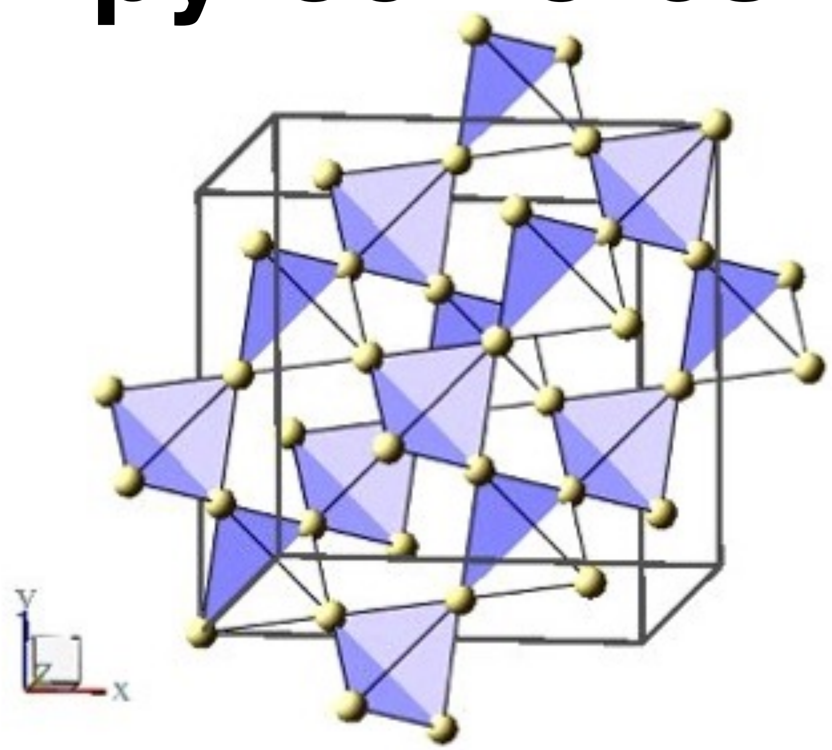
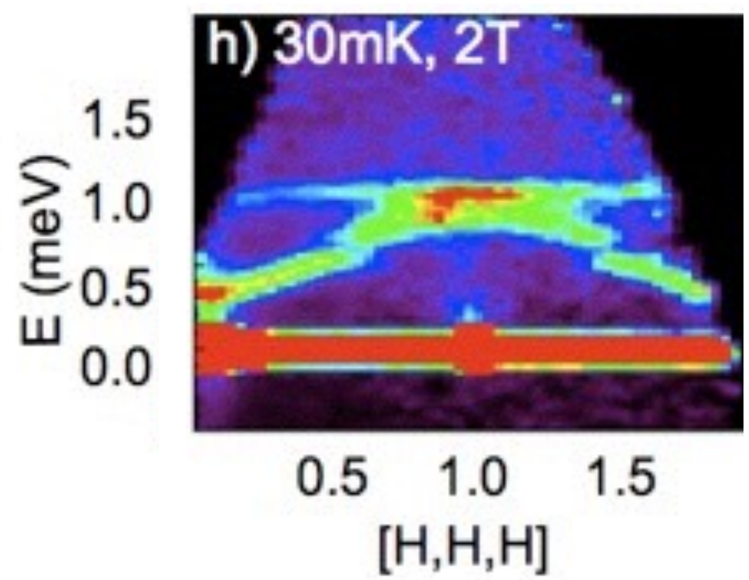
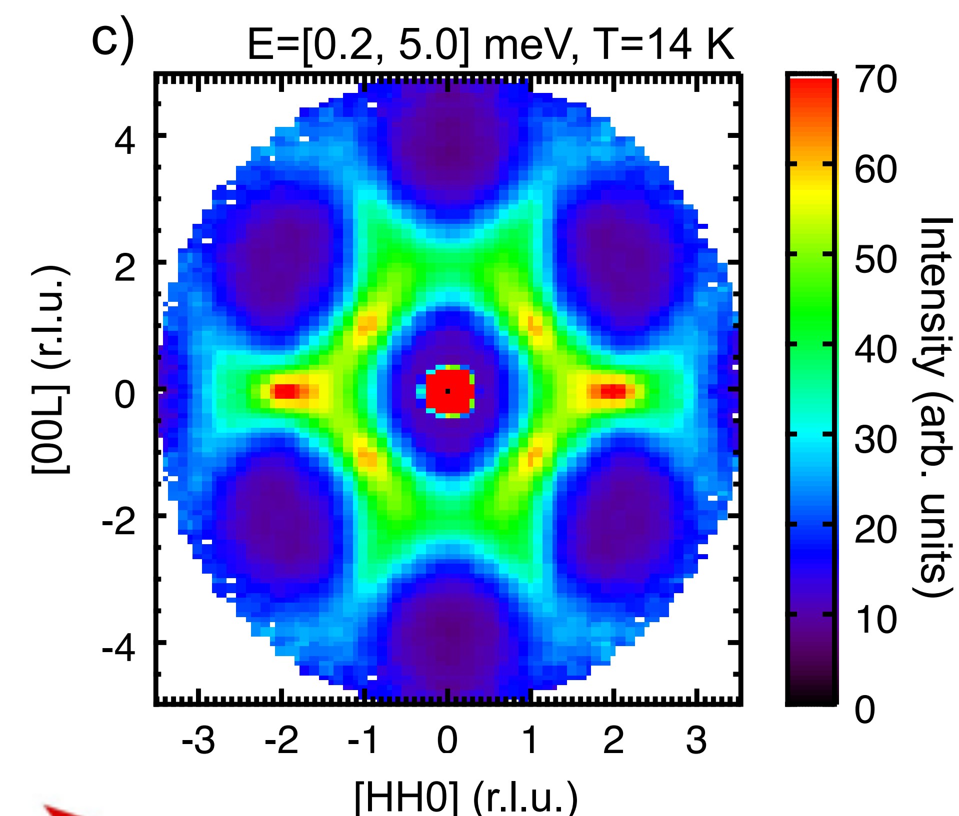
Quantum phenomena in S_{eff} = 1/2 pyrochlores revealed by neutron scattering







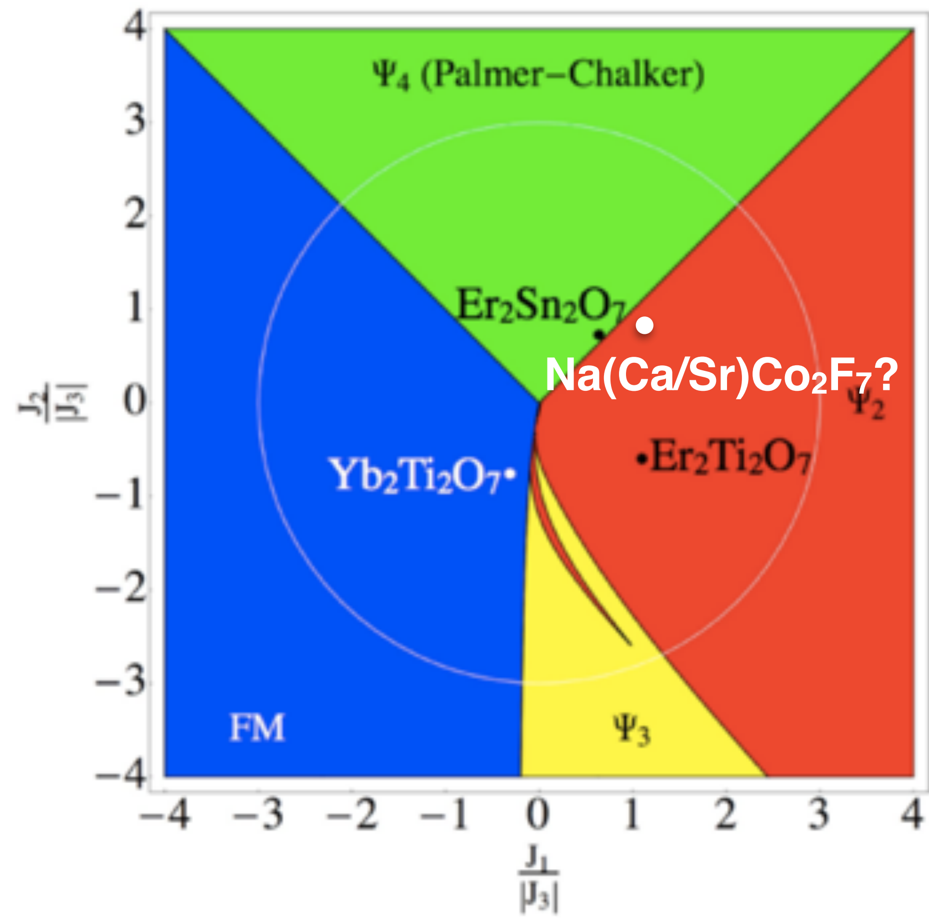
Kate A. Ross
Colorado State University

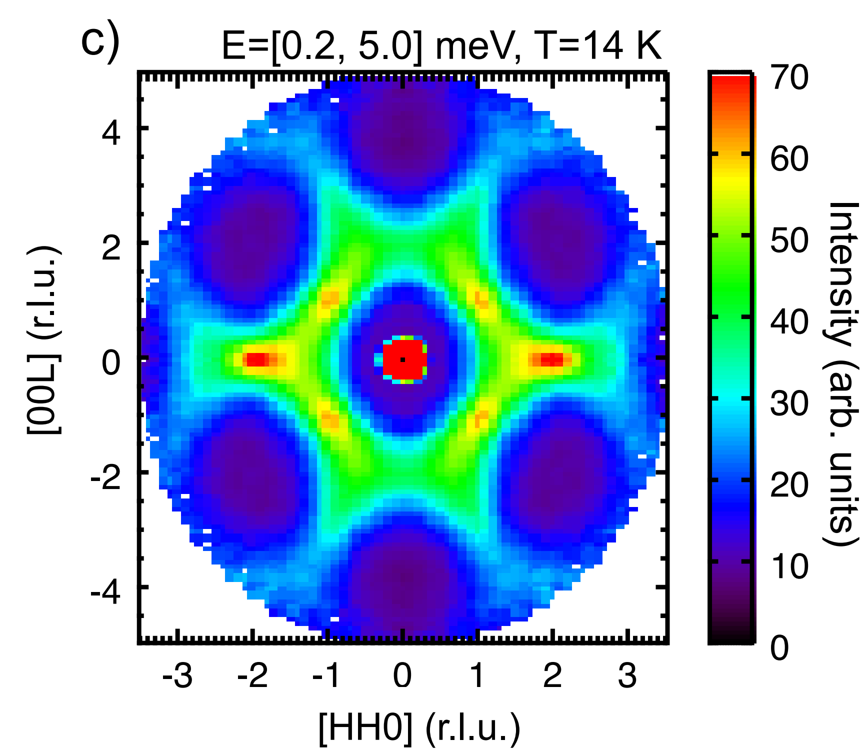
CIFAR AZRIELI Global Scholars

NCNR Neutron Scattering Summer School
NIST, June 22, 2017

Outline

- Geometric Frustration
- General anisotropic exchange phase diagram for pyrochlores
- Phase competition in real pyrochlores: **quantitative understanding using neutrons**
  - $Yb_2Ti_2O_7$, $Er_2Ti_2O_7$, and $NaCaCo_2F_7$



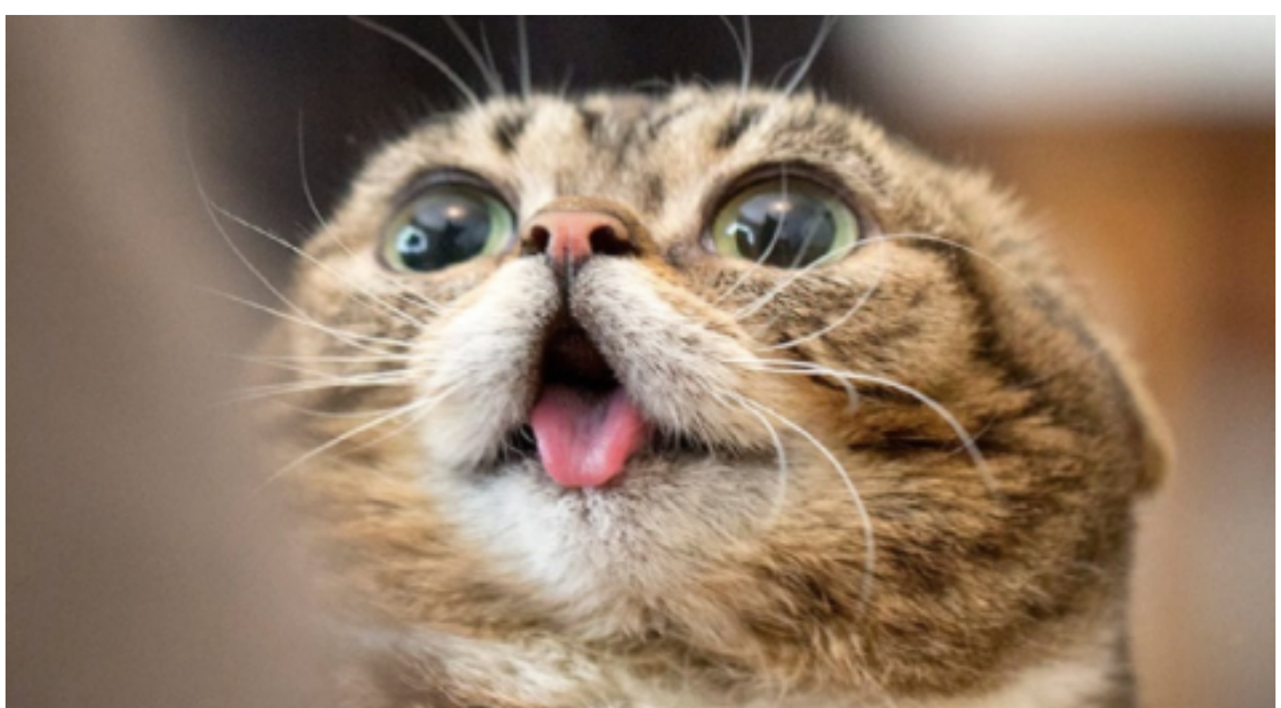


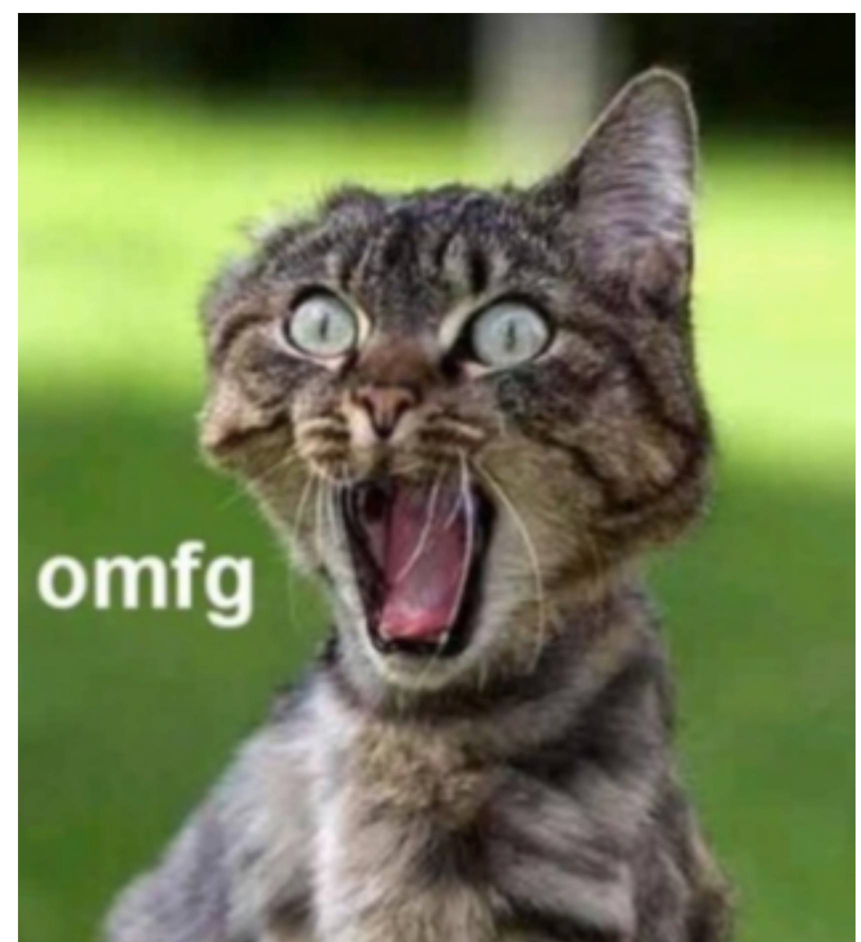
Overchoice

- Wikipedia:“**Overchoice** or **choice overload** is a cognitive process in which people have a difficult time making a decision when faced with many options.”

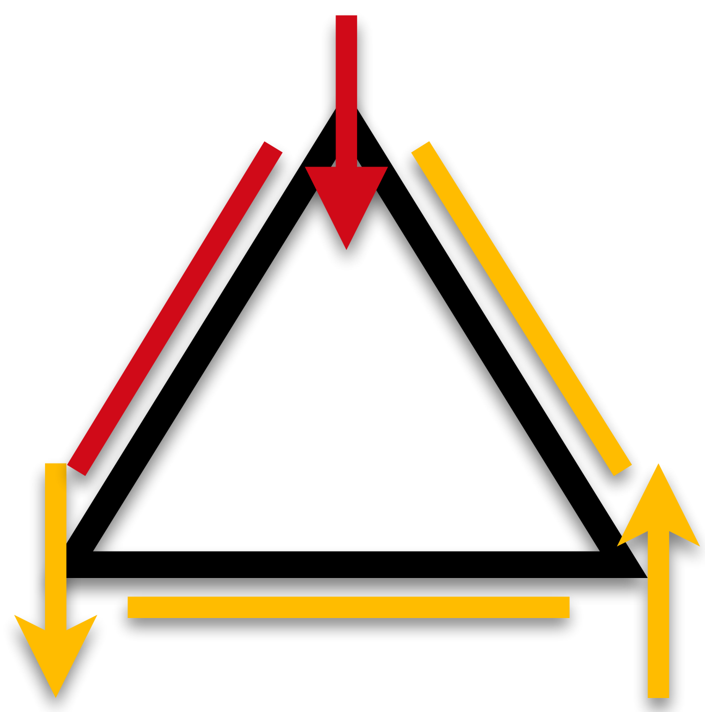
Overchoice = Frustration

- ***Frustration*** from overchoice leads to interesting excited states

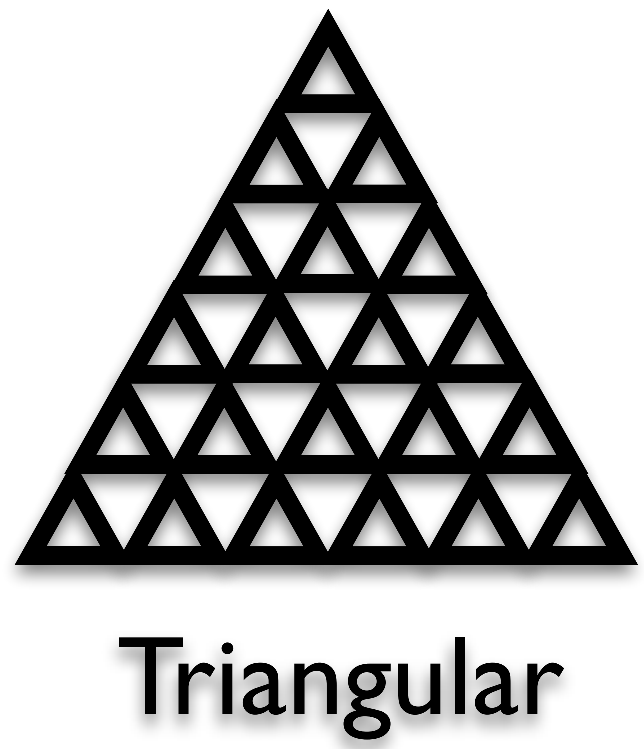


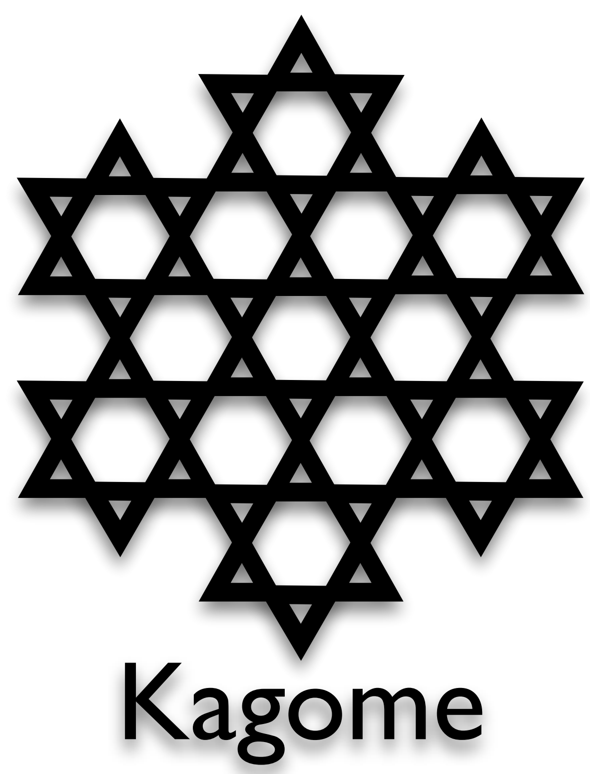


Geometric Frustration in 2D magnets

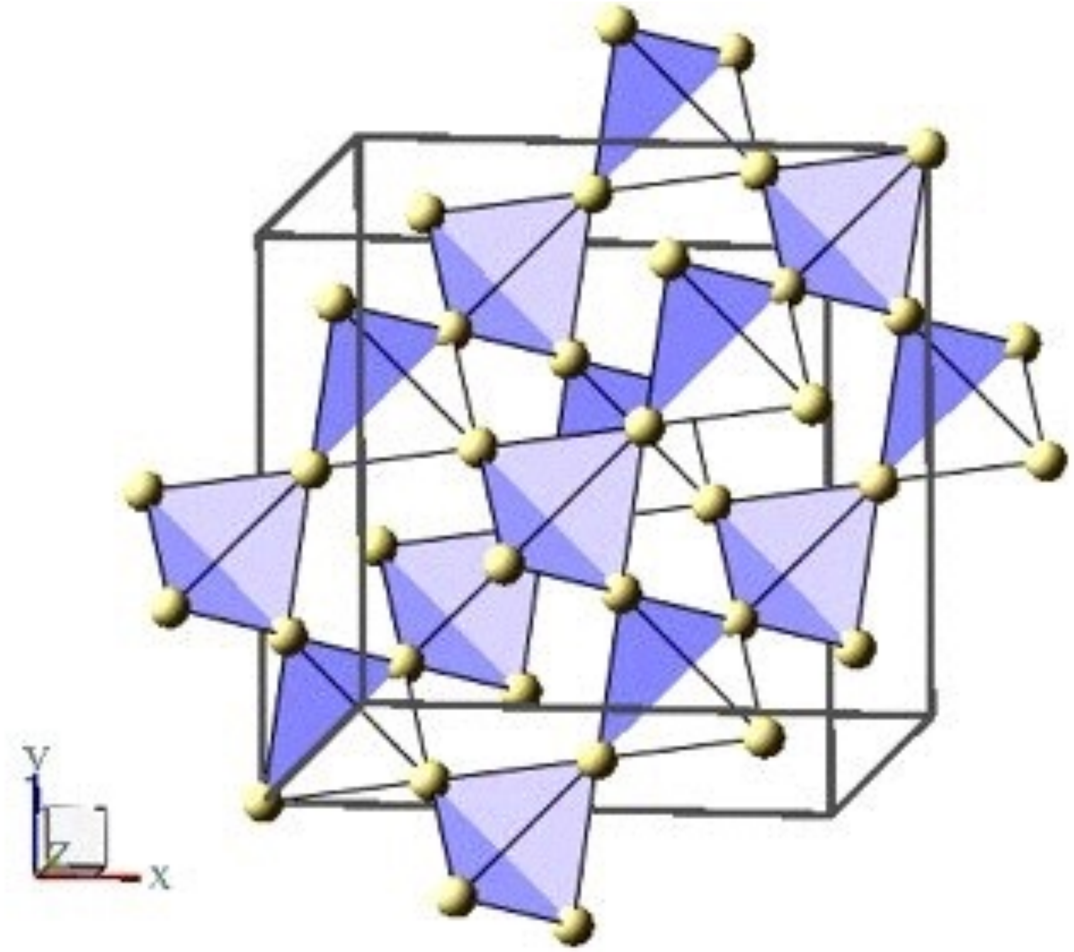


prefer ↑↓ alignment, but choice of 3rd spin direction is unclear





Geometric Frustration in 3D magnets



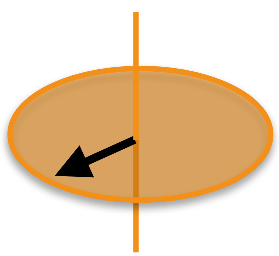
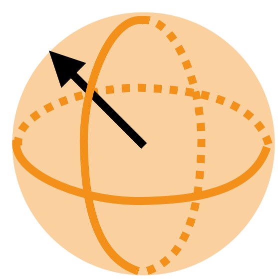
Pyrochlore

freedom of choice for each tetrahedron leads to a macroscopic degeneracy: **NO Long Range Order**

Local Anisotropy on the Pyrochlore Lattice

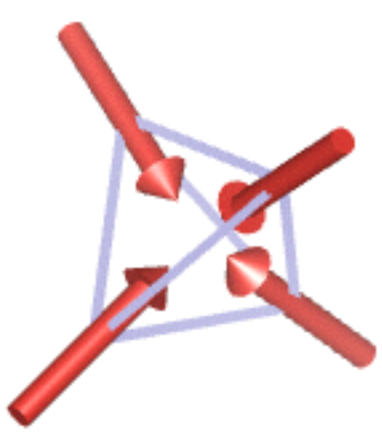
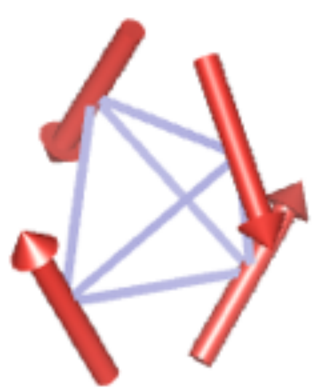
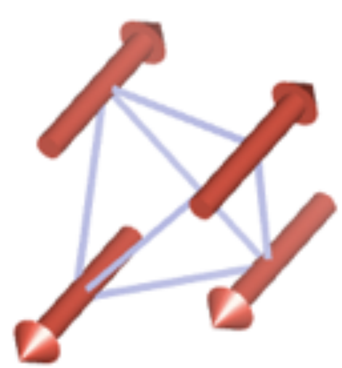
Types of Anisotropy

Ising **XY** **Heisenberg**

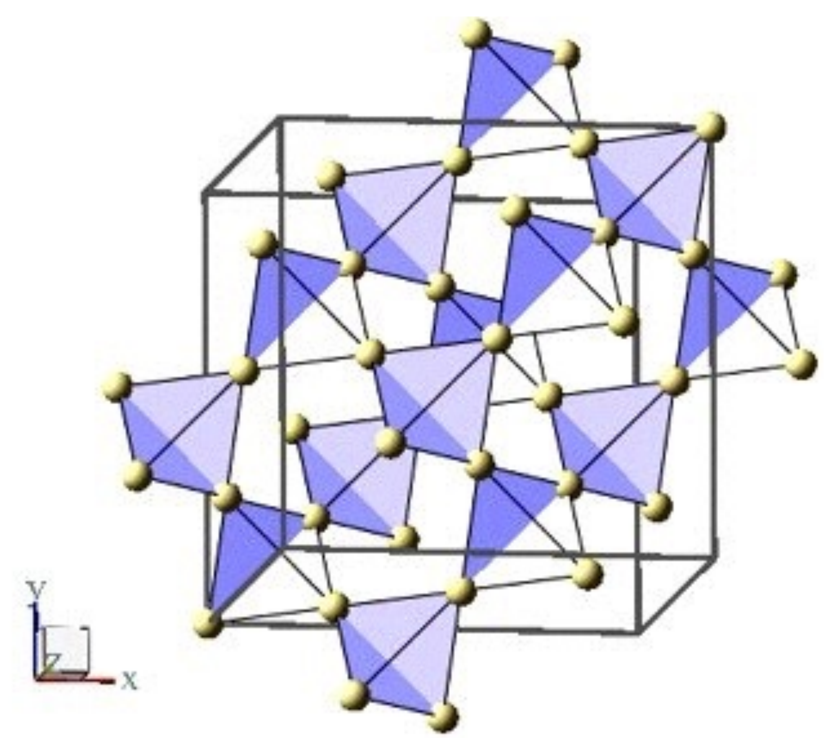




Some anisotropic AFM configurations

Ising **XY** **Heisenberg**

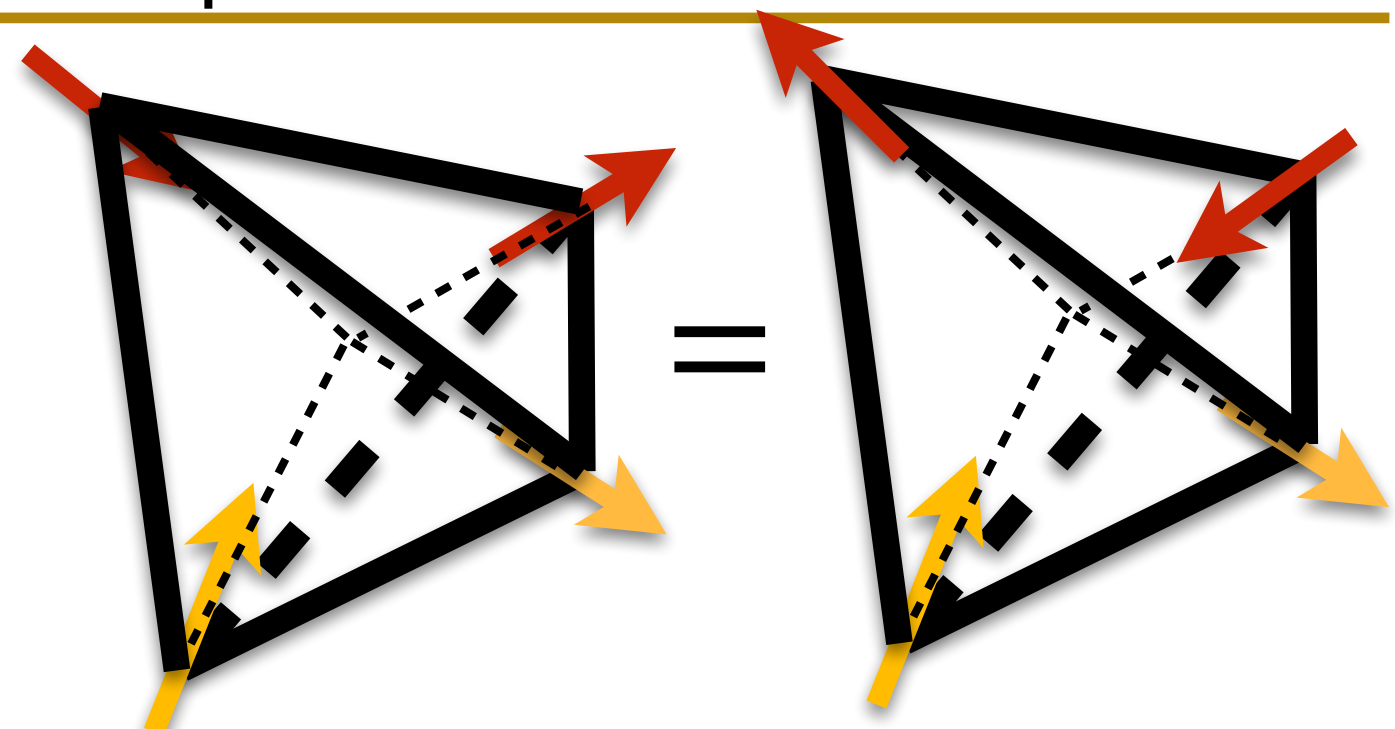
- crystal symmetry requires local axes for each sublattice
- "z" (Ising) is along *local* <111> ("In-to" or "out-of" tetrahedron)



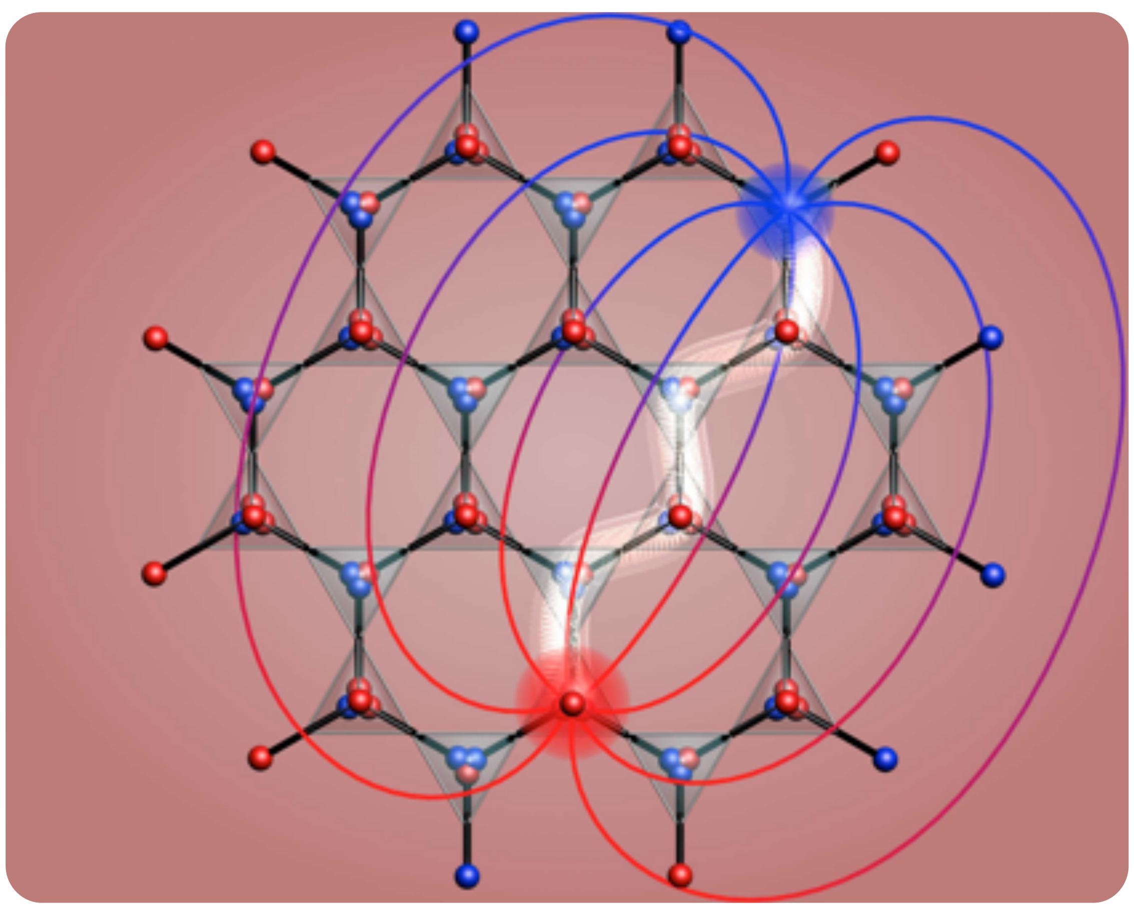
Example: Ising Ferromagnetic Pyrochlore Classical Spin Ice

ferromagnetic Ising exchange

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



Ferromagnetic Ising exchange gives "Ice Rules": Two-in Two-out

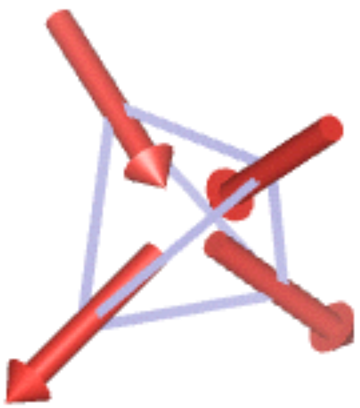


Castelnovo, Moessner, Sondhi. Nature, 451 (2008)

- "Spin ice" chooses between many disordered states obeying 2-in-2-out rules
- Excitations: **deconfined emergent magnetic monopoles**
- **Quantum spin ice:** tunneling between ice like ground states, produces additional emergent excitations

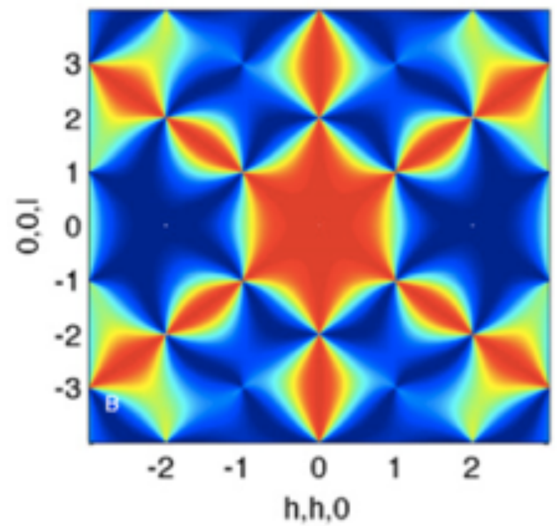
Magnetic Ground States in Pyrochlores (incomplete list!)

Spin Ice

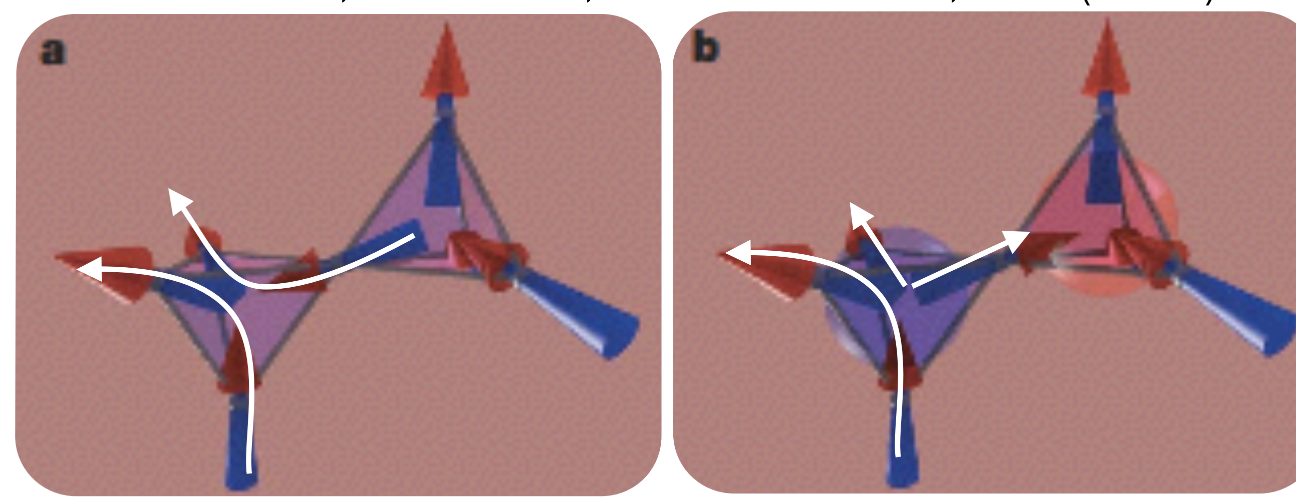


FM Ising

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



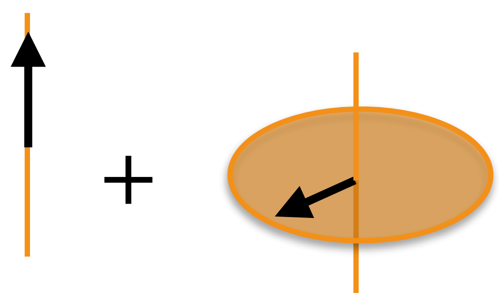
Castelnovo, Moessner, Sondhi. Nature, 451 (2008)



Emergent magnetic monopole excitations

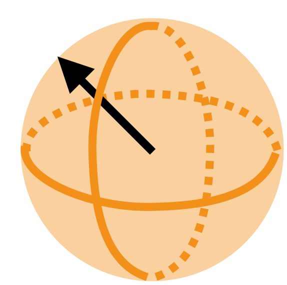
Quantum Spin Liquids

FM Ising **XY**



Or

AFM S=1/2 Heisenberg



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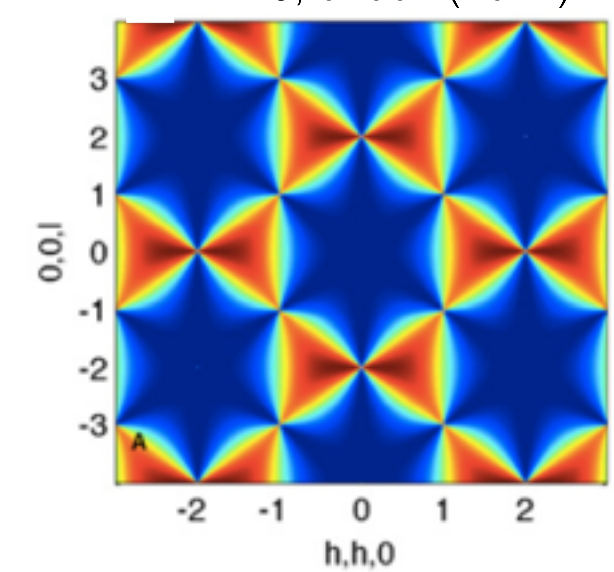
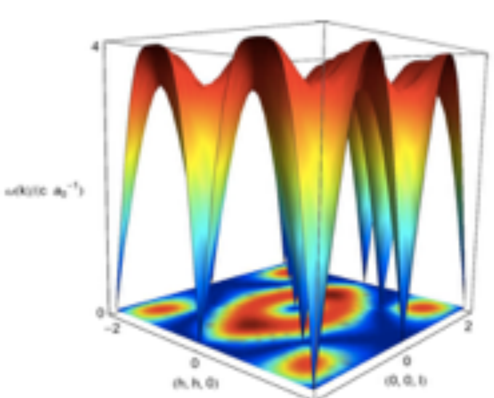




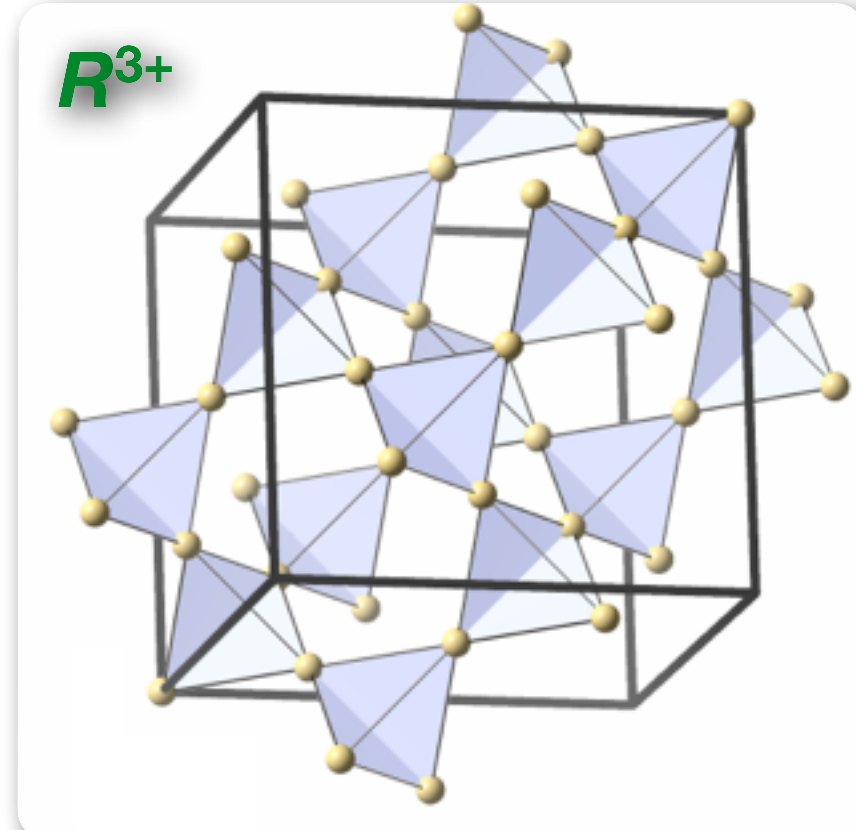
"Quantum Spin Ice"

Coulomb phase

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

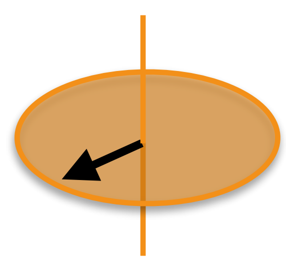
Real Pyrochlores: playgrounds for frustration

$R_2Ti_2O_7$ "Rare earth titanates"

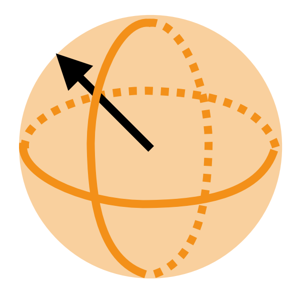


Ising

XY



Heisenberg



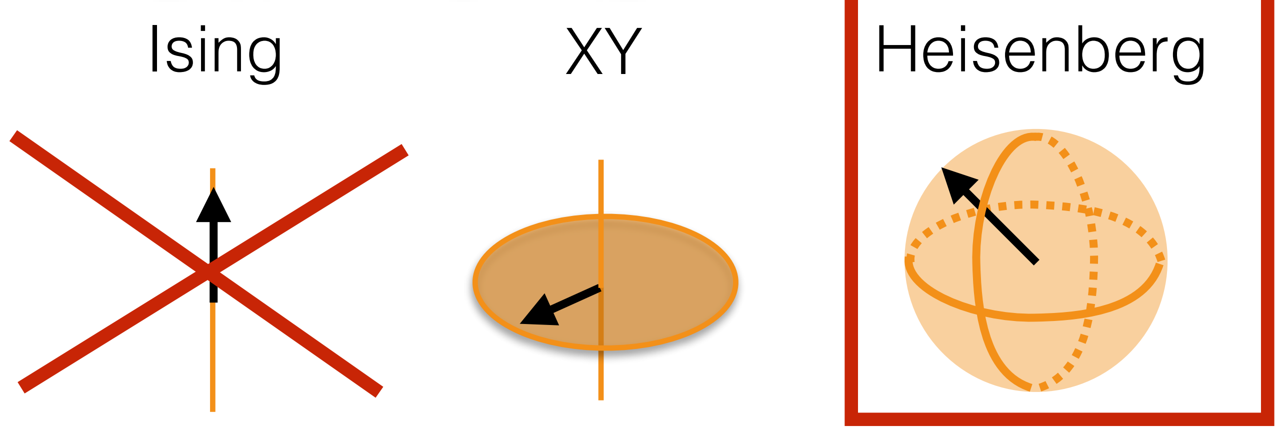
Differences in **single ion anisotropy** is very important

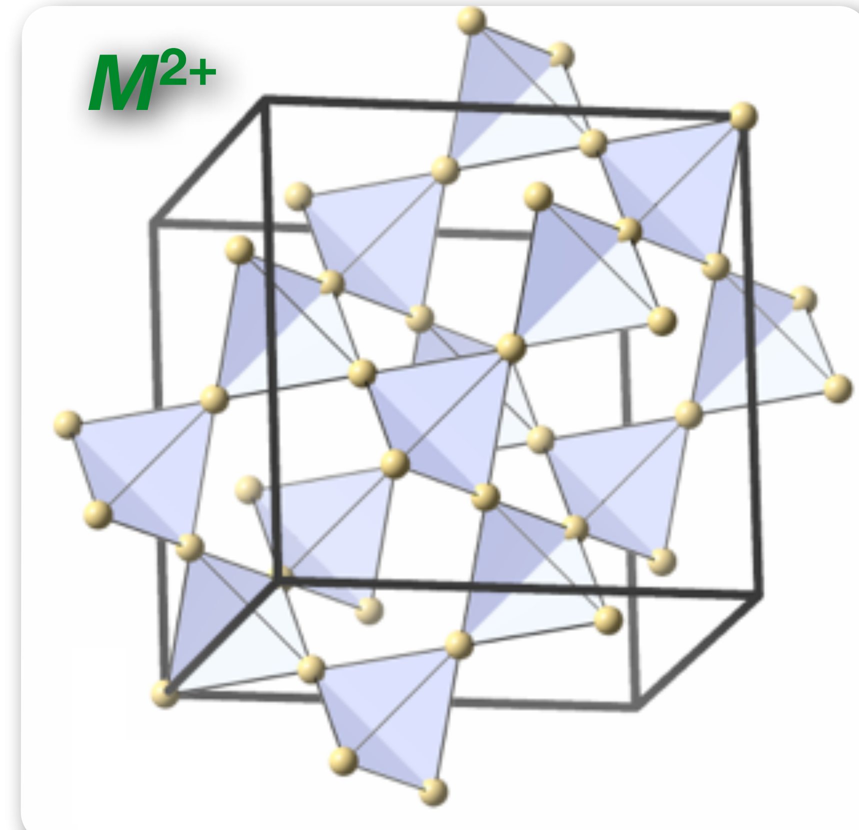
	Single Ion Anisotropy	Interactions	Ground state
Ho, Dy	Ising	FM	spin ice
Tb	Ising	AFM	spin liquid
Gd	Heisenberg	AFM	partial order
Er	XY	AFM	"order by disorder"
Yb	XY	FM	"quantum spin ice"? Phase competition

Real Pyrochlores: playgrounds for frustration

$(Na/A')_2 M_2 O_7$

$A' = Ca^{2+}$ or Sr^{2+}





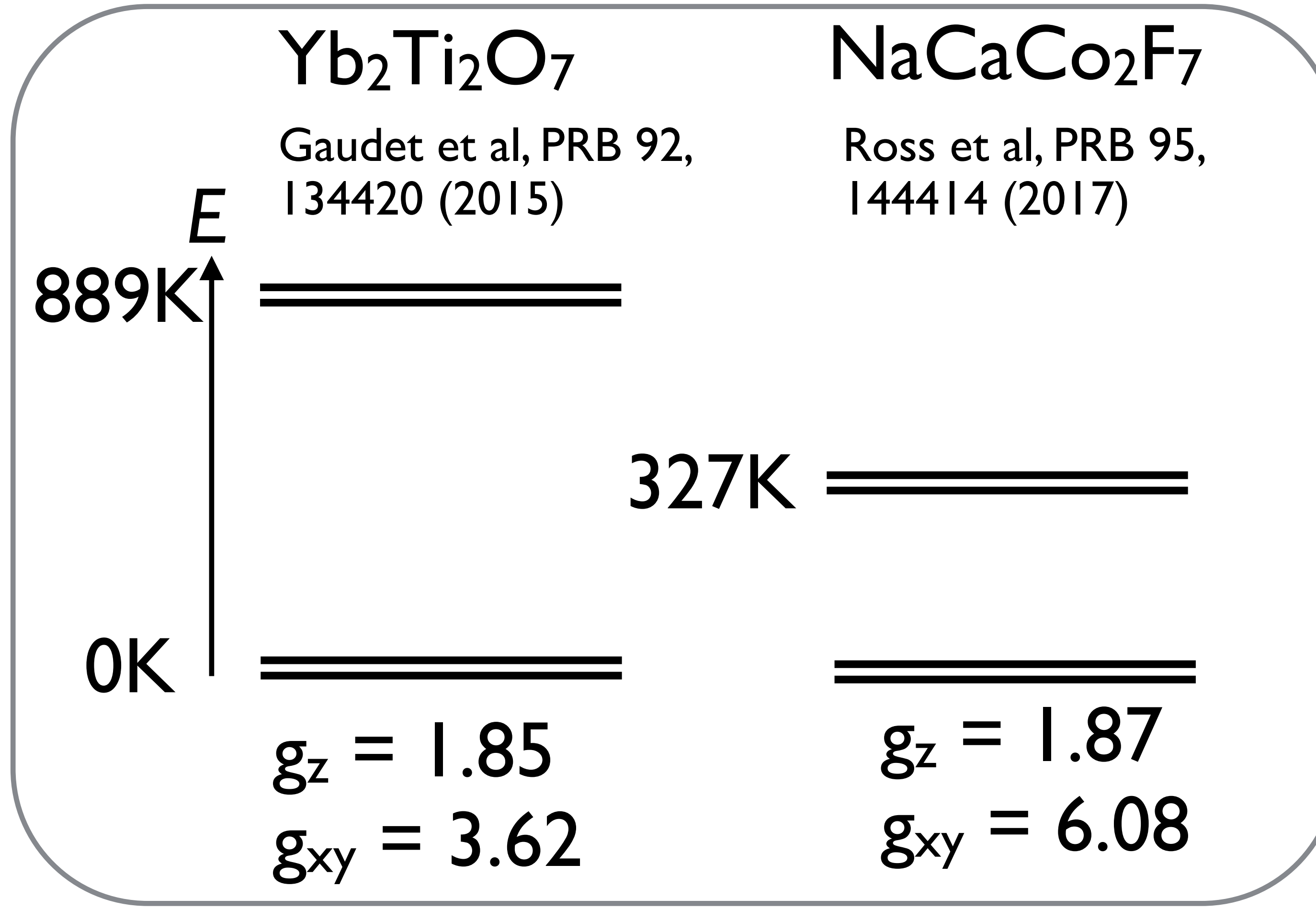
In 3d transition metals, usually Heisenberg — except Co^{2+}

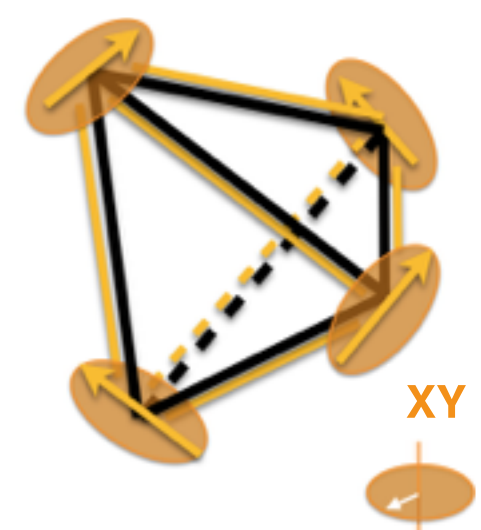
M^{2+}	Single Ion Anisotropy	Interactions	Ground state
Co	XY, $S_{eff}=1/2$	AFM	**spin frozen only at low effective T**
Mn	Heisenberg? S=5/2	AFM	spin frozen
Ni	Heisenberg? S=1	AFM	spin frozen
Fe	Heisenberg? S=5/2	AFM	spin frozen

Origin of anisotropy in Pyrochlores

$\boldsymbol{R}_2B_2O_7$ (R^{3+} = rare earth, B^{4+} = Ti, Sn, Pt, Ge),
$NaCa\mathbf{Co}_2F_7$, $NaSr\mathbf{Co}_2F_7$

- **Spin orbit coupling plus crystal field** in both Co^{2+} and R^{3+} : *J* instead of *S* and *L*
- ***Effective* S=1/2 doublets**
- **g-tensor:** describes size of single-ion magnetic moment in various directions
- **anisotropic exchange couplings:** Distinct from g-tensor anisotropy!





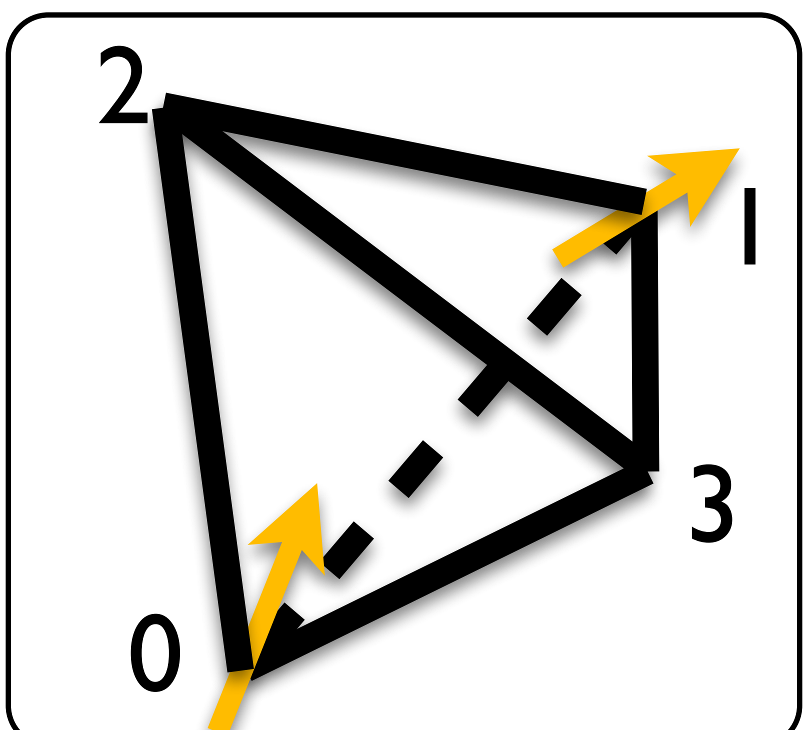
General Anisotropic Exchange

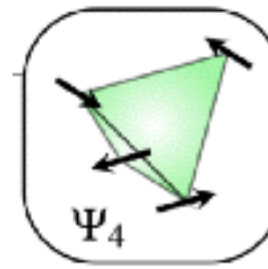
Tensor with 4 unique elements:

$$J_2 S_1^x S_2^x + J_1(S_1^y S_2^y + S_1^z S_2^z) + J_3(S_1^y S_2^z + S_1^z S_2^y) + \ldots$$

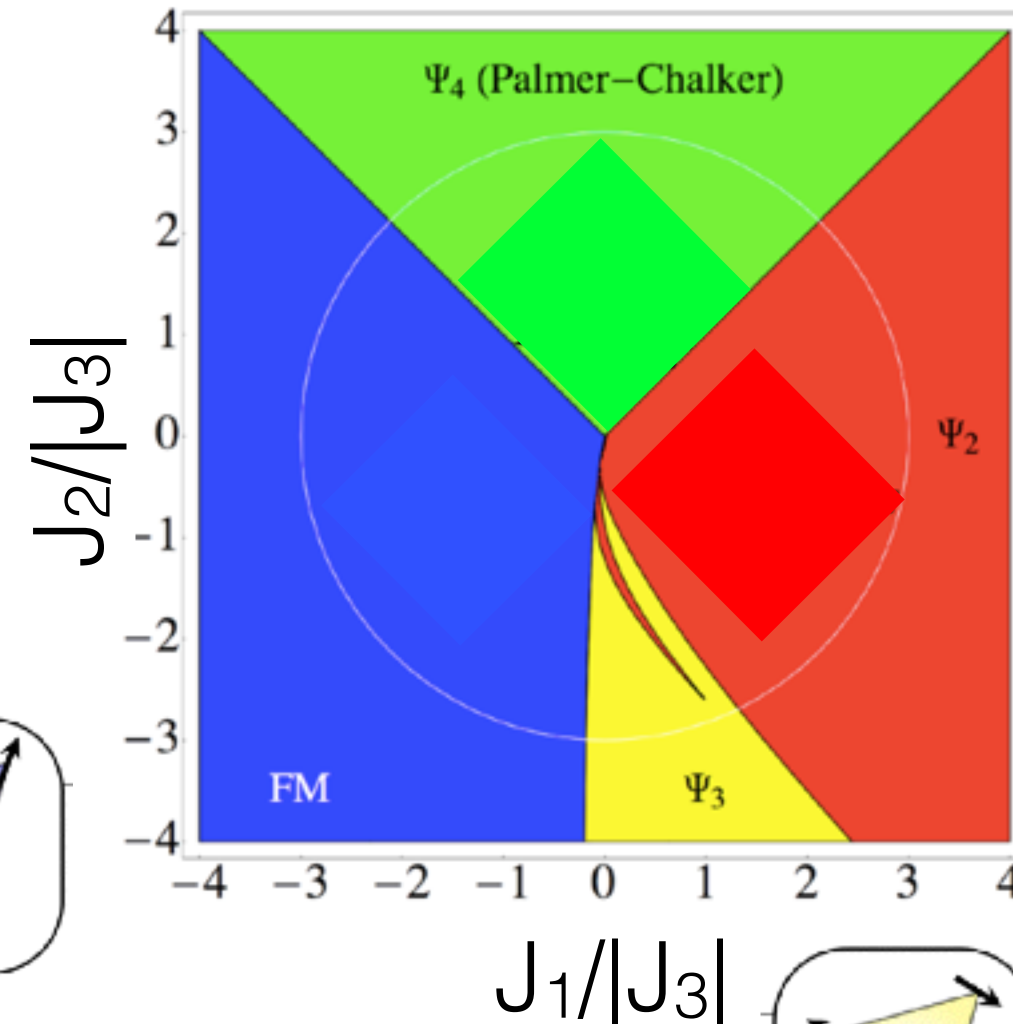
$$H = \frac{1}{2}\sum_{ij} J_{ij}^{\mu\nu} S_i^\mu S_j^\nu$$

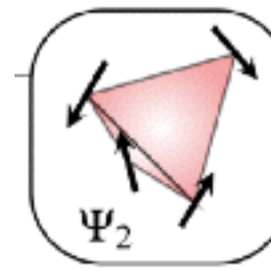
$$J_{01} = \begin{pmatrix} J_2 & J_4 & J_4 \\ -J_4 & J_1 & J_3 \\ -J_4 & J_3 & J_1 \end{pmatrix}$$

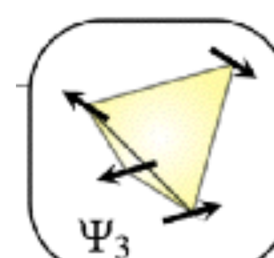




Classical phase diagram: Types of Long Range Order (for $J_4 = 0$)







Yan et al, "**General theory of anisotropic exchange on the pyrochlore lattice**", PRB **95**, 094422 (2017)

General Anisotropic Exchange

Tensor with 4 unique elements:

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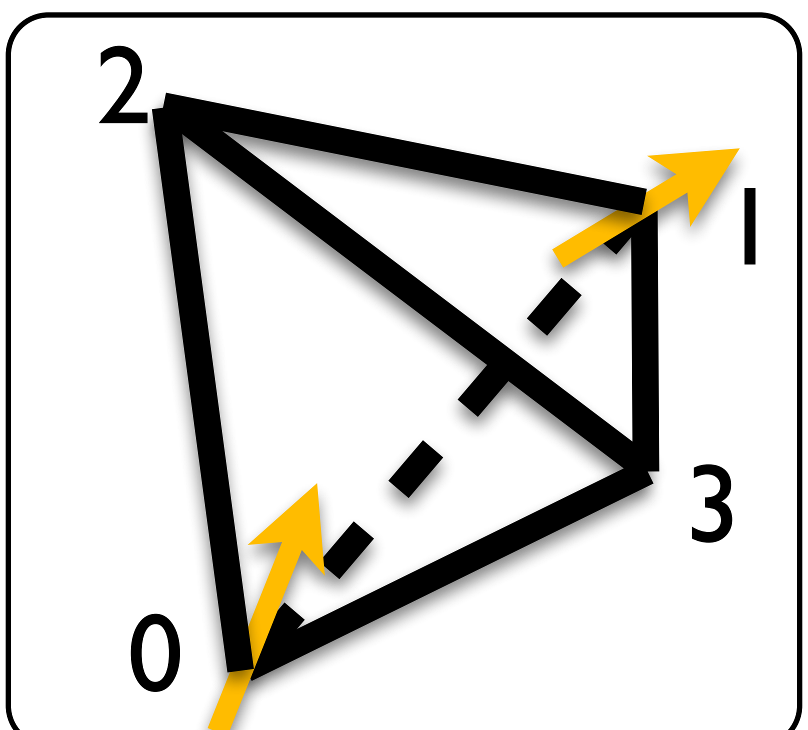
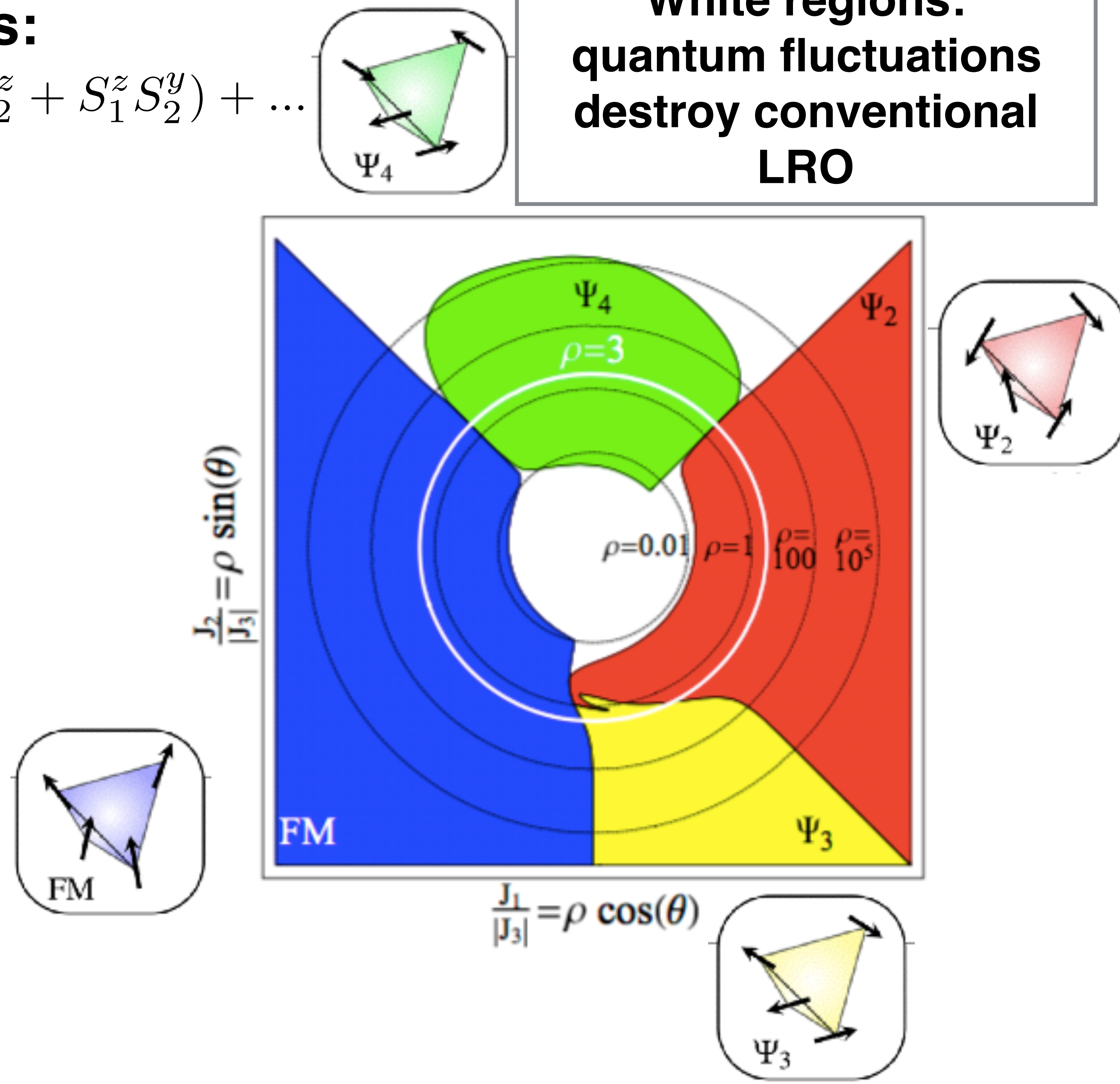
$$H = \frac{1}{2} \sum_{ij} J_{ij}^{\mu\nu} S_i^\mu S_j^\nu$$

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



White regions: quantum fluctuations destroy conventional LRO

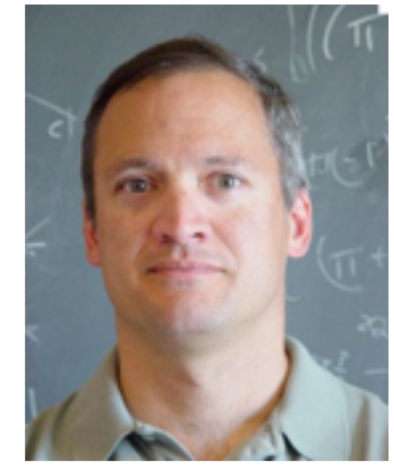


Yan et al, “**General theory of anisotropic exchange on the pyrochlore lattice**”, PRB **95**, 094422 (2017)

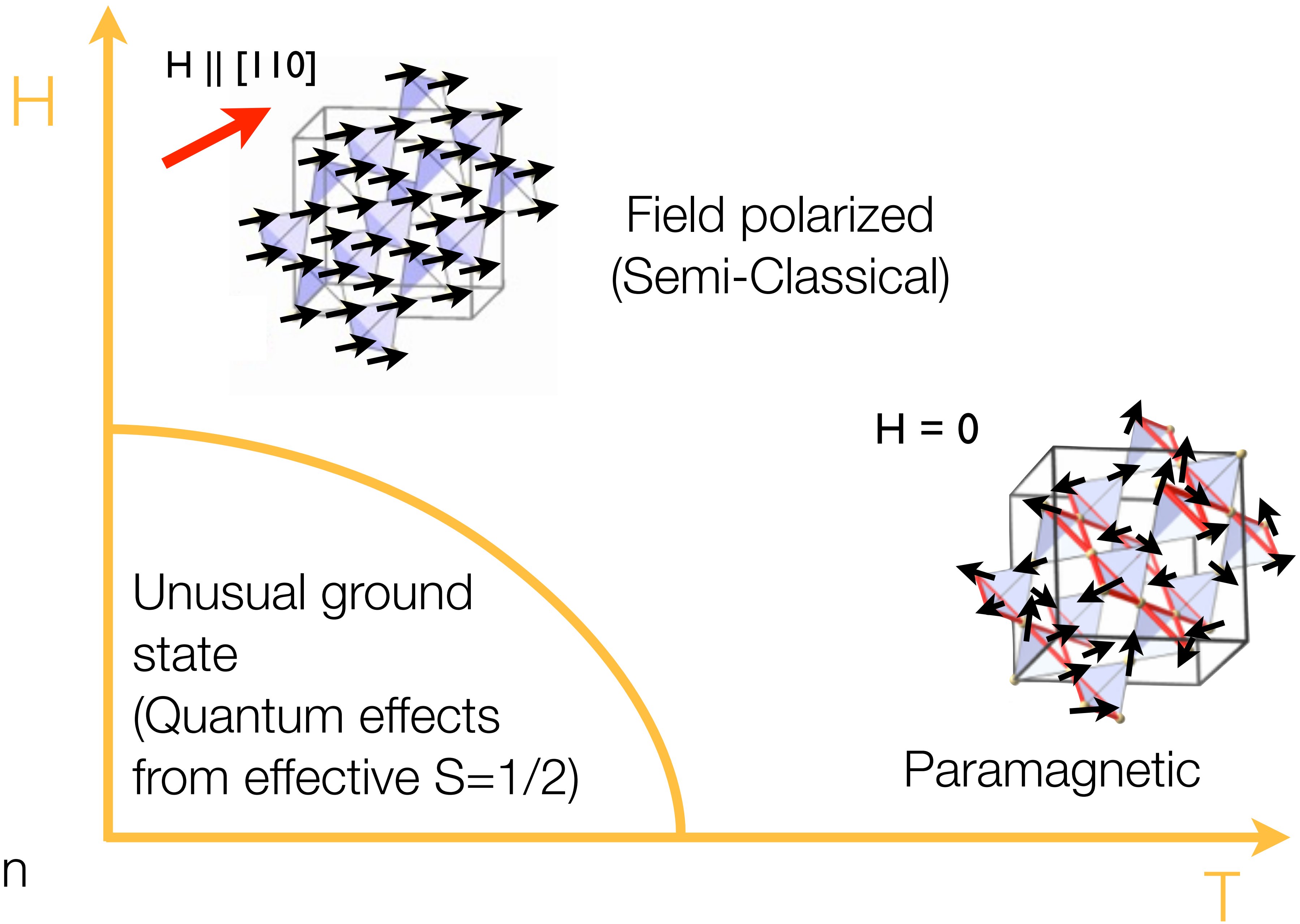
Determining exchange interactions from field polarized states

Can extract quantitative values for J_1-J_4

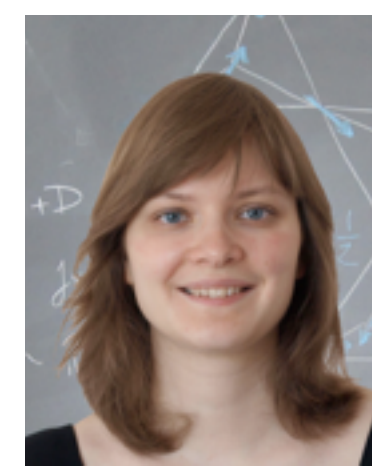
Linear Spin Wave Theory + Neutron Scattering



Leon Balents



Bruce Gaulin

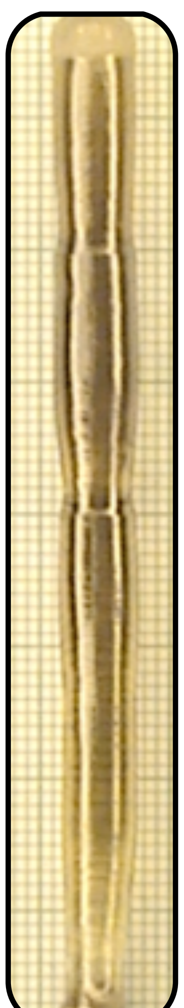


Lucile Savary

"Time of Flight" Inelastic Neutron Scattering

"Disk Chopper Spectrometer" (DCS)

@ NIST Center for Neutron Research



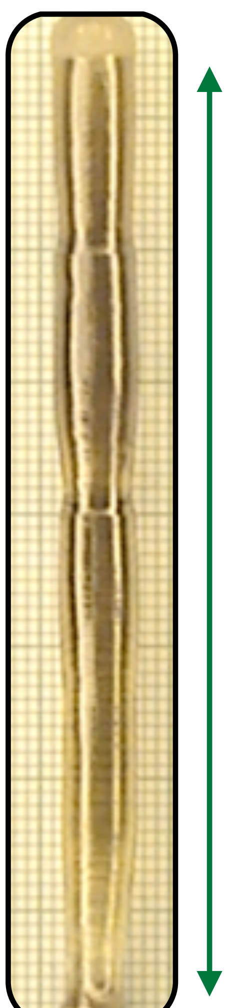
Single Crystal $Yb_2Ti_2O_7$

7.5 cm

“Time of Flight” Inelastic Neutron Scattering

“Disk Chopper Spectrometer” (DCS)

@ NIST Center for Neutron Research



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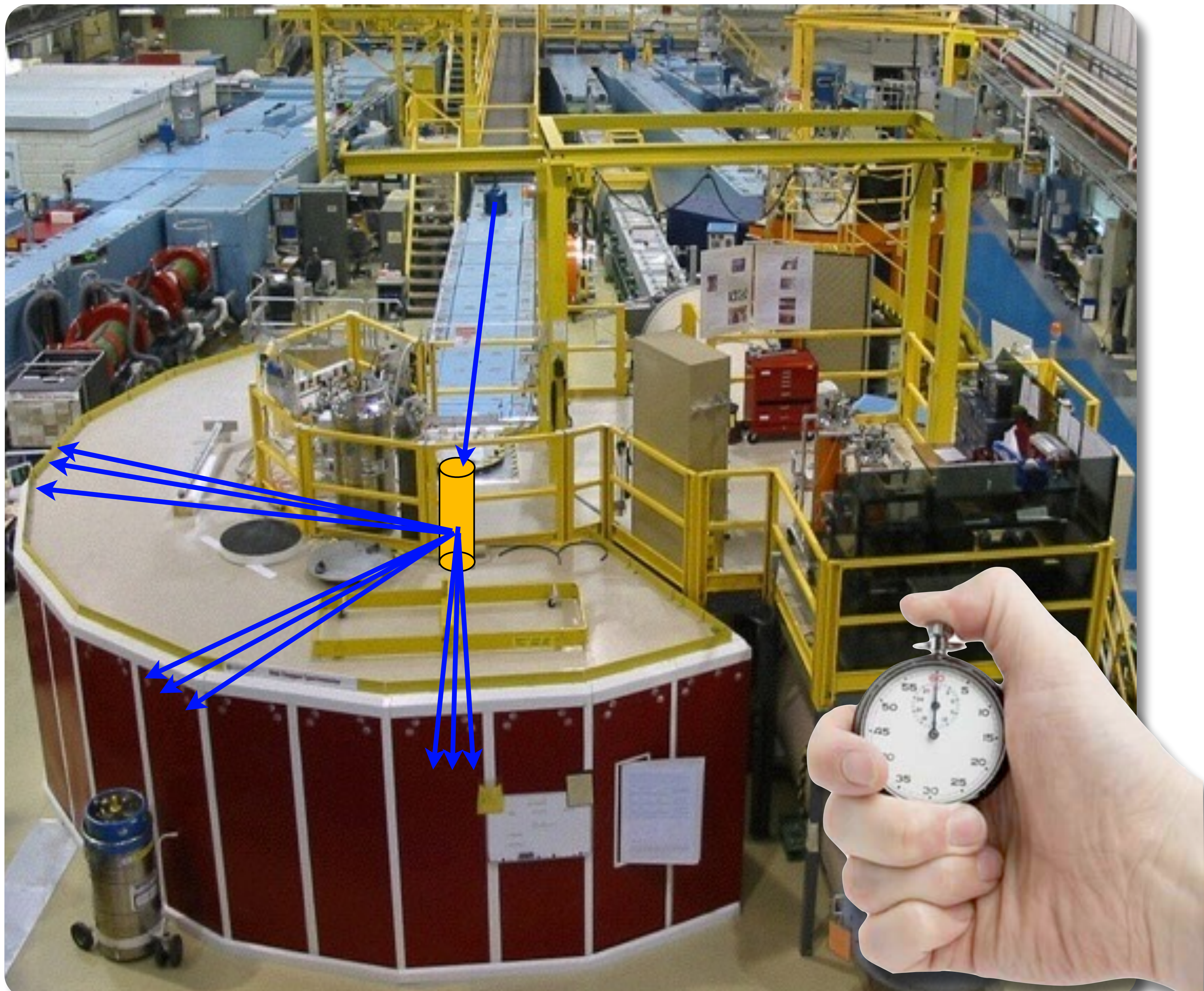
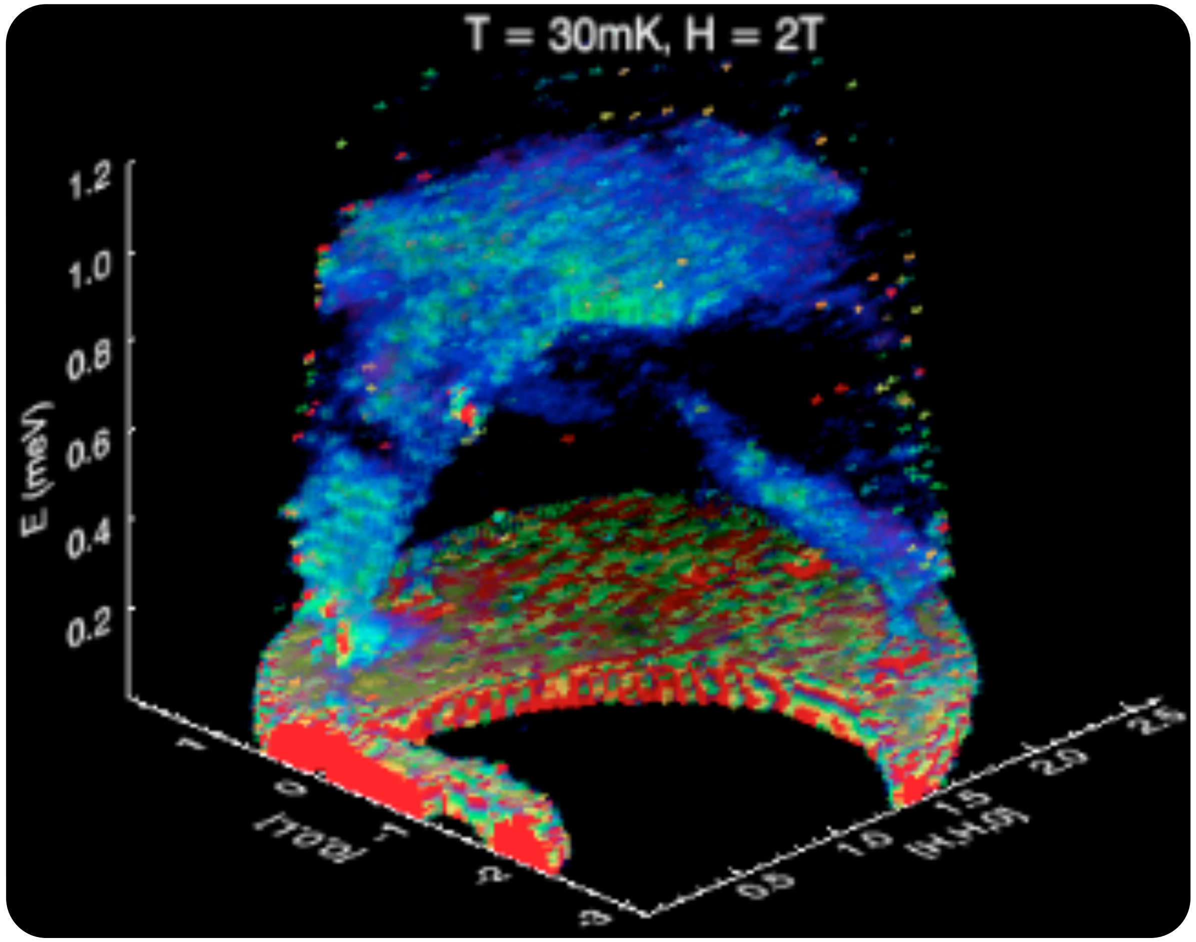


Volume of "Time of Flight" Data

Can slice through this volume in several directions



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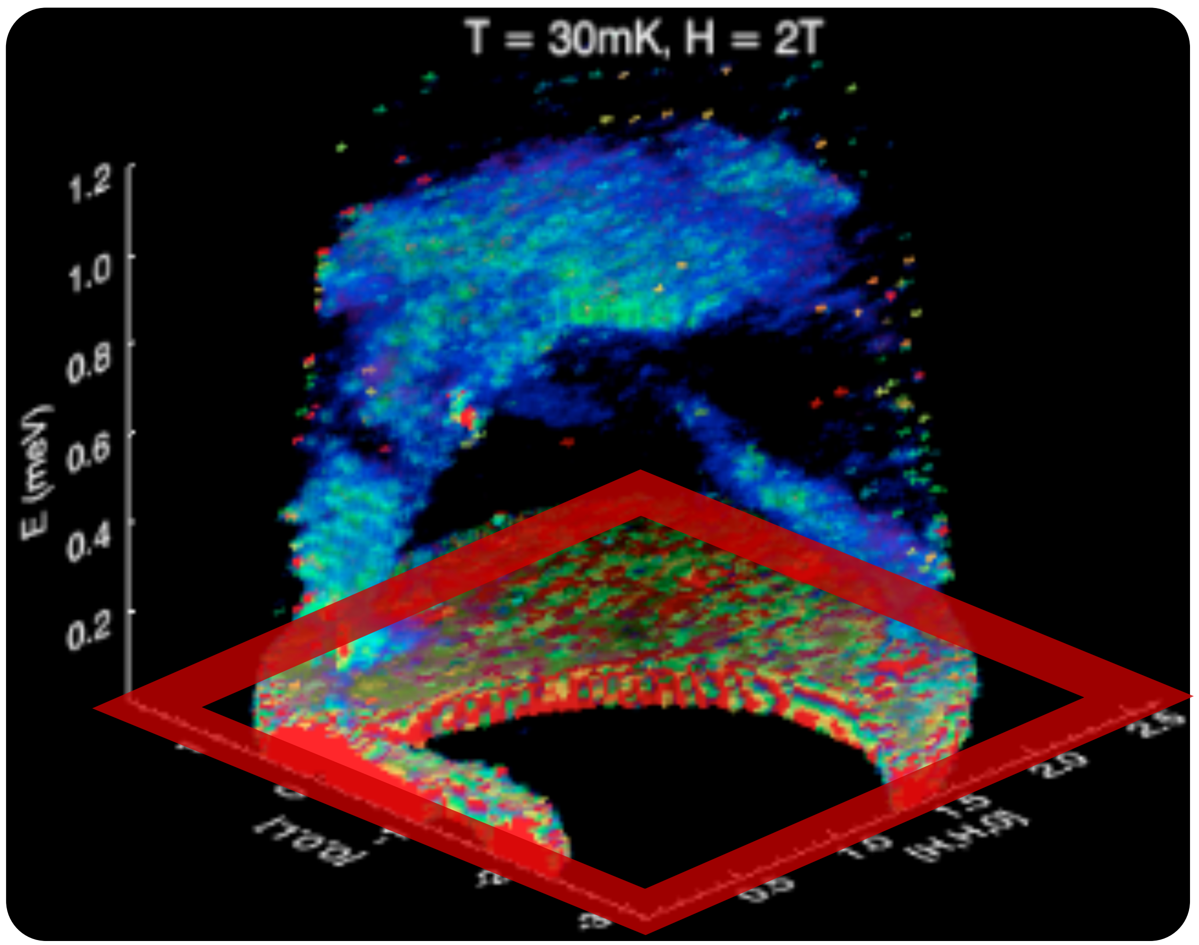

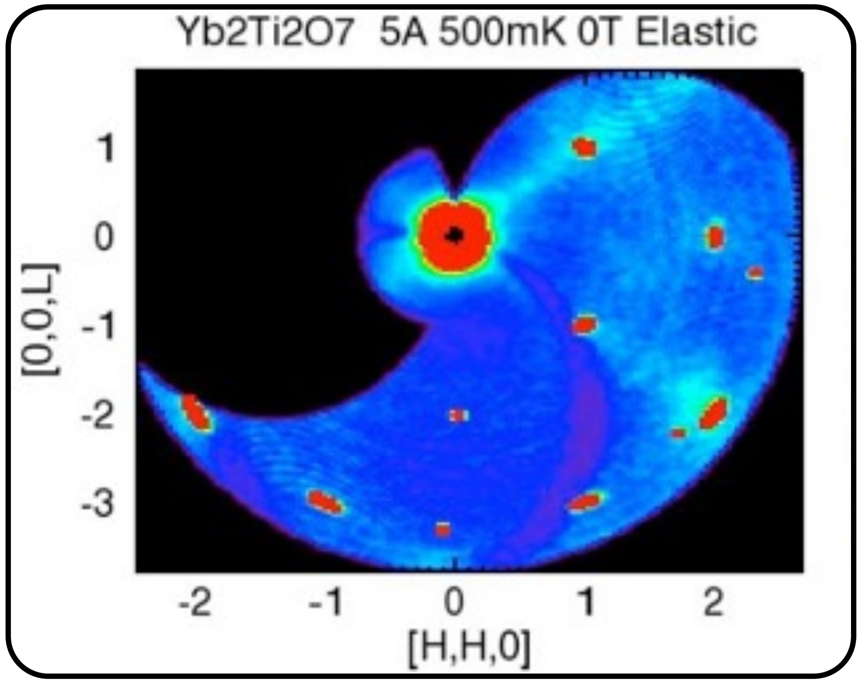

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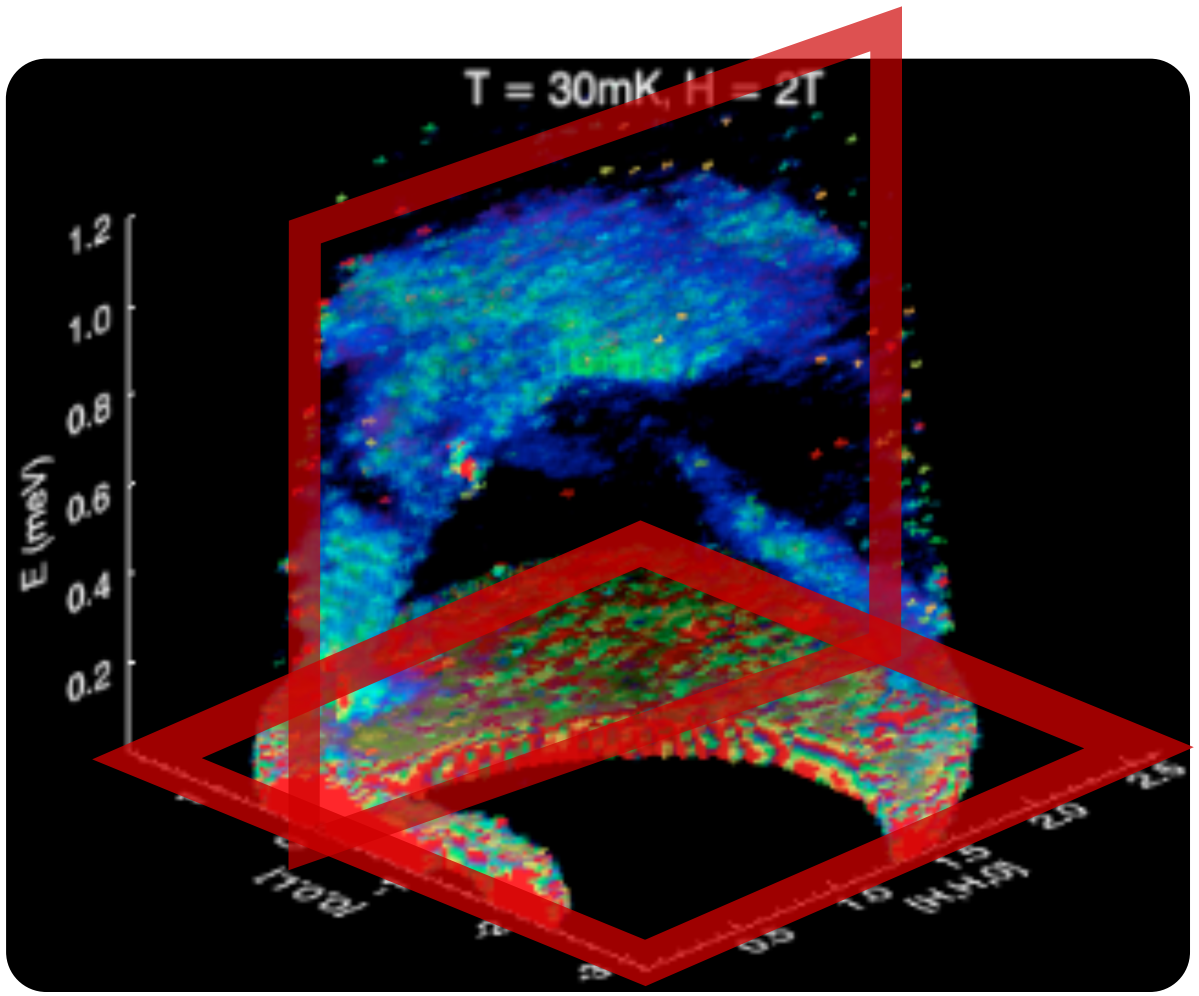
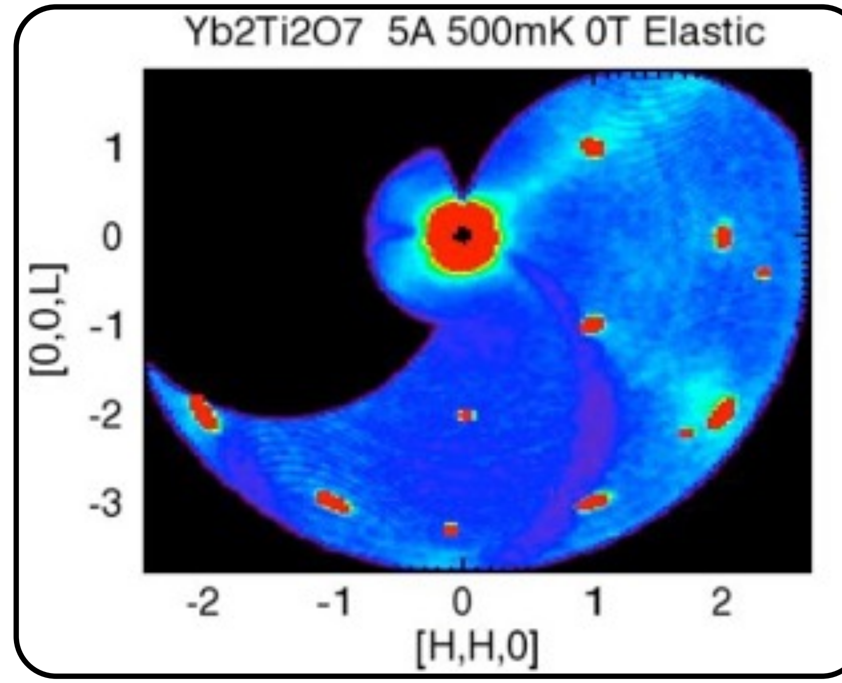
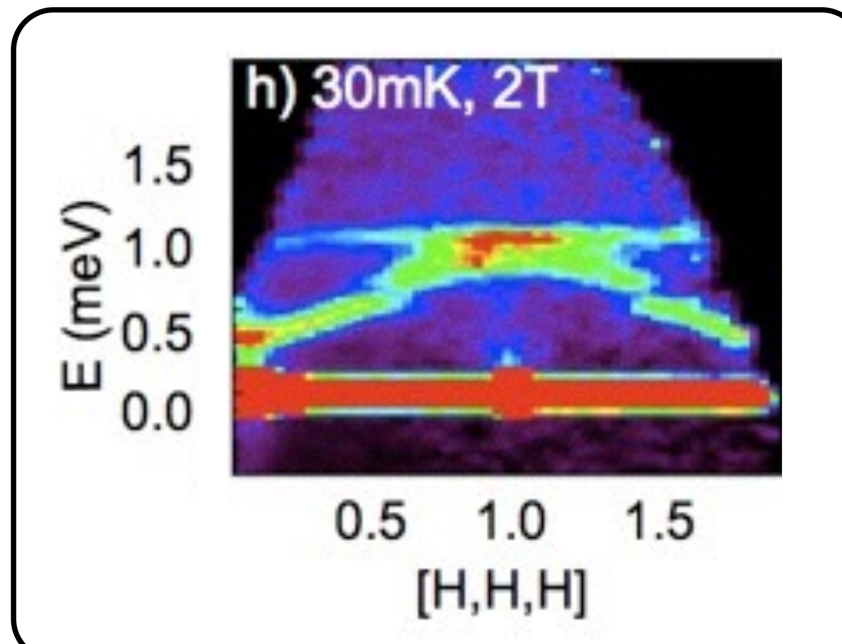


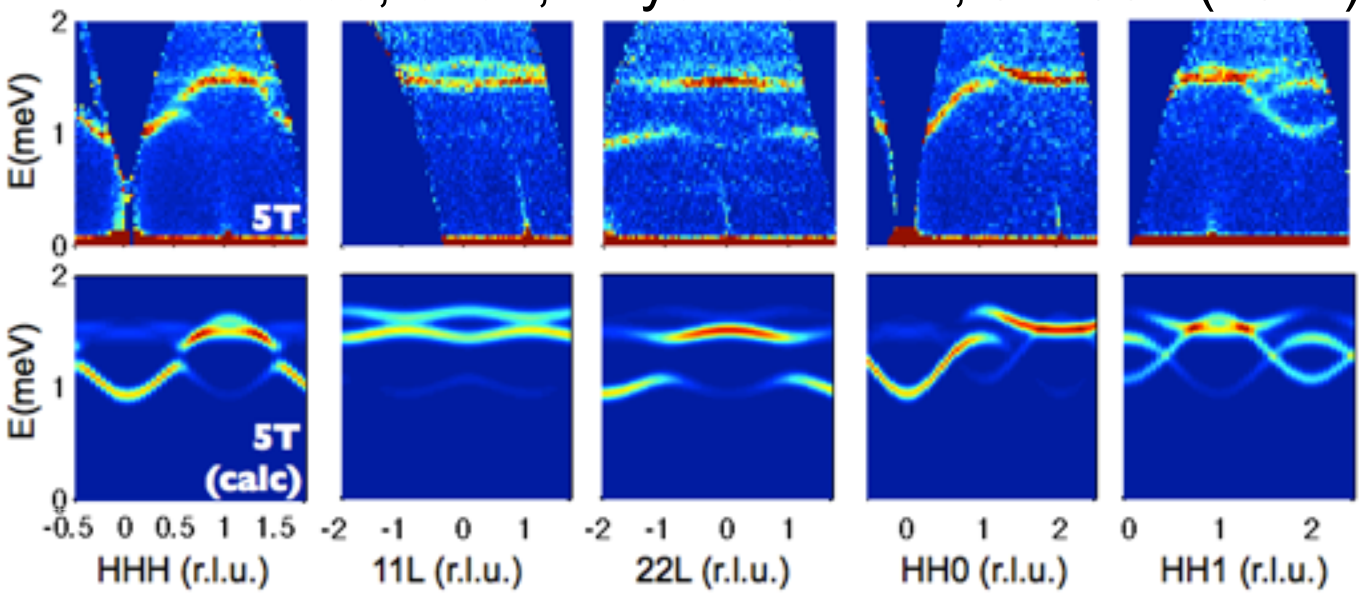




Determining exchange interactions with spin waves from field polarized state

$Yb_2Ti_2O_7$

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



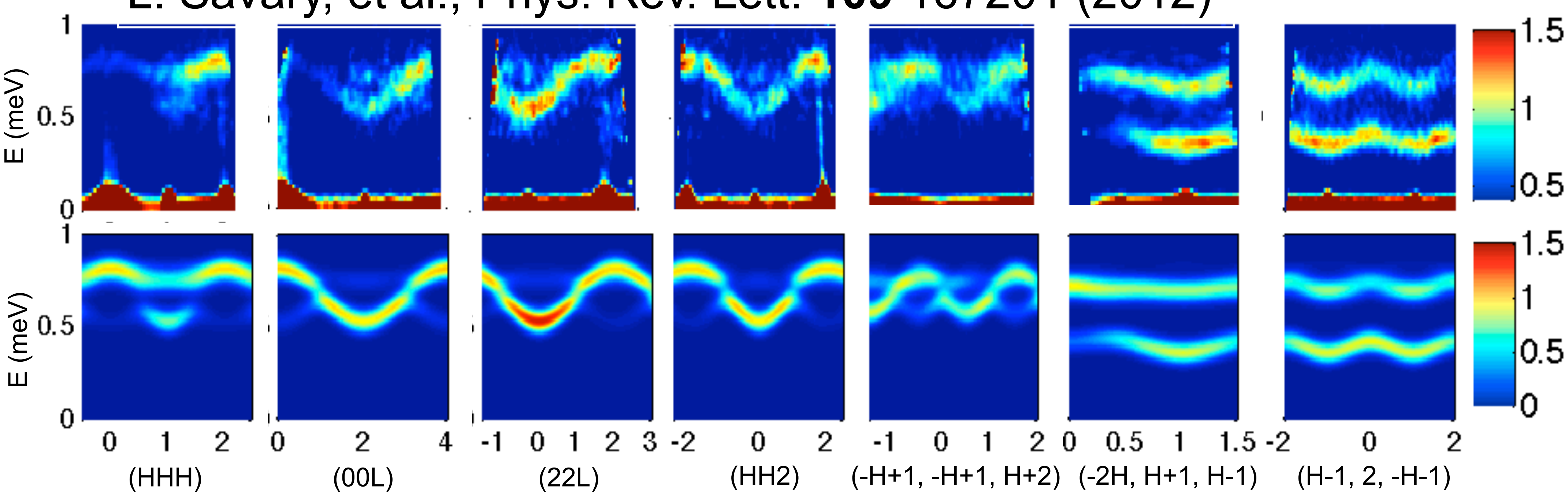
data, H=5T

fit

	$Yb_2Ti_2O_7$	$Er_2Ti_2O_7$
J1	-0.09	0.11
J2	-0.22	-0.06
J3	-0.29	-0.10
J4	0.01	0.00

$Er_2Ti_2O_7$

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



data, H=3T

fit

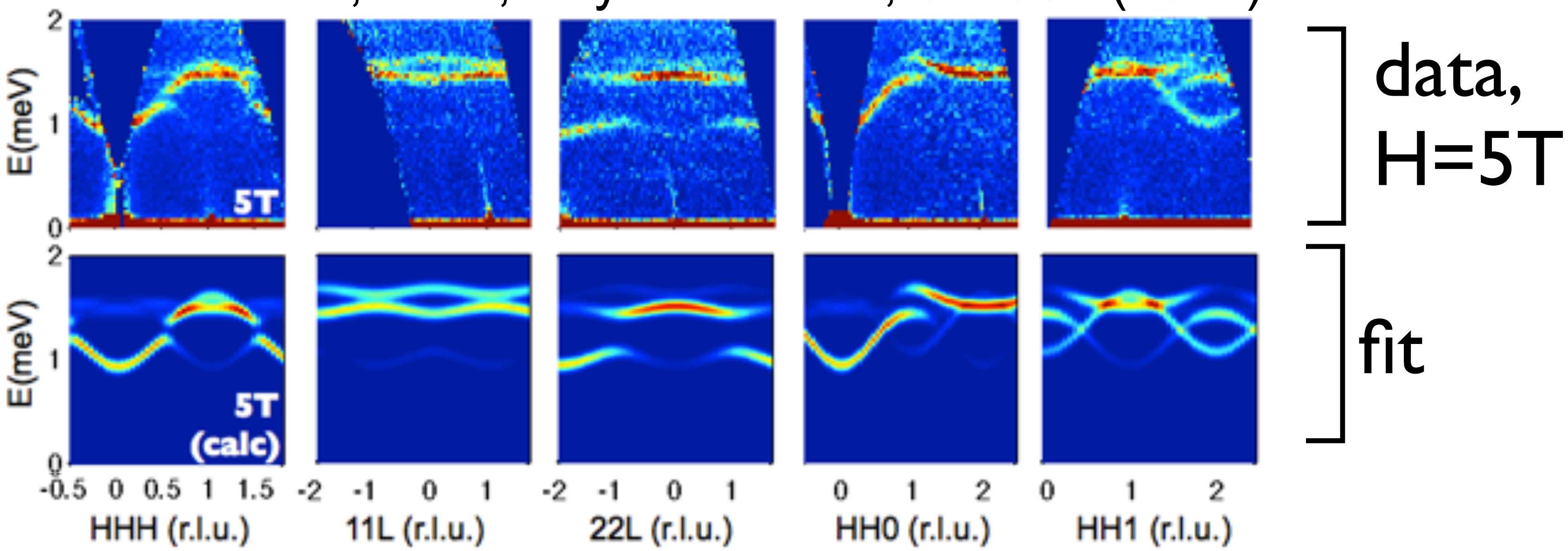
H || to [1-10]

H || to [111]

Determining exchange interactions with spin waves from field polarized state

$Yb_2Ti_2O_7$

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



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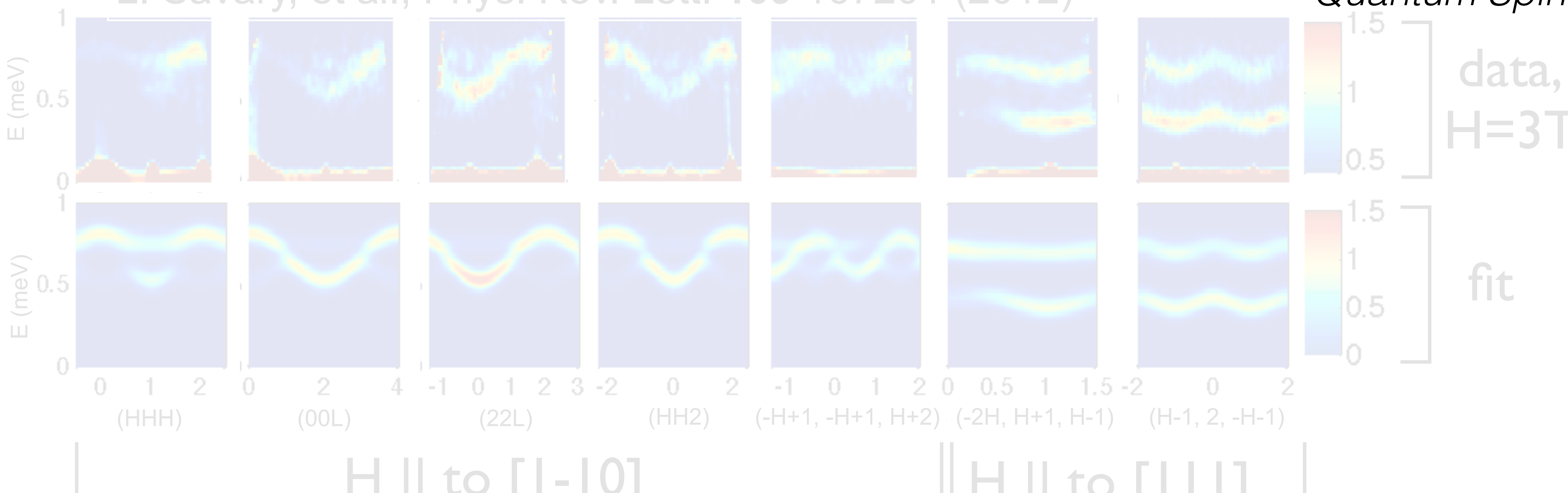
J3	-0.29	-0.10
J4	0.01	0.00

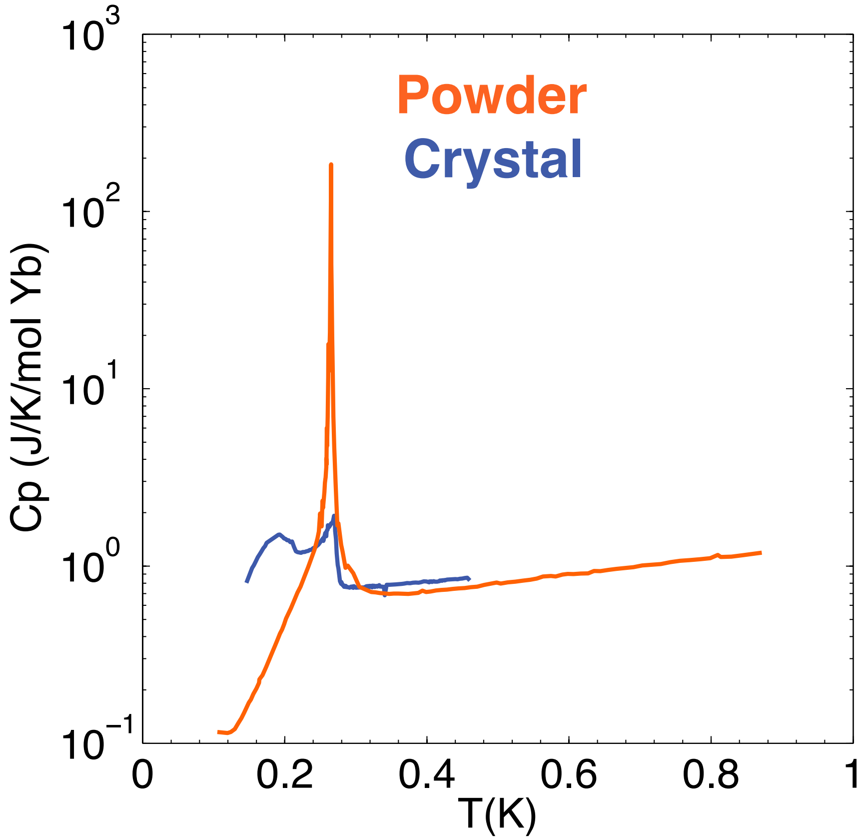
Params lead to phase competition, and possible *Quantum Spin Ice*

$Er_2Ti_2O_7$

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

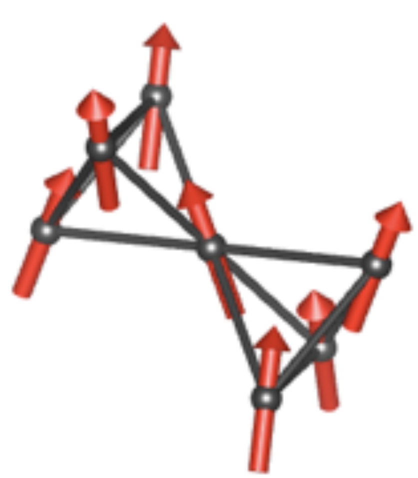


$Yb_2Ti_2O_7$: splayed ferromagnet with gapless “continuum” excitations



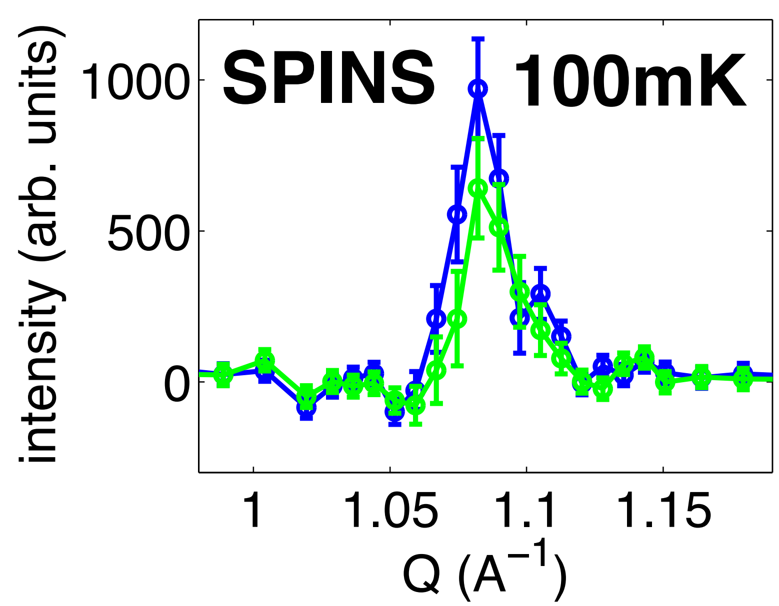
J. Gaudet, *et al* PRB **93**, 064406 (2015)

- Heat capacity anomaly at low temperatures, with some sample dependence
- **“Best” samples** (usually powders) show Ice-like **splayed ferromagnetic order** at 265 mK
- Despite this, excitations are relatively unstructured below T_C - **unlike conventional magnons**

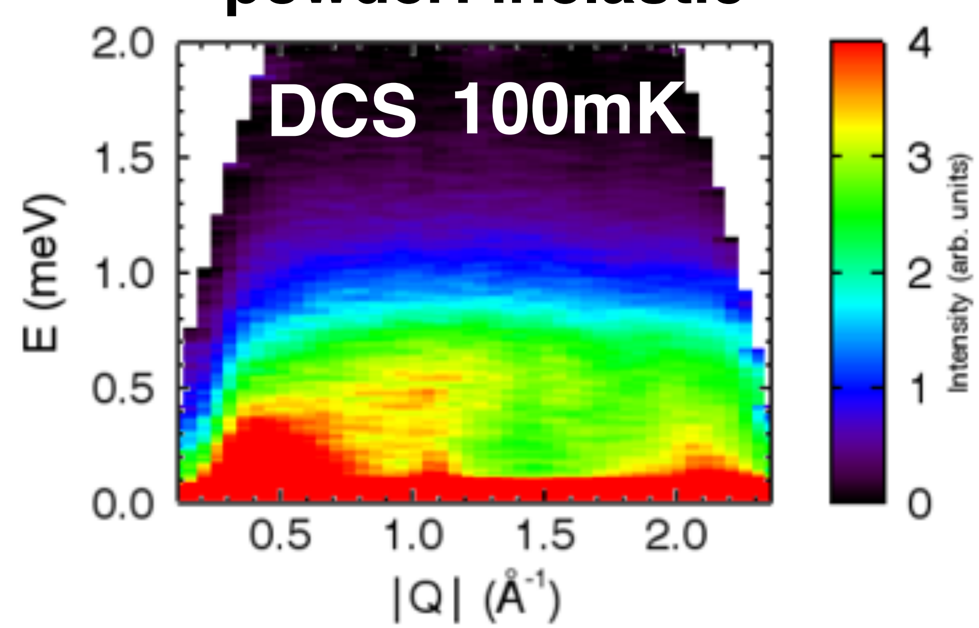


“Spin Ice-Like”
(2-in 2-out) Splaying

powder: elastic

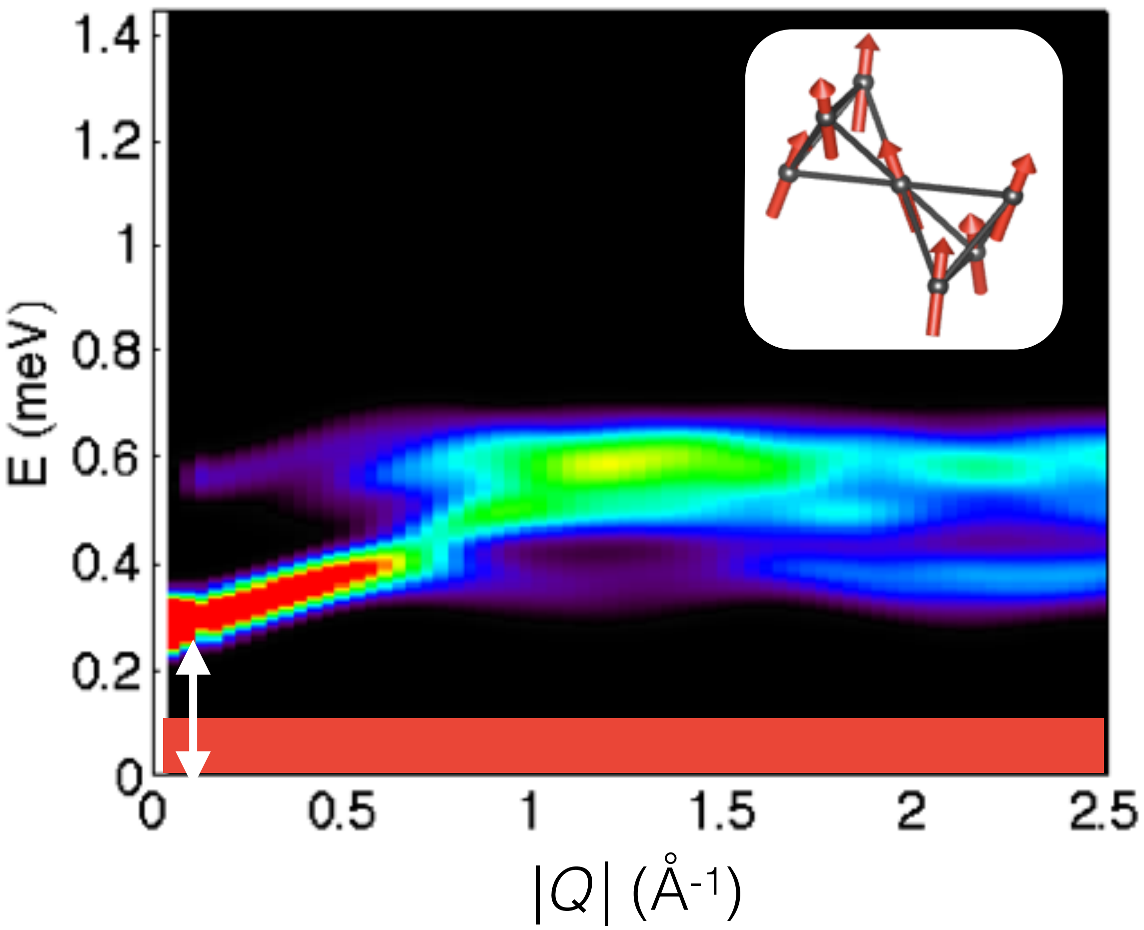


powder: inelastic



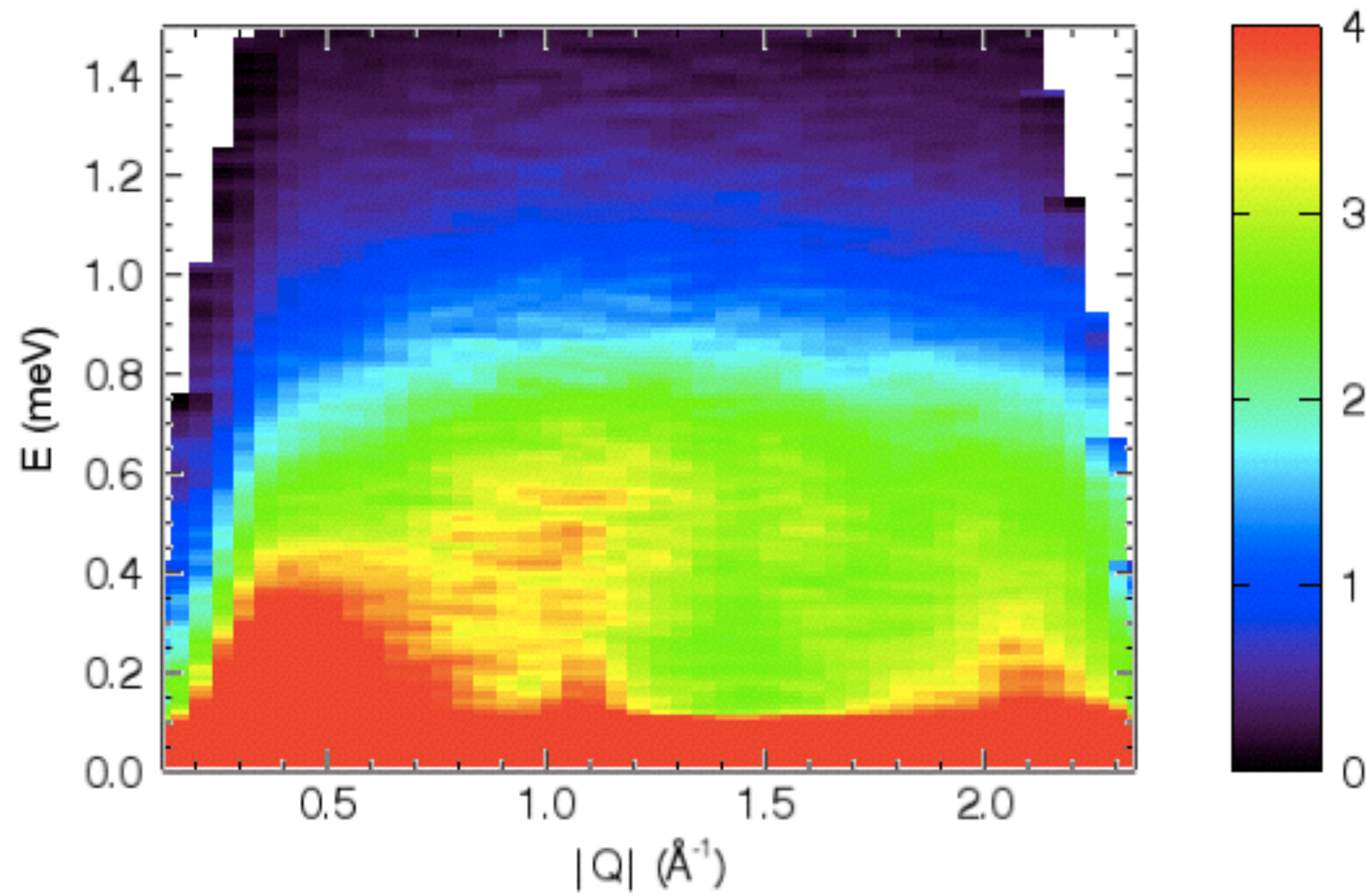
Compare zero field spin waves to Linear Spin Wave Theory

Calculated zero-field spin waves



Using Exchange parameters from
Ross *et al*, Phys. Rev. X **1**, 021002 (2011)

Measured $Yb_2Ti_2O_7$ 100 mK

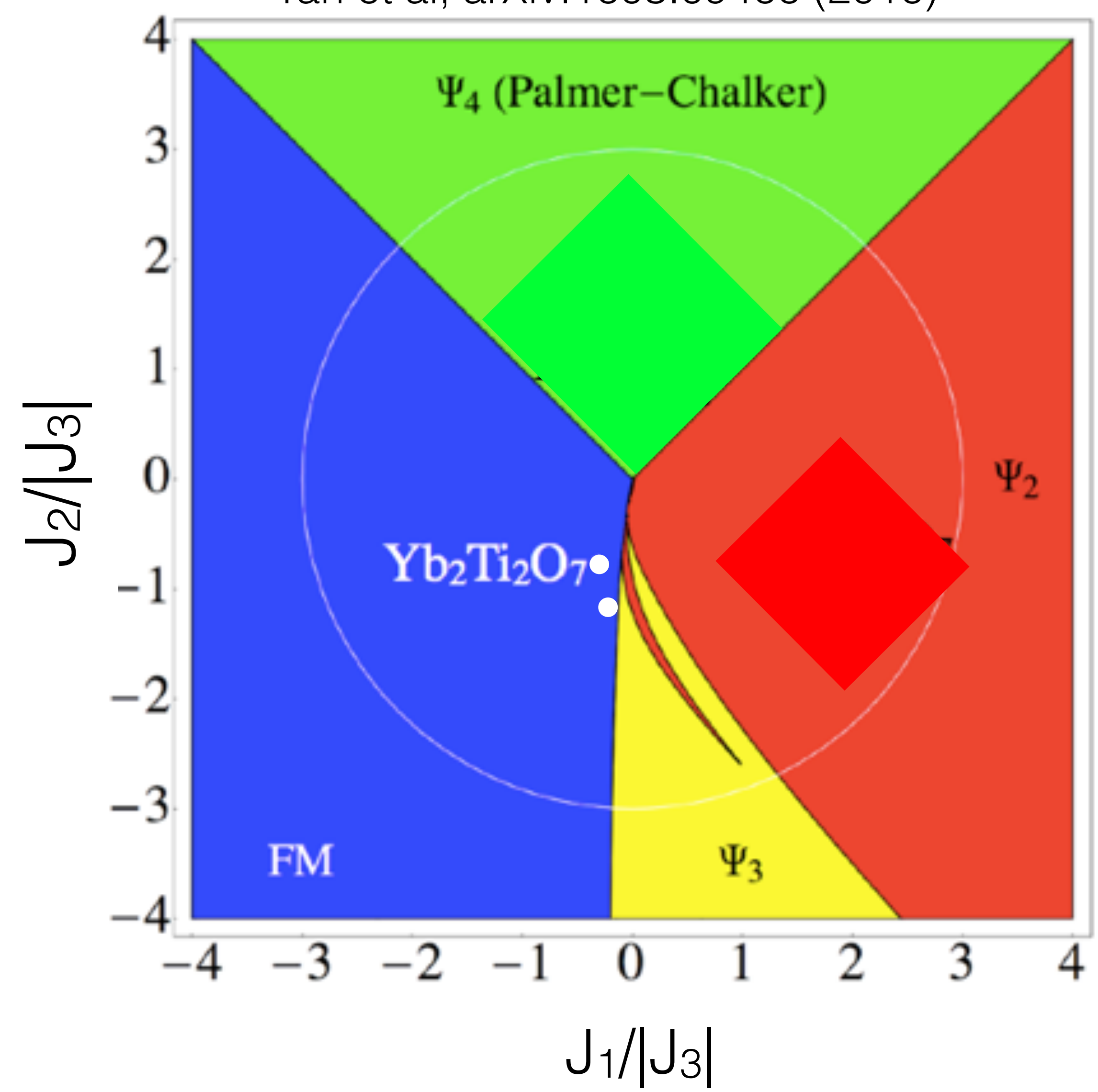


Time-of-Flight Spectrometer
(DCS)

$Yb_2Ti_2O_7$ on phase diagram

- Modified parameters from other groups[1,2] suggest $Yb_2Ti_2O_7$ is right on the edge of AFM order
- Do quantum fluctuations arise from proximity to AFM state, i.e. competing orders?
- **What role does the known sample dependence play?**

Yan et al, arXiv:1603.09466 (2016)



All proposed parameters put $Yb_2Ti_2O_7$ close to a classical phase boundary with AFM order

$J_1 = -0.09, J_2 = -0.22, J_3 = -0.29, J_4 = 0.01$

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

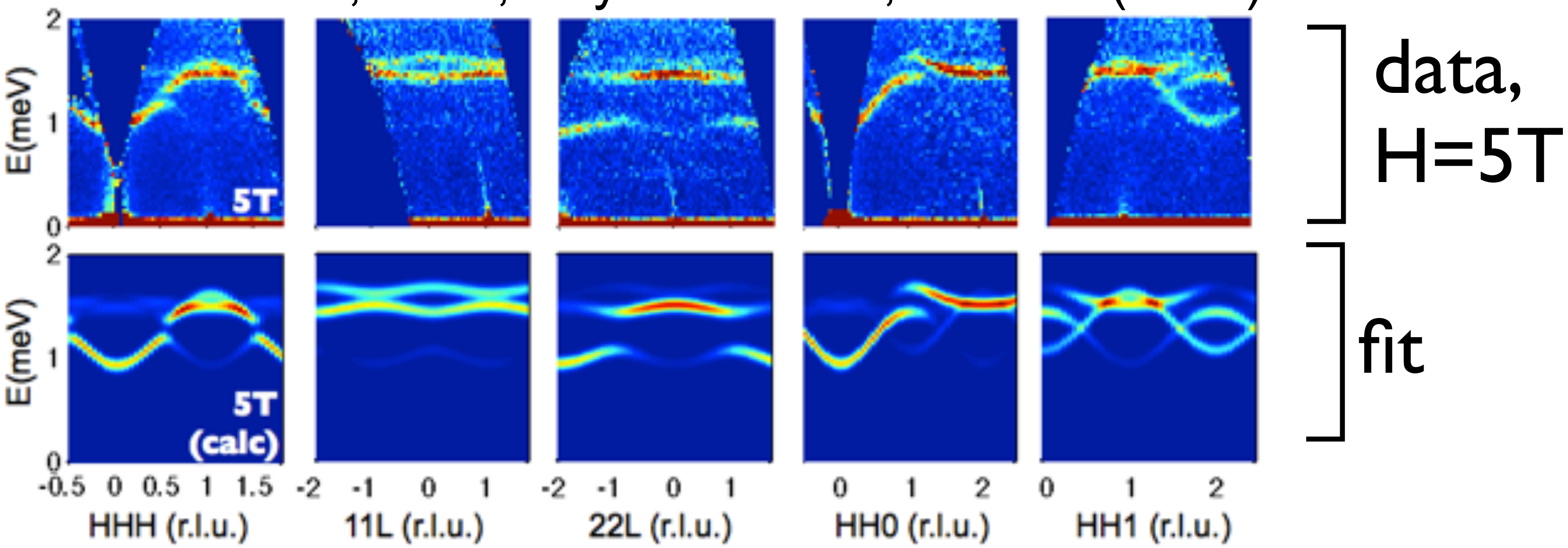
$J_1 = -0.03, J_2 = -0.32, J_3 = -0.28, J_4 = 0.02$

[1] J. Robert, Phys. Rev. B **92**, 064425 (2015)
[2] J. Thompson et al, arXiv:1703.04506 [cond-mat.str-el]

Determining exchange interactions with spin waves from field polarized state

$Yb_2Ti_2O_7$

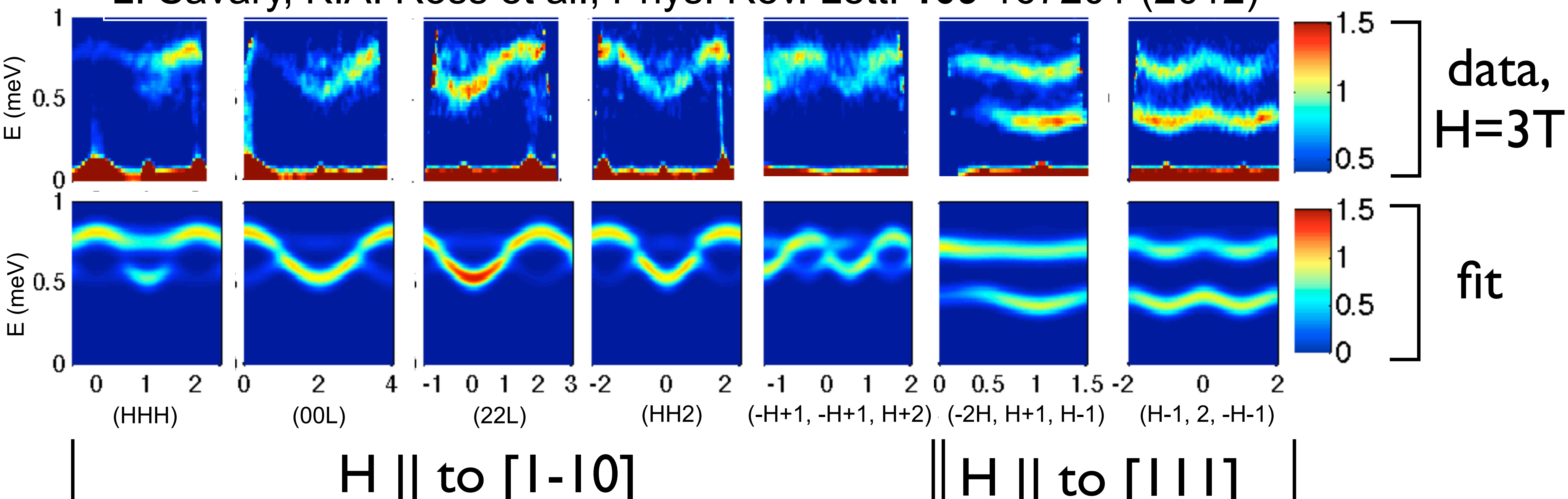
K.A. Ross, et al., Phys. Rev. X **1**, 021002 (2011)



	$Yb_2Ti_2O_7$	$Er_2Ti_2O_7$
J1	-0.09	0.11
J2	-0.22	-0.06
J3	-0.29	-0.10
J4	0.01	0.00

$Er_2Ti_2O_7$

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



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Params lead to "Order by Disorder"

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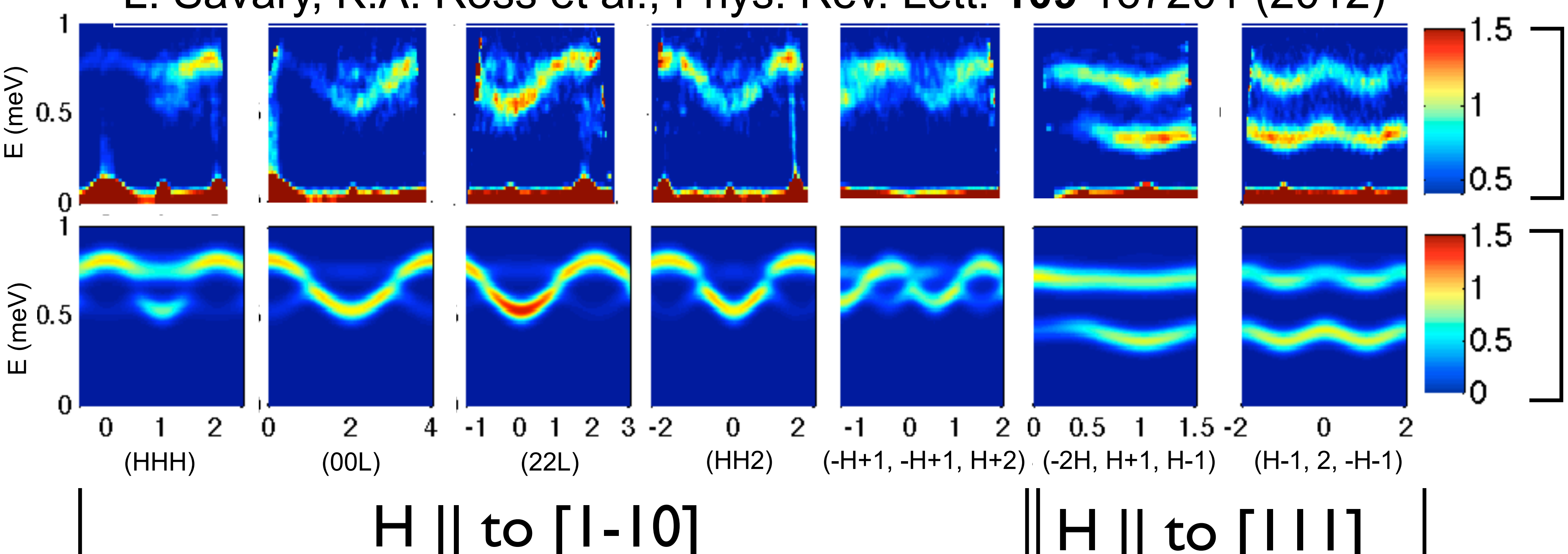
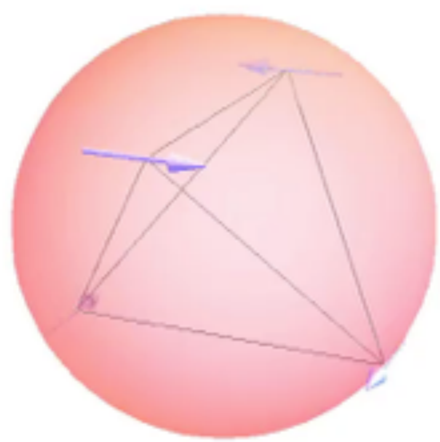
L. Savary, K.A. Ross et al., Phys. Rev. Lett. **109** 167201 (2012)



Determining exchange interactions with spin waves from field polarized state



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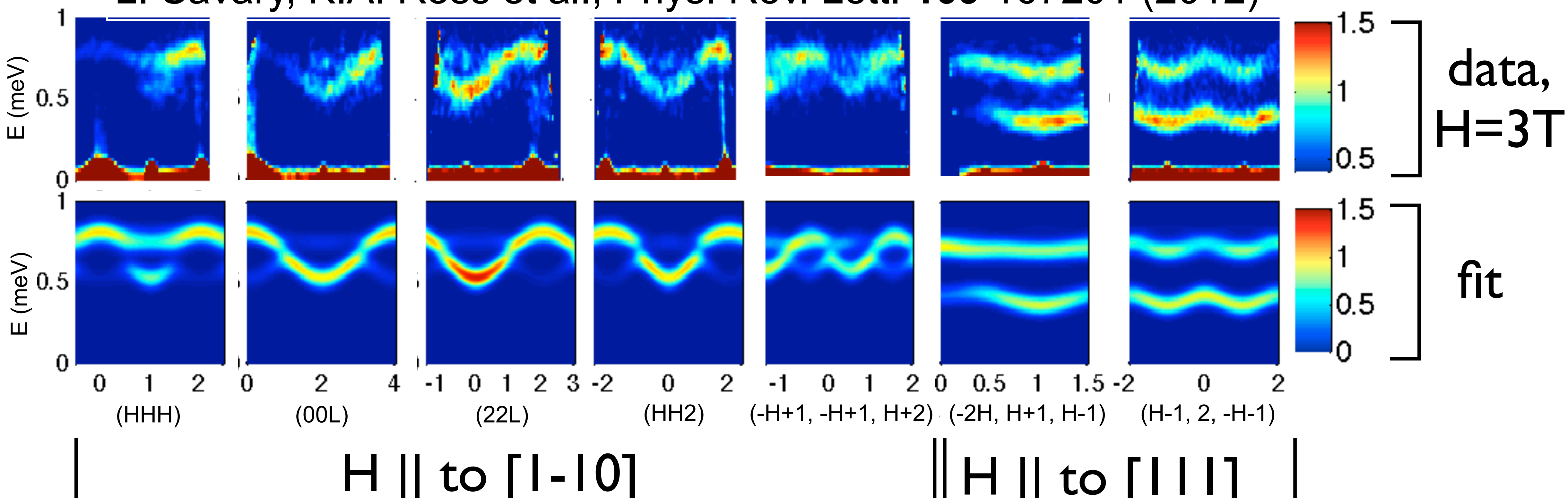
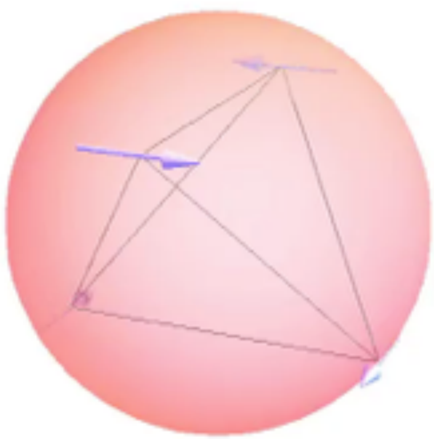


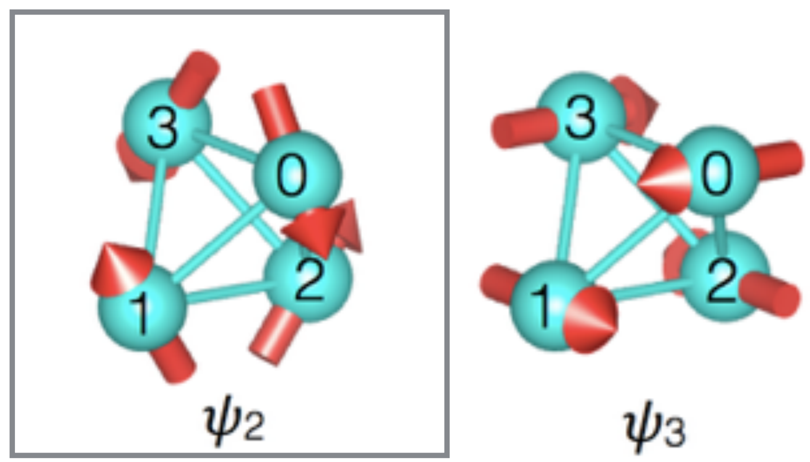
Determining exchange interactions with spin waves from field polarized state

***Γ*₅ manifold:**

Accidentally Degenerate



ψ_2 basis state selected by thermal and quantum fluctuations



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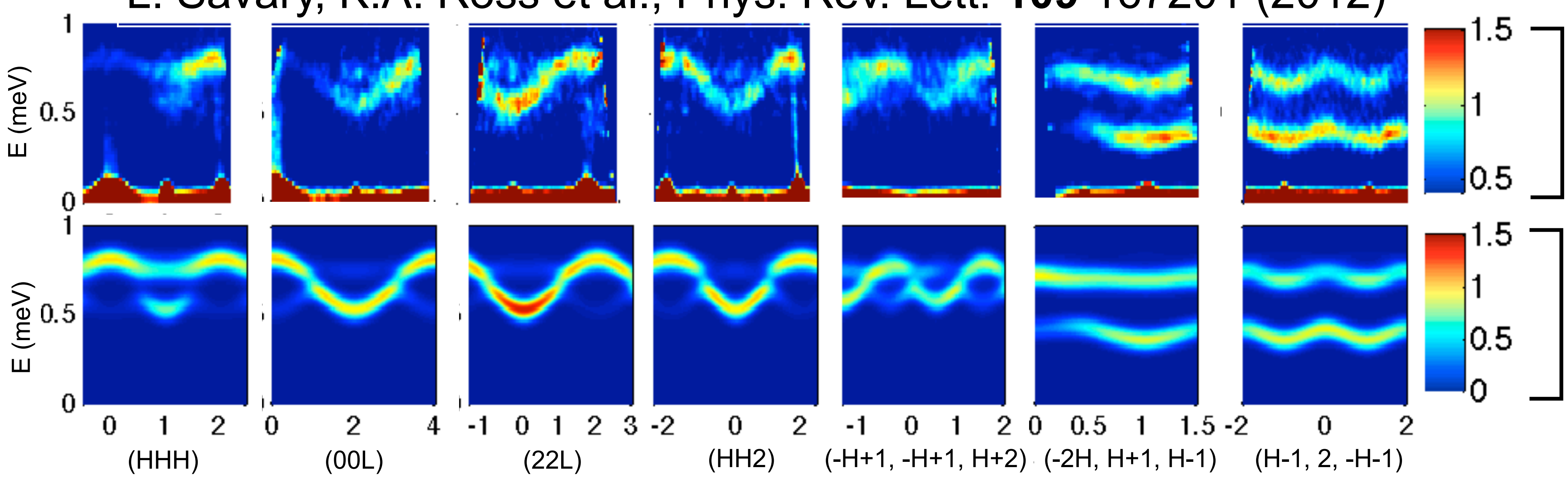
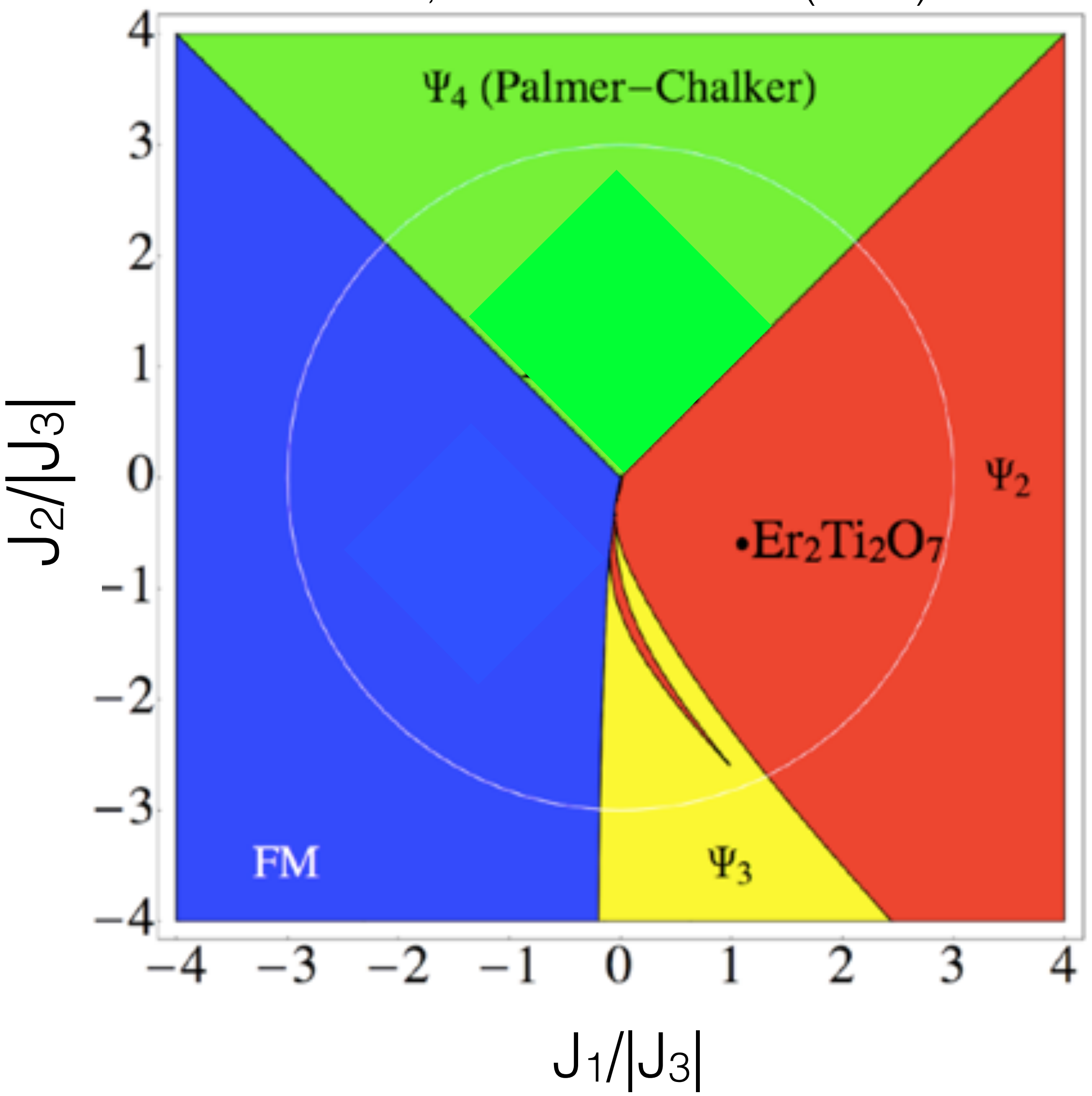


H || to [1-10] | H || to [111]

$Er_2Ti_2O_7$ on phase diagram

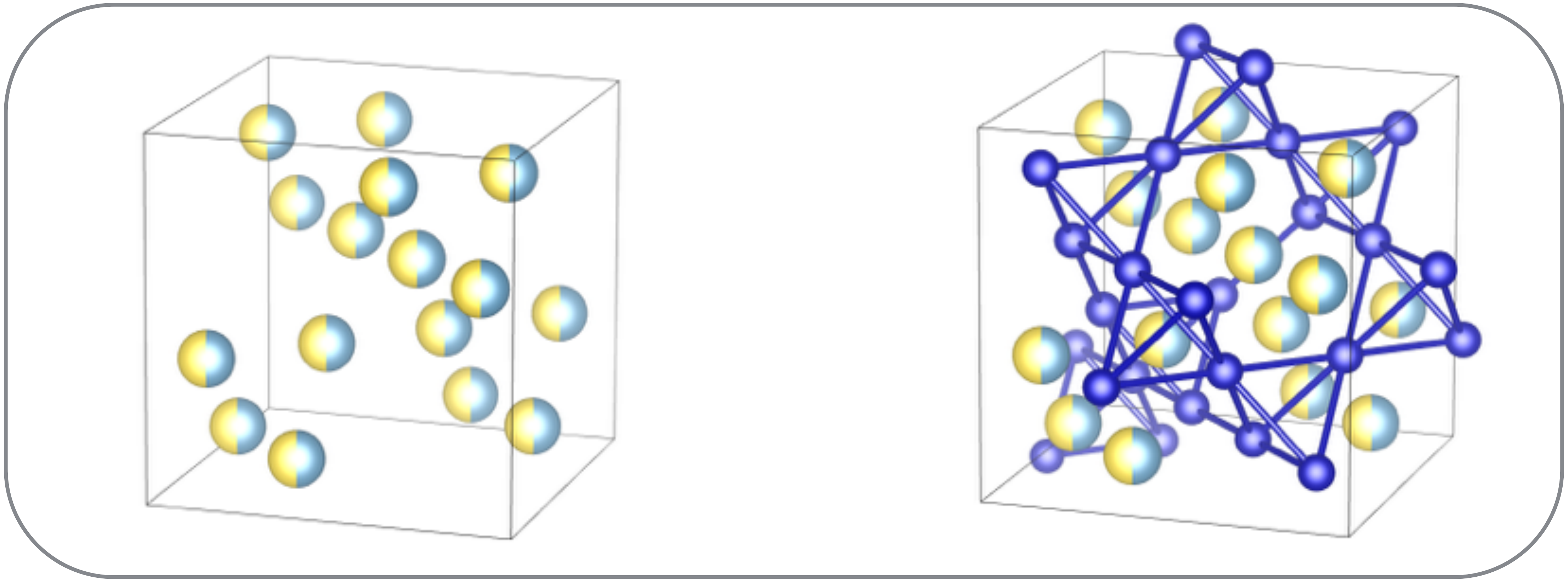
- Classical Monte Carlo agrees and puts $Er_2Ti_2O_7$ squarely inside ψ_2
- **Not as close to the phase boundary**
  - But remember, *thermal* (and quantum) *fluctuations put it there*
- Helps to explain why **no sample dependence** has been observed over the 12 years it's been studied! (despite similar synthesis as $Yb_2Ti_2O_7$)

Yan et al, arXiv:1603.09466 (2016)



$NaCaCo_2F_7$ and $NaSrCo_2F_7$

$A_2B_2X_7$: A = Na/(Ca,Sr), B = Co, X = F

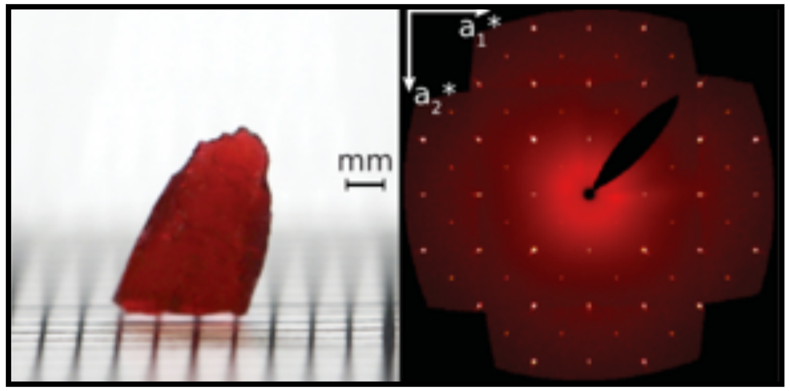


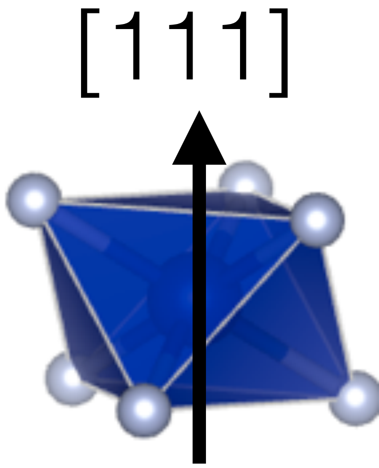
Na^{+}/Ca^{2+} or Sr^{2+}
non-magnetic, disordered site

Co^{2+}
high spin S=3/2, L=3

CEF + SOC

$S_{eff} = 1/2$

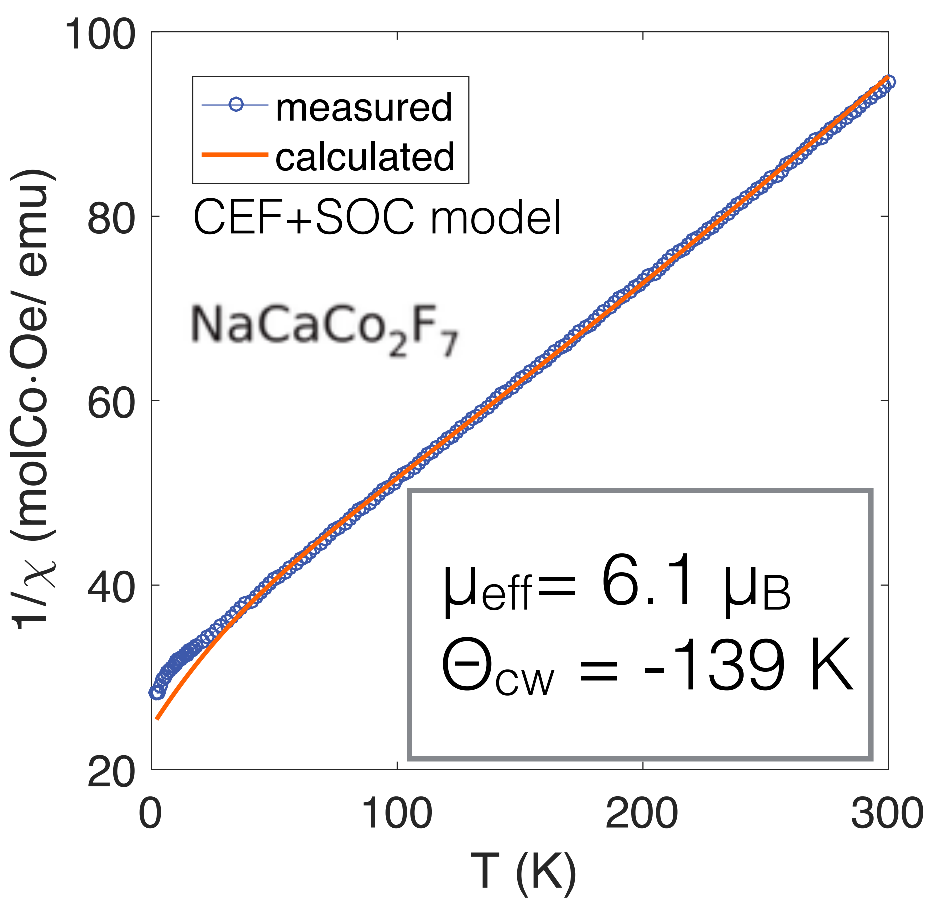




J.W. Krizan, R.J. Cava, PRB **89**, 214401 (2014)

XY AFM pyrochlores with S_{eff} = 1/2

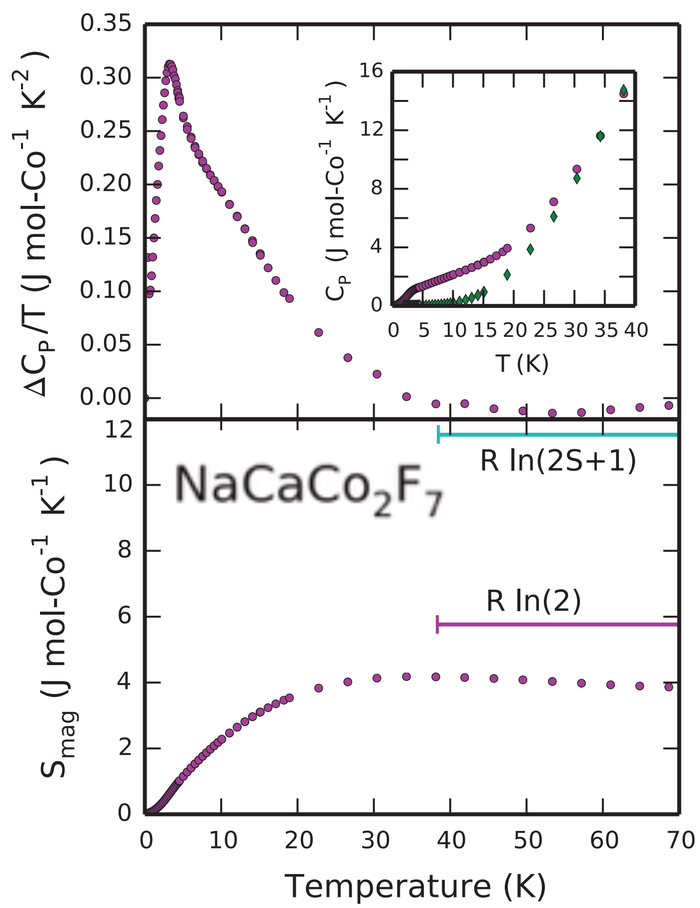
Strong AFM interactions



Single ion analysis:
K.A. Ross, et al,
PRB 95 (2017)

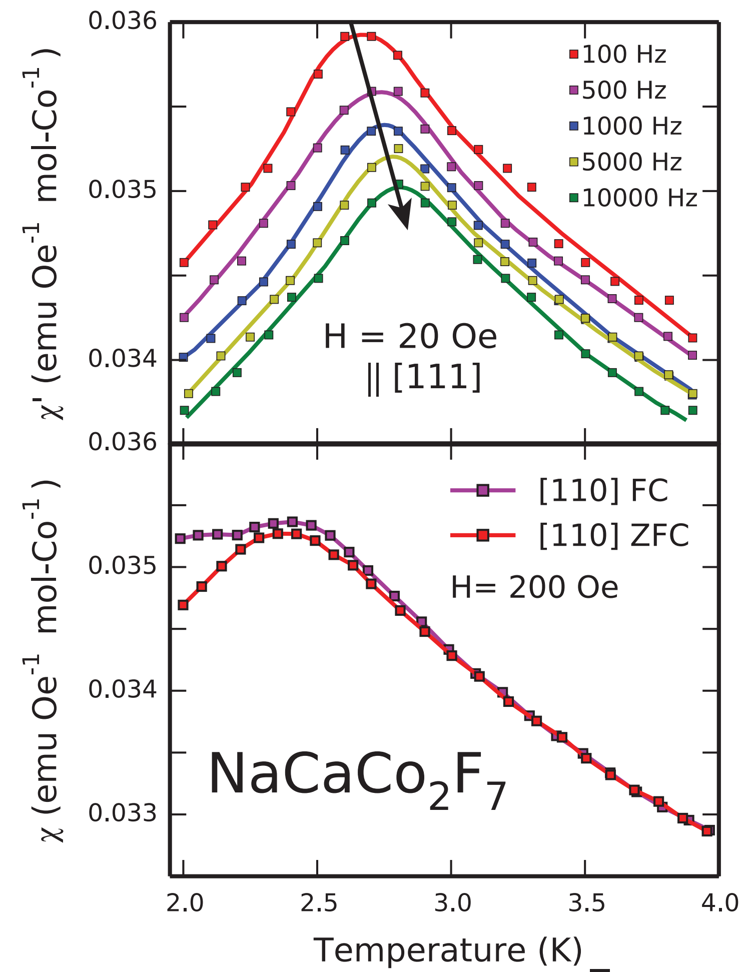
Broad feature in C_p

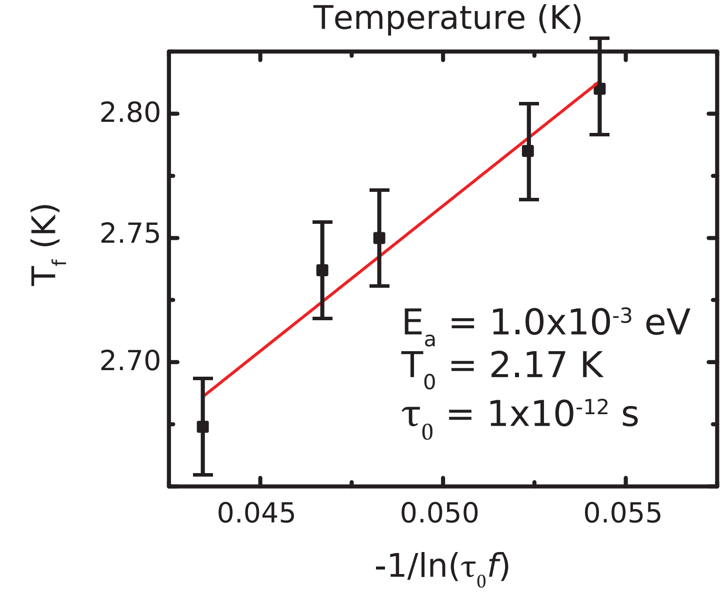
Releases Rln(2) entropy



Crystal growth and thermodynamics:
J.W. Krizan, R.J. Cava,
PRB **89**, (2014)

Spin freezing at T_F = 2.4 K



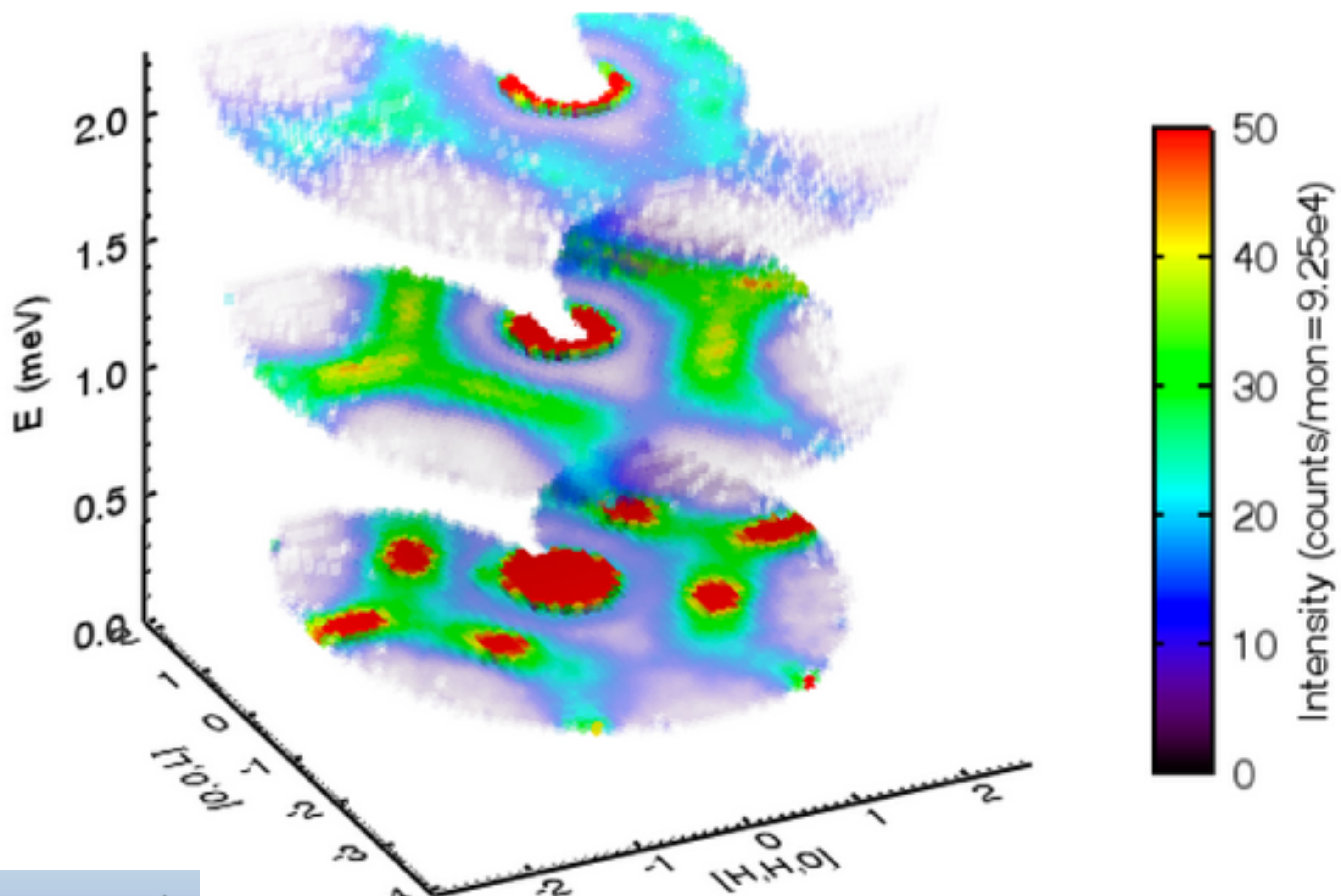


Neutron scattering from frozen state

zig-zag pattern persists to finite energies

It is telling us about the **low energy fluctuations** in the **thermal spin liquid state**

- With **MACS**, we build up S(**Q**,w) using constant energy slices
- Can we interpret the **Q** dependence of finite energy slices?
- **Fourier components of spin fluctuations** away from static configuration

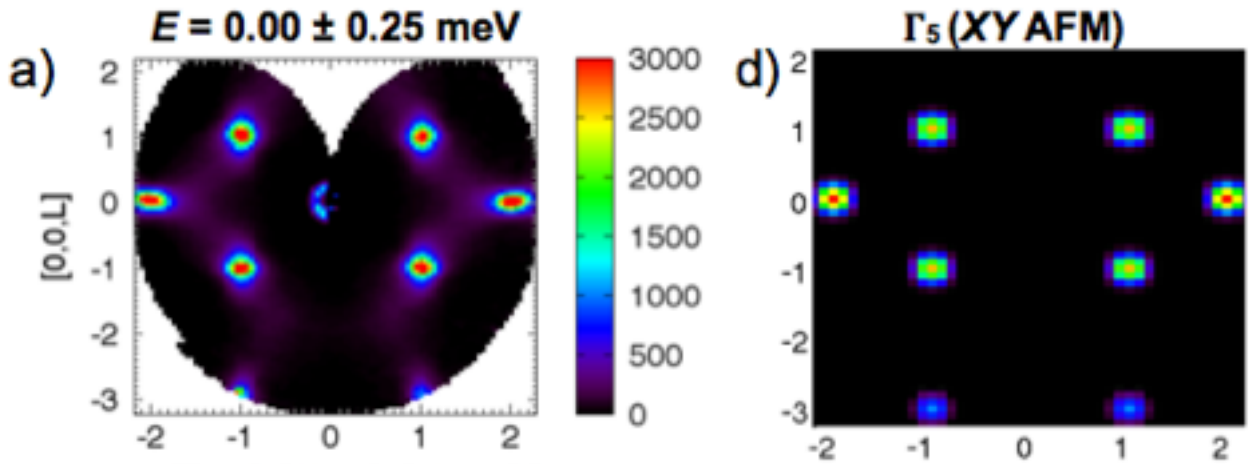


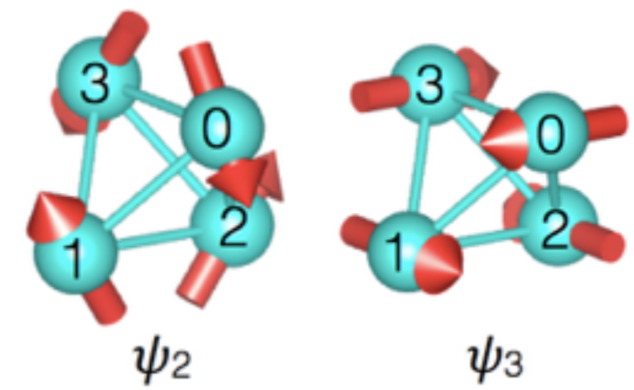
$$\mathcal{S}^{\alpha\beta}(\mathbf{Q},\omega) \equiv \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t}\,\frac{1}{N}\sum_{ll'} e^{i\mathbf{Q}\cdot(\mathbf{r}_l-\mathbf{r}_{l'})}\left\langle S_l^{\alpha}(0)\,S_{l'}^{\beta}(t)\right\rangle$$

T = 1.7K

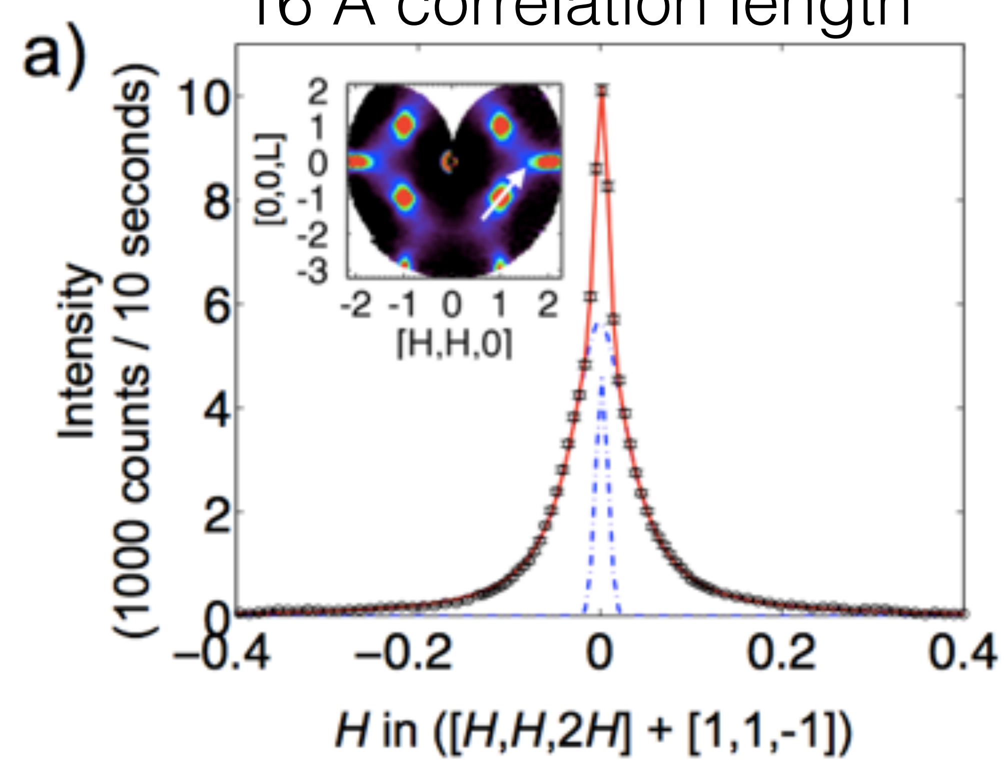
Inelastic scattering in frozen state

Same manifold of states as $Er_2Ti_2O_7$!





16 Å correlation length



MACS spectrometer NCNR

Ross,et al.. Phys. Rev. B 93, 014433 (2016)

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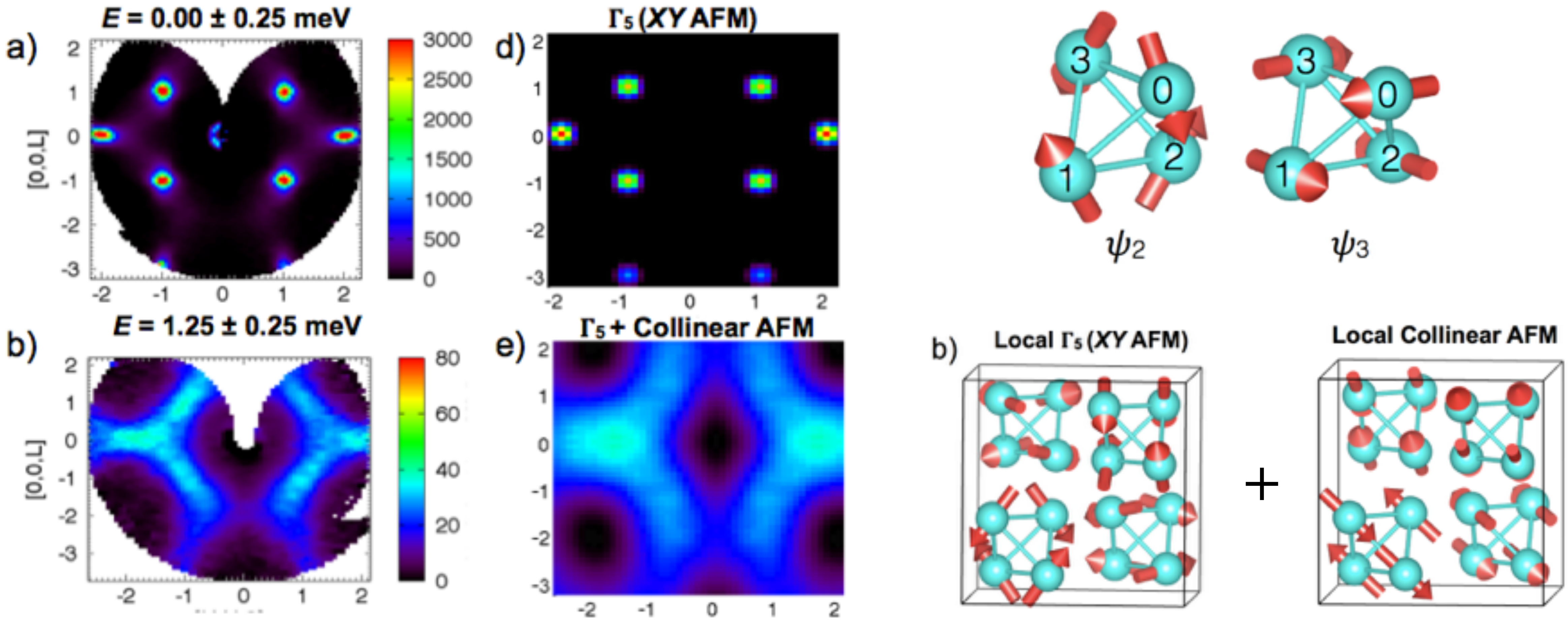

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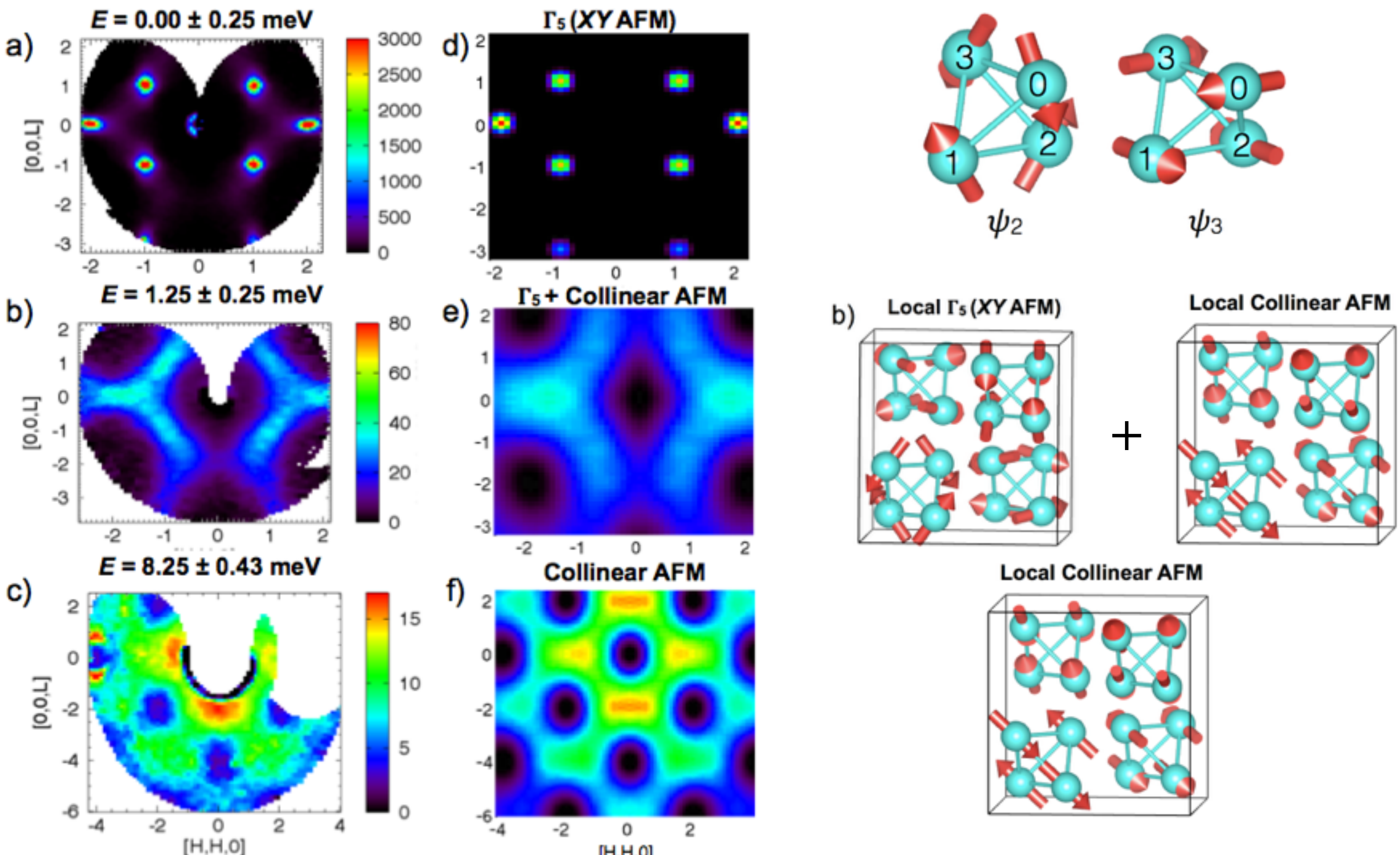
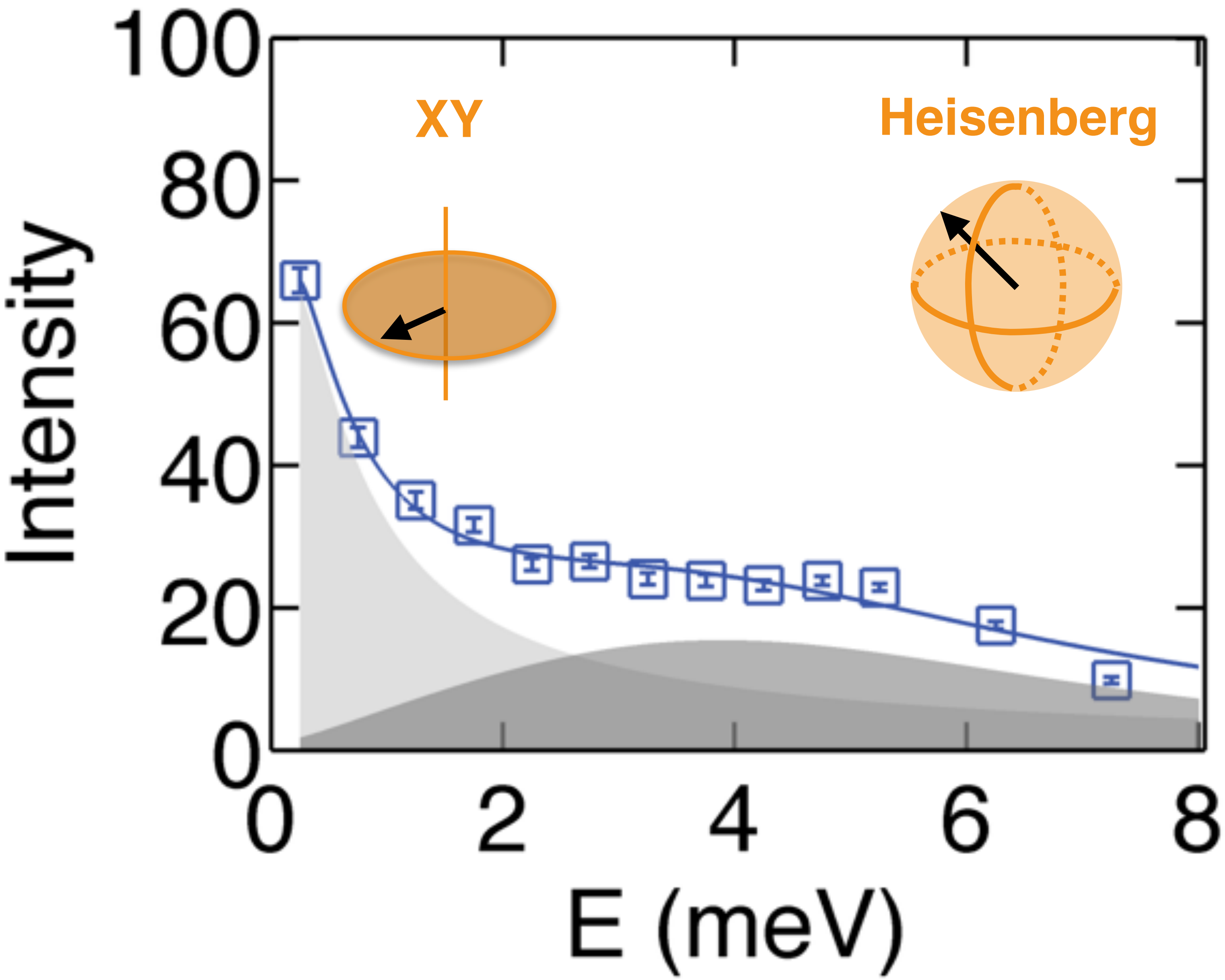


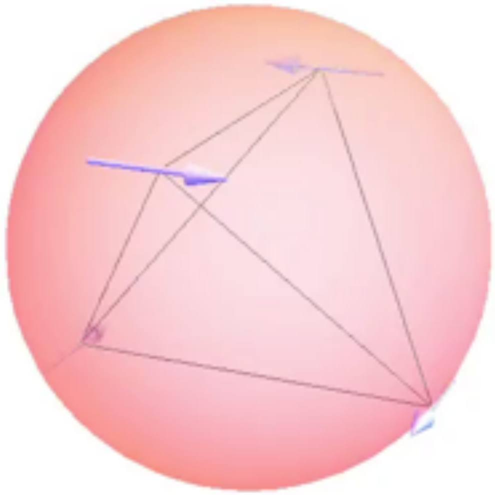
MACS spectrometer NCNR

Ross,et al.. Phys. Rev. B 93, 014433 (2016)

Damped Spin Excitations



- XY clusters relax slowly: explore the continuous manifold



- Crossover to **Heisenberg local mode** at 5.5 meV

Ross,et al.. Phys. Rev. B 93, 014433 (2016)

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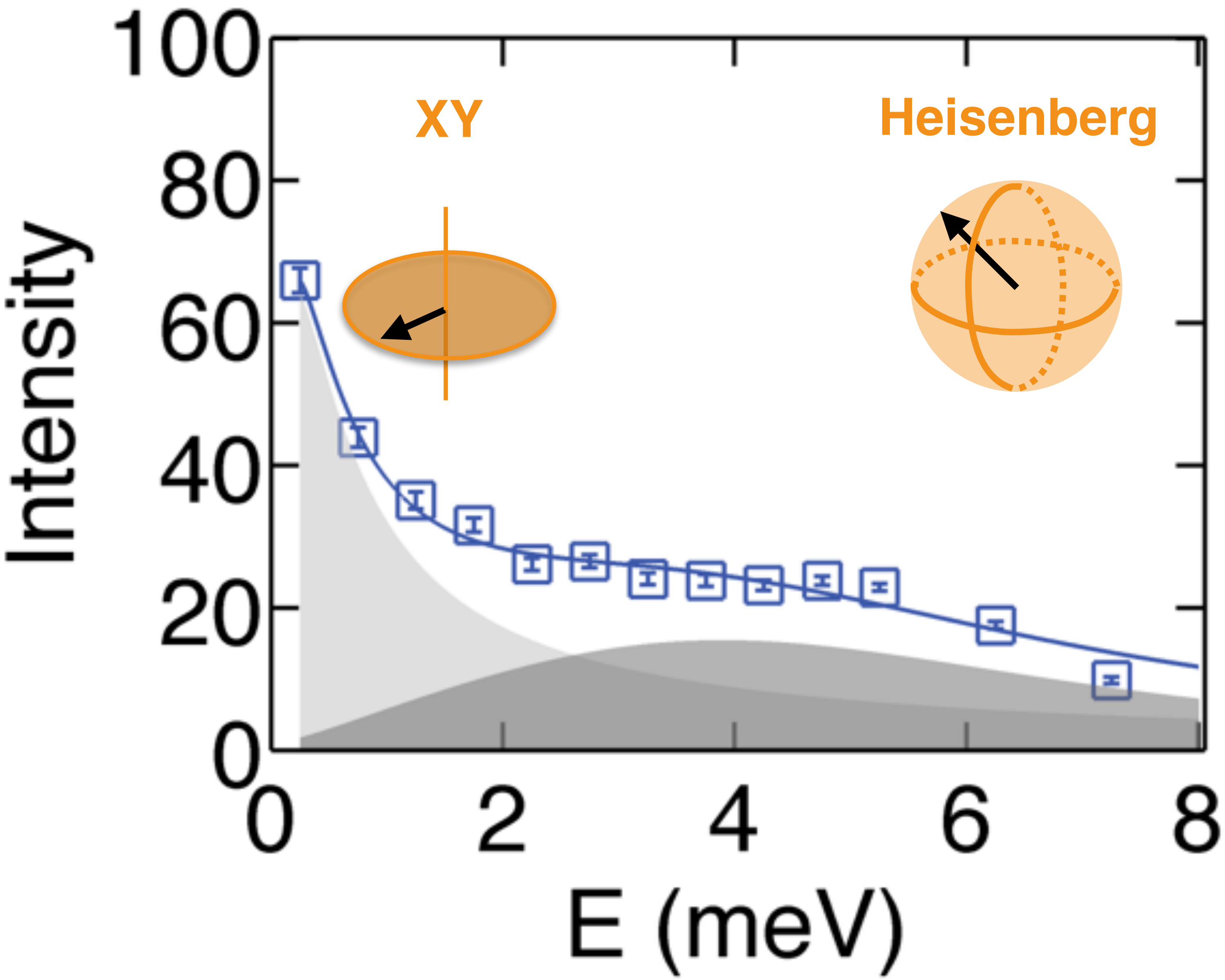

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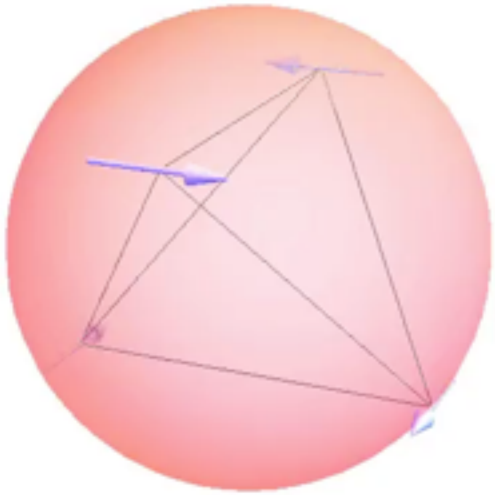

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Ross,et al.. Phys. Rev. B 93, 014433 (2016)

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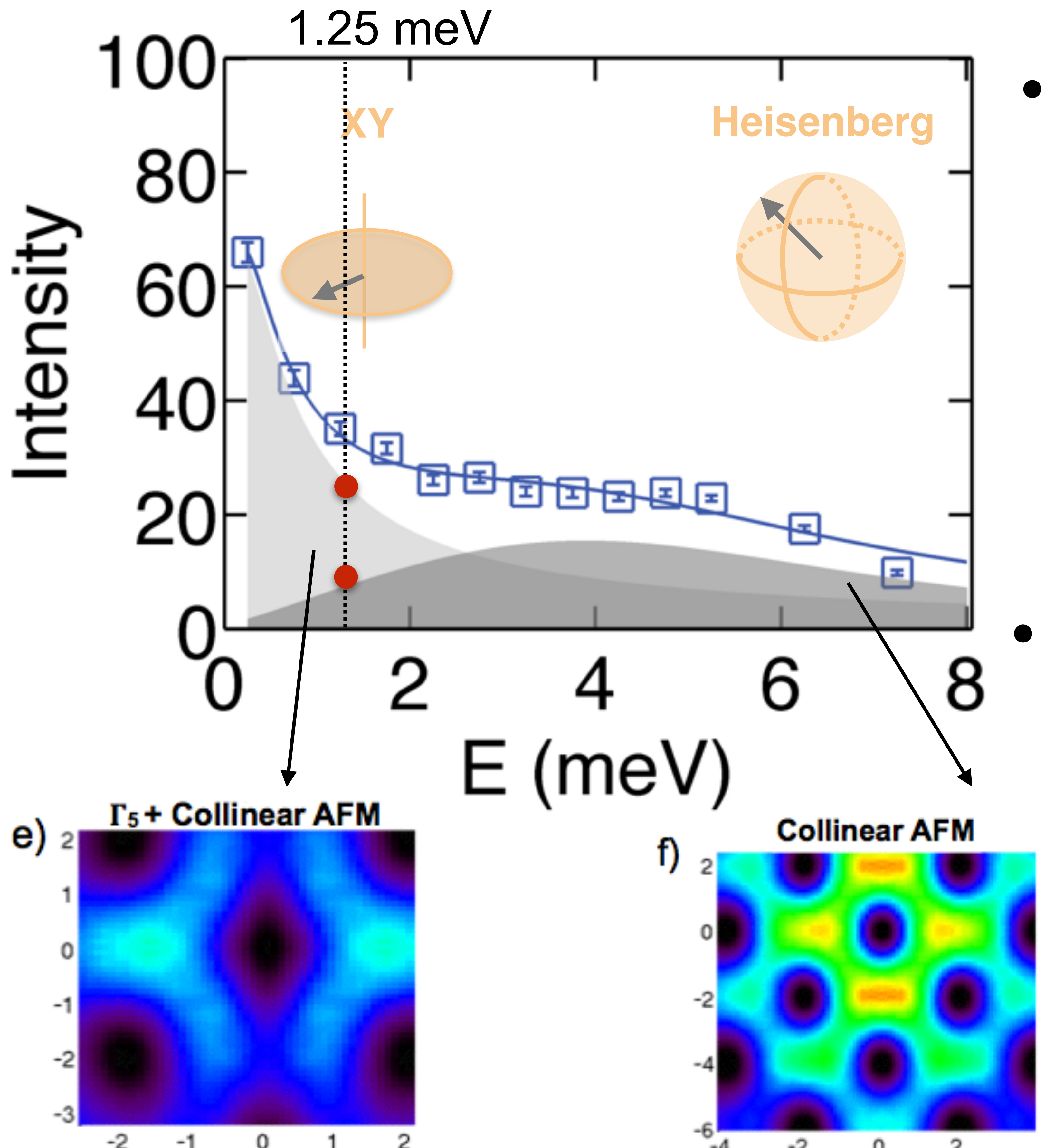

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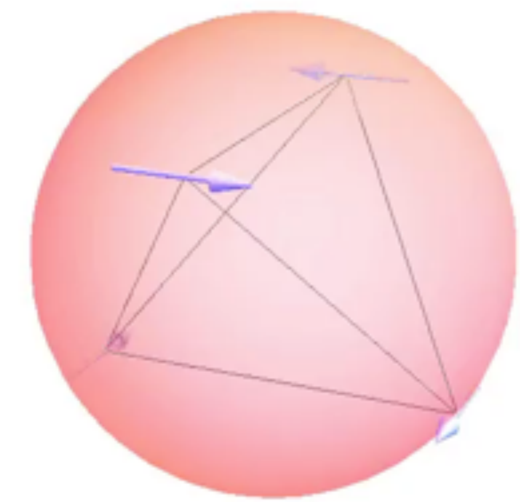

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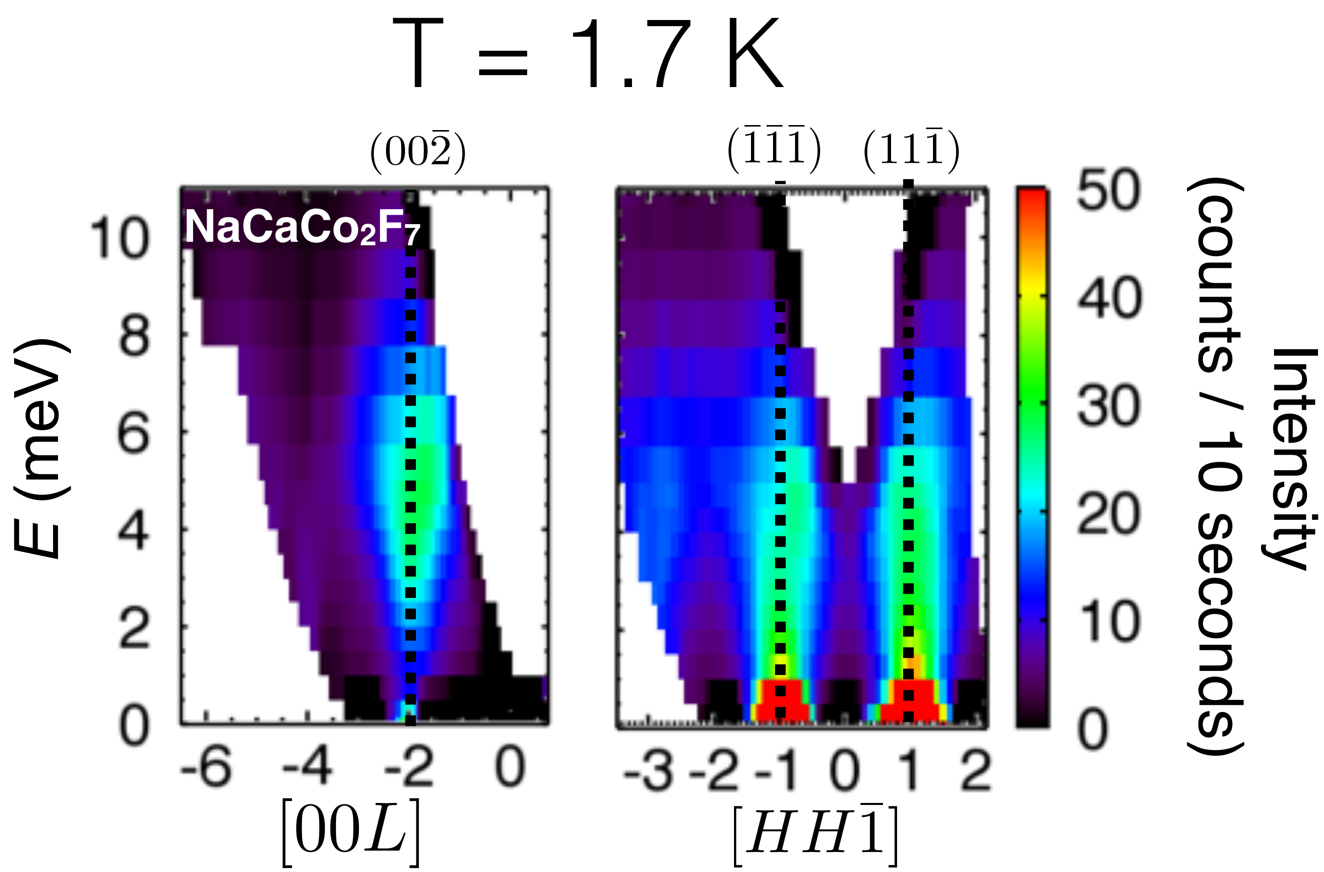
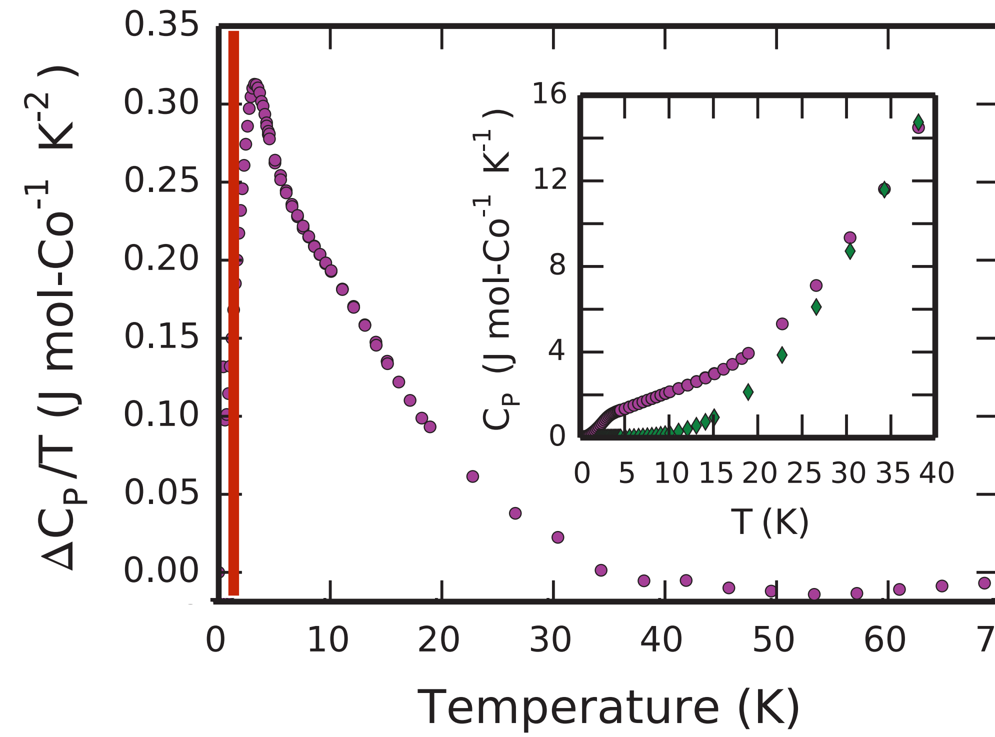
Ross,et al.. Phys. Rev. B 93, 014433 (2016)

Above T_F, thermal spin liquid



- **Broad excitations** consistent with strongly correlated paramagnet
- Above T_F, Thermal spin liquid over range of nearly 140 K
- **Highly *frustrated***:
  - $f = \theta_{CW}/T_F = 58$ in $NaCaCo_2F_7$
  - compared to $f = 18$ in $Er_2Ti_2O_7$



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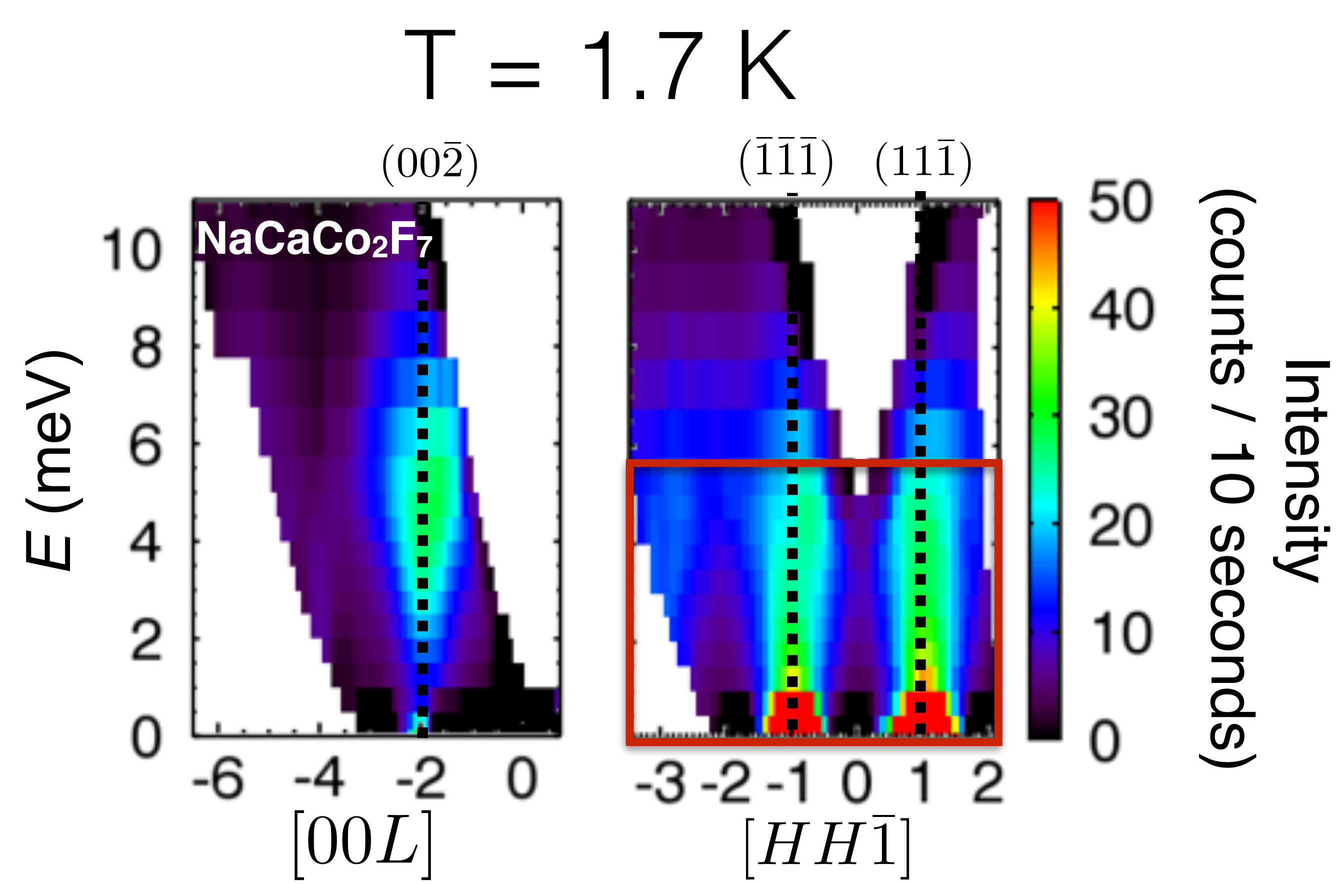

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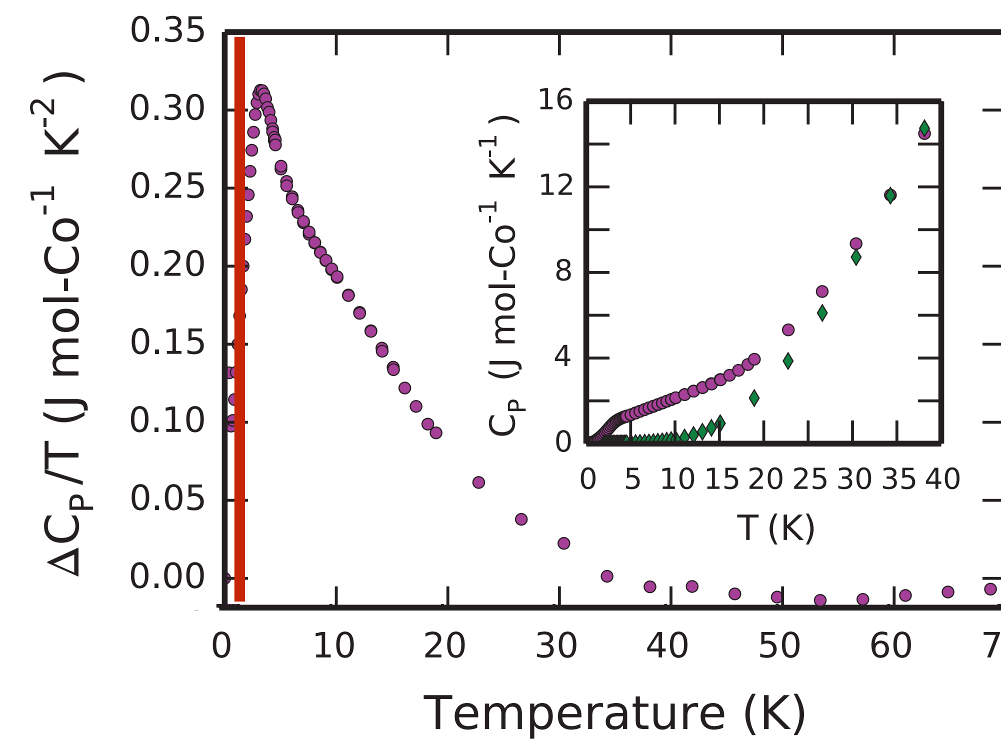

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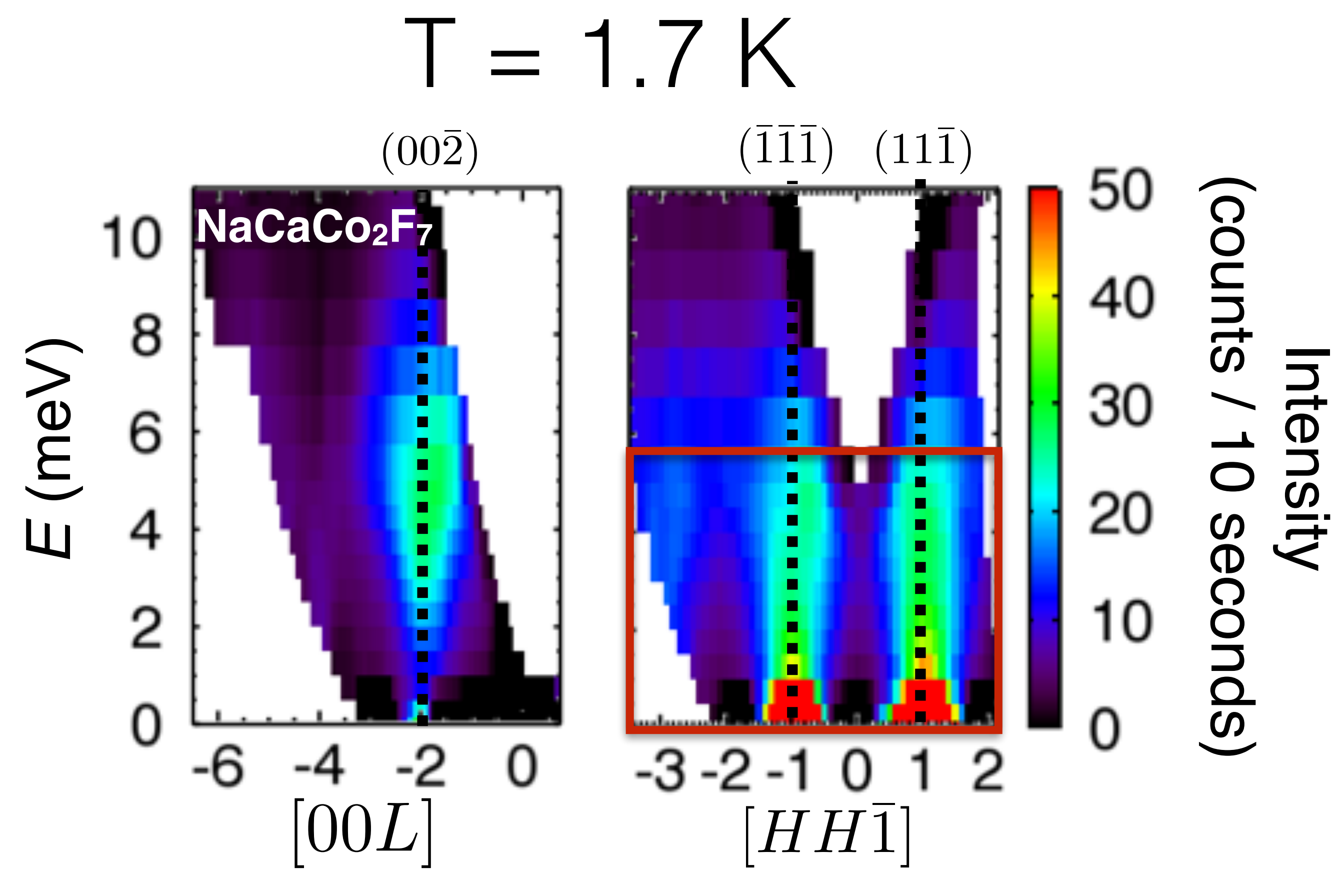

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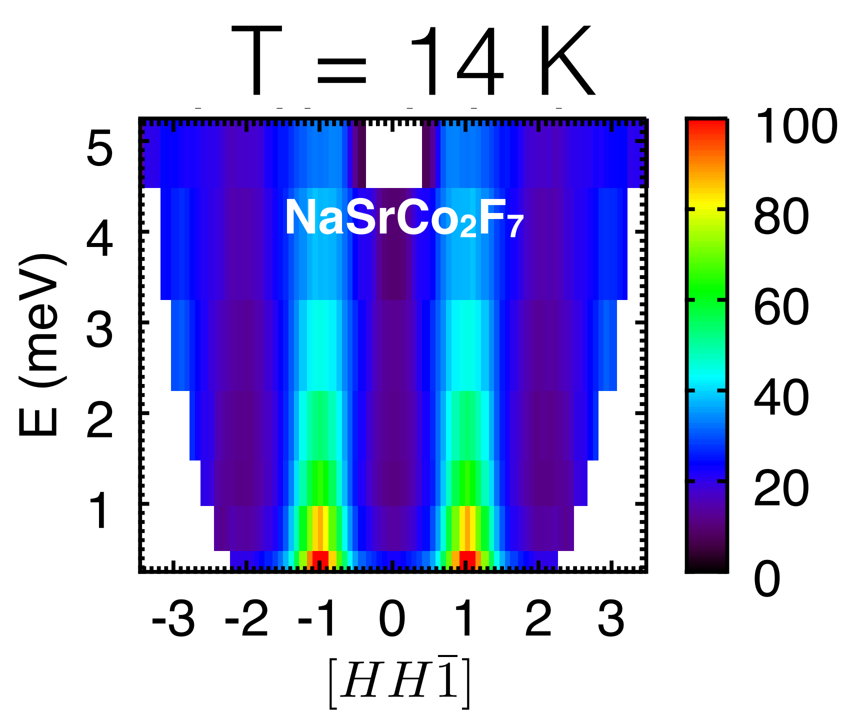
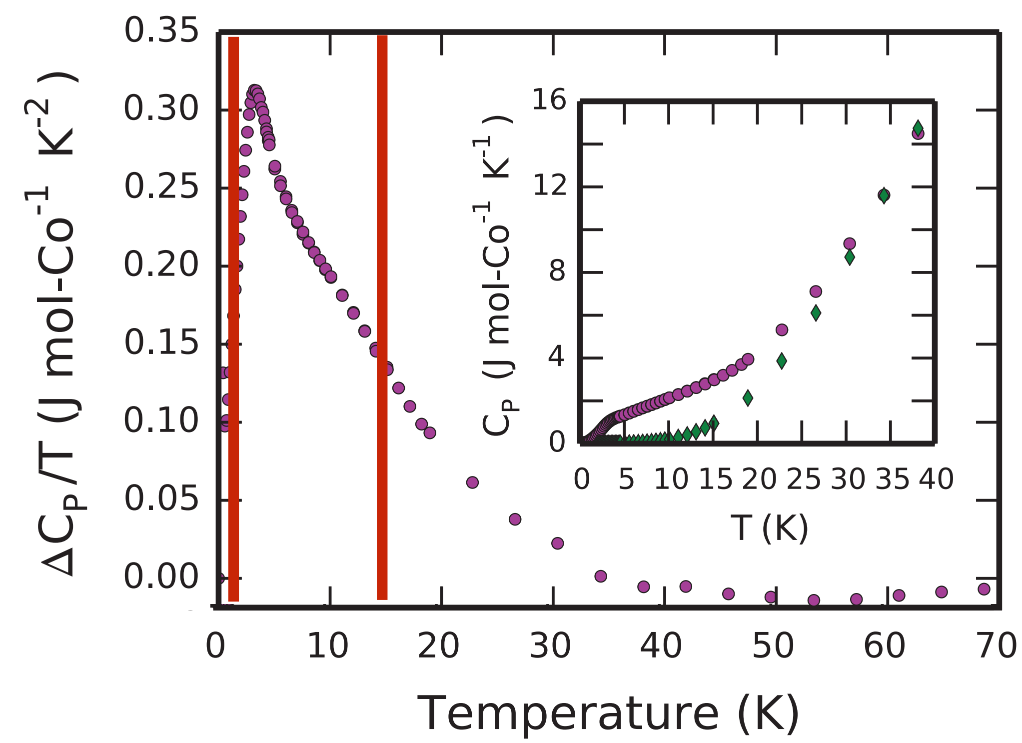
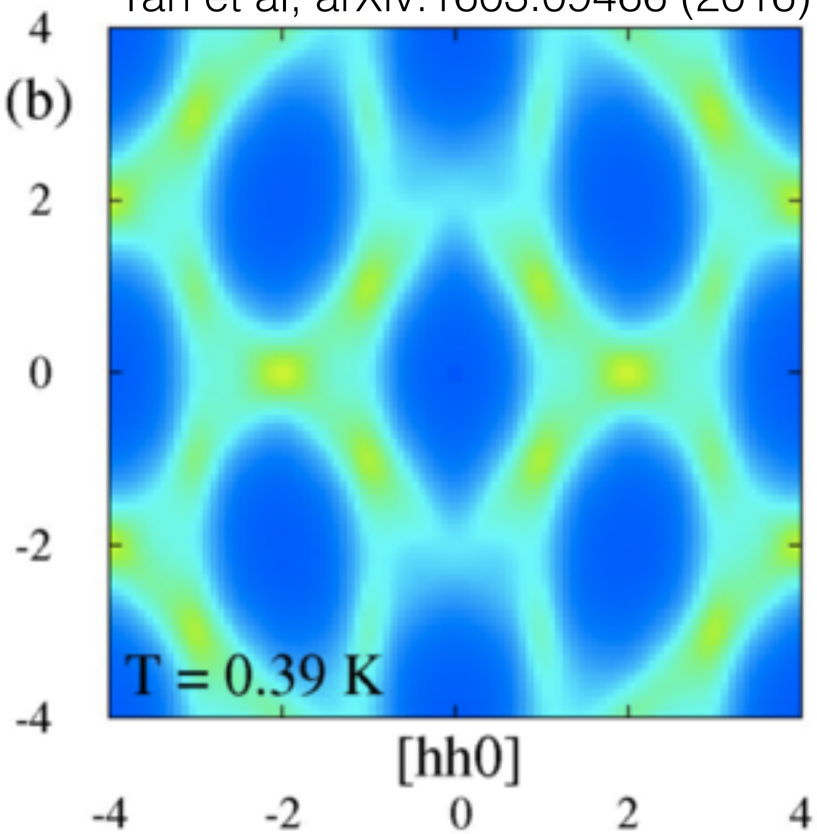




Comparison to Effective-Spin 1/2 Hamiltonian

Yan et al, arXiv:1603.09466 (2016)



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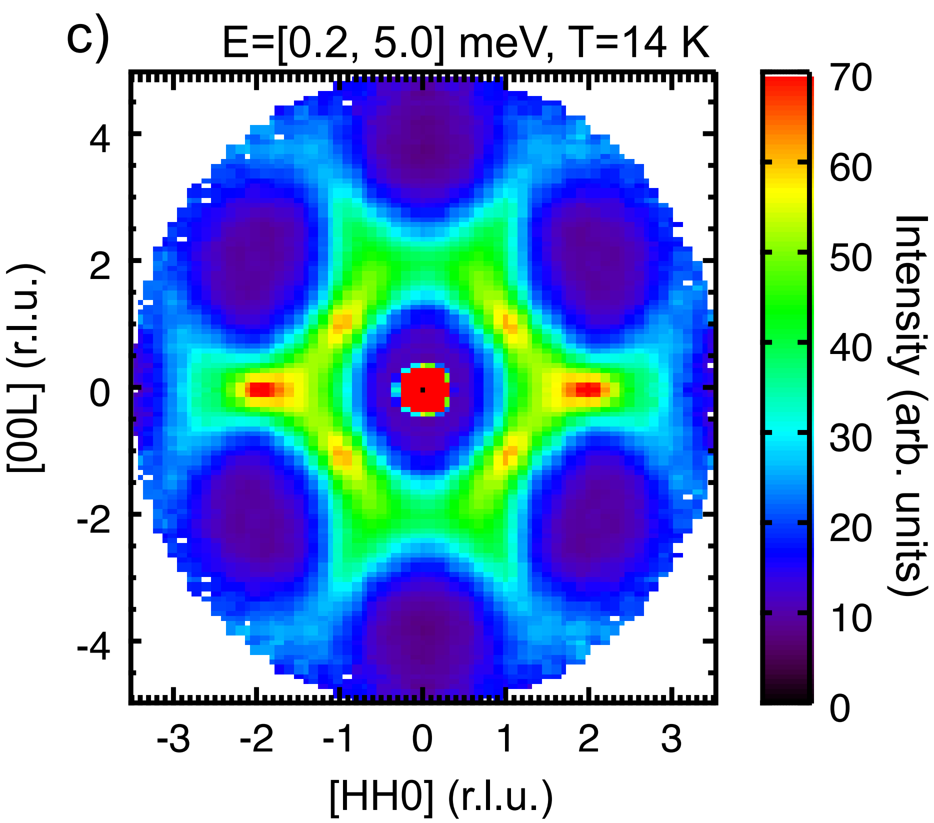
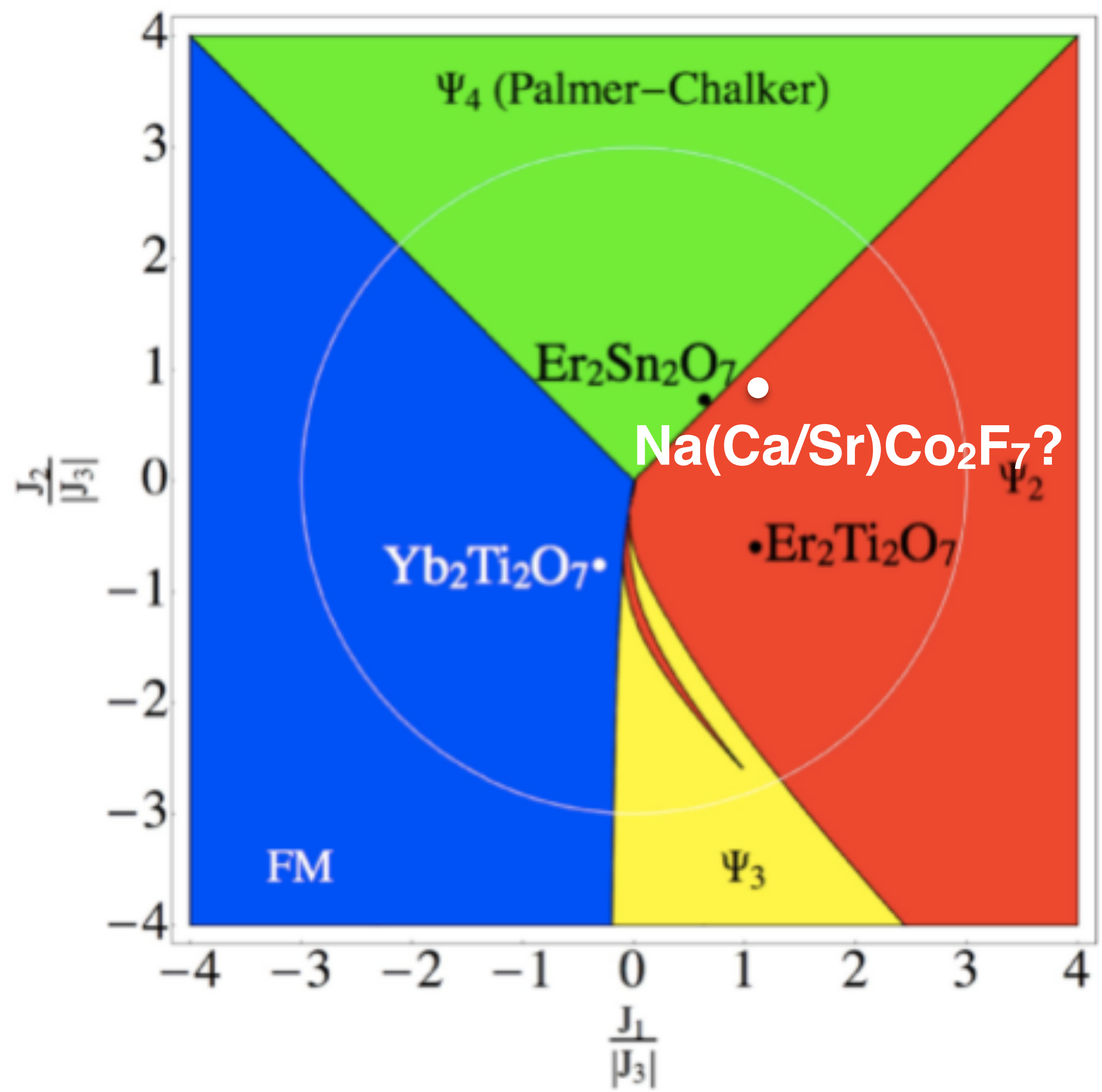


$S_{eff} = 1/2$ with
XY anisotropic exchange



Yan et al, PRB **95**, 094422 (2017)

Summary

- Frustrated pyrochlore materials based on R^{3+} earths and Co^{2+} act as ***effective*** **S=1/2** - the "most quantum" they can be
- The same **spin orbit coupling** effects responsible for establishing S_{eff}=1/2 also lead to **anisotropic exchange**
- A general 4-parameter anisotropic exchange model can be used to describe S_{eff}=1/2 pyrochlores
- **Neutron scattering** allows us to probe the diffuse magnetic scattering and field-polarized spin waves, to extract parameters for real pyrochlores, and understand spin correlations
- **Amazing diversity of ground states** can be understood from the deduced relative positions in the **unified phase diagram**
- **MACS, DCS, SPINS** - cold neutron spectrometers used for these studies

Thanks to…

Collaborators

- Bruce Gaulin
- Edwin Kermarrec
- Jonathan Gaudet
- Lucile Savary
- Leon Balents
- Collin Broholm
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- Juscelino Leao
- Jose Rodriguez
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- Yiming Qiu

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- Colorado State University (startup)