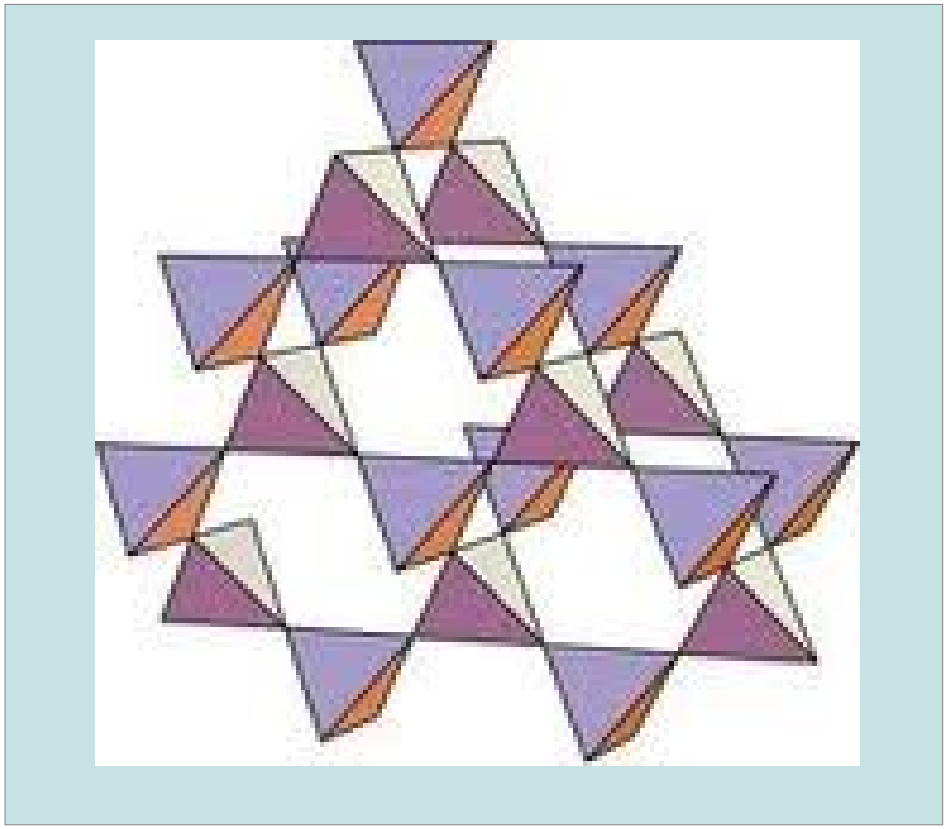
CRETE CENTER FOR QUANTUM COMPLEXITY AND NANOTECHNOLOGY

UNIVERSITY OF BIRMINGHAM

$Er_2Ti_2O_7$
A fight between crystal fields and quantum fluctuations

Amy Briffa, R.J. Mason, M.W. Long



Pyrochlore lattice
Image by Balents group

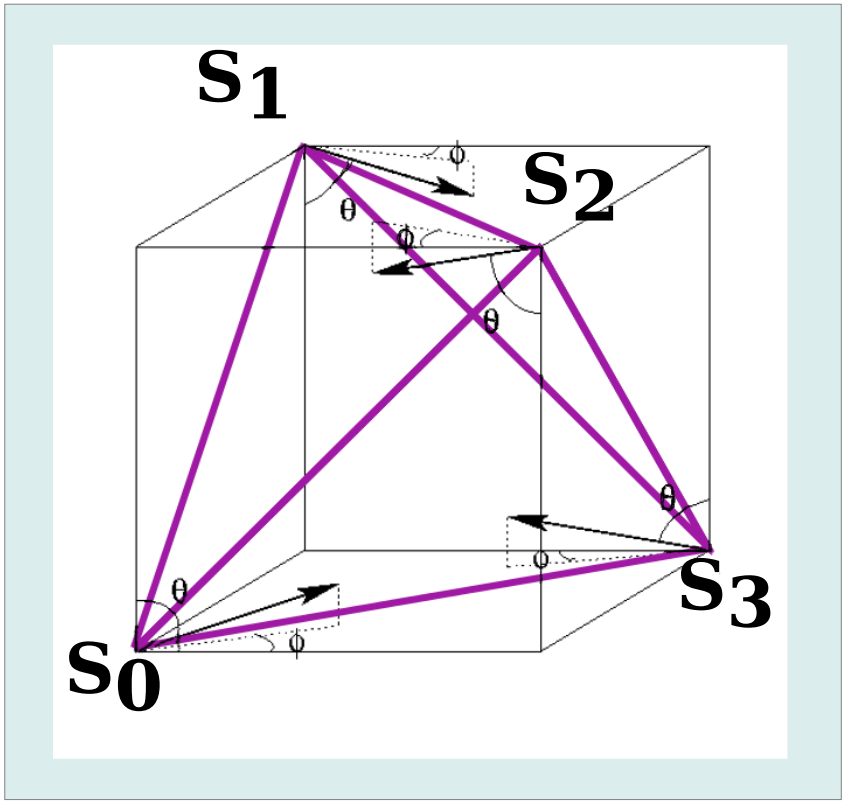
Overview

(1) Introduction to frustration in rare-earth pyrochlores

(2) Long-range ordering and the gapless spin-wave mode

(3) Semi-classical spin-wave model via a minimal pseudo-spin projection

(1) Frustration on the pyrochlore lattice



Heisenberg model

$$H = \frac{1}{2}\sum_{jj\prime} J_{jj\prime}\mathbf{S}_j \cdot \mathbf{S}_{j\prime}$$

$$= 2J_0 \sum_t \mathbf{T} \cdot \mathbf{T}$$

$$\mathbf{T} = \frac{1}{2}\left[\mathbf{S}_0 + \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3\right]$$

Alternatively consider degeneracy in reciprocal space...

Block transforming to k-space gives

$$H = \frac{1}{2}\sum_{jj\prime} J_{jj\prime}\mathbf{S}_j \cdot \mathbf{S}_{j\prime} = \sum_{\mathbf{k}} \mathbf{S}^*_{\mathbf{k}}.\mathbf{S}_{\mathbf{k}} J(\mathbf{k})$$

Ground state minimises Structure factor: J(k)

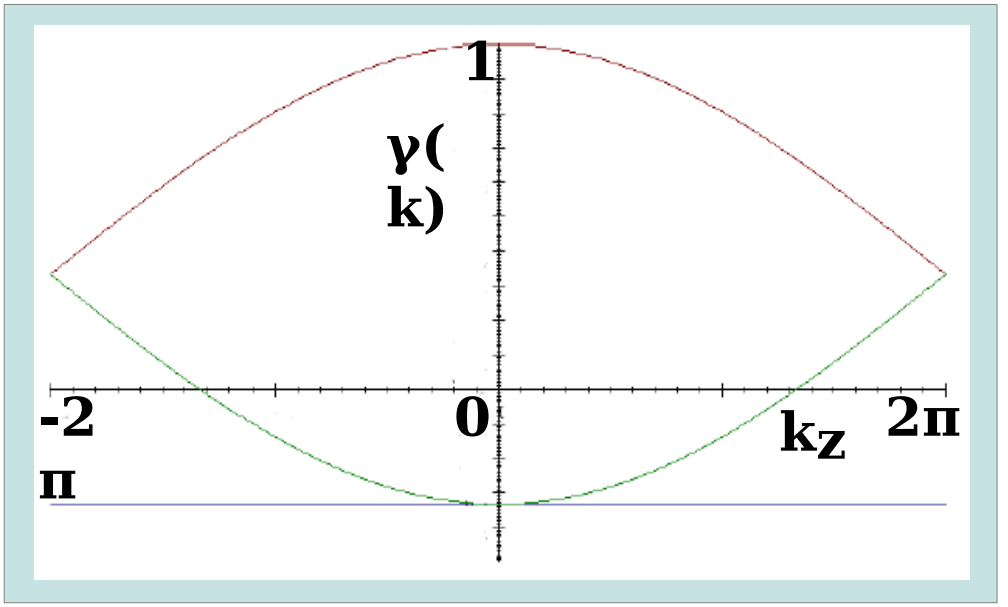
But n.n. Heisenberg on a pyrochlore lattice has **huge degeneracy**

$$J(\mathbf{k}) = \sum_s J_s Z_s \gamma_s(\mathbf{k}) \qquad \gamma_s(\mathbf{k}) = \frac{1}{Z_s}\sum_{\langle 0n\rangle_s} e^{i\mathbf{k}.\mathbf{R}_n}$$

Two flat bands

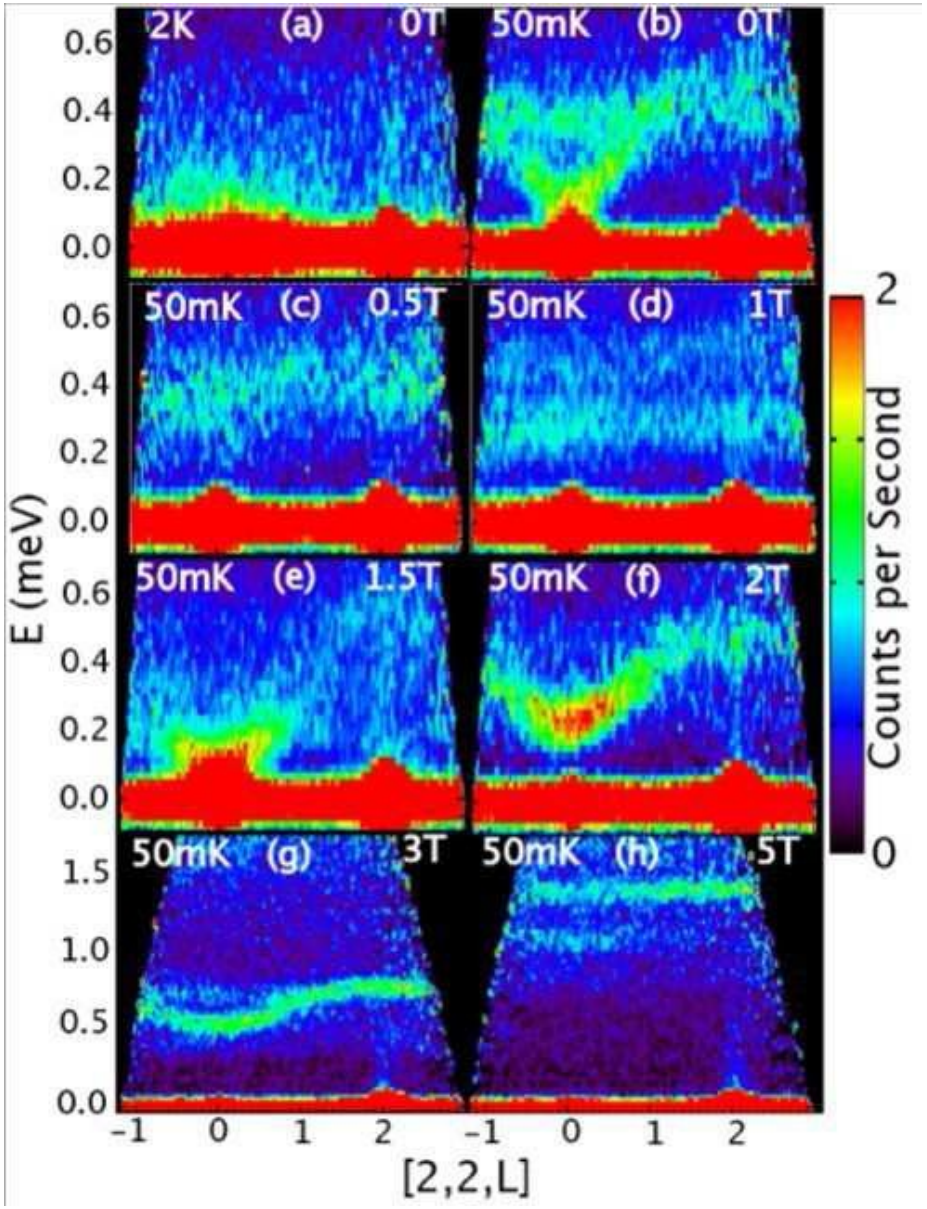
Corresponds to half of k-points

Degeneracy lifted by:
Crystal Field
Dipole interactions
Further neighbour Heisenberg



Plotted for $k_x = k_y = 0$

Why study Erbium Titanate? (Nearly) gapless spin-wave mode



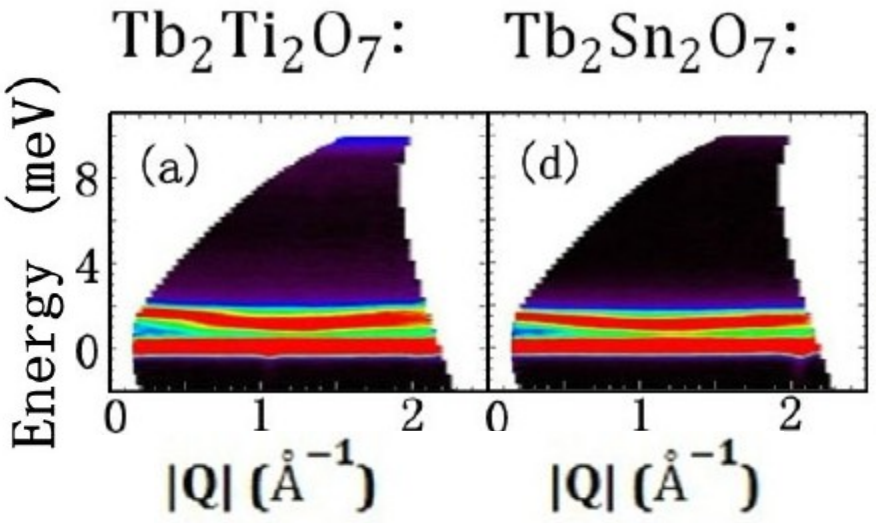
JPC Ruff; PRL **101**, 147205 (2008)

Gap < 0.05 meV

KA Ross; PRL **112**, 057201 (2014)

Compare to terbium pyrochlores

Gap ~ 1 meV



J Zhang; PRB **89**, 134410 (2014)

(2) Long-range magnetic order

Chemistry

Ti^{4+} and O^{2+}: closed shell so zero magnetic moment

Er^{3+}: $[Xe]4f^{11}$ → model as three holes using Hund's rules

S = 3/2 L = 6 J=15/2 16 degenerate J_Z states

Curie-Weiss Θ_C ~ -20K →

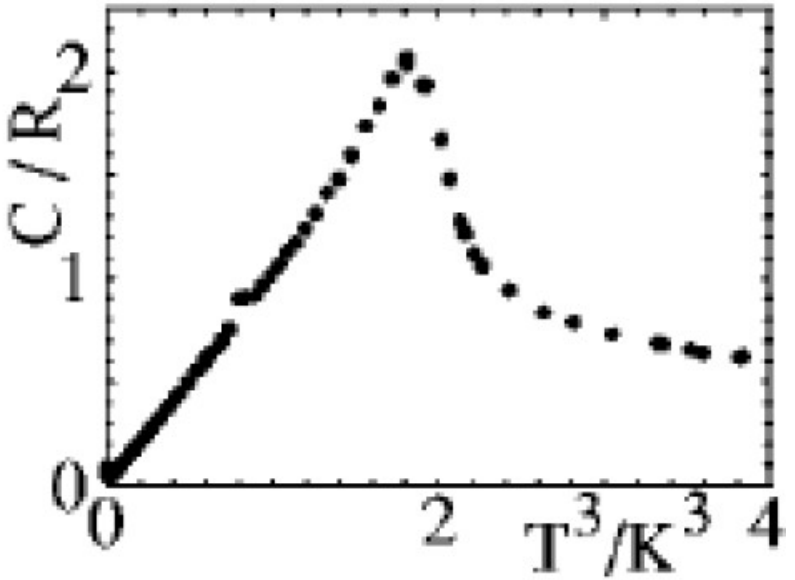
frustrated AFM: T_N = 1.3K

Specific heat linear below T_N

signature of gapless spin-wave

Entropy from transition ~ ln2 →

pseudo-spin ½ low energy effective model



JDM Champion; PRB **68** 020401 (2003)

Elastic powder neutron scattering find **k=0** order with a reduced moment of about 1/3 of theoretical maximum value for Er^{3+}

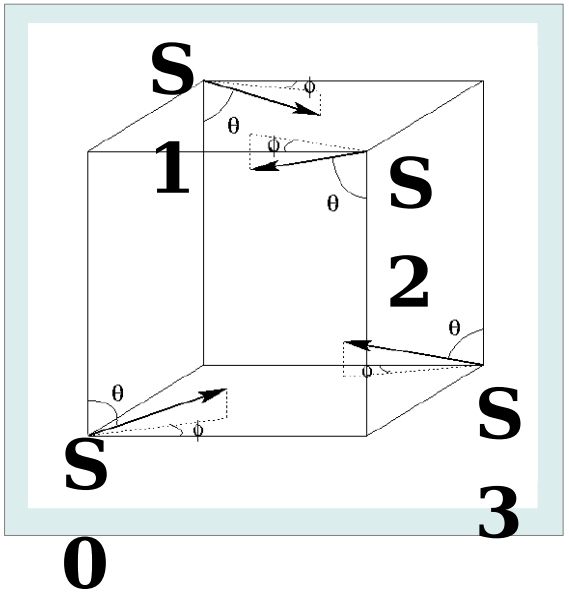
Elastic neutron scattering for pyrochlores

Bragg spot intensity

$$I\left(\mathbf{k}, \mathbf{S}_{\mathbf{k}}\right) \sim \left|\mathrm{f}\left(\mathbf{k}\right)\right|^2 \left[1 - \left|\hat{\mathbf{k}} \cdot \hat{\mathbf{S}}_{\mathbf{k}}\right|^2\right] \left|\mathbf{S}_{\mathbf{k}}\right|^2$$

Structure factor

$$\mathbf{S}_{\mathbf{k}} = \frac{1}{N_0} \sum_{\alpha} e^{i\mathbf{k}\cdot(\mathbf{c}_\alpha)} \mathbf{S}_{j\alpha}$$



$$\mathbf{c}_0 = \langle 000 \rangle$$
$$\mathbf{c}_1 = \frac{a}{4}\langle 011 \rangle$$
$$\mathbf{c}_2 = \frac{a}{4}\langle 101 \rangle$$
$$\mathbf{c}_3 = \frac{a}{4}\langle 110 \rangle$$

For **k=0**, structure factors are a linear combination of only four spins, eg.

$$\mathbf{S}_{\mathbf{Q}_0} = \frac{1}{4}\left(\mathbf{S}_0 + \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3\right)$$
$$\mathbf{S}_{\mathbf{K}_0} = \frac{1}{4}\left(\mathbf{S}_0 - \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3\right)$$

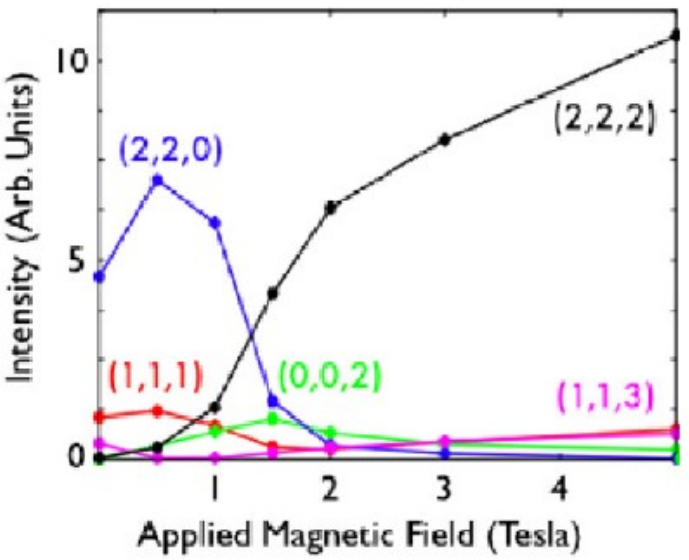
$$\mathbf{Q}_0 = (000), \quad \mathbf{Q}_1 = (200), \quad \mathbf{Q}_2 = (020), \quad \mathbf{Q}_3 = (002),$$
$$\mathbf{K}_0 = (111), \quad \mathbf{K}_1 = (1\bar{1}\bar{1}), \quad \mathbf{K}_2 = (\bar{1}1\bar{1}), \quad \mathbf{K}_3 = (\bar{1}\bar{1}1).$$

The k-points of the eight different structure factors

Structure factors not independent for pyrochlores

$$\mathbf{S}_{\mathbf{K}_0} = \frac{1}{2}\left(-\mathbf{S}_{\mathbf{Q}_0} + \mathbf{S}_{\mathbf{Q}_1} + \mathbf{S}_{\mathbf{Q}_2} + \mathbf{S}_{\mathbf{Q}_3}\right), \qquad \mathbf{S}_{\mathbf{K}_1} = \frac{1}{2}\left(+\mathbf{S}_{\mathbf{Q}_0} - \mathbf{S}_{\mathbf{Q}_1} + \mathbf{S}_{\mathbf{Q}_2} + \mathbf{S}_{\mathbf{Q}_3}\right)$$
$$\mathbf{S}_{\mathbf{K}_2} = \frac{1}{2}\left(+\mathbf{S}_{\mathbf{Q}_0} + \mathbf{S}_{\mathbf{Q}_1} - \mathbf{S}_{\mathbf{Q}_2} + \mathbf{S}_{\mathbf{Q}_3}\right), \qquad \mathbf{S}_{\mathbf{K}_3} = \frac{1}{2}\left(+\mathbf{S}_{\mathbf{Q}_0} + \mathbf{S}_{\mathbf{Q}_1} + \mathbf{S}_{\mathbf{Q}_2} - \mathbf{S}_{\mathbf{Q}_3}\right)$$

Single Crystal Data in a <110> magnetic field



JPC Ruff; PRL **101**, 147205 (2008)

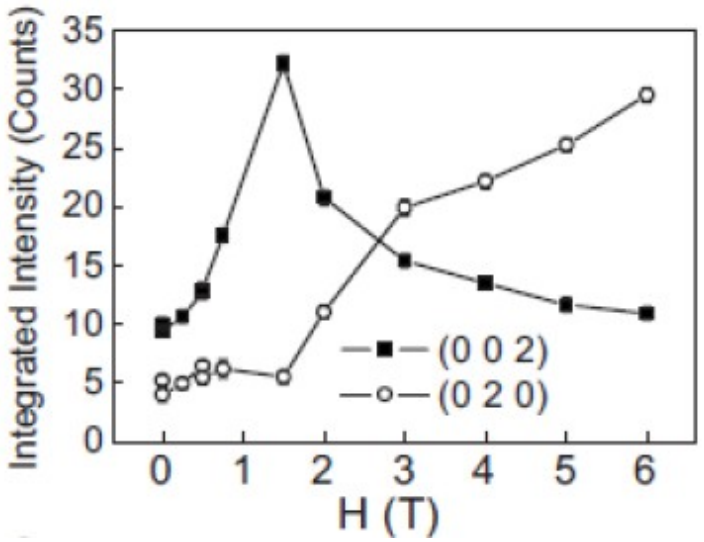
(222) spot absent: no ferromagnetism

$(22\overline{2})$ is a reciprocal lattice vector, so (002) and (220) share the same structure factor

(002) absent but (220) dominant: consider orientational factor:

$$\left[1 - \left|\hat{\mathbf{k}} \cdot \hat{\mathbf{S}}_{\mathbf{k}}\right|^2\right]$$

$$\mathbf{S}_{(200)} = S_x\hat{\mathbf{x}} \quad \mathbf{S}_{(020)} = S_y\hat{\mathbf{y}} \quad \mathbf{S}_{(002)} = S_z\hat{\mathbf{z}}$$

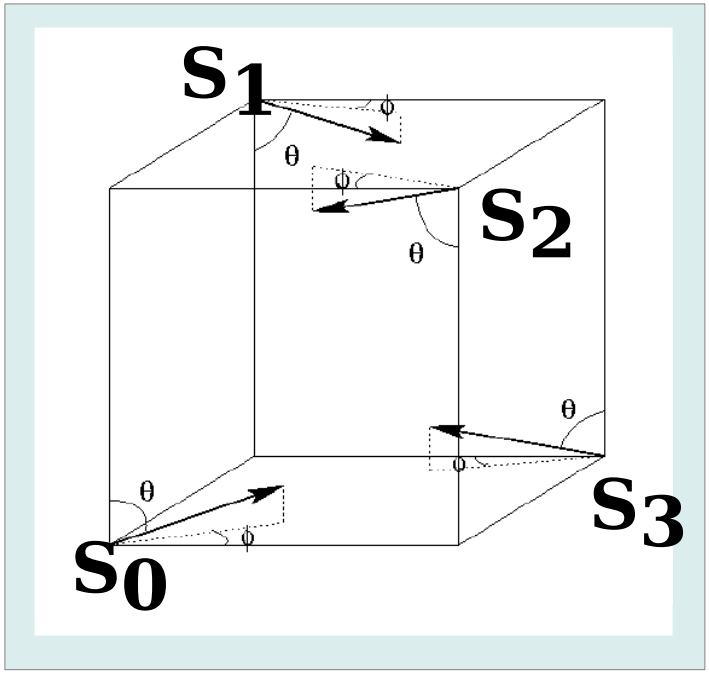


HB Cao PRB **82** 104431 (2010)

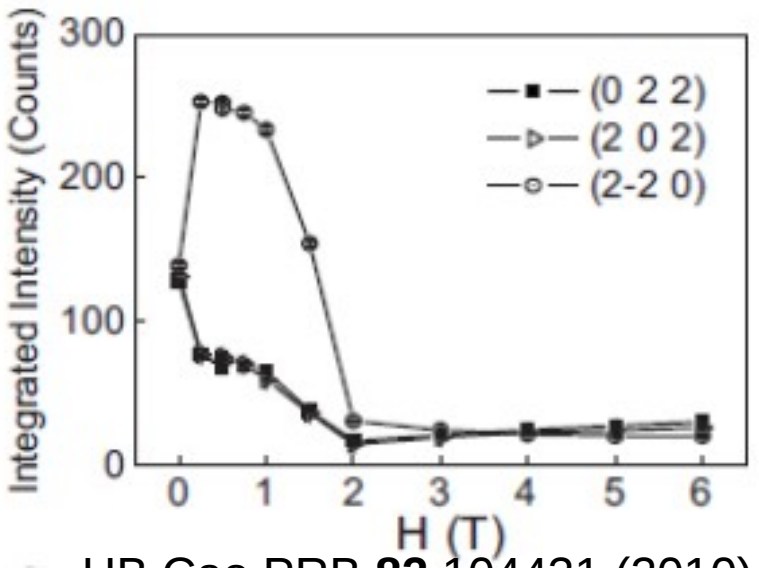
And invert back to real-space

$$\mathbf{S}_0 = S_x\hat{\mathbf{x}} + S_y\hat{\mathbf{y}} + S_z\hat{\mathbf{z}}$$
$$\mathbf{S}_1 = S_x\hat{\mathbf{x}} - S_y\hat{\mathbf{y}} - S_z\hat{\mathbf{z}}$$
$$\mathbf{S}_2 = -S_x\hat{\mathbf{x}} + S_y\hat{\mathbf{y}} - S_z\hat{\mathbf{z}}$$
$$\mathbf{S}_3 = -S_x\hat{\mathbf{x}} - S_y\hat{\mathbf{y}} + S_z\hat{\mathbf{z}}$$

We have determined the relative spin orientations:



Magnetic field selects z-direction as special: biases domain population



HB Cao PRB **82** 104431 (2010)

Two remaining degrees of freedom
View as orientation of $\mathbf{S_0}$
i.e. the angles θ and φ

$$I((002))=I((202)) \rightarrow Sx=Sy > 0$$

$$\sin^2\theta\left(\cos^2\phi-\sin^2\phi\right)=0 \quad \phi=\pm\tfrac{\pi}{4},\pm\tfrac{3\pi}{4}$$

$$\frac{I\left((2,-2,0)\right)}{I\left((0,2,2)\right)}=2\cot^2\theta\approx\frac{260}{80}$$

$$\theta\approx\pm0.2\pi,\pm1.2\pi$$

Next (022), (202) and (220) peaks
All have maximal orientational factor
All have an equal form factor

$$\mathbf{S}_{(022)}=S_x\hat{\mathbf{x}}\ \mathbf{S}_{(202)}=S_y\hat{\mathbf{y}}\ \mathbf{S}_{(220)}=S_z\hat{\mathbf{z}}$$

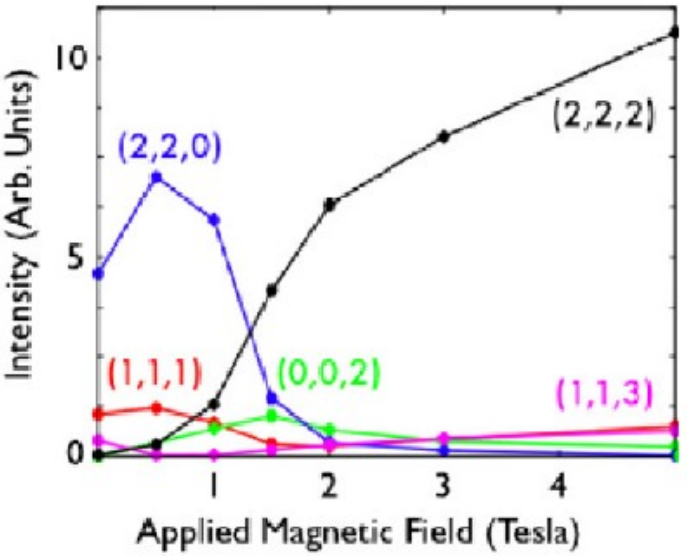
$$\mathbf{S}_0\approx\frac{1}{\sqrt{6}}\langle\pm1,\pm1,\pm2\rangle$$

Finally there is still the (111) Bragg spot to consider

Structure factors are not independent
Which leads to

$$\boldsymbol{S}_{(000)} = \boldsymbol{0} \rightarrow \boldsymbol{S}_{(111)} = \boldsymbol{S_0}/2 \neq \boldsymbol{0}$$

So consider orientational factor
$I((111))$ is weak so
$\boldsymbol{S_0}$ must point close to <111> direction.



Single crystal data by Ruff *et al.* shows

$$\frac{I\left((1,1,1)\right)}{I\left((2,2,0)\right)} \sim \frac{1}{5}$$

Consider the three (non-symmetrically related) possibilities for $\boldsymbol{S_0}$

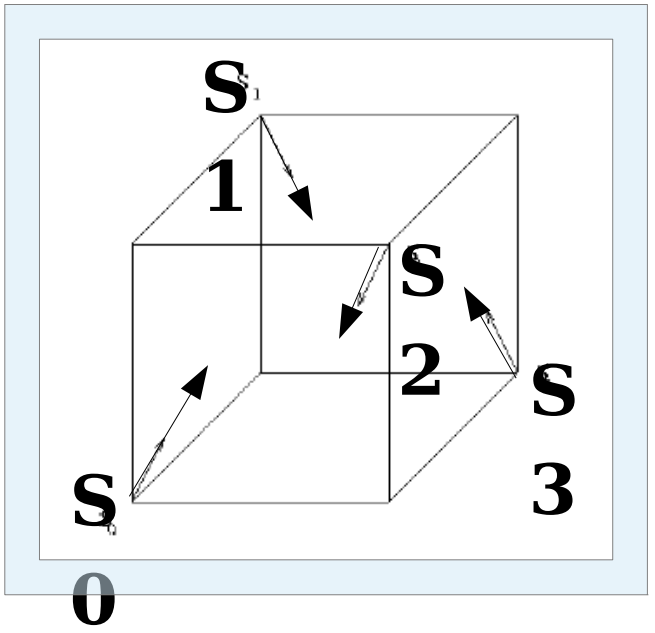
(We use a very crude estimate for the form factor)

$$\mathbf{S}_0 = \frac{1}{\sqrt{6}}\langle 1,1,-2\rangle \qquad \frac{I\left((1,1,1)\right)}{I\left((2,2,0)\right)} \sim \frac{9}{8}$$

$$\mathbf{S}_0 = \frac{1}{\sqrt{6}}\langle -1,1,2\rangle \qquad \frac{I\left((2,2,0)\right)}{I\left((1,1,1)\right)} \sim \frac{8}{7}$$

$$S_0 = \frac{1}{\sqrt{6}}\langle 1,1,2\rangle \qquad \frac{I\left((2,2,0)\right)}{I\left((1,1,1)\right)} \sim 8$$

Physical Interpretation of ordered state and gapless spin-wave



Domain selected by <110> field

$$\mathbf{S}_0 = \frac{1}{\sqrt{6}}\langle 1,1,2\rangle, \quad \mathbf{S}_1 = \frac{1}{\sqrt{6}}\langle 1,-1,-2\rangle$$

$$\mathbf{S}_2 = \frac{1}{\sqrt{6}}\langle -1,1,-2\rangle, \quad \mathbf{S}_3 = \frac{1}{\sqrt{6}}\langle -1,-1,2\rangle$$

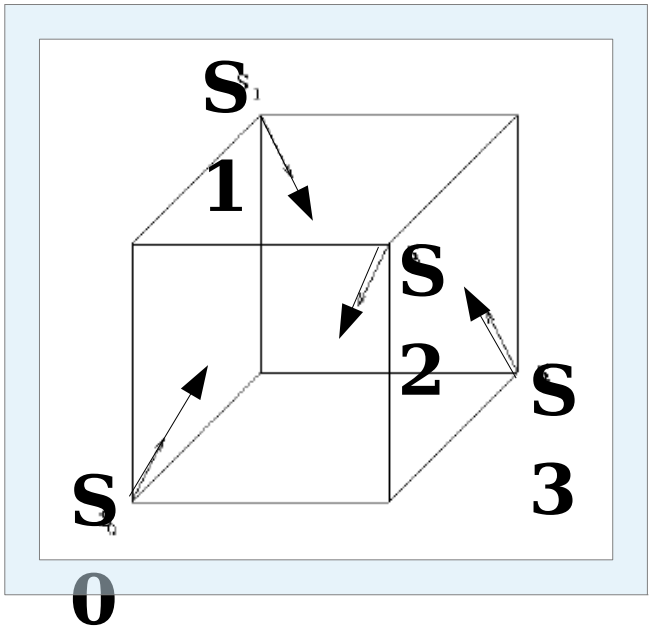
Can re-write as 'triple-q' state plus co-linear AFM along z-direction

$$\mathbf{S}_0 = \frac{1}{\sqrt{6}}\langle 1,1,1\rangle + \frac{1}{\sqrt{6}}\langle 0,0,1\rangle, \quad \mathbf{S}_1 = \frac{1}{\sqrt{6}}\langle 1,-1,-1\rangle + \frac{1}{\sqrt{6}}\langle 0,0,-1\rangle,$$

$$\mathbf{S}_2 = \frac{1}{\sqrt{6}}\langle -1,1,-1\rangle + \frac{1}{\sqrt{6}}\langle 0,0,-1\rangle, \quad \mathbf{S}_3 = \frac{1}{\sqrt{6}}\langle -1,-1,1\rangle + \frac{1}{\sqrt{6}}\langle 0,0,1\rangle$$

<112> is not a natural crystallographic direction.
Crystal field interaction must be frustrated via a competition with other interactions.
How can this be understood energetically?

Physical Interpretation of ordered state and gapless spin-wave



Domain selected by <110> field

$$\mathbf{S}_0 = \frac{1}{\sqrt{6}}\langle 1,1,2\rangle, \quad \mathbf{S}_1 = \frac{1}{\sqrt{6}}\langle 1,-1,-2\rangle$$

$$\mathbf{S}_2 = \frac{1}{\sqrt{6}}\langle -1,1,-2\rangle, \quad \mathbf{S}_3 = \frac{1}{\sqrt{6}}\langle -1,-1,2\rangle$$

Remember structure factors

$$\mathbf{S}_{(200)} = S_x\hat{\mathbf{x}} \quad \mathbf{S}_{(020)} = S_y\hat{\mathbf{y}} \quad \mathbf{S}_{(002)} = S_z\hat{\mathbf{z}}$$

Normally for rare-earth magnets: Strong crystal field interaction provides a finite energy penalty for global spin rotations.

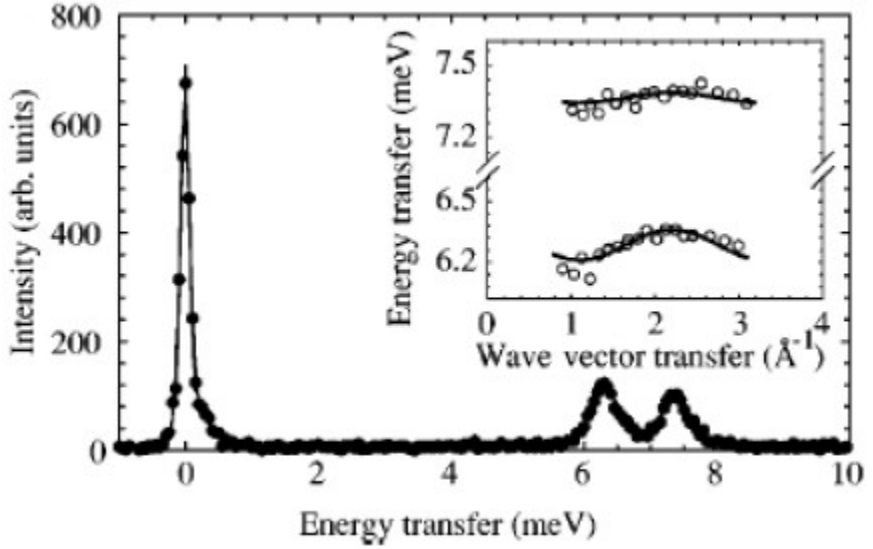
So the standard transverse spin-waves are strongly gapped.

Here spin-wave mode at (220) consistent with transferring weight between to (022); (202) and (220) Bragg peaks.

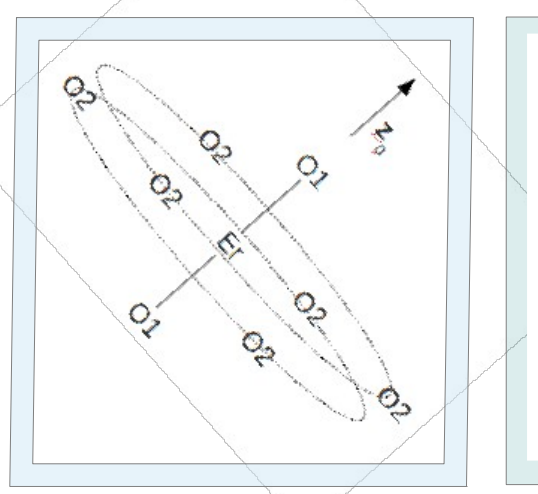
This changes θ and φ of $\mathbf{S_0}$ (with relative spin directions maintained)

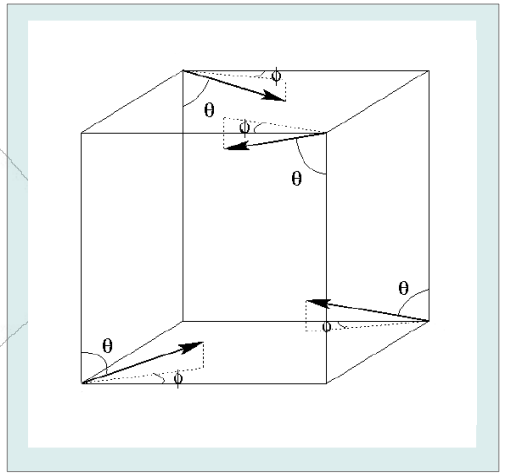
(3) Energetic modelling

Crystal field largest energy scale
Energy gap from ground-state doublet
To first excited state 70K



JDM Champion; PRB **68** 020401 (2003)





Oxygen at centre of tetrahedron dominates
So choose each local quantisation axis
to point towards the cube centre

For one hole, use Y_{30} orbital so project onto minimal J_z

Er^{3+} has 3 holes so only approximate (other low Jz states will be mixed in)

Resulting pseudo-spin ½ state
can be orientated in any direction

$$|\psi^{\pm}\rangle = e^{\mp\frac{i\phi}{2}}\cos\frac{\theta}{2}\left|J,\pm\frac{1}{2}\right\rangle \pm e^{\pm\frac{i\phi}{2}}\sin\frac{\theta}{2}\left|J,\mp\frac{1}{2}\right\rangle$$

Angles θ and φ determined by
n.n. Heisenberg and n.n Dipole
Both have energy scale of ~1K

Energetically motivated phenomenological Hamiltonians

Local dipole interaction $H_D = J_D \left\{ \frac{7}{4} H_1 + \frac{3}{4} H_4 + \frac{9}{2} H_0 - \frac{9}{4} H_2 \right\}$

Anisotropic n.n Heisenberg as $H_{\mathrm{Ex}} = a_{\mathrm{Ex}} H_1 - b_{\mathrm{Ex}} H_4$

Orbitally generated exchange anisotropy out of control
– forces us to use phenomenological coefficients.

$$H_0 = \frac{1}{2} \sum_{\alpha} \left(\hat{\mathbf{z}}_\alpha \cdot \hat{\mathbf{J}}_\alpha \right)^2 \qquad H_1 = \frac{1}{2} \hat{\mathbf{T}} \cdot \hat{\mathbf{T}} \qquad H_2 = \hat{\mathbf{T}} \cdot \hat{\mathbf{z}}_\alpha \sum_{\alpha} \left(\hat{\mathbf{z}}_\alpha \cdot \hat{\mathbf{J}}_\alpha \right)$$

$$H_3 = \frac{1}{8} \left(\sum_{\alpha} \hat{\mathbf{z}}_\alpha \cdot \hat{\mathbf{J}}_\alpha \right)^2 \qquad H_4 = \frac{1}{2} \hat{\mathbf{A}} \cdot \hat{\mathbf{A}}$$

$$\hat{\mathbf{T}} = \hat{\mathbf{J}}_0 + \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 + \hat{\mathbf{J}}_3$$

$$\hat{\mathbf{A}} = \left(\hat{J}_0^x + \hat{J}_1^x - \hat{J}_2^x - \hat{J}_2^x \right) \hat{\mathbf{x}} + \left(\hat{J}_0^y - \hat{J}_1^y + \hat{J}_2^y - \hat{J}_3^y \right) \hat{\mathbf{y}} + \left(\hat{J}_0^z - \hat{J}_1^z - \hat{J}_2^z + \hat{J}_3^z \right) \hat{\mathbf{z}}.$$

Z_α describes local quantisation axis directed towards cube centre

Pseudo-spin projection

To project onto maximal J_z states
[appropriate for modelling spin-ice]

$$\hat{\mathbf{J}}_\alpha \mapsto 2J\left(\hat{\mathbf{S}}_\alpha \cdot \hat{\mathbf{z}}_\alpha\right)\hat{\mathbf{z}}_\alpha$$

We choose to use minimal J_z projection

$$\hat{\mathbf{J}}_\alpha \mapsto \left(J+\frac{1}{2}\right)\hat{\mathbf{S}}_\alpha - \left(J-\frac{1}{2}\right)\left(\hat{\mathbf{S}}_\alpha \cdot \hat{\mathbf{z}}_\alpha\right)\hat{\mathbf{z}}_\alpha$$

Anisotropic Exchange and Dipole Hamiltonians project onto:

$$H_{\mathrm{Ex}} \rightarrow \lambda_{\mathrm{Ex}1}H_1 - \lambda_{\mathrm{Ex}2}H_2 + \lambda_{\mathrm{Ex}3}H_3 - \lambda_{\mathrm{Ex}4}H_4 + \lambda_{\mathrm{Ex}5}\left(H_0 - H_3\right)$$

$$H_D \rightarrow \lambda_{D0}H_0 + \lambda_{D1}H_1 - \lambda_{D2}H_2 + \lambda_{D4}H_4 + \lambda_{D5}\left(H_0 - H_3\right)$$

Combines to give phenomenological Hamiltonian

$$H = J_0(H_1 - \delta H_4 - \eta H_0 + \xi(H_0 - H_3) - \mu H_2$$

Coefficients chosen to be positive: provides classical g.s. manifold with previously discussed θ and φ degeneracy [except H_0: triple-q g.s. state]

Coefficient choice consistent with energetics, but notice sign of H_4: dipole frustrated; turns out consistent with heavily reduced (111) spot

Minimal model for gap-less spin waves

$$H = J_0(H_1 - \delta H_4)$$

$$H_1 = \frac{1}{2}\hat{\mathbf{T}} \cdot \hat{\mathbf{T}}$$

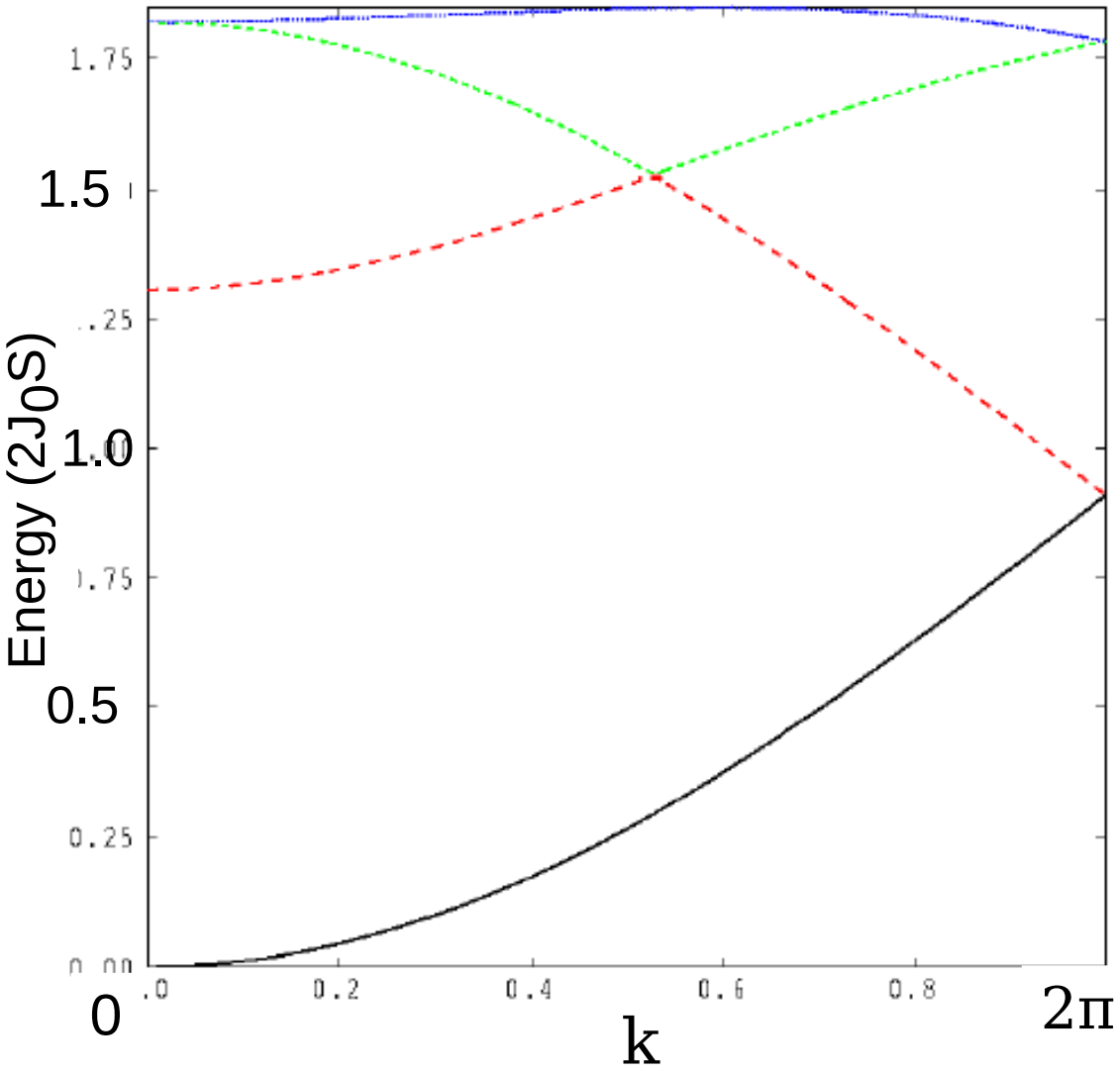
$$H_4 = \frac{1}{2}\hat{\mathbf{A}} \cdot \hat{\mathbf{A}}$$

Dispersion shown for experimentally observed $\theta \sim 0.2\pi$ and $\varphi = \pi$; i.e.

$$S_0 = \frac{1}{\sqrt{6}}\langle 1, 1, 2\rangle.$$

Classical g.s. has θ and φ degeneracy ($\boldsymbol{S_0}$ orientation)

Lifted by quantum fluctuations?

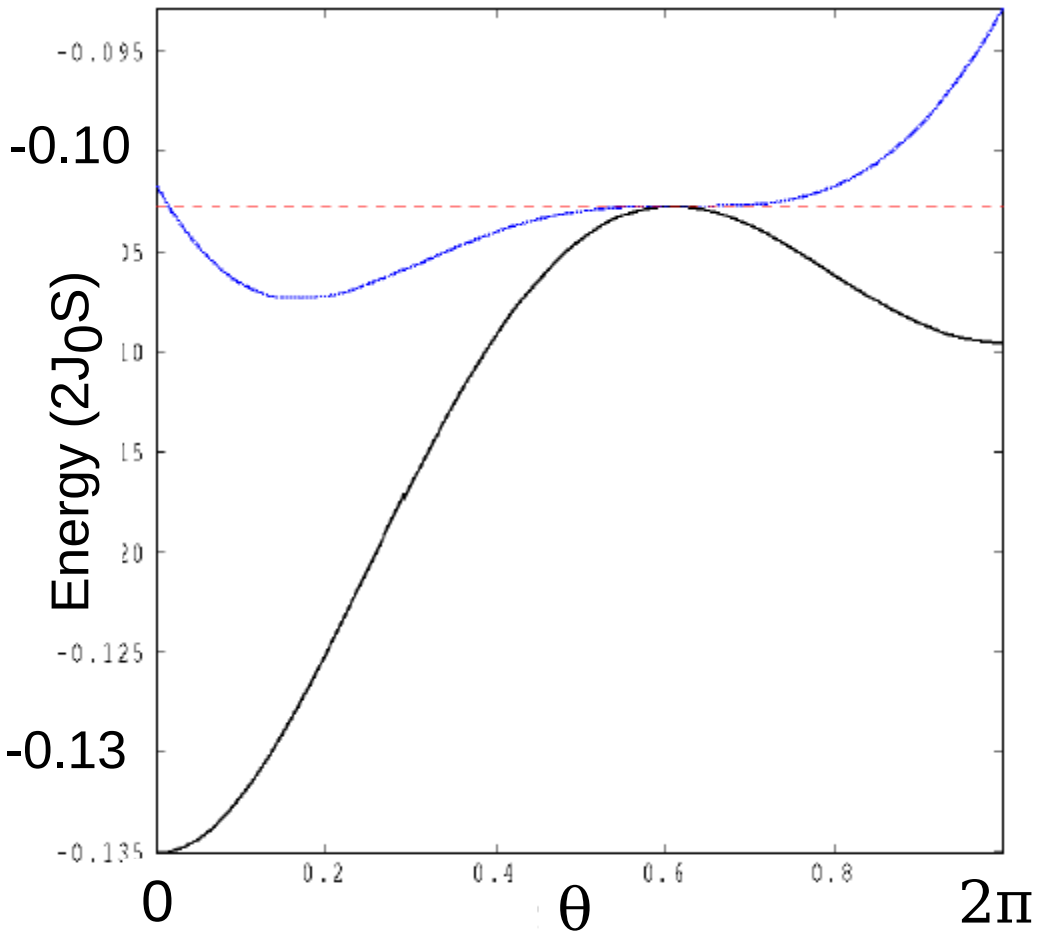


Where:

$$\hat{\mathbf{T}} = \hat{\mathbf{J}}_0 + \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 + \hat{\mathbf{J}}_3$$

$$\hat{\mathbf{A}} = \left(\hat{J}_0^x + \hat{J}_1^x - \hat{J}_2^x - \hat{J}_2^x\right)\hat{\mathbf{x}} + \left(\hat{J}_0^y - \hat{J}_1^y + \hat{J}_2^y - \hat{J}_3^y\right)\hat{\mathbf{y}} + \left(\hat{J}_0^z - \hat{J}_1^z - \hat{J}_2^z + \hat{J}_3^z\right)\hat{\mathbf{z}}.$$

Competing crystal field and quantum fluctuations



Black curve: Quantum fluctuation energy: QFE(θ) for δ=0.2 and η=0

Minimimum: co-linear single-q magnet (spins point along a Cartesian axis)

$$H = J_0(H_1 - \delta H_4 - \eta H_0)$$

Residual crystal field term

$$H_0 = \frac{1}{2}\sum_{\alpha}\left(\hat{\mathbf{z}}_\alpha \cdot \hat{\mathbf{J}}_\alpha\right)^2$$

η>0: triple-q classical ground state. Spins point along tetrahedral axis Generates spin-wave gap ~ η

But for pseudo-spin ½ expect large QFE. Crude resolution:

Find θ that minimises a sum of QFE (for η=0) and classical ground state energy (for η=0).

Blue curve: above linear combination tuned to stabilise experimentally seen θ value.

All calculations we choose the experimental value of φ=π/4

Conclusions

- The gapless spin-wave is not the usual transverse Goldstone mode. It describes a transferral of weight between the (022), (202) and (220) Bragg peaks. In real-space this corresponds to a rotation of the pseudo-spin angles θ and φ (but maintaining the relative spin orientations within the unit cell).

- External-field single crystal elastic neutron measurements consistent with a surprising long-range ordered state. The magnetic moments do NOT lie along minima of the crystal field. [The n.n. dipole interaction also frustrated].

- We make a (phenomenological) Holstein-Primakoff analysis of the classically degenerate pseudo-spin model and find competition between this zero point energy and the residue of the classical single ion anisotropy. This produces a gapless mode which is invisible in the classical limit of the the effective Hamiltonian of this material.