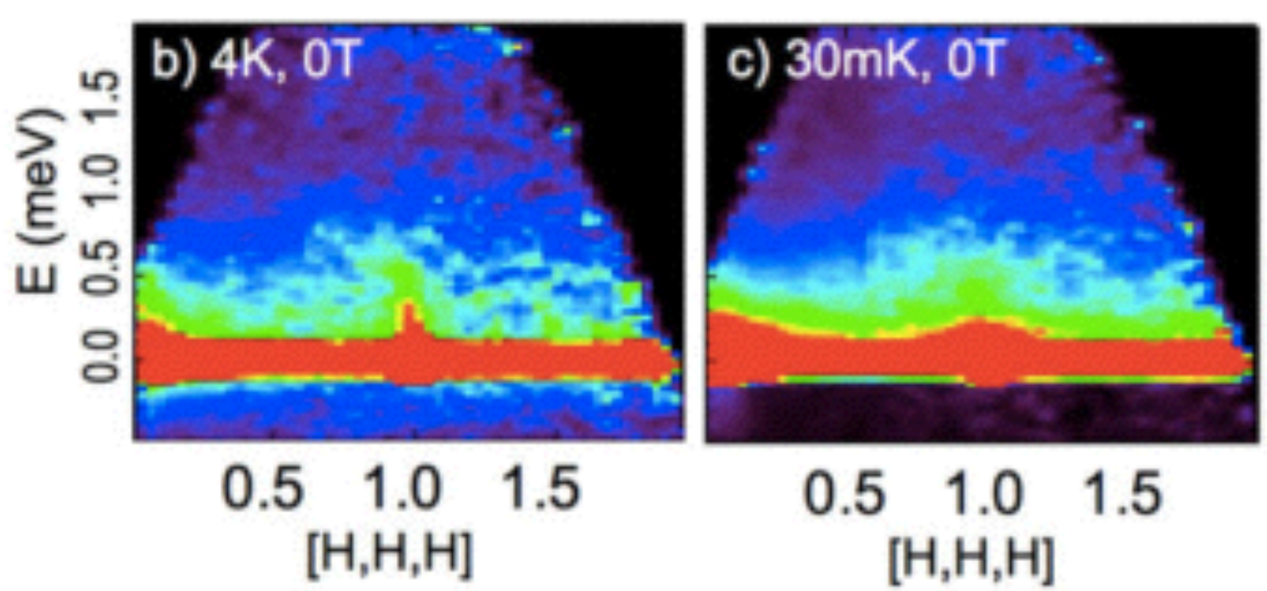

J. A. Hodges et al, Phys Rev Lett, **88**, 077204 (2002)



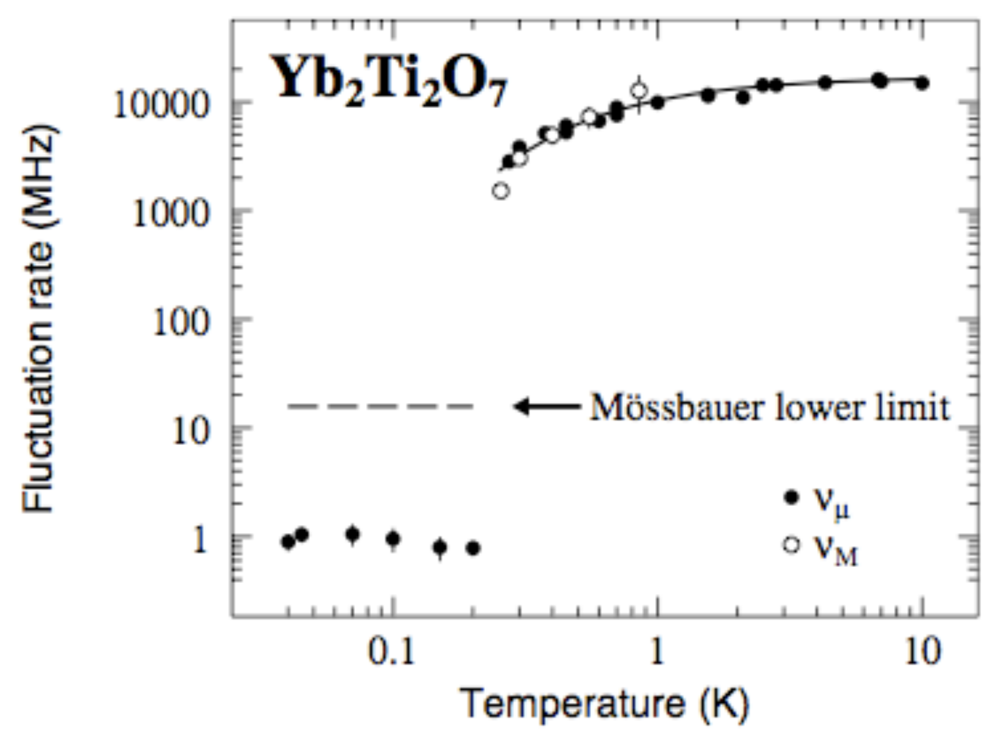
# Effect of Phase Transition



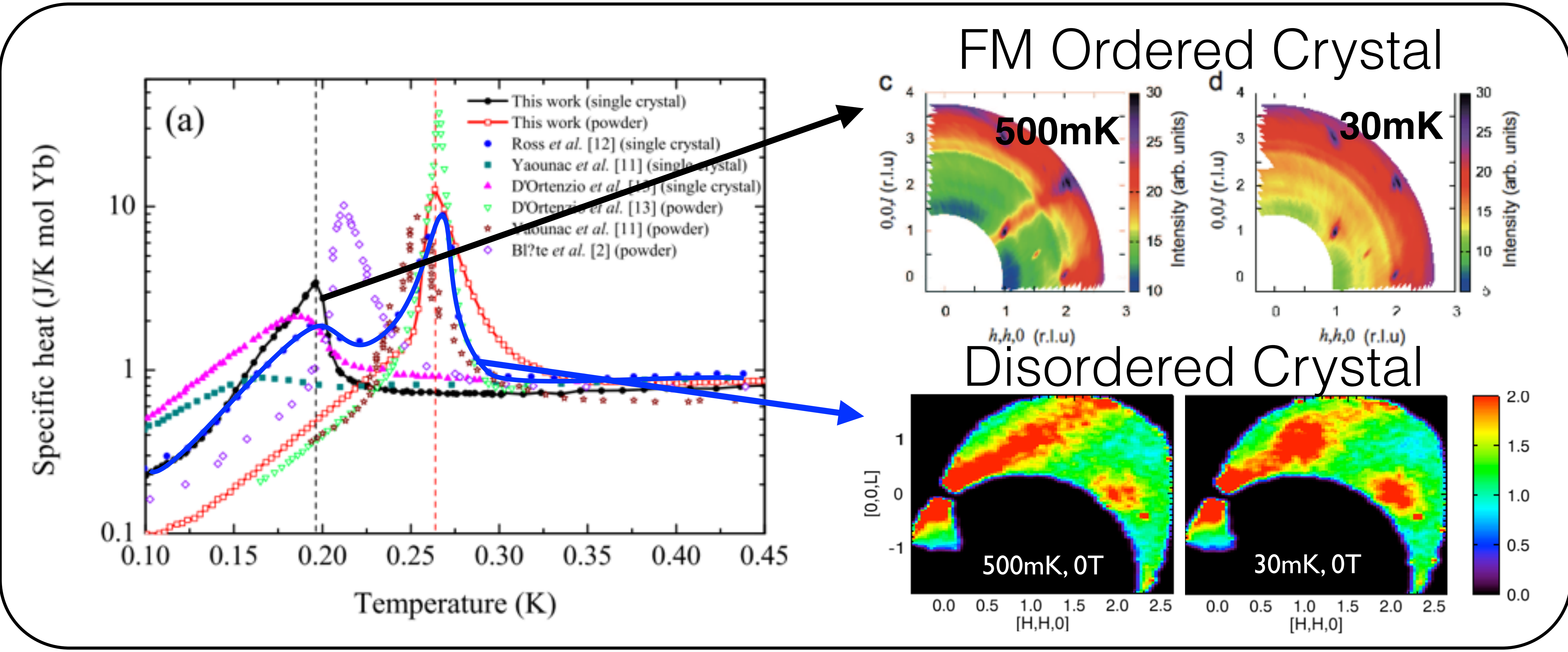




K.A. Ross, et al. Phys. Rev. Lett., **103**, 227202 (2009)




J. A. Hodges et al, Phys Rev Lett, **88**, 077204 (2002)

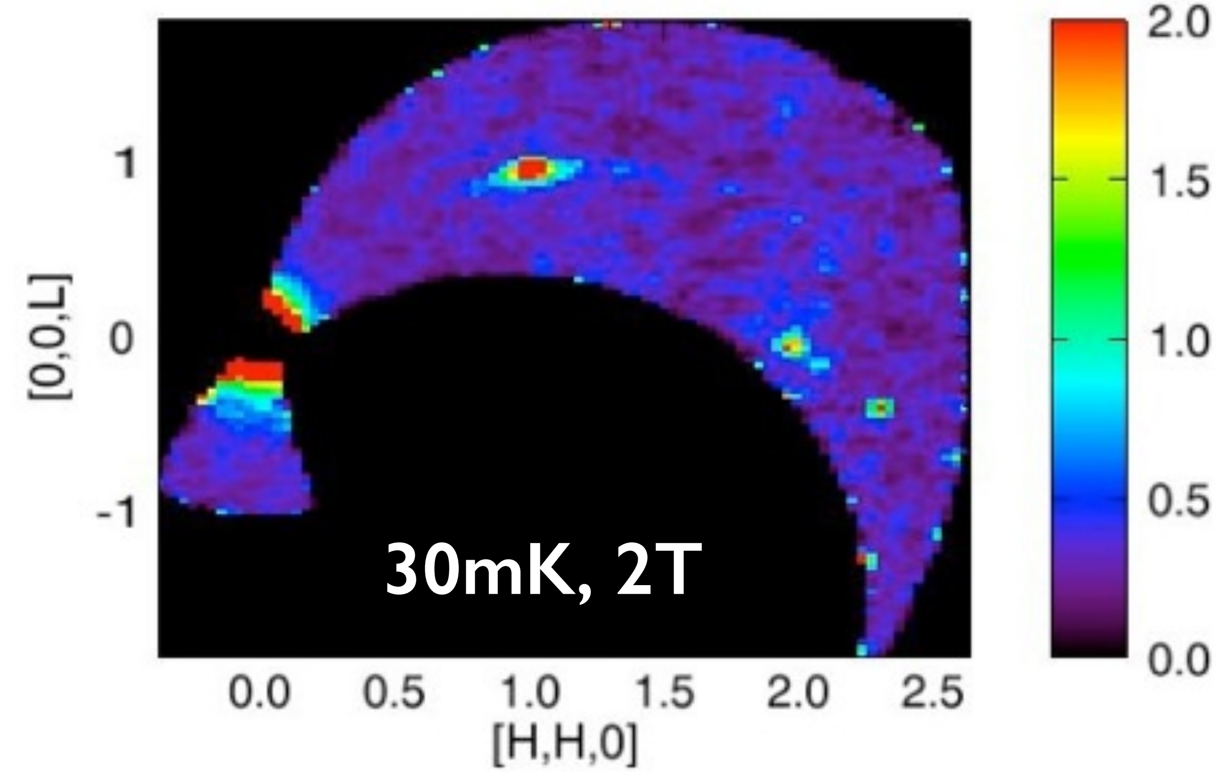
# Debate: small differences in sample quality?



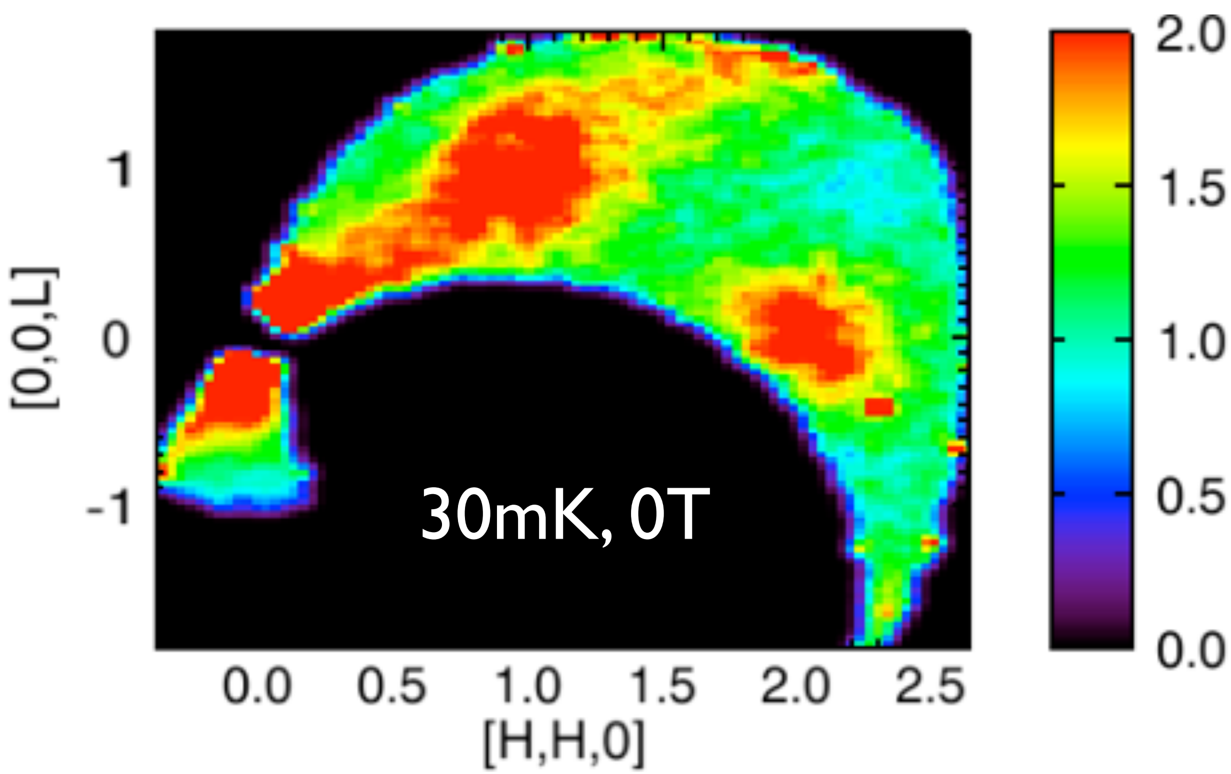

L-J. Chang, et al ,Nat. Comm. **3**, 992, (2012)

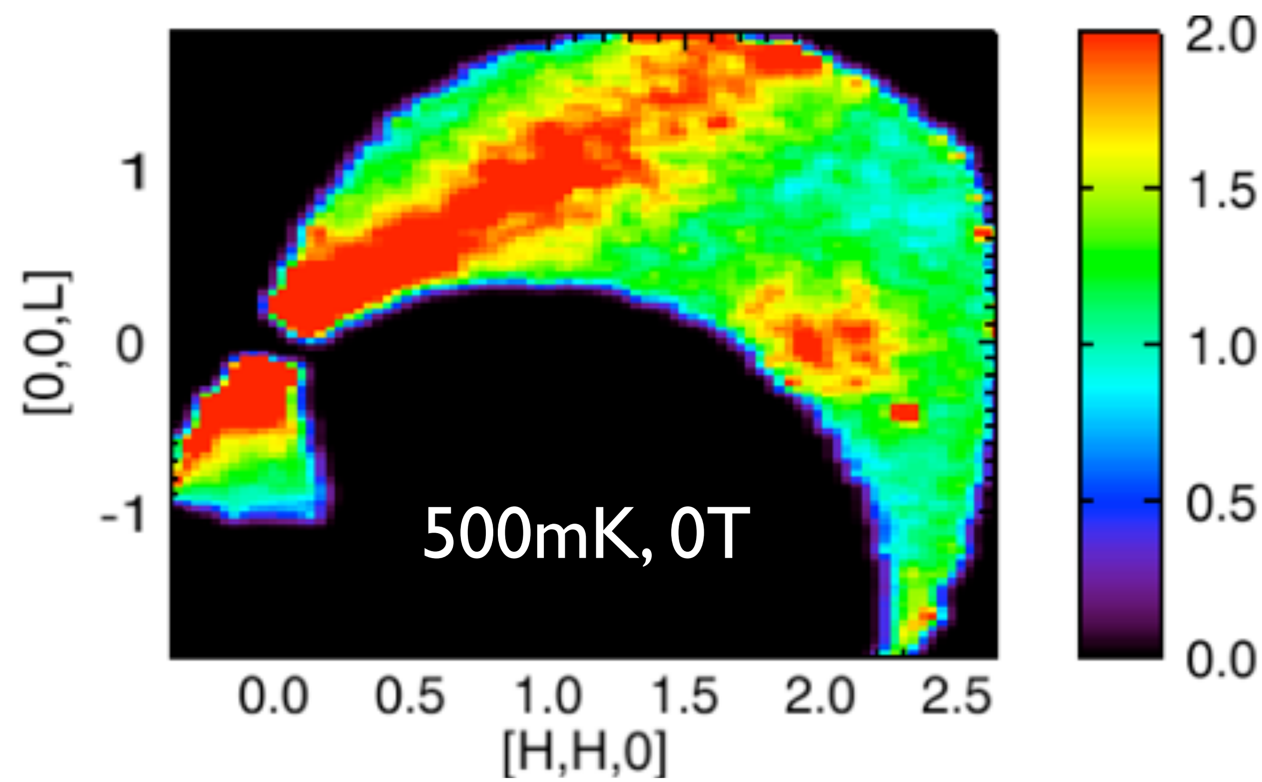
- Bimodality of $C_p$ features
- One crystal shows evidence for ordering below 200 mK
- One is very short range correlated down to 30 mK

# In a Magnetic Field

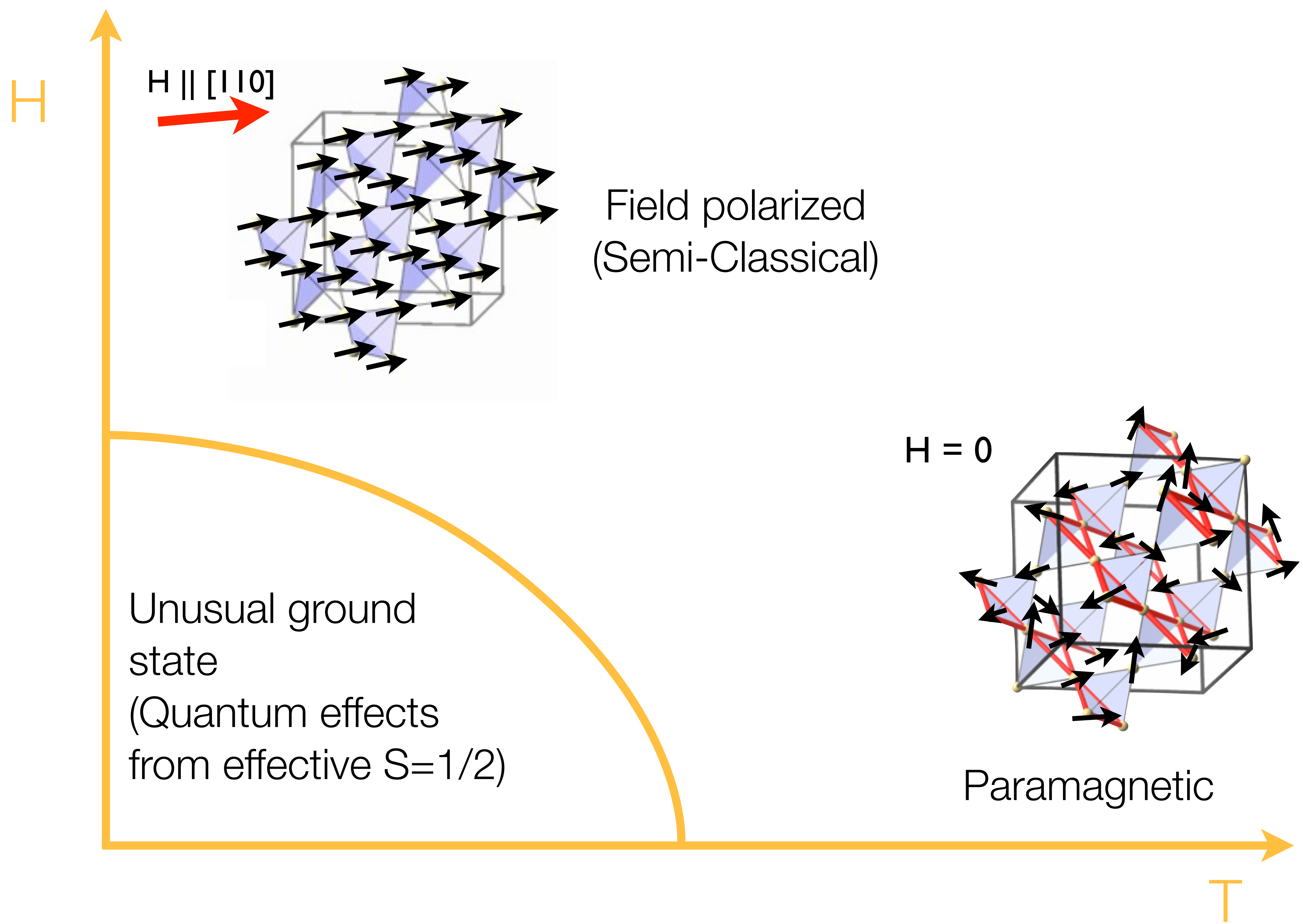



**Field removes diffuse scattering**

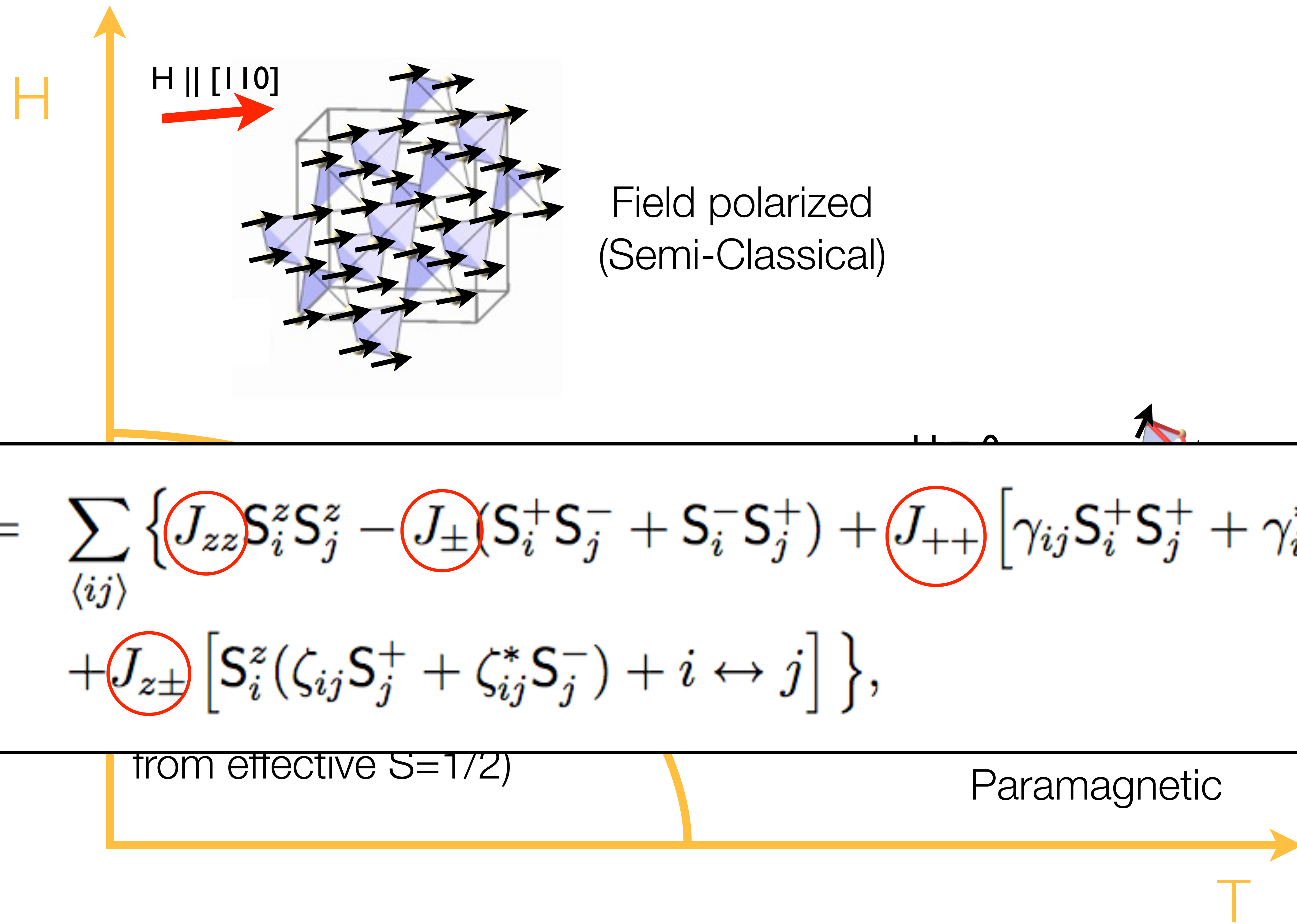


# General Phase Diagram



# General Phase Diagram

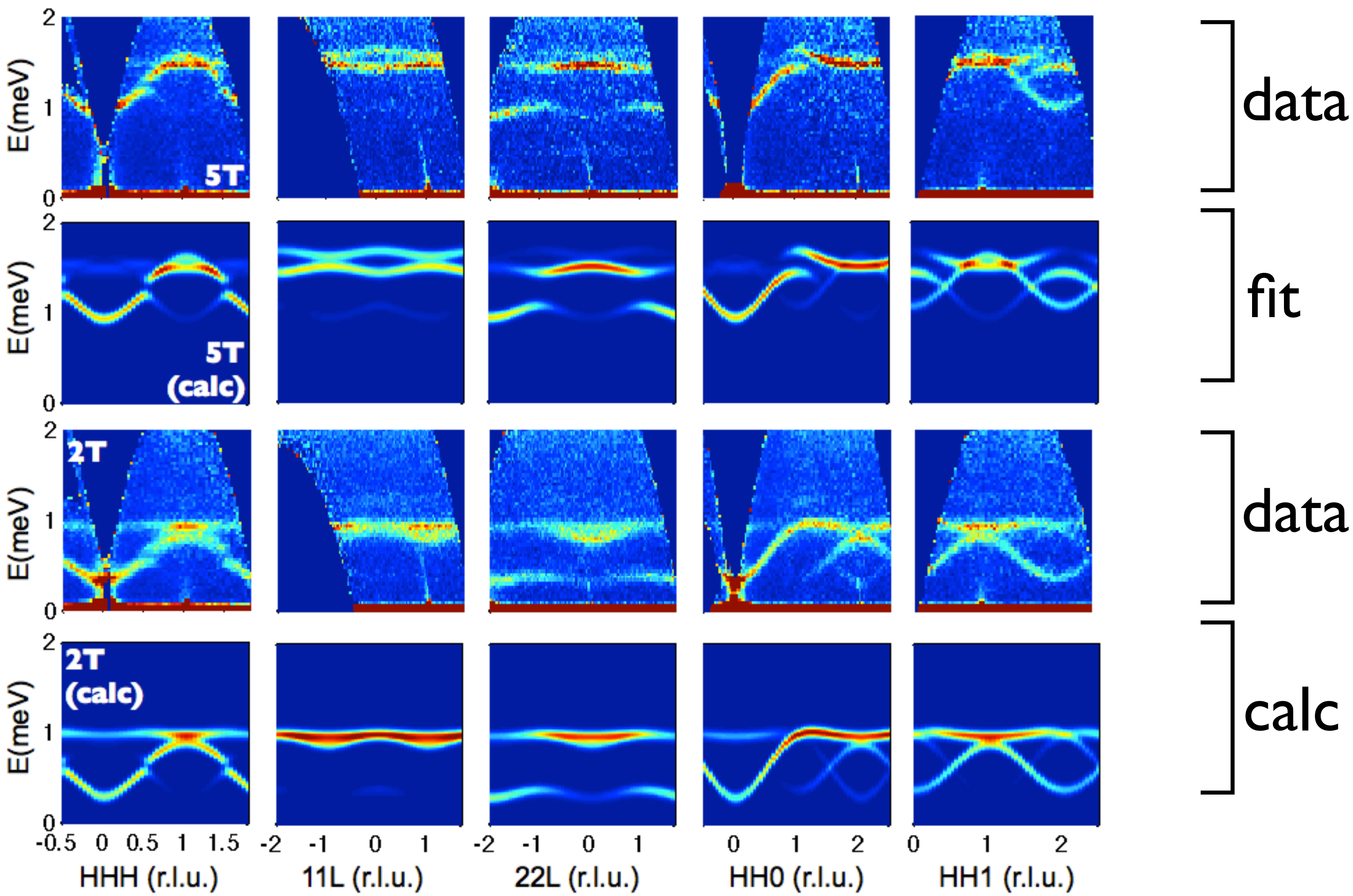


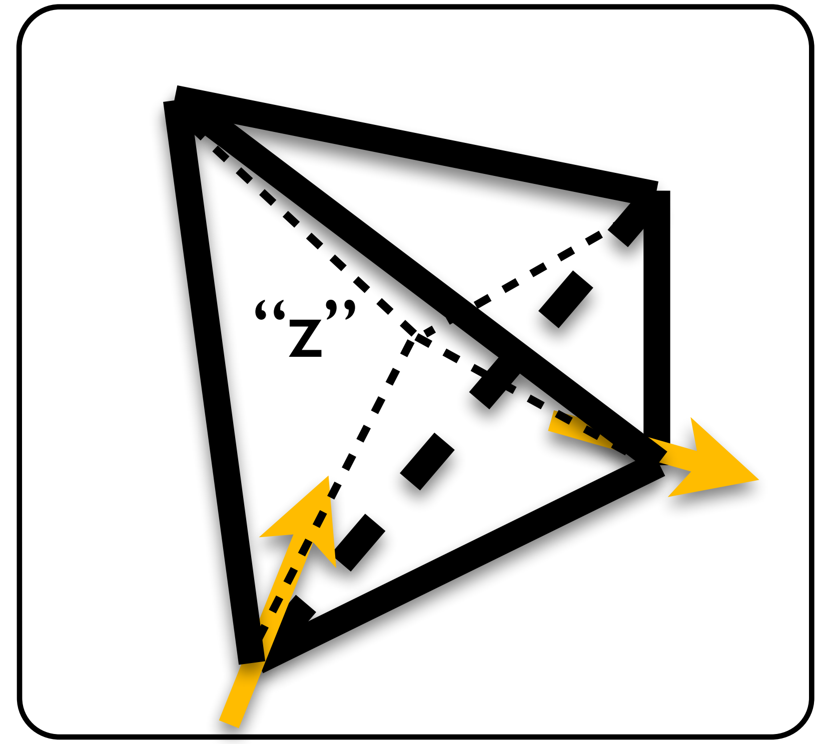

$$H = \sum_{\langle ij\rangle} \Big\{ J_{zz} \mathsf{S}_i^z \mathsf{S}_j^z - J_{\pm}\left(\mathsf{S}_i^+ \mathsf{S}_j^- + \mathsf{S}_i^- \mathsf{S}_j^+\right) + J_{++}\left[\gamma_{ij} \mathsf{S}_i^+ \mathsf{S}_j^+ + \gamma_{ij}^* \mathsf{S}_i^- \mathsf{S}_j^-\right] + J_{z\pm}\left[\mathsf{S}_i^z\left(\zeta_{ij} \mathsf{S}_j^+ + \zeta_{ij}^* \mathsf{S}_j^-\right) + i \leftrightarrow j\right] \Big\},$$

# Field Polarized Phase

H along [1-10]

K.A. Ross, L. Savary, B. D. Gaulin, and L. Balents, Phys. Rev. X **1**, 021002 (2011)

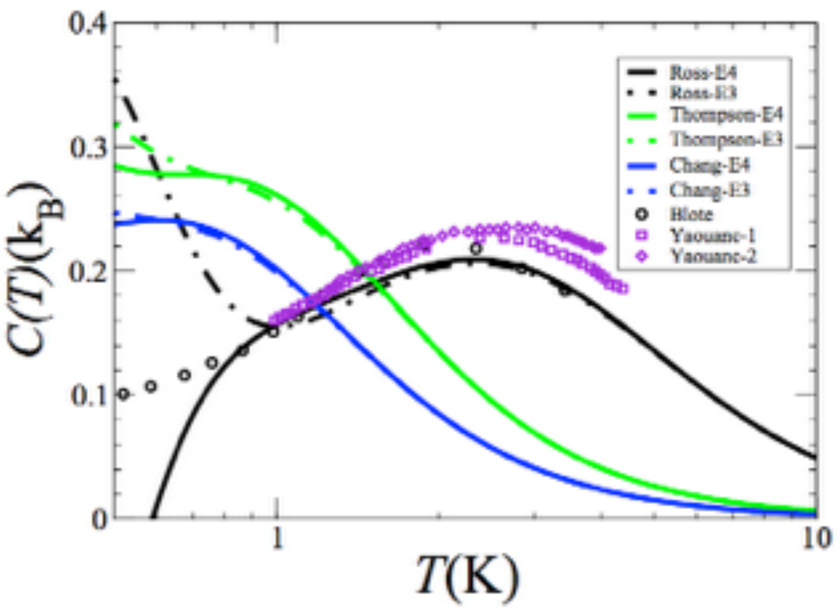


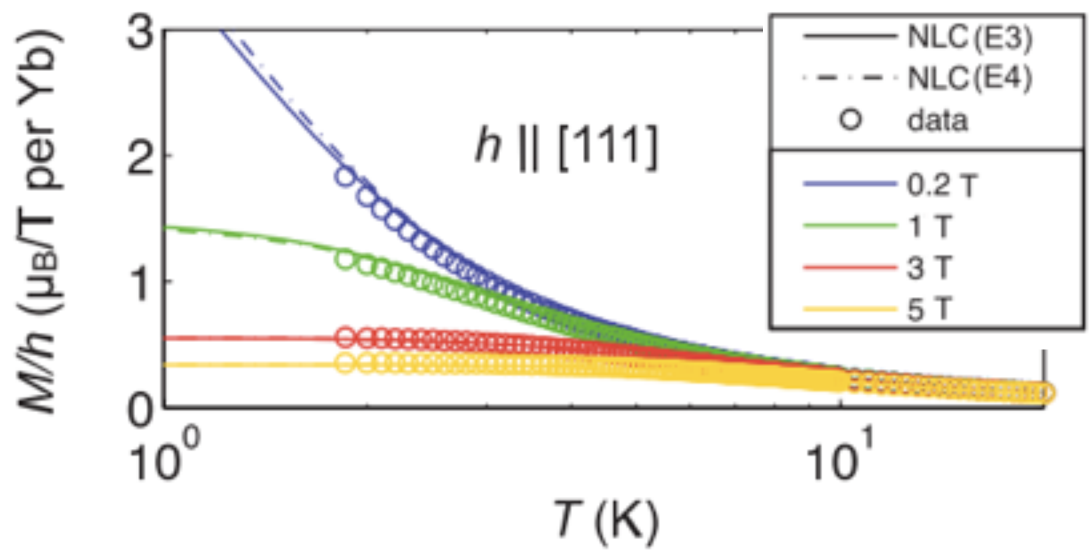

Frustration plus quantum fluctuations

$$J_{zz} = 0.17 \pm 0.04, \; J_{\pm} = 0.05 \pm 0.01, \; J_{\pm\pm} = 0.05 \pm 0.01, \; J_{z\pm} = -0.14 \pm 0.01 \; \text{(meV)}$$

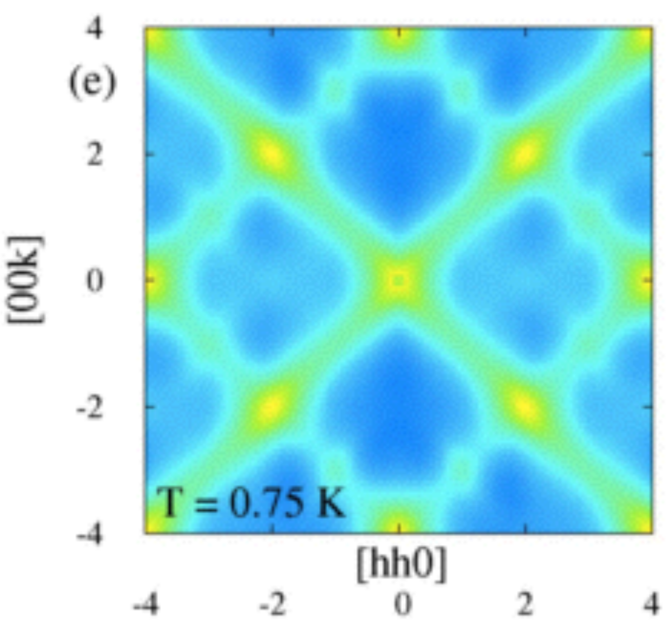
# Successes for the model




R. Applegate *et al*,
Phys. Rev. Lett. **109**, (2012)




N. R. Hayre *et al*, Phys. Rev. B **87**, (2013)




H. Yan *et al*,
arXiv:1311.3501 (2013)

**Specific heat:**

no adjusted params

**Magnetization:**

no adjusted params

**Diffuse scattering:**

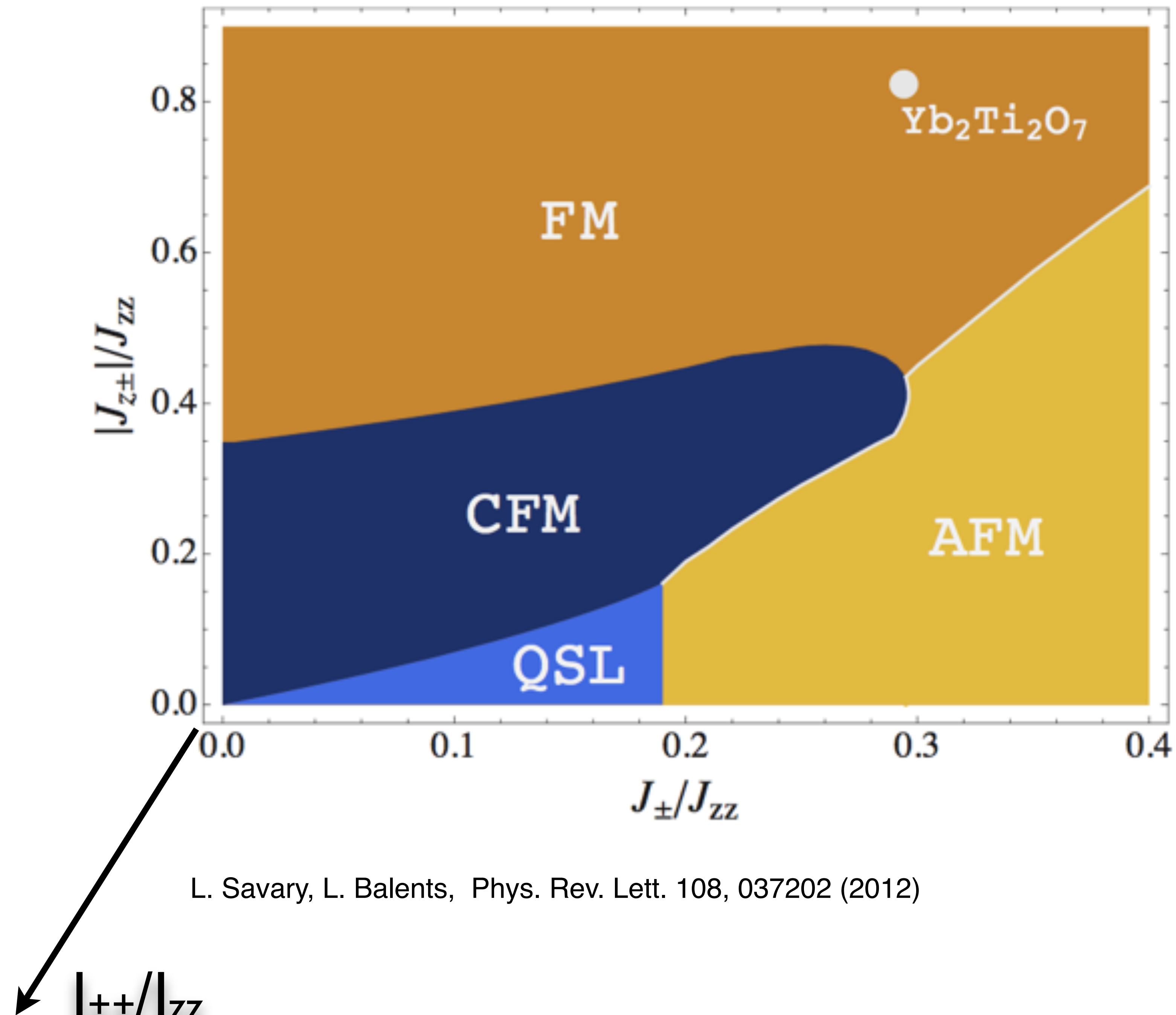
no adjusted params

Our parameters have been used to reproduce high temperature, zero field effects

# What is the ground state with our J's?

## Gauge Mean Field Phase Diagram

$Yb_2Ti_2O_7$ if $J_{\pm\pm} = 0$

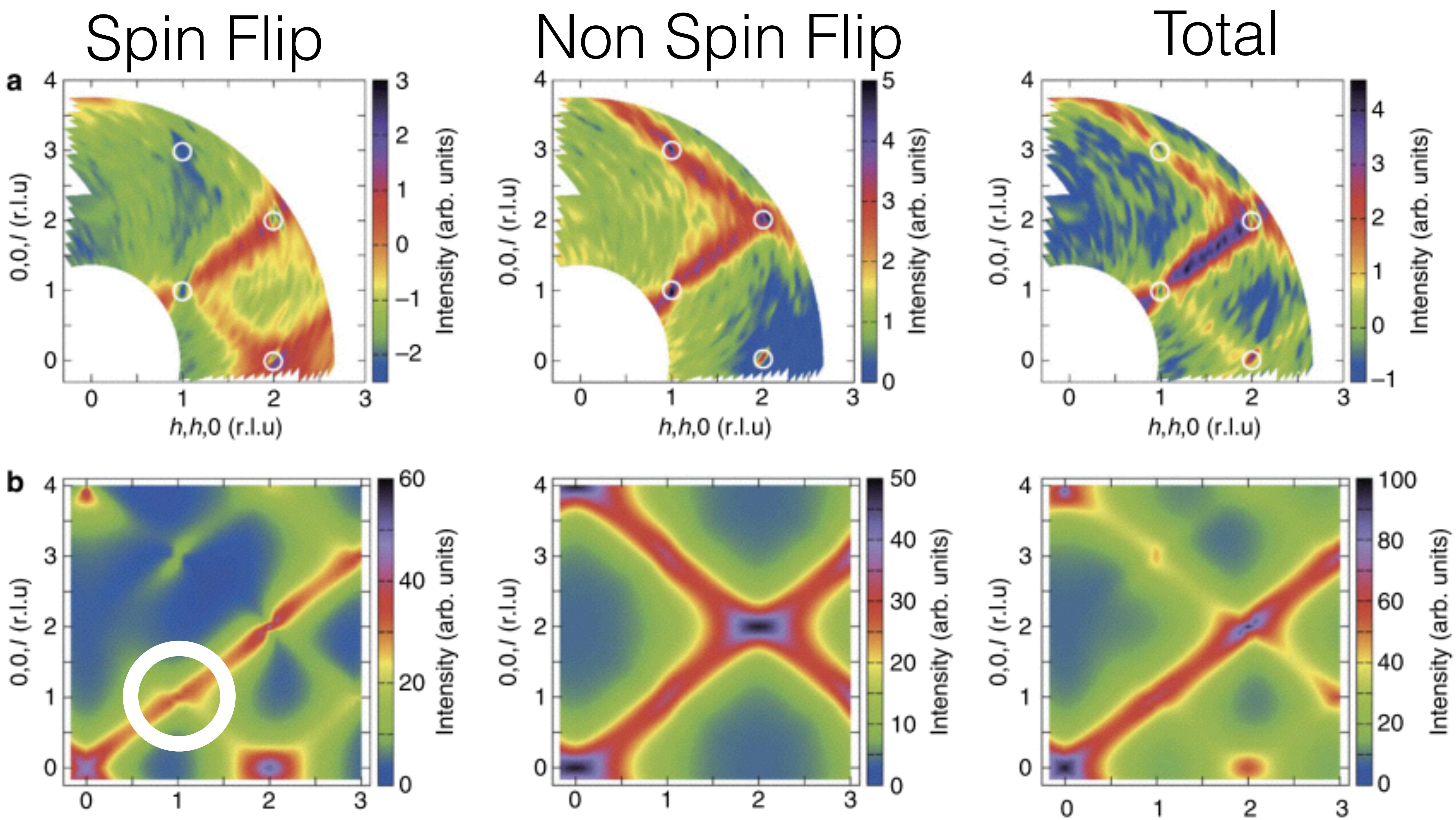



L. Savary, L. Balents, Phys. Rev. Lett. 108, 037202 (2012)

How close are we to the Coulomb QSL phase or Coulomb FM phase?

# Pinch Points in $Yb_2Ti_2O_7$?

Energy Integrated Diffraction using Polarized Neutrons at **300 mK**

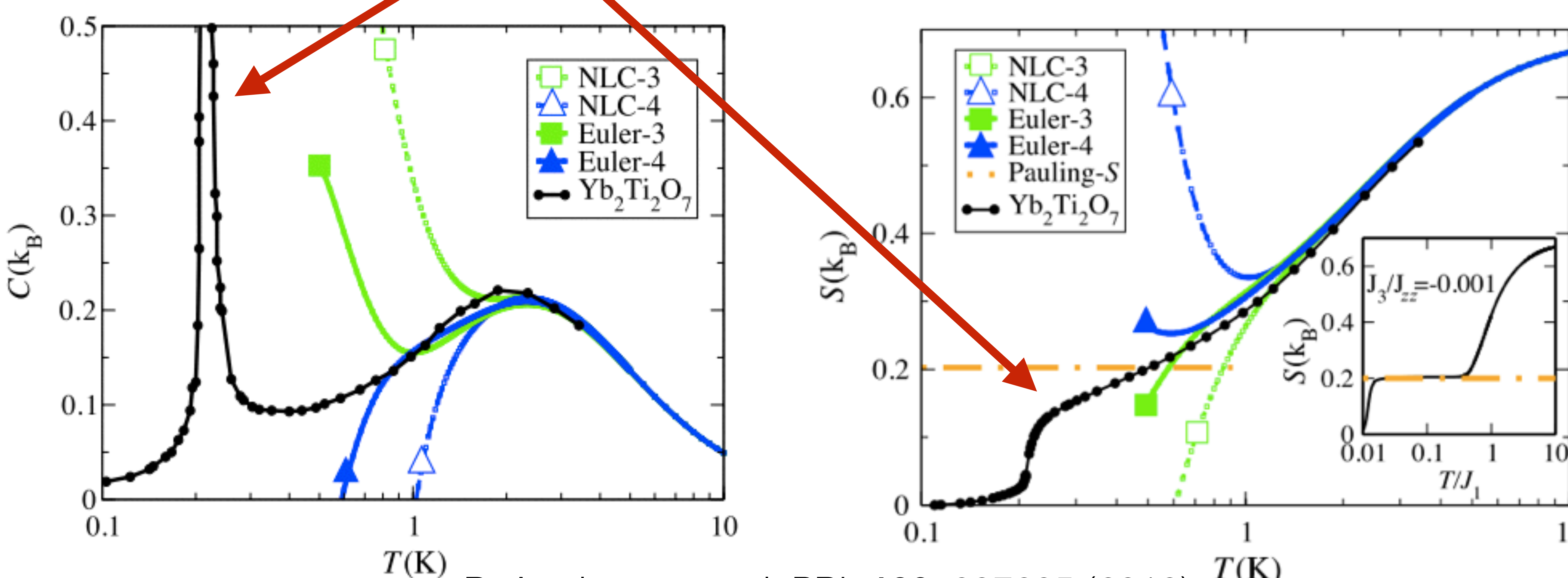



L-J. Chang, et al ,Nat. Comm. **3**, 992, (2012)

Calculated using params **similar to (but not the same as!)** Ross *et al*

# Entropy Plateau at Pauling Level

**This transition removes the macroscopic degeneracy of spin ice**



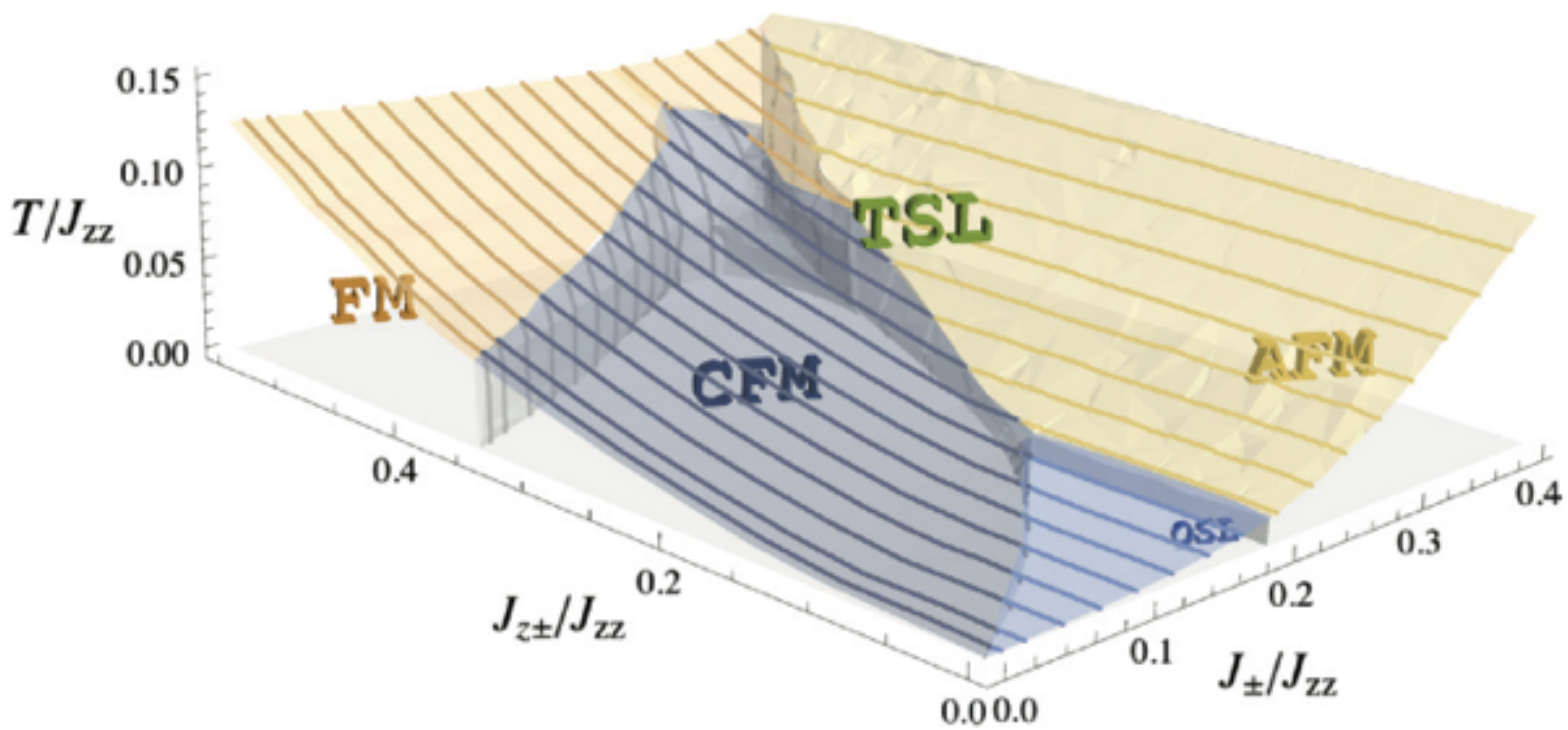

R. Applegate, et al, PRL **109**, 097205 (2012)

See also: Y. Kato, S. Onoda, arXiv:1411.1918 [cond-mat.stat-mech] (2014)

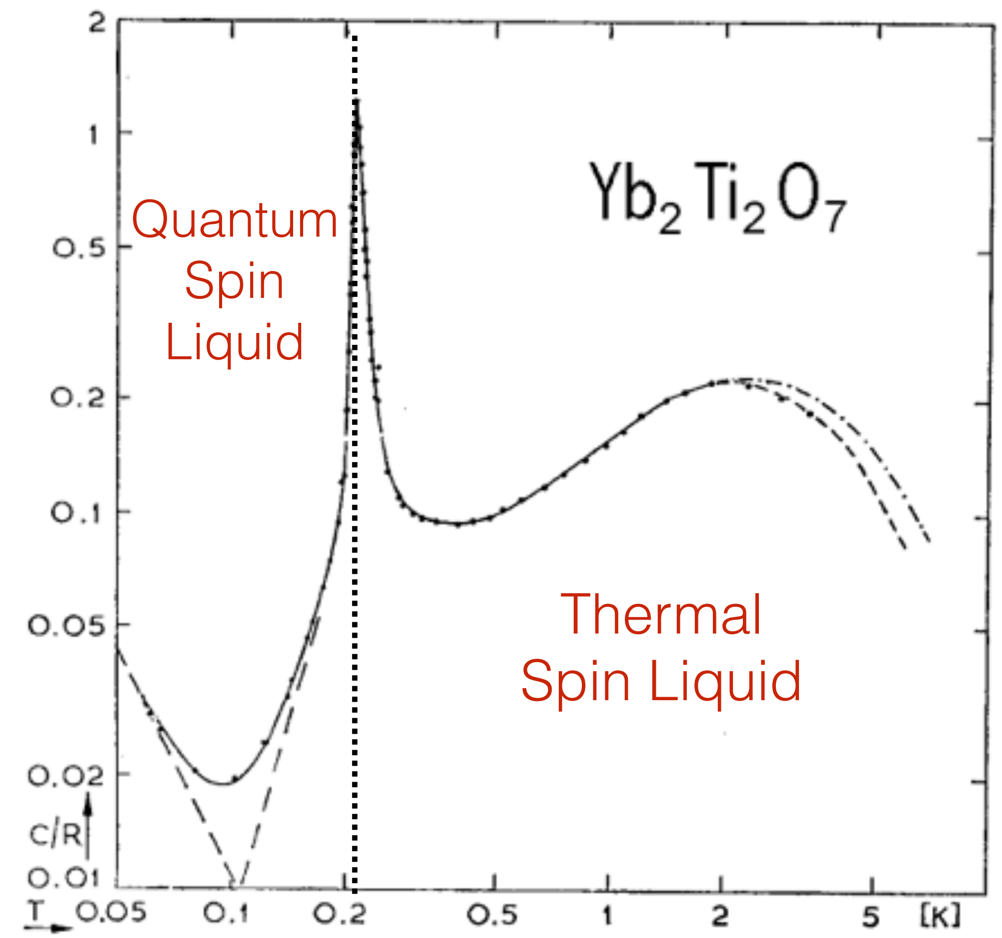
# Nature of transition

- <u>On the side of ordering to FM state ("Higgs Phase"):</u>
    - Magnetic Bragg peaks in some crystals (Chang *et al*)
    - muSR results from Chang *et al*
- <u>On the side of an exotic state related to QSL</u>
    - muSR from Luke *et al* and original Hodges *et al*
    - Neutron Scattering on some single crystals (Ross *et al*)
    - Magnetization measurements on powders and crystals showing small ordered moment (50% or less)

# First Order Thermal Spinon Confinement?




L. Savary, L. Balents, PRB **87**, 205130 (2013)

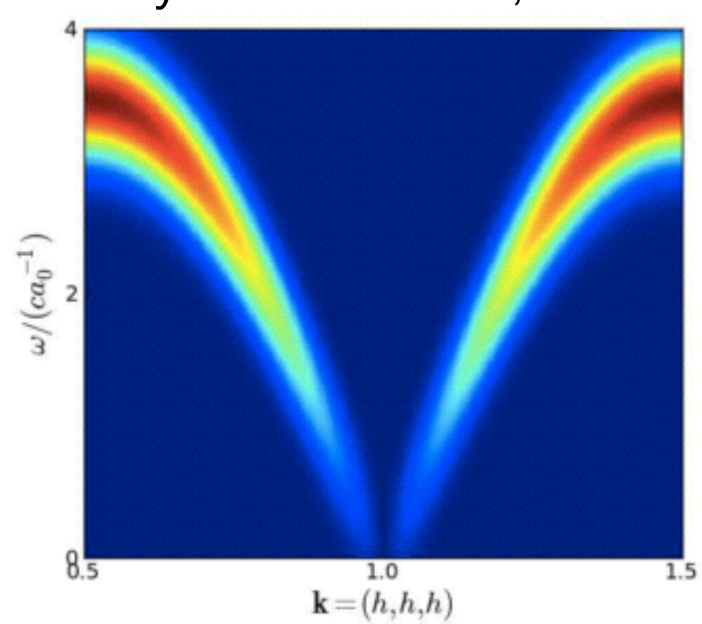



- Savary and Balents argue for a thermal confinement of spinons at a first order transition
- Above Tc, thermal spin liquid (like classical spin ice)
- Below Tc, coherently propagating spinons, photons, etc.
- Removes the entropy associated with spin ice

# Summary of Quantum Spin Ice

- Arises in systems where dominant interactions are *exchange* (rather than dipolar)
- **dominant nearest neighbor Ising** exchange leads to spin ice character
- Bilinear **transverse coupling** leads to quantum fluctuations
- U(1) quantum spin liquid phases exist with analogs to **magnetic monopoles, electrons, and photons** as elementary excitations
- Several material candidates: **$Yb_2Ti_2O_7$**, $Yb_2Sn_2O_7$, $Pr_2Zr_2O_7$, $Pr_2Sn_2O_7$, $Pr_2Ir_2O_7$, $Tb_2Ti_2O_7$, $Tb_2Sn_2O_7$

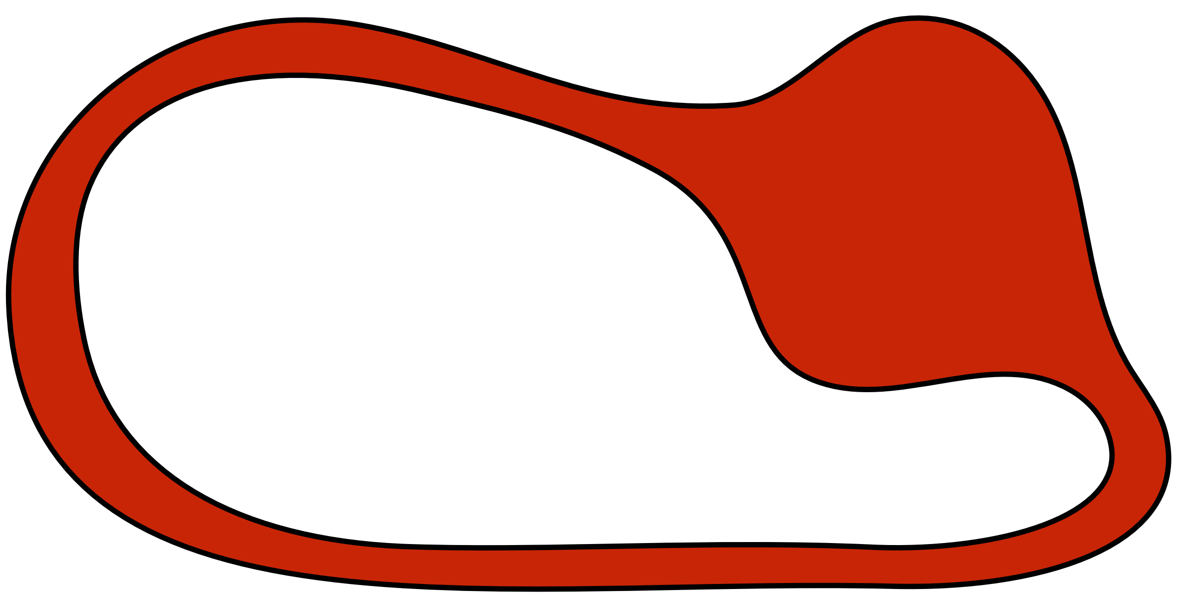
O. Benton et al,
Phys. Rev. B **86**, 2002

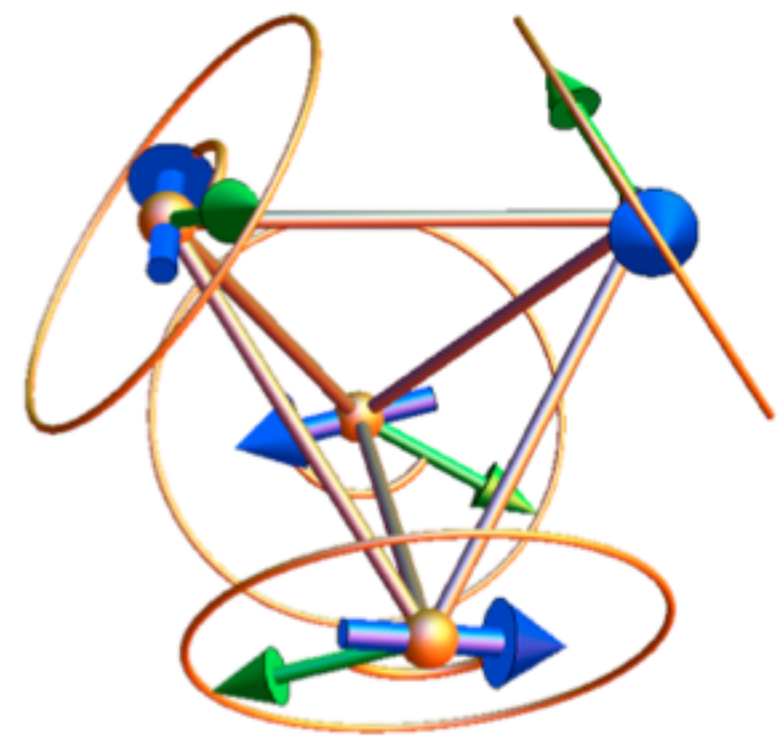


# Quantum Spin Ice Papers


- M. Hermele, M. P. A. Fisher, L. Balents. *Pyrochlore photons: The U(1) spin liquid in a S=1/2 three-dimensional frustrated magnet.* PRB **69**, 064404 (2004)
- K.A. Ross, L. Savary, B. D. Gaulin, and L. Balents, *Quantum Excitations in Quantum Spin Ice*, Phys. Rev. X **1**, 021002 (2011)
- O. Benton, O. Sikora, N. Shannon. *Seeing the light: Experimental signatures of emergent electromagnetism in a quantum spin ice.* PRB **86**, 075154 (2012)
- M. J. P. Gingras and P. A. McClarty, *Quantum spin ice: a search for gapless quantum spin liquids in pyrochlore magnets*, Rep. Prog. Phys. **77** 056501 (2014)

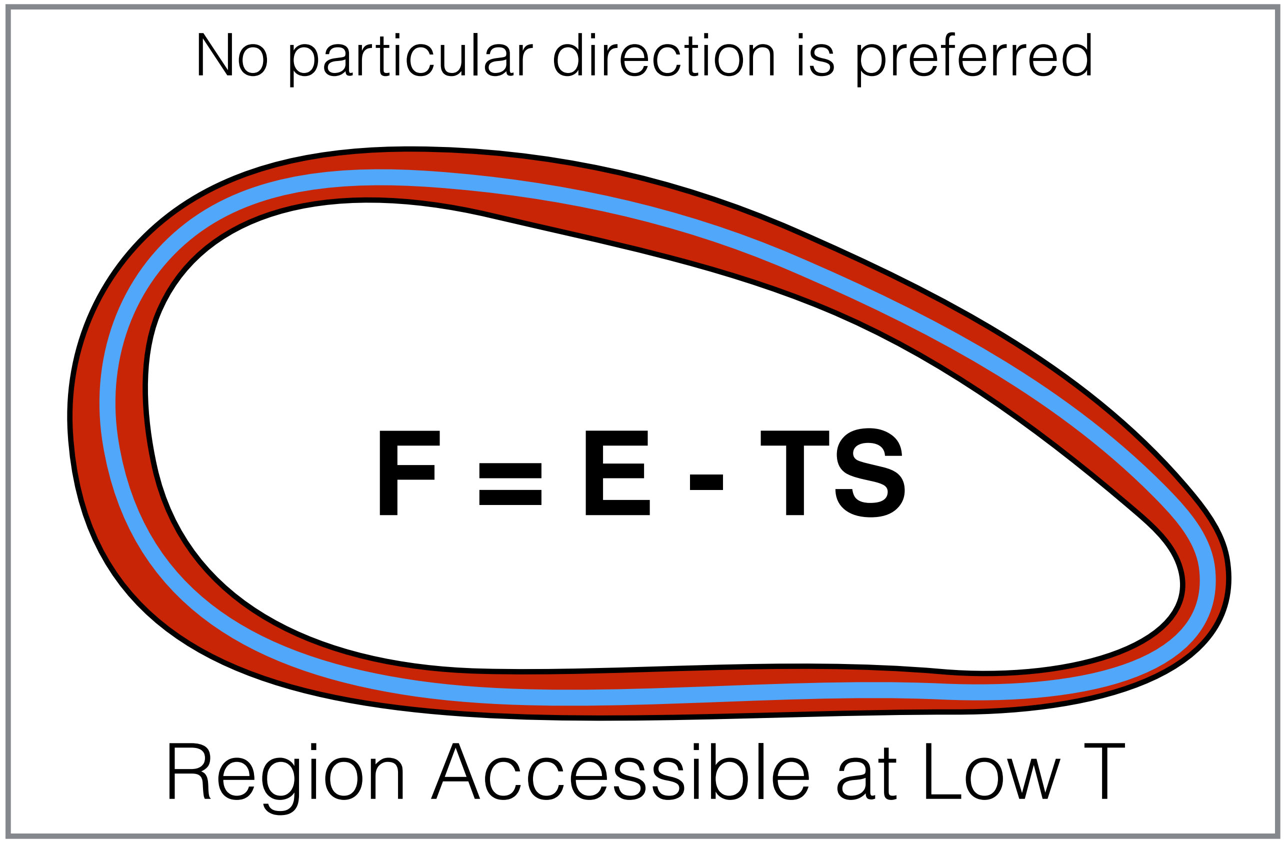
# 3) XY Pyrochlore and Order by Disorder

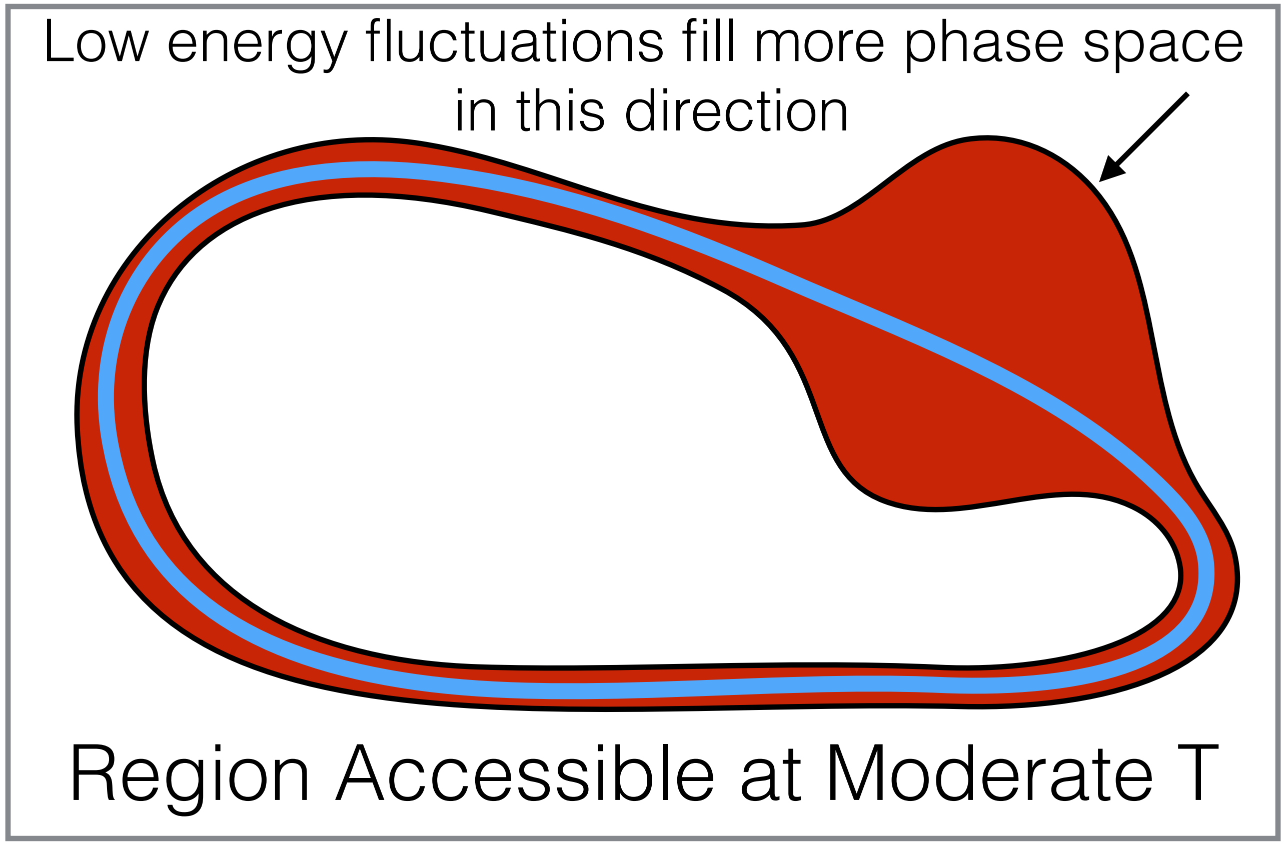




# *Thermal* Order By Disorder

Phase Space




- When an "accidental" degeneracy arises in a model (i.e. not protected by the symmetry of the Hamiltonian), it can be broken by fluctuations

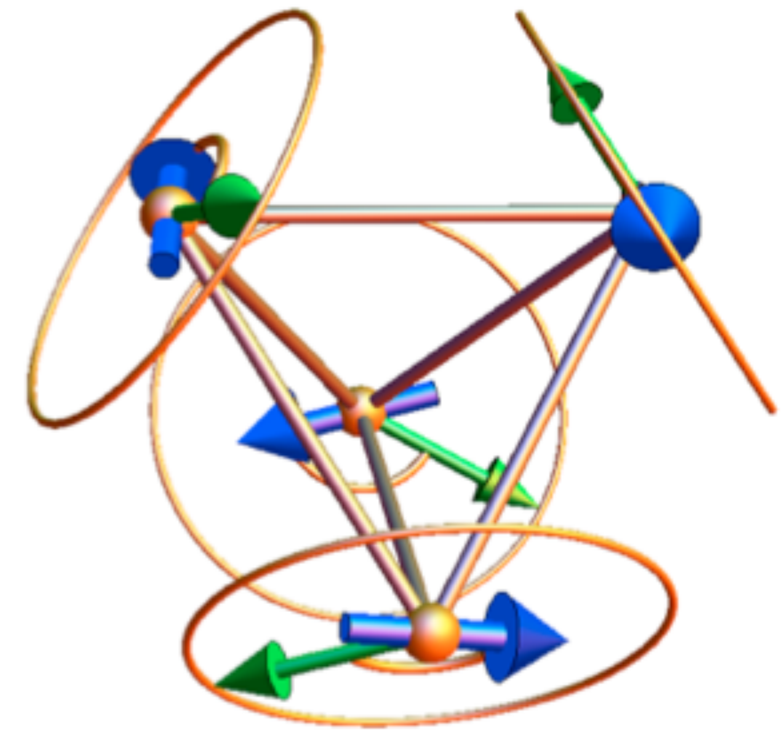
# XY AFM pyrochlore model

Single Ion Anisotropy
D<0

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i . \vec{S}_j - D \sum_i (\vec{S}_i . \vec{d}_i)^2,$$

**Isotropic** exchange
J<0

local <111> axis

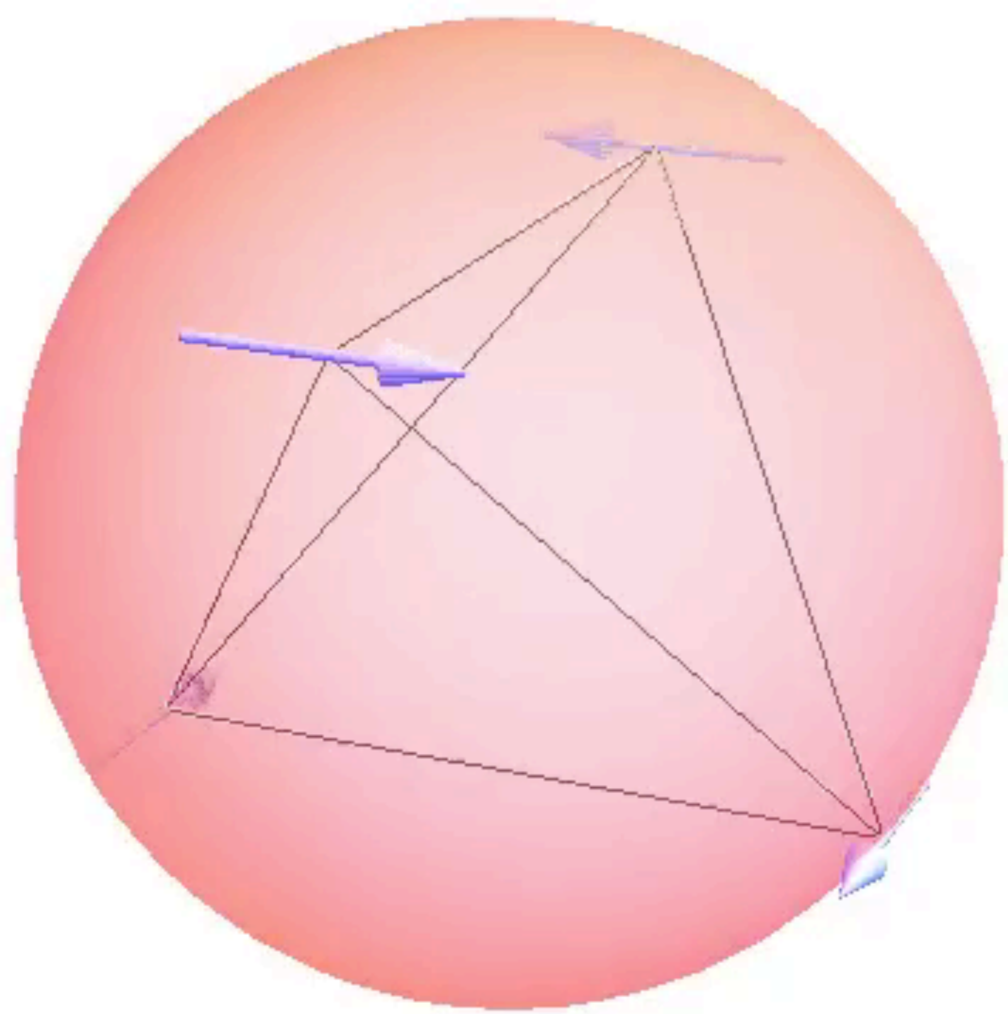


- Accidental continuous degeneracy at mean field level

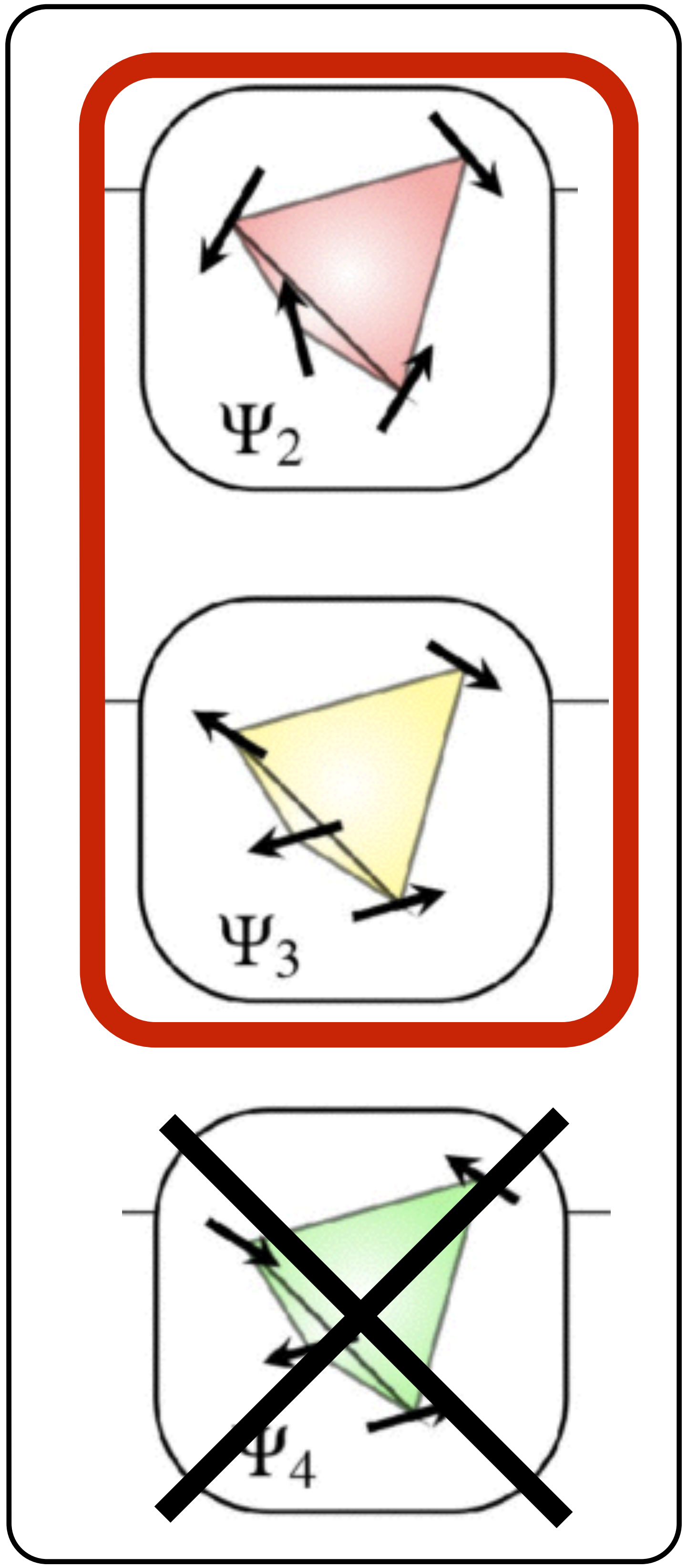
J. D. M. Champion, et al,**PRB** 68 (2003) S. T. Bramwell, *et al*, J. Appl. Phys. 75, 5523 (1994)

# XY Antiferromagnet Accidental Degeneracy

e.g. J. D. M. Champion et al, PRB **68**, 020401R (2003)



Producer:
Oleg Tchernyshyov



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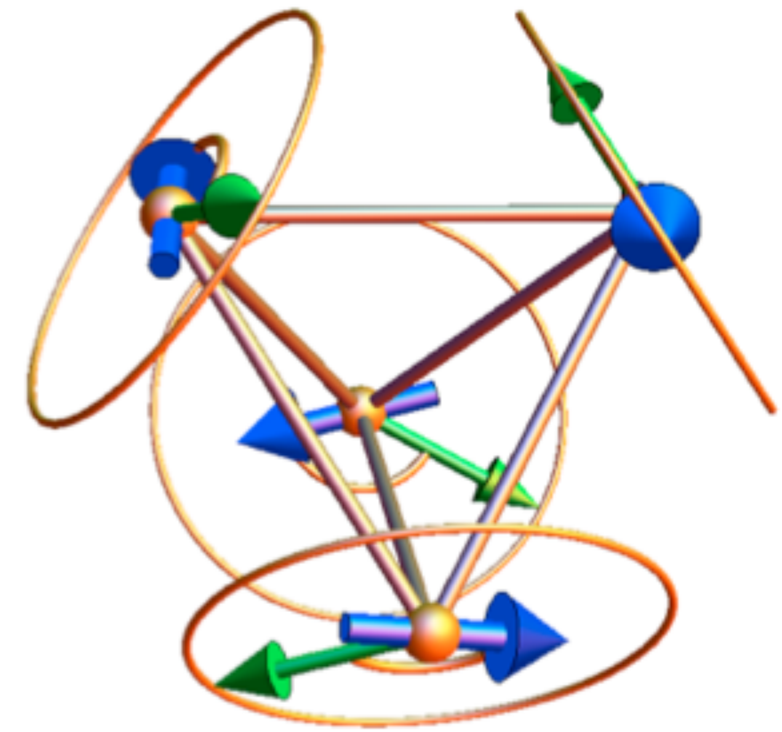
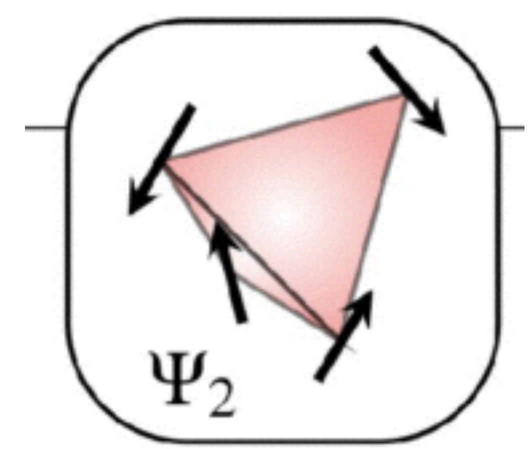


- soft **quantum fluctuations** select the **k** = 0 “psi2” state (*quantum* order by disorder)
- **First order** transition predicted

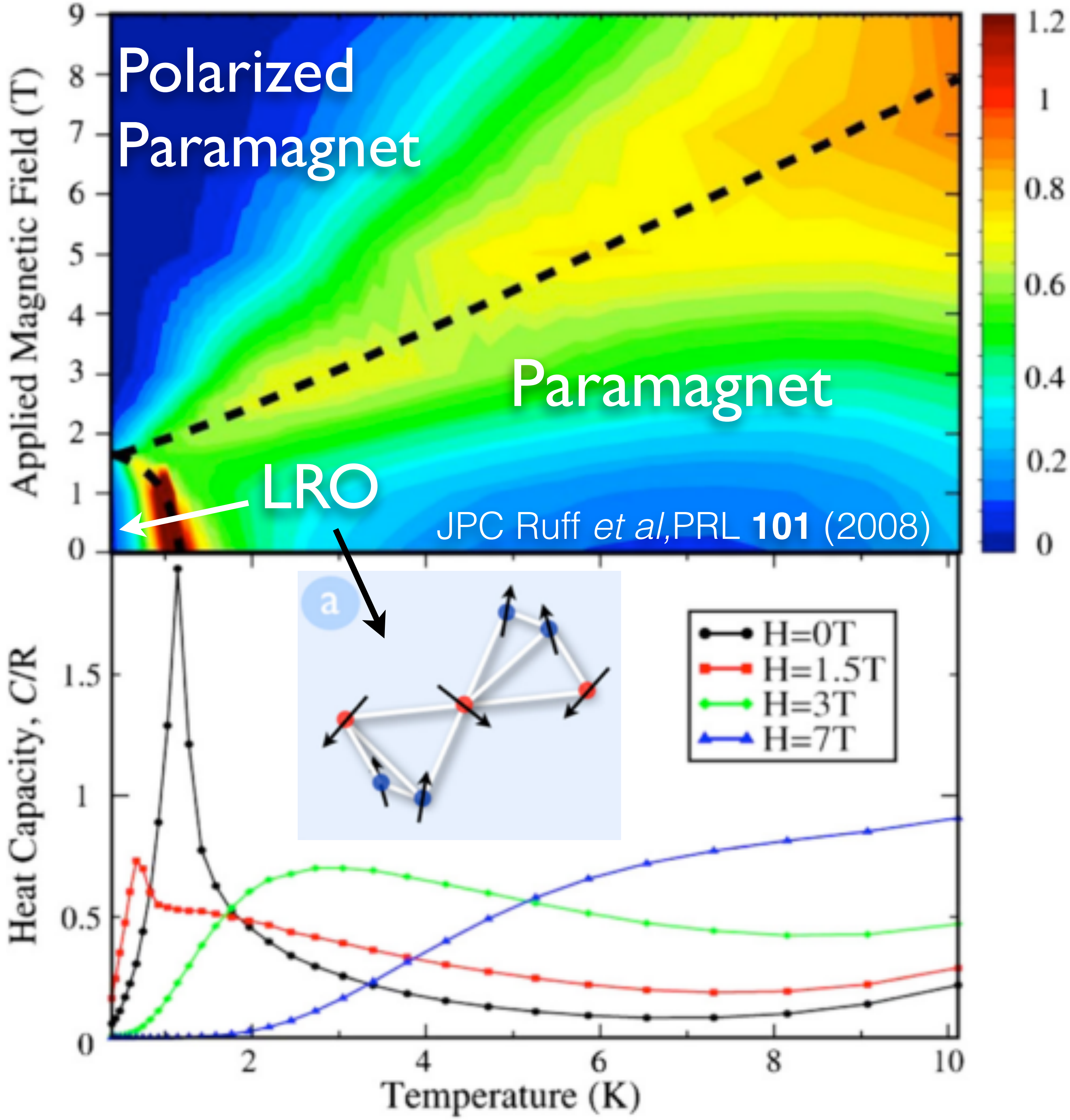


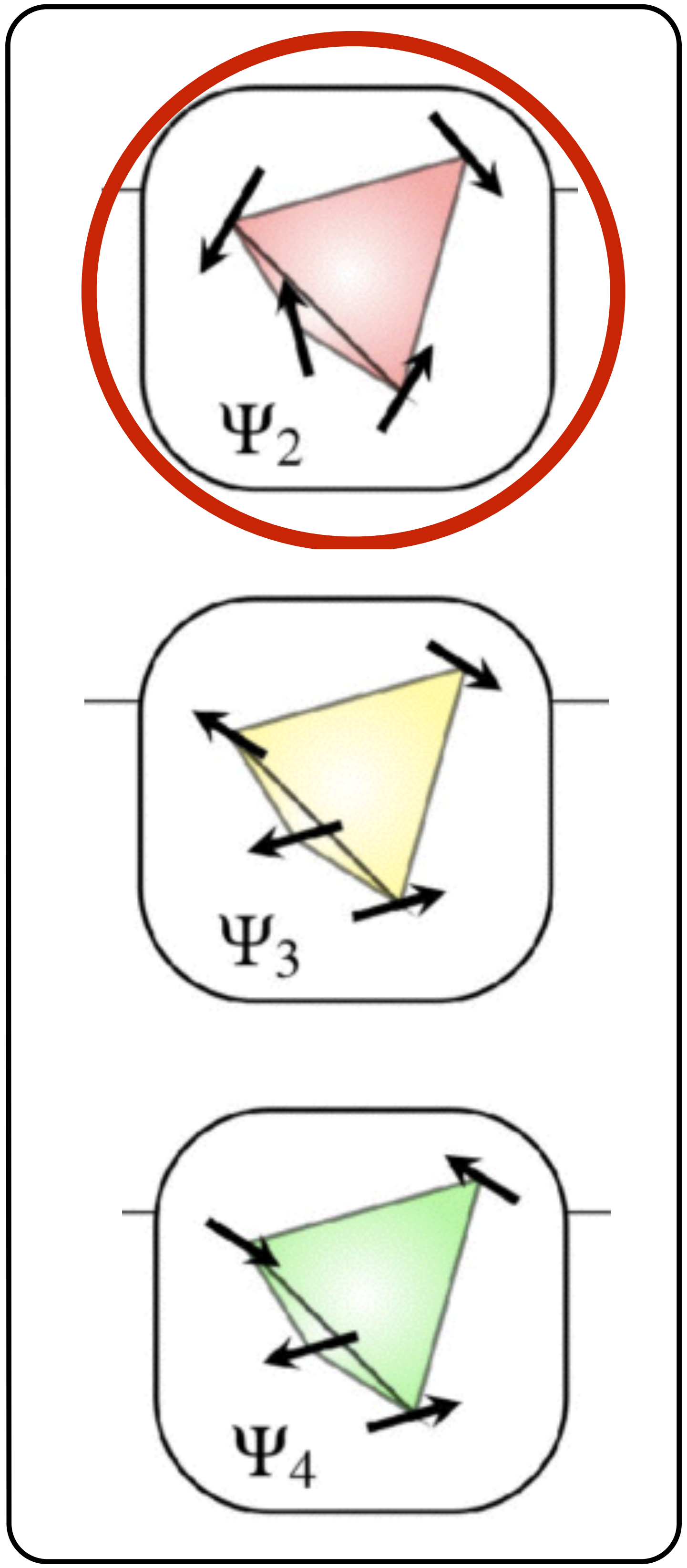

J. D. M. Champion, et al,**PRB** 68 (2003)

S. T. Bramwell, *et al*, J. Appl. Phys. 75, 5523 (1994)

# $Er_2Ti_2O_7$: XY Antiferromagnet

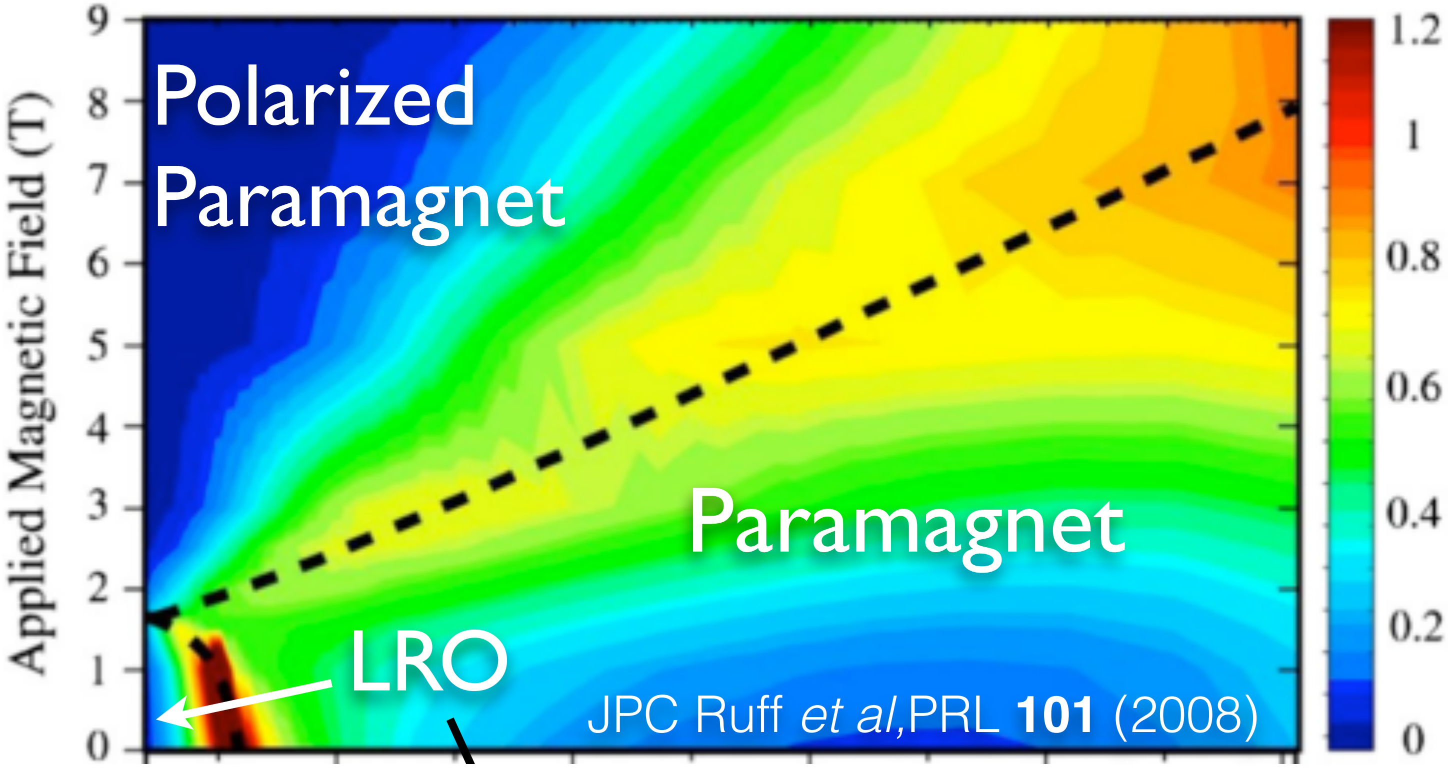
$\theta_{CW}$ = -22K   $g_{\|}$ = 2.32, $g_{\perp}$ = 6.80

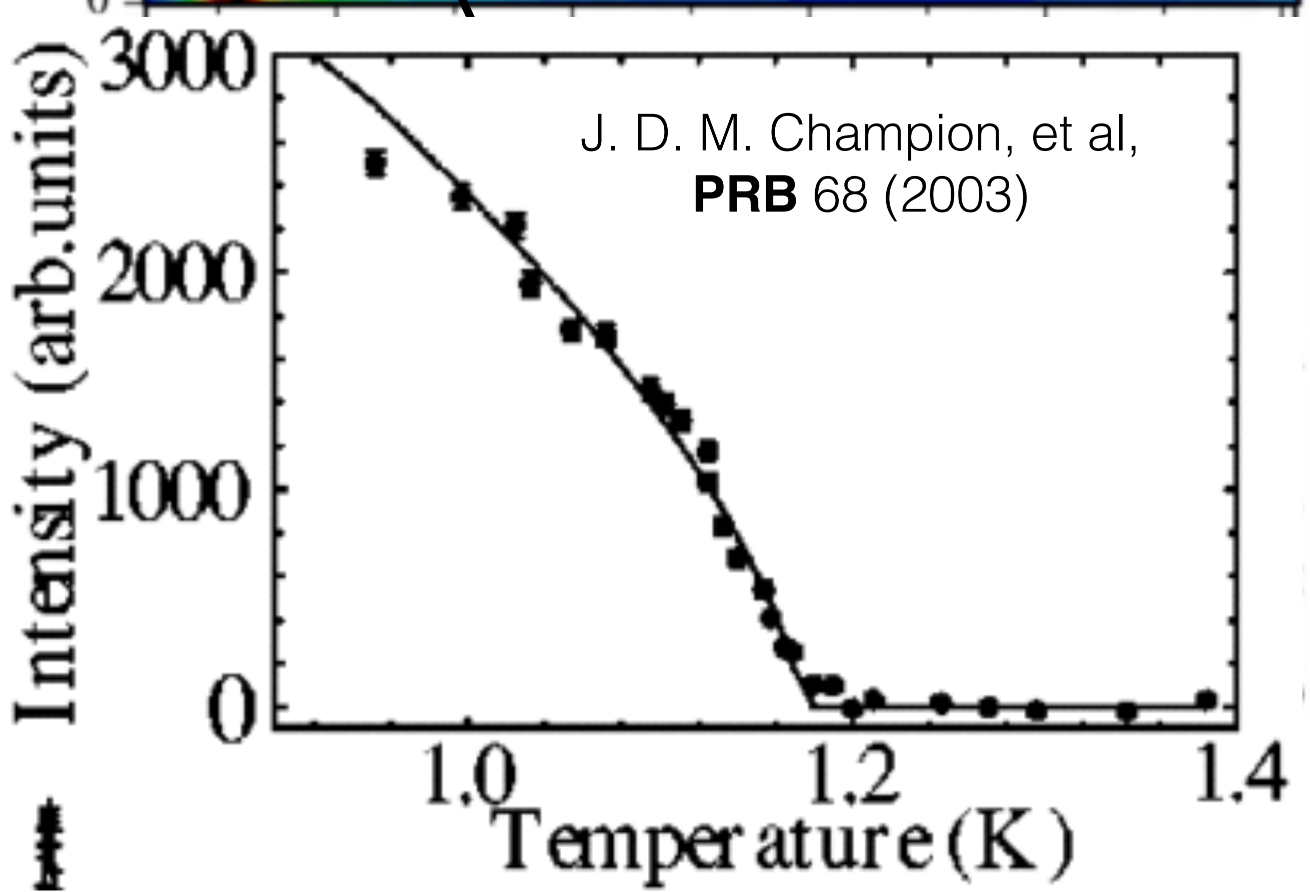


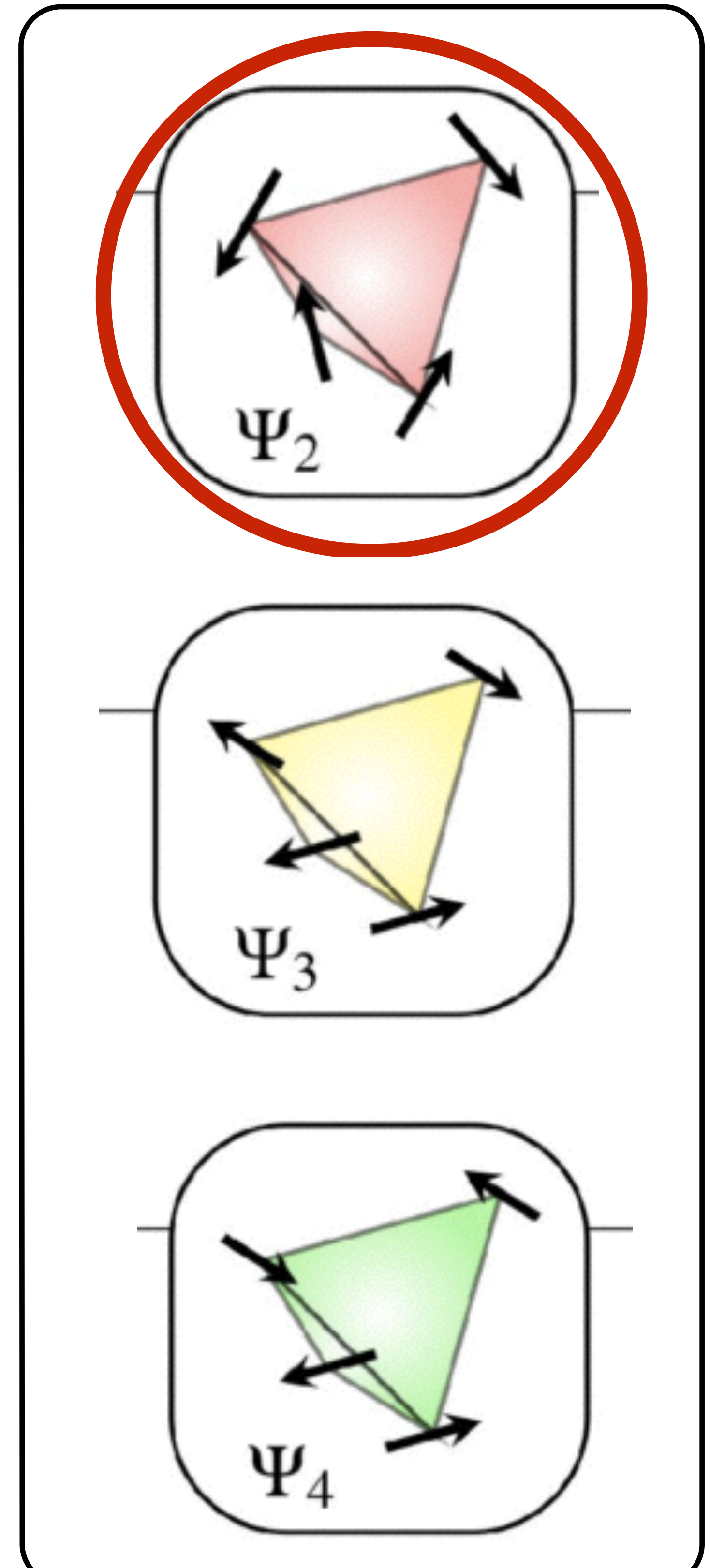



# $Er_2Ti_2O_7$: XY Antiferromagnet

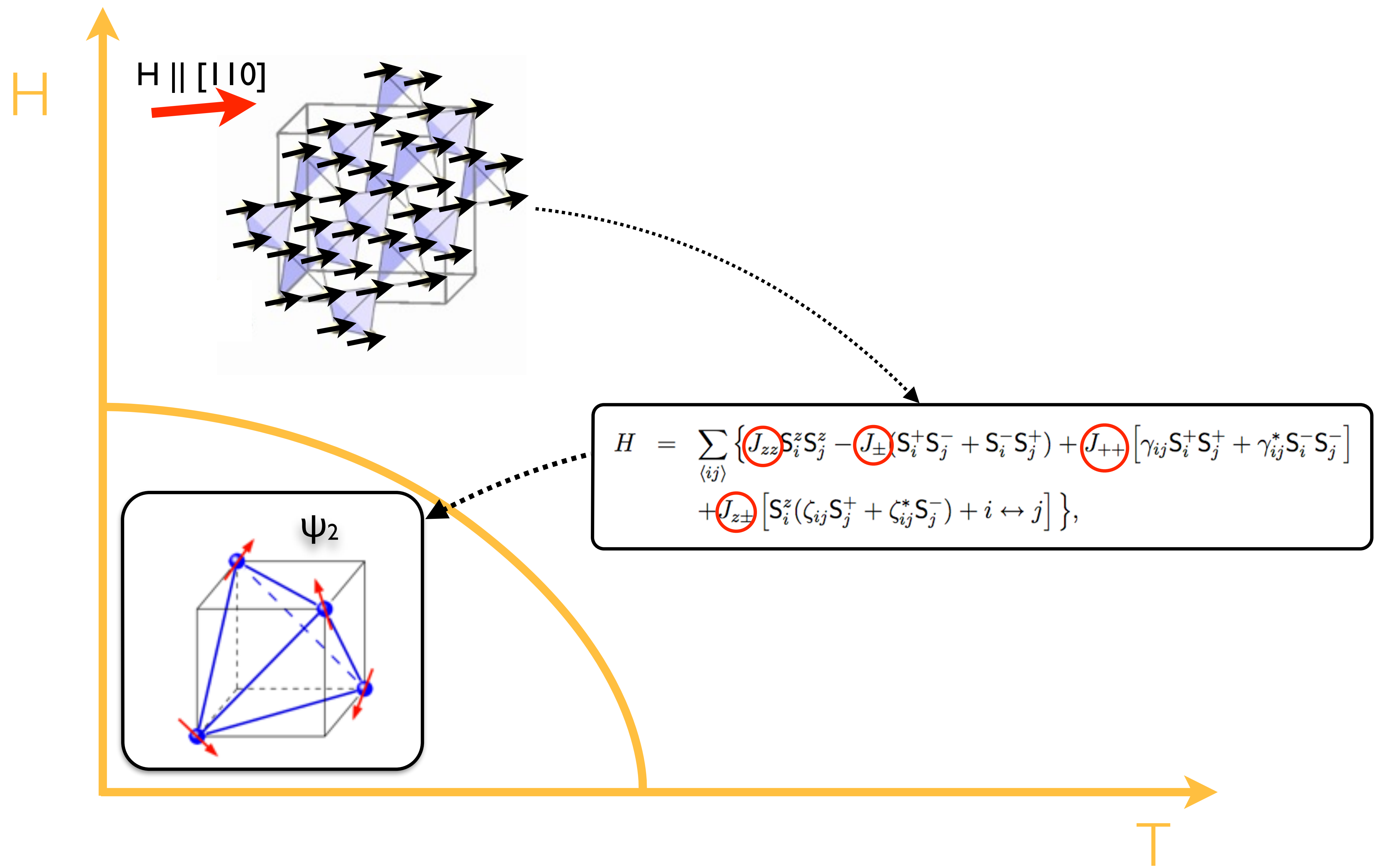
$\theta_{CW}$ = -22K  $g_{||}$ = 2.32, $g_{\perp}$ = 6.80



# General Phase Diagram



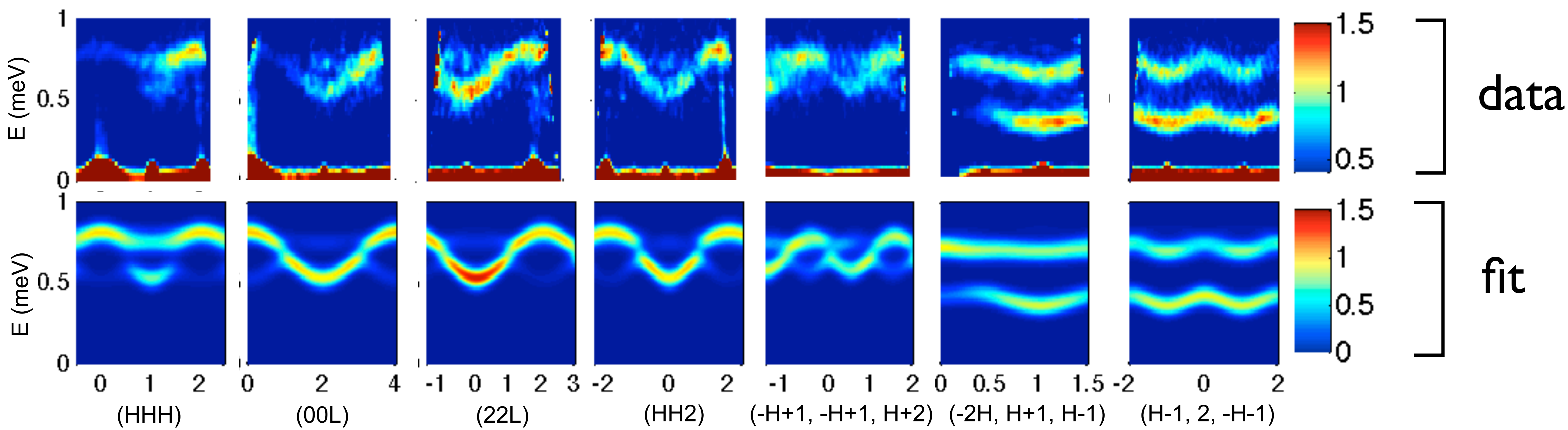

$$H = \sum_{\langle ij\rangle} \Big\{ J_{zz} S_i^z S_j^z - J_{\pm}(S_i^+ S_j^- + S_i^- S_j^+) + J_{++}\left[\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-\right] + J_{z\pm}\left[S_i^z(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^-) + i \leftrightarrow j\right] \Big\},$$

Task: Find the four exchange parameters

# Exchange Hamiltonian Extracted

L. Savary, et al. Phys. Rev. Lett. **109** 167201 (2012)

**H = 3T**




H || to [1-10] | H || to [111]

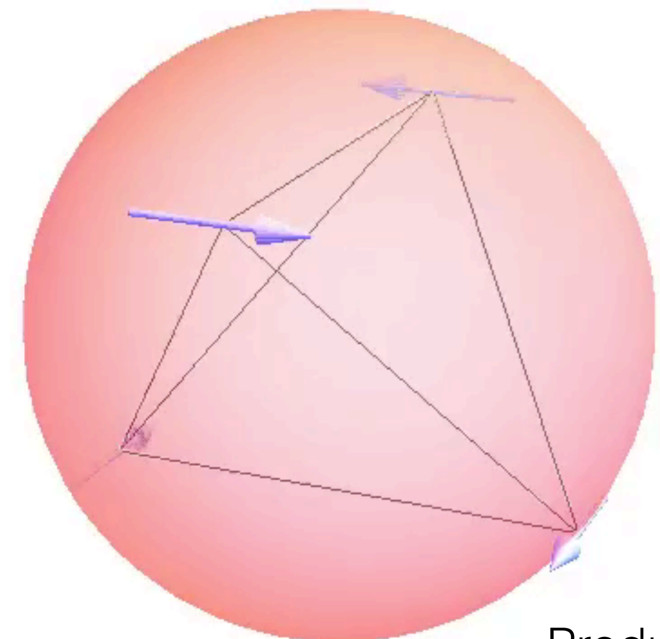
$$J_{zz} = -2.5\times10^{-2} \pm 1.8\times10^{-2},\ J_{\pm} = 6.5\times10^{-2} \pm 7.5\times10^{-3}$$

$$J_{\pm\pm} = 4.2\times10^{-2} \pm 5.0\times10^{-3},\ J_{z\pm} = -8.8\times10^{-3} \pm 1.5\times10^{-2}$$

(meV)

# Accidental Degeneracy of Model

- Continuous "accidental" degeneracy at Mean Field level
- Parameterized by single angular parameter: *α*

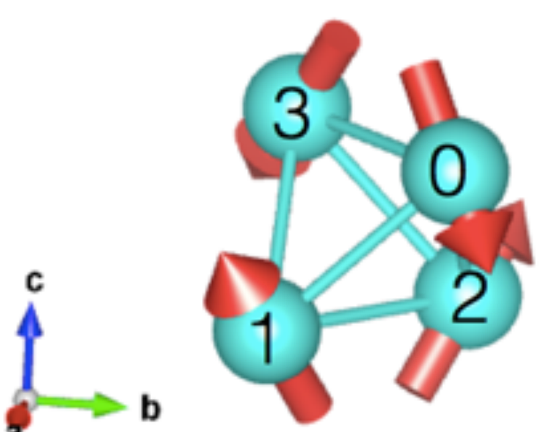


Producer:
Oleg Tchernyshyov

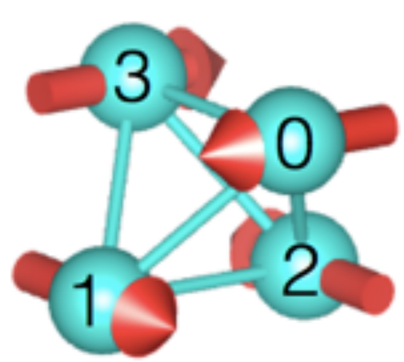
$$\vec{\chi}(\alpha) = \cos\alpha \cdot \vec{\psi}_2 + \sin\alpha \cdot \vec{\psi}_3$$

$\alpha = n\pi/3$ $\quad$ $\alpha = \pi/6 + n\pi/3$

$$\vec{\psi}_2 \begin{cases} \hat{\mathbf{s}}_0 = (1,1,\bar{2})/\sqrt{6} \\ \hat{\mathbf{s}}_1 = (1,\bar{1},2)/\sqrt{6} \\ \hat{\mathbf{s}}_2 = (\bar{1},1,2)/\sqrt{6} \\ \hat{\mathbf{s}}_3 = (\bar{1},\bar{1},\bar{2})/\sqrt{6}, \end{cases} , \quad \vec{\psi}_3 \begin{cases} \hat{\mathbf{s}}_0 = (1,\bar{1},0)/\sqrt{2} \\ \hat{\mathbf{s}}_1 = (1,1,0)/\sqrt{2} \\ \hat{\mathbf{s}}_2 = (\bar{1},\bar{1},0)/\sqrt{2} \\ \hat{\mathbf{s}}_3 = (\bar{1},1,0)/\sqrt{2} \end{cases}$$




$\psi_2$




$\psi_3$

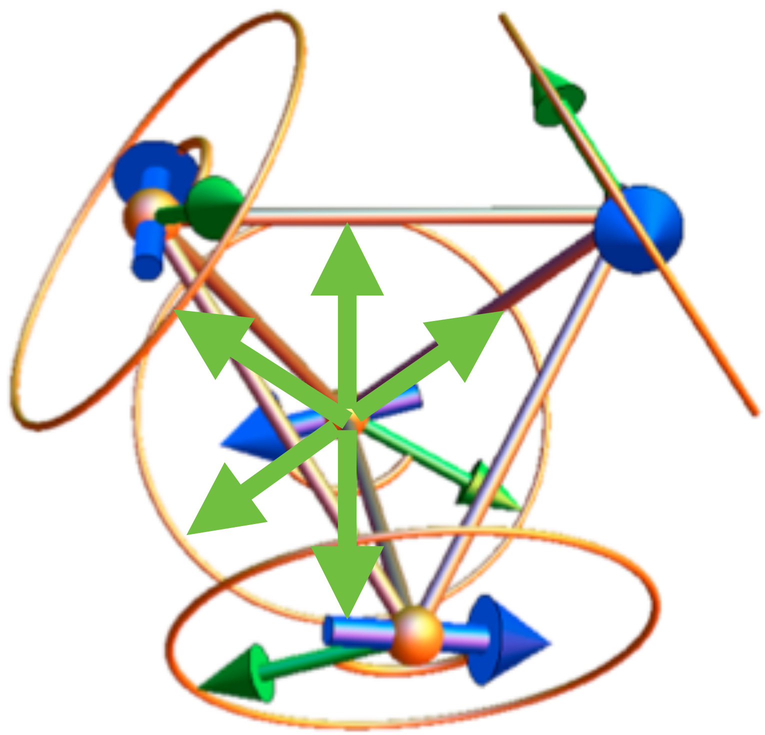

M. E. Zhitomirsky, Phys. Rev. Lett. **109** 077204 (2012)

L. Savary, et al. Phys. Rev. Lett. **109** 167201 (2012)

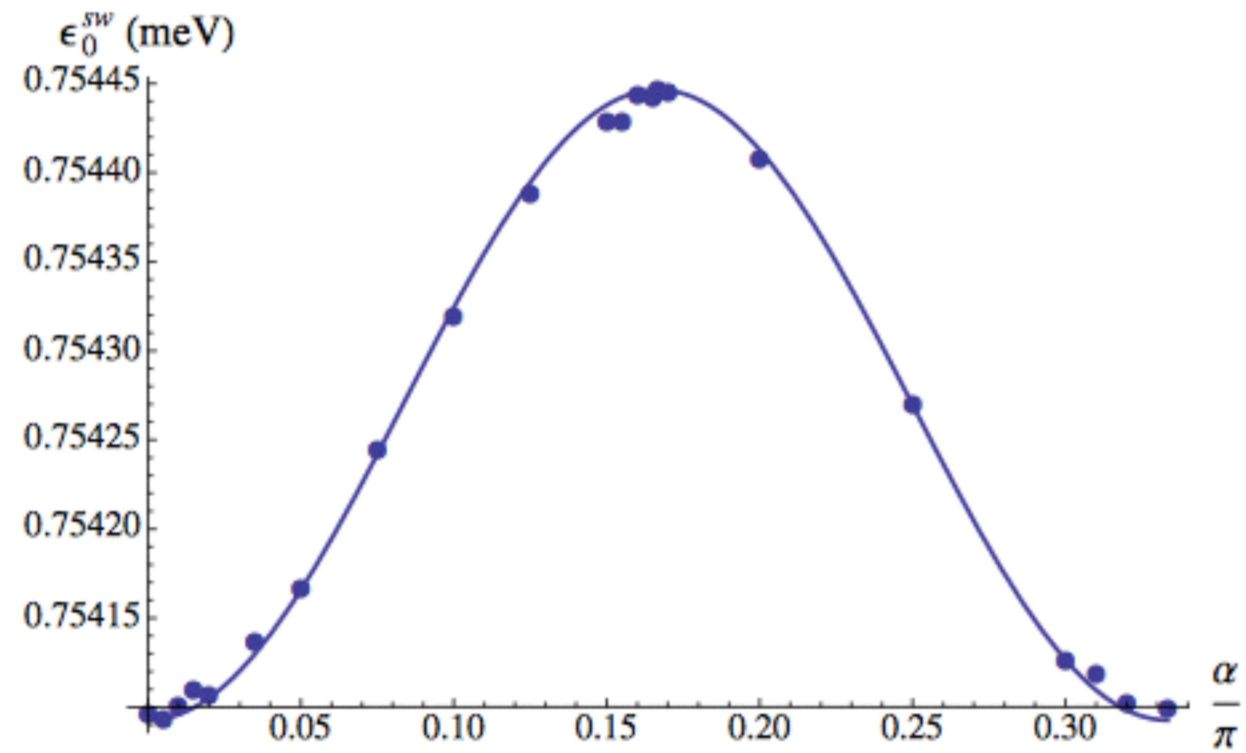
# Accidental Degeneracy of Model

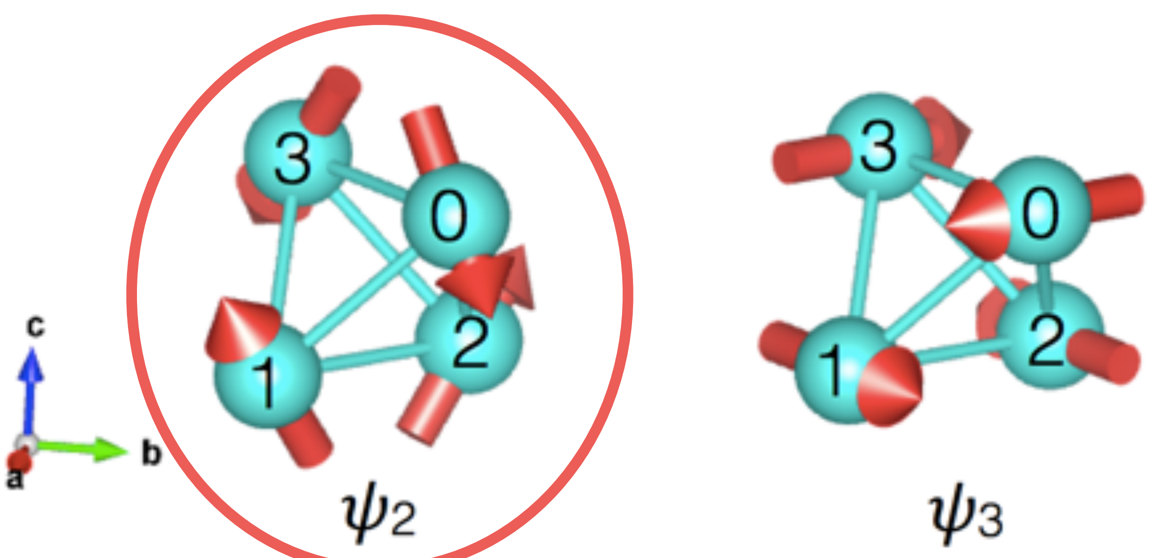
Robust deneracy of the pseudo-spin 1/2 model

- bilinear, biquadratic…etc. up to 6-spin interactions **cannot** break the degeneracy
- **quantum fluctuations** can lift the degeneracy!



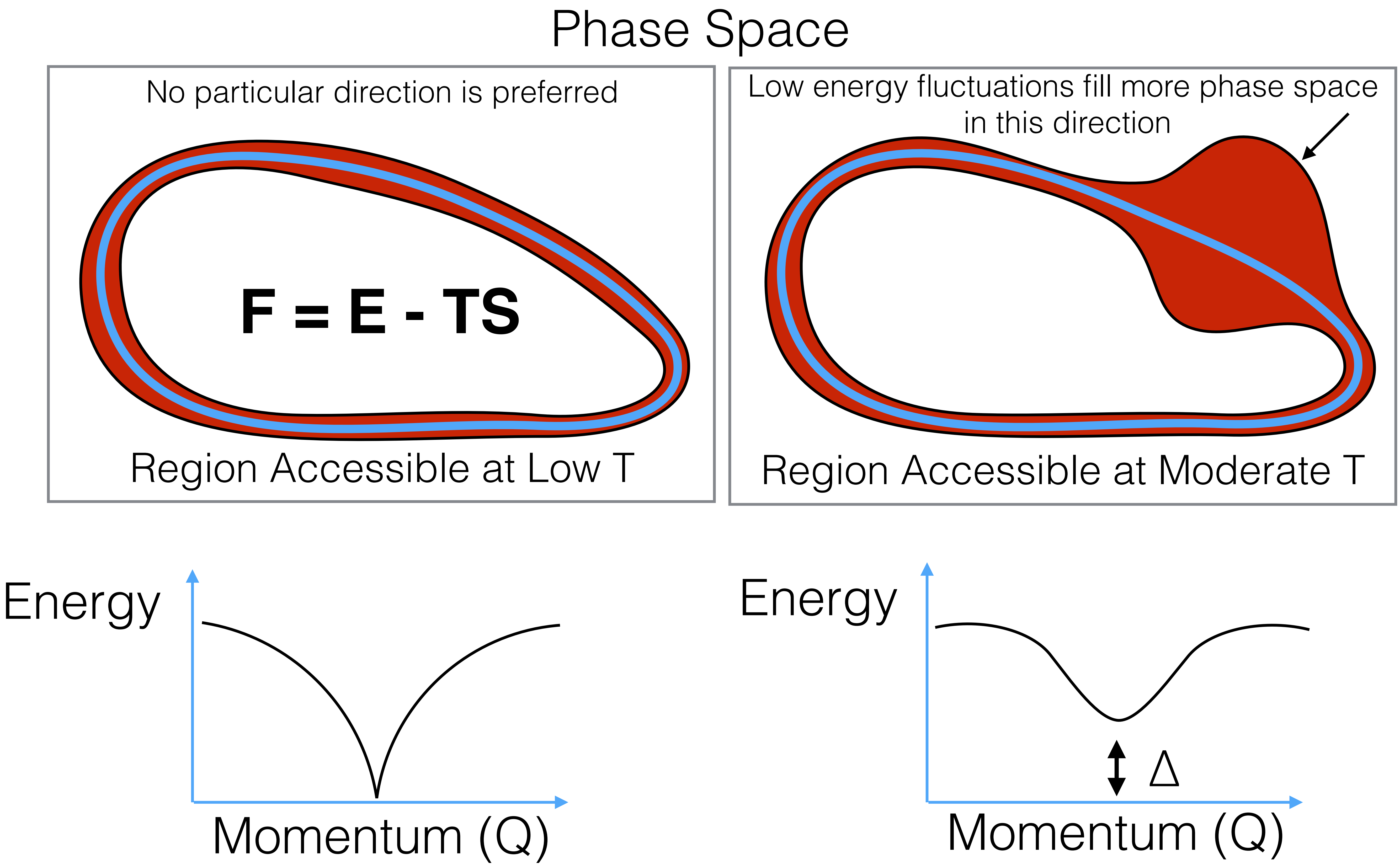
$$\epsilon_0^{\mathrm{SW}} = V_{\mathrm{BZ}}^{-1} \sum_{i=1}^{4} \int_{\mathbf{k}\in\mathrm{BZ}} \omega_{\mathbf{k}}^{i}/2,$$



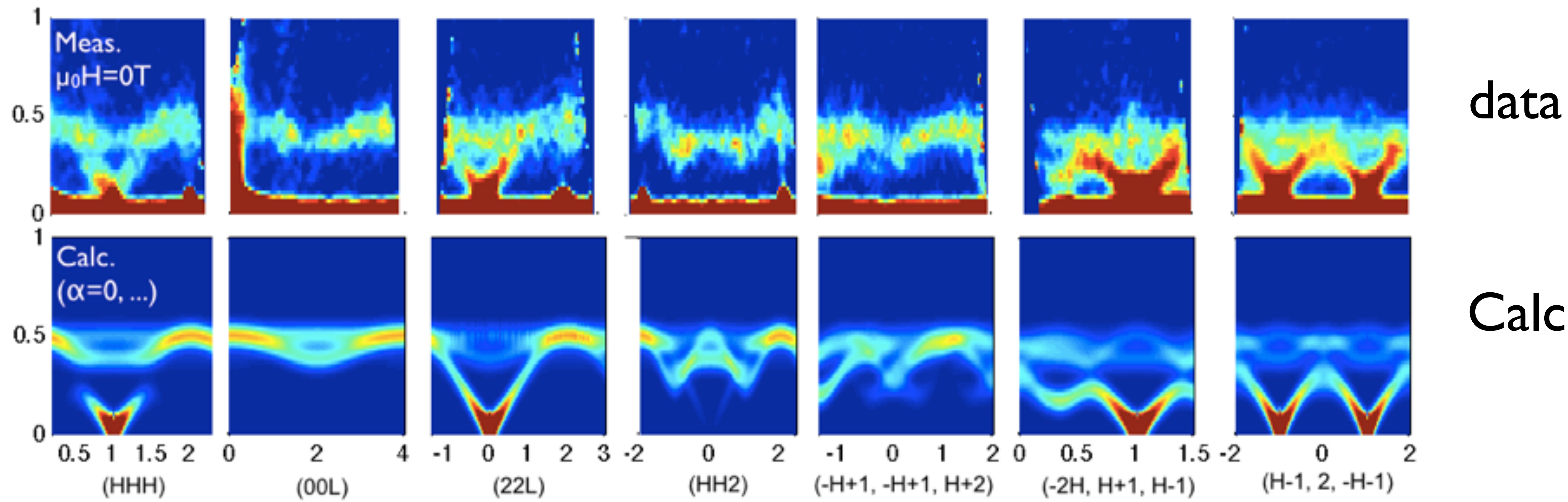

L. Savary, et al. Phys. Rev. Lett. **109** 167201 (2012)

# Pseudo-Goldstone Modes



# $Er_2Ti_2O_7$ in Zero Field

H = 0T



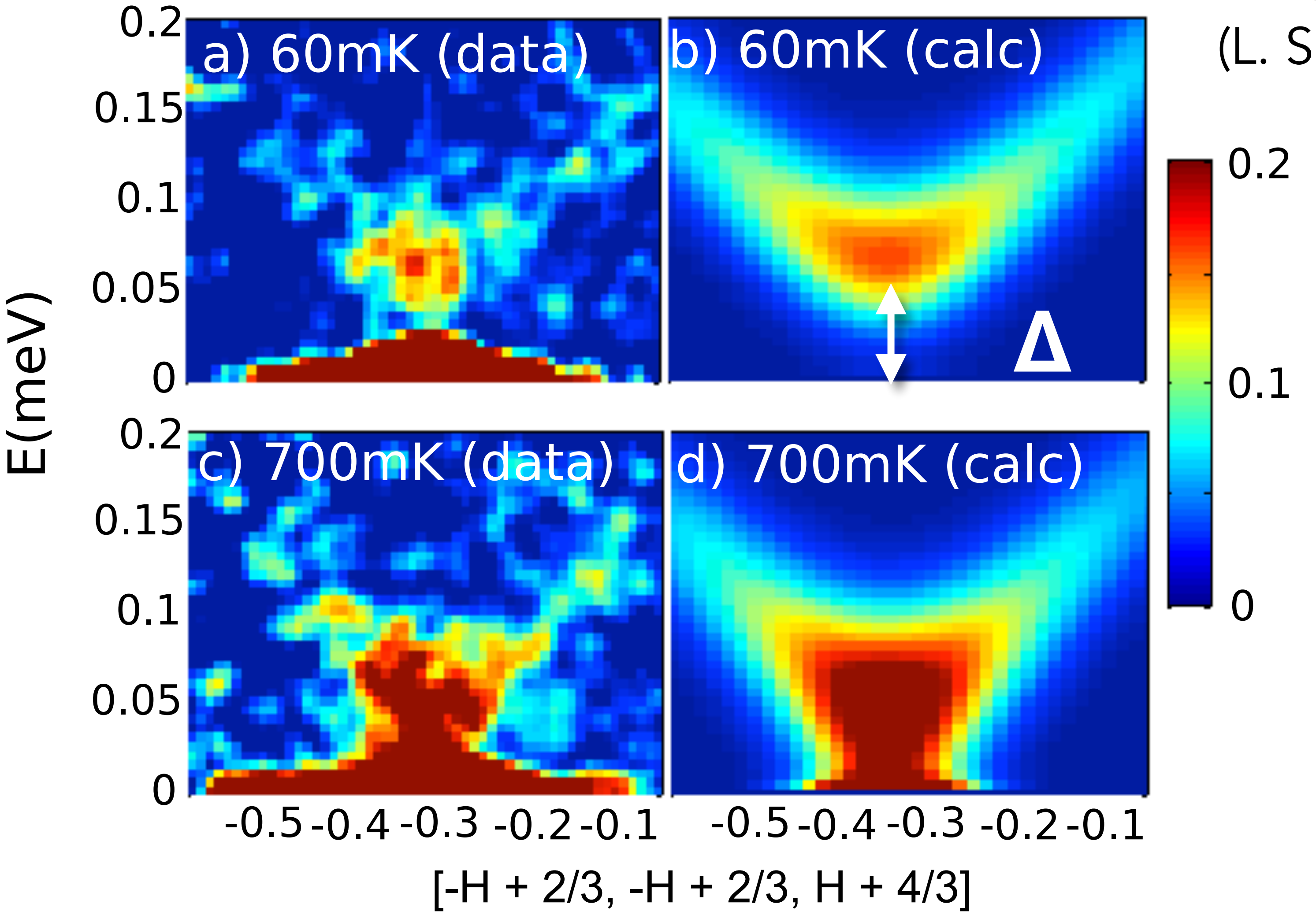

States selected by Order by Disorder agree with zero field spin waves

## But there seem to be Goldstone Modes?

Gap Predicted to be only 0.02 meV!

(L. Savary, et al. Phys. Rev. Lett. **109** 167201 (2012))

# A small gap is found: within a factor of 2 from prediction

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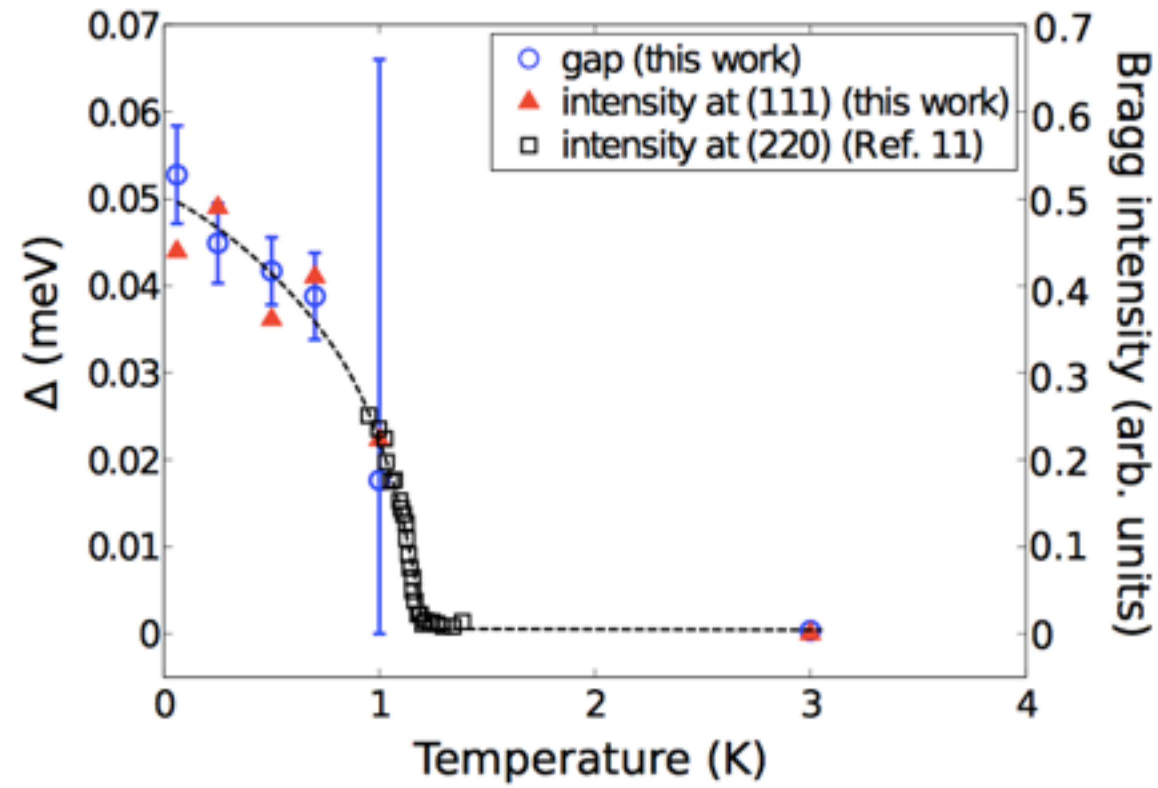
(L. Savary, et al. Phys. Rev. Lett. **109** 167201 (2012))




**Extremely high energy resolution (δE = 0.013 meV) measurements at the NCNR (NIST)**

24 hours of counting on a 7 gram crystal

K.A.Ross, et al. PRL **112** (2014)

# Summary of XY AFM Pyrochlore and $Er_2Ti_2O_7$

- $Er_2Ti_2O_7$ is one of the only material realizations of the XY AFM pyrochlore

- Both **quantum** and **thermal** order by disorder select the same state in $Er_2Ti_2O_7$, $\psi_2$, as originally expected from "simple" Hamiltonian. (*See Ref. 4 on next page for alternative view outside of pseudo-spin 1/2 manifold*)

J. Oitmaa, et al, PRB **88** 220404(R) (2013)

- **BUT** we needed to determine, and include, the **anisotropic exchange** interaction to account for the nature of the phase transition and details of the excitation spectrum for $Er_2Ti_2O_7$

- **Recent proposal**: quenched **configurational** disorder (site dilution) selects the "opposite" state ($\psi_3$) — yet to be confirmed

A. Andreanov, P.A. McClarty, arXiv:1408.7119v1 (2014)

V. S. Maryasin, et al, **PRB** 90, 094412 (2014)

# XY AFM Pyrochlore Papers

(1) J. D. M. Champion et al, *Er2Ti2O7: Evidence of quantum order by disorder in a frustrated antiferromagnet,*PRB **68**, 020401R (2003)

(2) M. E. Zhitomirsky, et al, Quantum Order by Disorder and Accidental Soft Mode in Er2Ti2O7, PRL **109**, 077204 (2012)

(3) L. Savary et al, *Order By Quantum Disorder in Er2Ti2O7*, PRL **109**, 167201 (2012)

(4) S. Petit *et al*, *Order by disorder or energetic selection of the ground state in the XY pyrochlore antiferromagnet* $Er_2Ti_2O_7$*: An inelastic neutron scattering study,* PRB **90**, 060410(R) (2014)

# Summary: experimental pyrochlore systems

- Pyrochlore materials can harbor a remarkable variation in electronic behavior - from spin ice, to spin liquids, to superconductors
- The materials can often be successfully modeled: great feedback between theory and experiment
- I spoke in detail about Spin Ice and Quantum Spin Ice - these phases open the door to interesting emergent properties, like magnetic monopoles and U(1) gauge photons (lets keep looking for the latter in our many candidate materials (i.e. $Yb_2Ti_2O_7$)!)
- The XY pyrochlore has an interesting history involving order-by-disorder - I showed you our material example, $Er_2Ti_2O_7$; it's properties are now known to be fully consistent with order by disorder once we include anisotropic exchange