

Anisotropic exchange in ytterbium magnets: Breathing pyrochlores, spinels and beyond

Jeffrey G. Rau

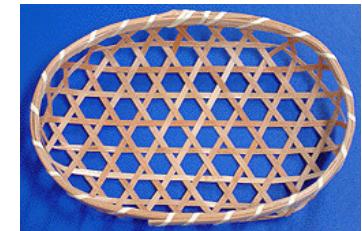
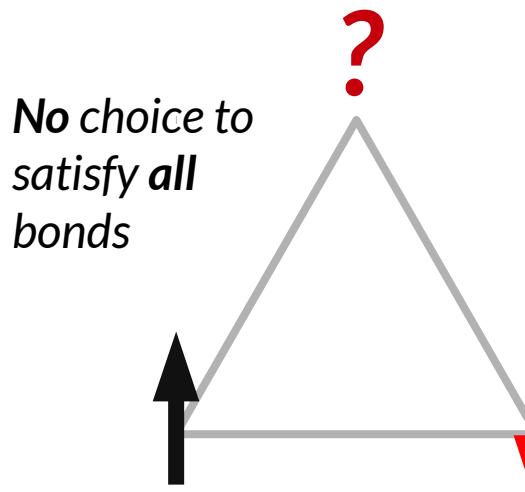
Max Planck Institute for the Physics of Complex Systems

In collaboration with: Michel Gingras, University of Waterloo

Highly Frustrated Magnetism 2018, July 10th, 2018 (UC Davis)

Frustration from anisotropy

- Geometrical frustration
- Lattices built from triangles, e.g.
 - Triangular
 - Kagome
 - Pyrochlore
- Frustration via anisotropic interactions
- Less dependent on the *geometrical* structure of lattice, more on nature of interactions



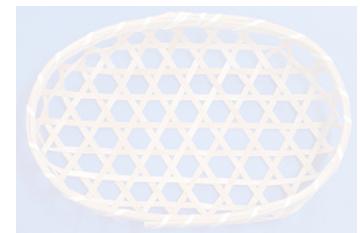
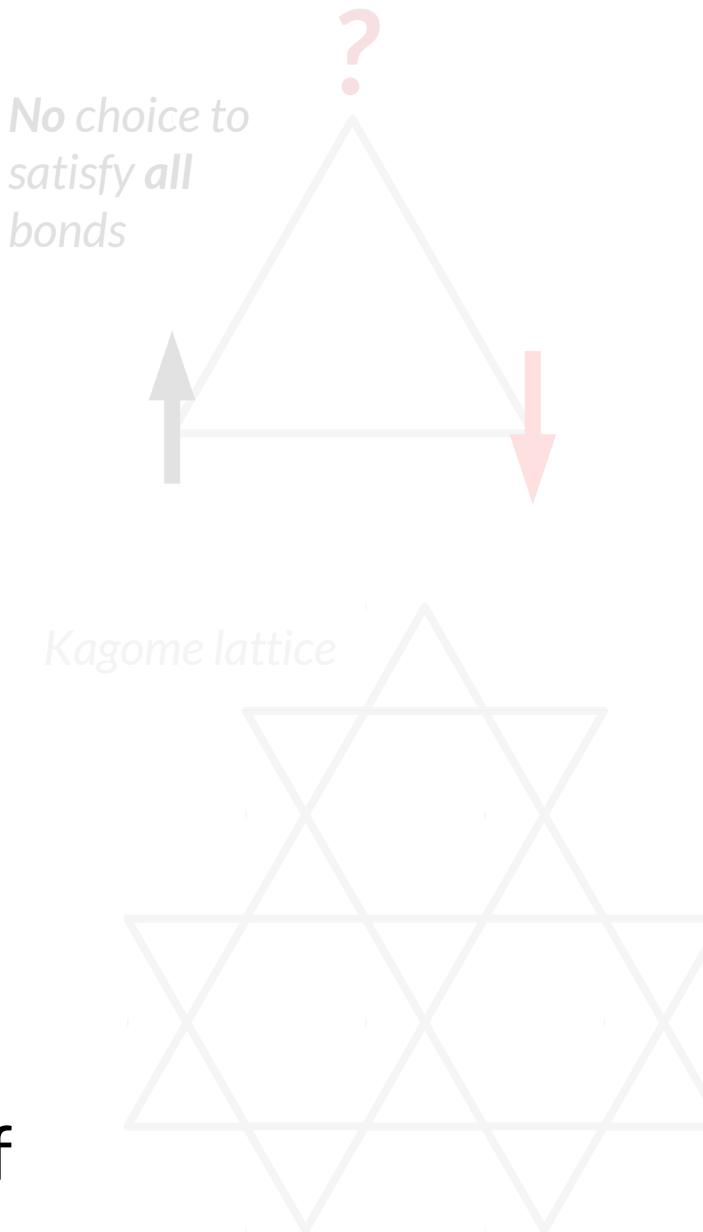
Etymology:
Kagome basket
weaving pattern

Corner-sharing
triangles

Example?

Frustration from anisotropy

- Geometrical frustration
- Lattices built from triangles, e.g.
 - Triangular
 - Kagome
 - Pyrochlore
- **Frustration via anisotropic interactions**
- Less dependent on the *geometrical structure* of lattice, more on nature of interactions



*Etymology:
Kagome basket
weaving pattern*

*Corner-sharing
triangles*

Example?

Kitaev's model

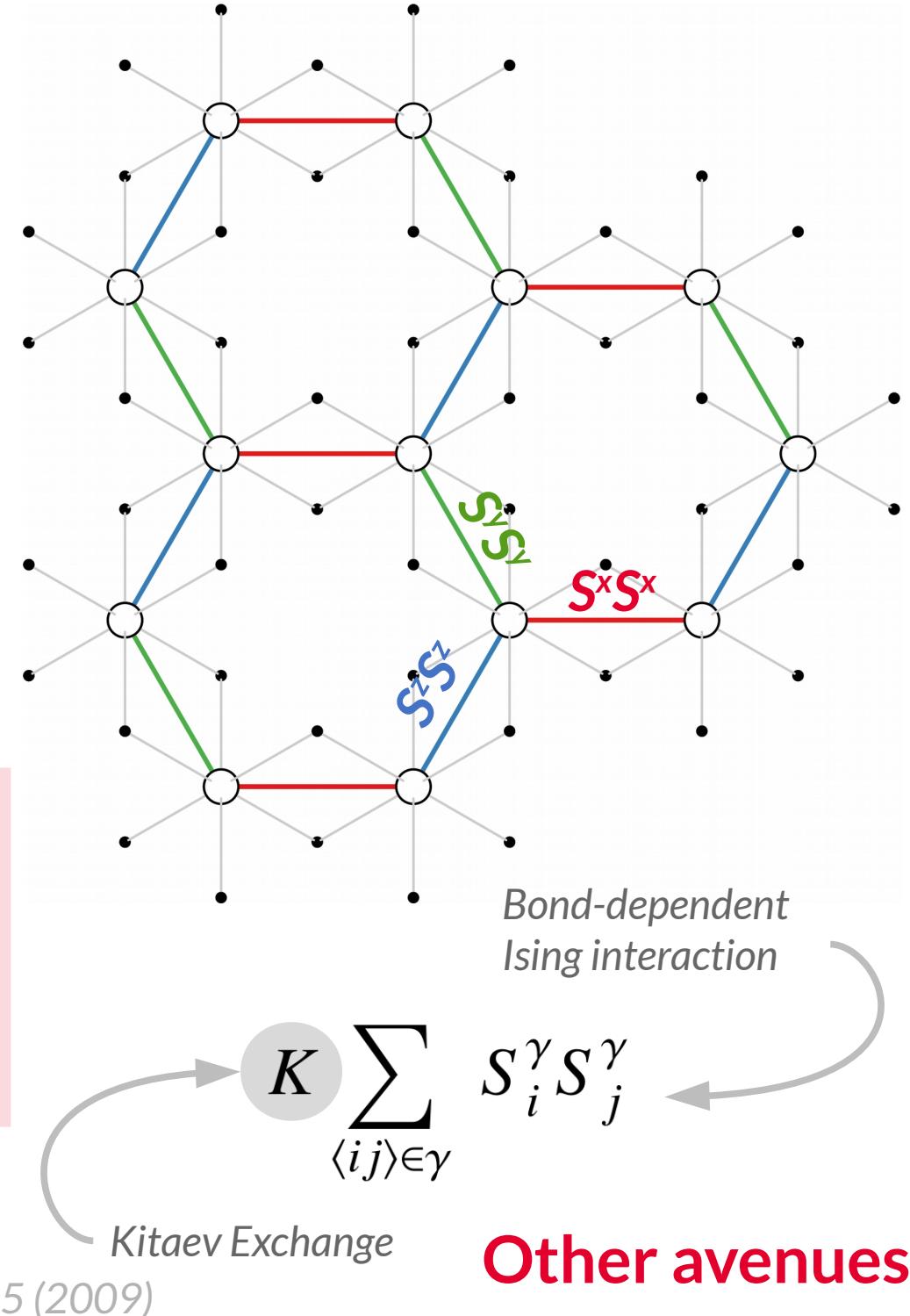
- Example: Kitaev's honeycomb model
- Solvable → Ground state is a Z_2 spin liquid
- Distinct from usual Heisenberg, XY, Ising limits

Jackeli/Khaliullin: Heavy transition metal magnets built of edge-shared octahedra

- e.g. $(\text{Na},\text{Li})_2\text{IrO}_3$, RuCl_3

Kitaev, Ann. Phys. 321, 2 (2006)

Jackeli and Khaliullin, Phys. Rev. Lett. 102, 017205 (2009)



Anisotropic exchange in rare-earths

- Can we do this in **rare-earth magnets?**

• Advantages

- Very localized,
 - Large SOC

- **Problems:**

- Small energy scale
 - Exchange hard to understand, predict

- No clear exchange regime
(usually)

Can be hard to pin down even with exp. input (c.f. $\text{Yb}_2\text{Ti}_2\text{O}_7$)

Simplest context?

1	¹ _{s_{1/2}} H Hydrogen 1.00 ⁸ 1s 13.5984	2 ¹ _{s₀} He Helium 4.026202 1s ² 24.5874
2	³ _{-s_{1/2}} Li Lithium 6.94 ¹ 1s ² 5.3917 9.3227	⁴ _{s₀} Be Beryllium 9.0121831 1s ² 5.3917 9.3227
3	¹¹ _{-s_{1/2}} Na Sodium 22.9897928 [Ne]3s ² 5.1391	¹² _{s₀} Mg Magnesium 24.305 ⁸ [Ne]3s ² 6.7642
4	¹⁹ _{-s_{1/2}} K Potassium 39.9983 [Ar]4s ¹ 4.3407 6.1132	²⁰ _{s₀} Ca Calcium 40.078 [Ar]4s ² 4.3407 6.5615
5	³⁷ _{-s_{1/2}} Rb Rubidium 85.4678 [Kr]5s ¹ 4.1771 5.6949	²¹ _{s₀} Sc Scandium 44.959908 [Ar]3d ¹ 4.7850 6.2173
6	⁵⁵ _{-s_{1/2}} Cs Cesium 132.9054520 [Xe]6s ¹ 3.8639 5.2117	²² _{s₀} Ti Titanium 47.867 [Ar]3d ² 4.7850 6.8281
7	⁸⁷ _{-s_{1/2}} Fr Francium (223) [Rn]7s ¹ 4.0727 5.2784	²³ _{s₀} V Vanadium 50.9415 [Ar]3d ³ 4.7850 6.7462
	¹⁰⁴ _{-f_{15/2}} Rf Rutherfordium (267) [Rn]5f ¹⁵ 6d ¹ 6.01	²⁴ _{s₀} Cr Chromium 51.9961 [Ar]3d ⁵ 4.7850 6.7665
	¹⁰⁵ _{-f_{15/2}} Db Dubnium (208)	²⁵ _{s₀} Mn Manganese 54.938044 [Ar]3d ⁵ 4.7850 7.4340
	¹⁰⁶ _{-f_{15/2}} Sg Seaborgium (271)	²⁶ _{d_{5/2}} Fe Iron 55.845 [Ar]3d ⁶ 4.7850 7.9022
	¹⁰⁷ _{-f_{15/2}} Bh Bohrium (272)	²⁷ _{f_{7/2}} Co Cobalt 58.933194 [Ar]3d ⁷ 4.7850 7.8810
	¹⁰⁸ _{-f_{15/2}} Hs Hassium (270)	²⁸ _{f_{5/2}} Ni Nickel 58.6934 [Ar]3d ⁸ 4.7850 7.6309
	¹⁰⁹ _{-f_{15/2}} Mt Meitnerium (276)	²⁹ _{s₀} Cu Copper 63.546 [Ar]3d ⁹ 4.7850 7.7264
	¹¹⁰ _{-f_{15/2}} Ds Darmstadtium (281)	³⁰ _{s₀} Zn Zinc 65.38 [Ar]3d ¹⁰ 4.7850 9.3942
	¹¹¹ _{-f_{15/2}} Rg Roentgenium (280)	⁴⁸ _{s₀} Pd Palladium 106.42 [Kr]4d ⁸ 5.7562
	¹¹² _{-f_{15/2}} Cn Copernicium (285)	⁴⁹ _{p_{1/2}} Ag Silver 107.8862 [Kr]4d ⁹ 5.7562
	¹¹⁴ _{-f_{15/2}} Fl Flerovium (289)	⁵⁰ _{p₀} Cd Cadmium 112.414 [Kr]4d ¹⁰ 5.7562
	¹¹⁶ _{-f_{15/2}} Lv Livermorium (293)	⁵¹ _{s₀} In Indium 114.214 [Kr]4d ¹¹ 5.7562
	¹¹⁷ _{-f_{15/2}} Uus Ununseptium (294)	⁵² _{p_{1/2}} Tl Thallium 127.60 [Kr]4d ¹² 5.7562
	⁸⁹ _{-f_{15/2}} Ac Actinium (232)	⁵³ _{p₀} Pb Lead 126.90447 [Kr]4d ¹³ 5.7562
	⁹⁰ _{-f_{15/2}} Th Thorium (232)	⁵⁴ _{s₀} Xe Xenon 131.2760 [Kr]4d ¹⁴ 5.7562
	⁹¹ _{-f_{15/2}} Pa Protactinium (231)	⁵⁵ _{p_{1/2}} Bi Bismuth 208.89040 [Kr]4d ¹⁵ 5.7562
	⁹² _{-f_{15/2}} U Uranium (238)	⁸⁴ _{p₀} Po Polonium (209) [Kr]4d ¹⁶ 5.7562
	⁵⁷ _{-f_{15/2}} La Lanthanum 136.95047 [Xe]6s ² 5.5769	⁸⁵ _{p_{1/2}} Rn Radon (222) [Kr]6s ² 5.7485
	⁵⁸ _{-f_{15/2}} Ce Cerium 140.116 [Xe]6s ² 5.5386	⁵⁶ _{-f_{15/2}} Pr Praseodymium 140.907 [Xe]6s ² 5.5250
	⁶⁰ _{-f_{15/2}} Nd Neodymium 144.242 [Xe]6s ² 5.5250	⁶¹ _{-f_{15/2}} Sm Samarium 150.36 [Xe]6s ² 5.6437
	⁶³ _{-f_{15/2}} Eu Europium 151.964 [Xe]6s ² 5.6704	⁶⁴ _{-f_{15/2}} Gd Gadolinium 157.25 [Xe]6s ² 6.1498
	⁶⁵ _{-f_{15/2}} Tb Terbium 158.9255 [Xe]6s ² 5.8683	⁶⁶ _{-f_{15/2}} Dy Dysprosium 162.500 [Xe]6s ² 5.9391
	⁶⁷ _{-f_{15/2}} Ho Holmium 164.9333 [Xe]6s ² 6.0215	⁶⁸ _{-f_{15/2}} Er Erbium 167.259 [Xe]6s ² 6.1077
	⁶⁹ _{-f_{15/2}} Tm Thulium 168.9342 [Xe]6s ² 6.1843	⁷⁰ _{-f_{15/2}} Yb Ytterbium 172.560 [Xe]6s ² 6.2542
	⁷¹ _{-f_{15/2}} Lu Lutetium 174.96024 [Xe]6s ² 5.4229	⁷² _{-f_{15/2}} Sr Lawrencium (262)

Tractable case?

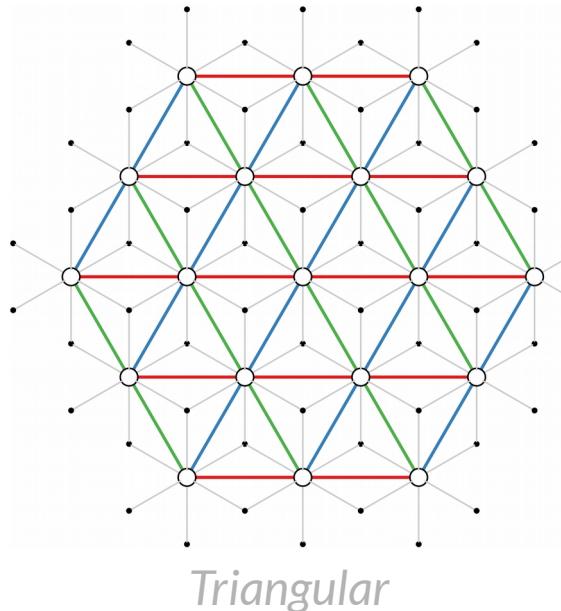
Trivalent Ytterbium ion →
Simplest atomic physics

Edge-shared octahedra →
Simpler exchange physics,
Well-characterized test case

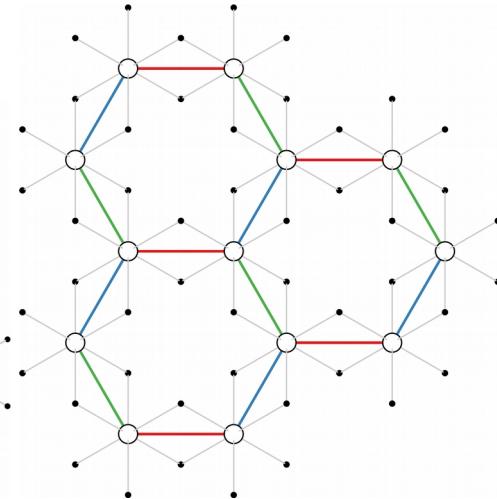
Should be able to make reliable statements about exchange

Edge-shared octahedra

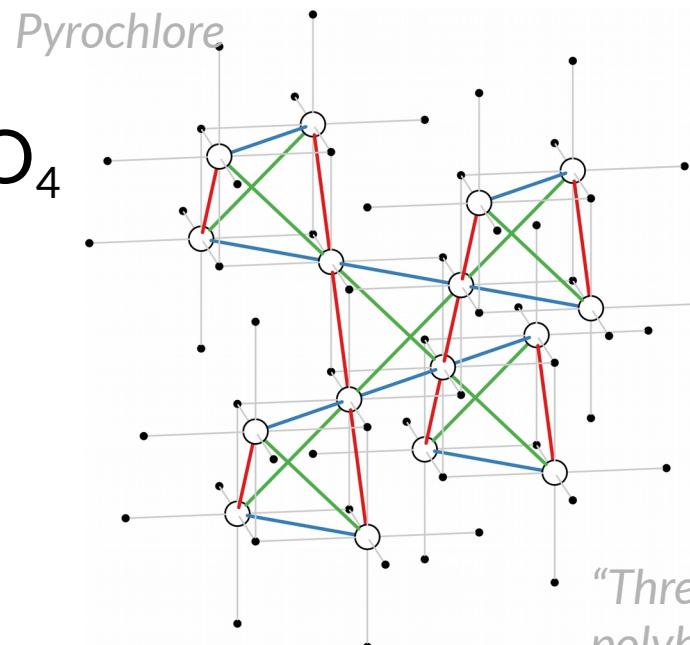
- Many structures can be built from edge-shared octahedra
- Materials of current interest
- Examples:
 - Pyrochlore spinels
 - Triangular YbMgGaO_4
 - Honeycomb
 - $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$,



Triangular



Honeycomb



Pyrochlore

- Kagome
- Hyper-honeycomb
- Hyper-kagome
- Harmonic honeycomb
- Hyper-octagon
-

"Three dimensional nets and polyhedra", Wells et al (1977)

Single ion physics

Only common magnetic valence

- $\text{Yb}^{3+} \rightarrow 4f_{13}$

- One hole in $4f$ shell

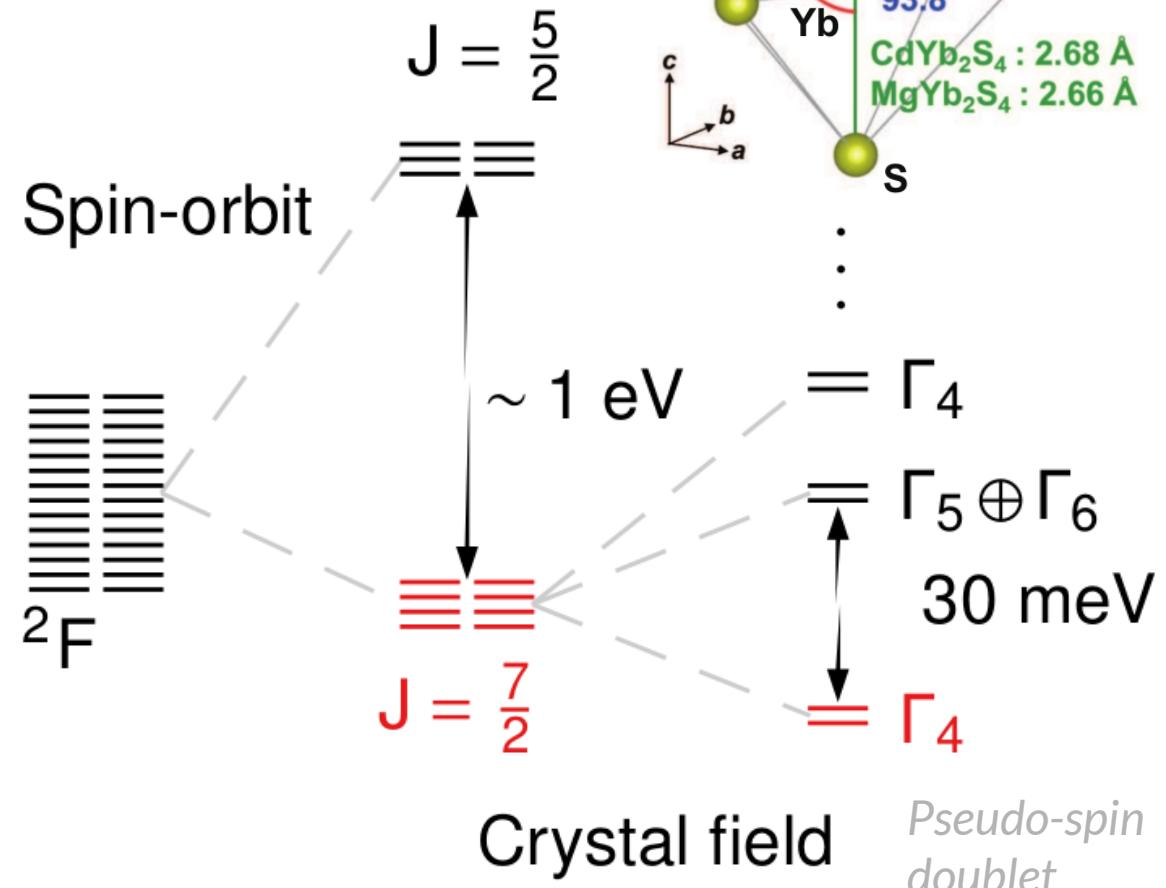
- Spin-orbit $\rightarrow J=7/2$

- Spilt by crystal field

 - Four Kramers doublets

- Much simpler

 - Single electron atomic states



$$|\pm\rangle = \sin \eta [\cos \zeta |\pm 7/2\rangle \pm \sin \zeta |\pm 1/2\rangle] + \cos \eta |\mp 5/2\rangle$$

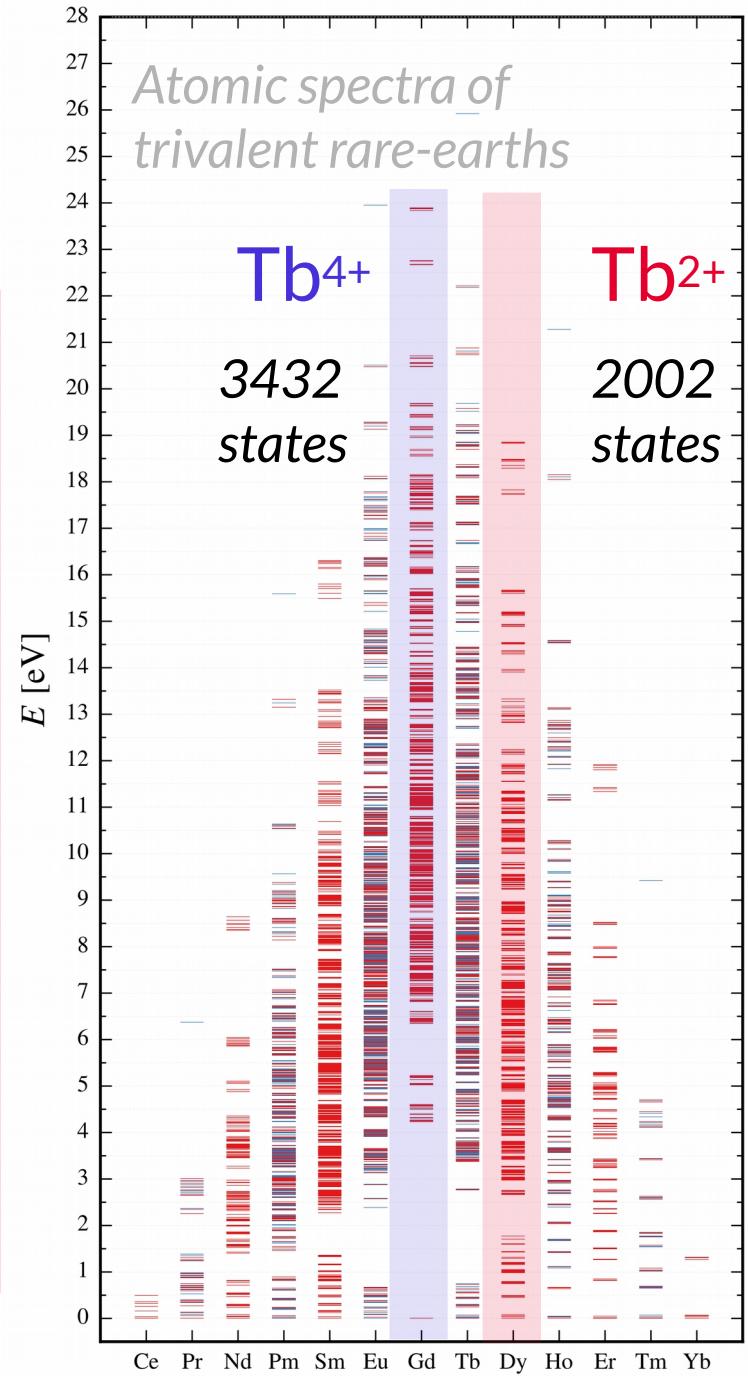
Composition of ground doublet – material dependent

Exchange?

Exchange physics

- Generate exchange through ligand mediated processes
- *Usually complicated* in rare-earths
 - Large orbital contributions to states
 - Large and varied set of **virtual atomic states** in process

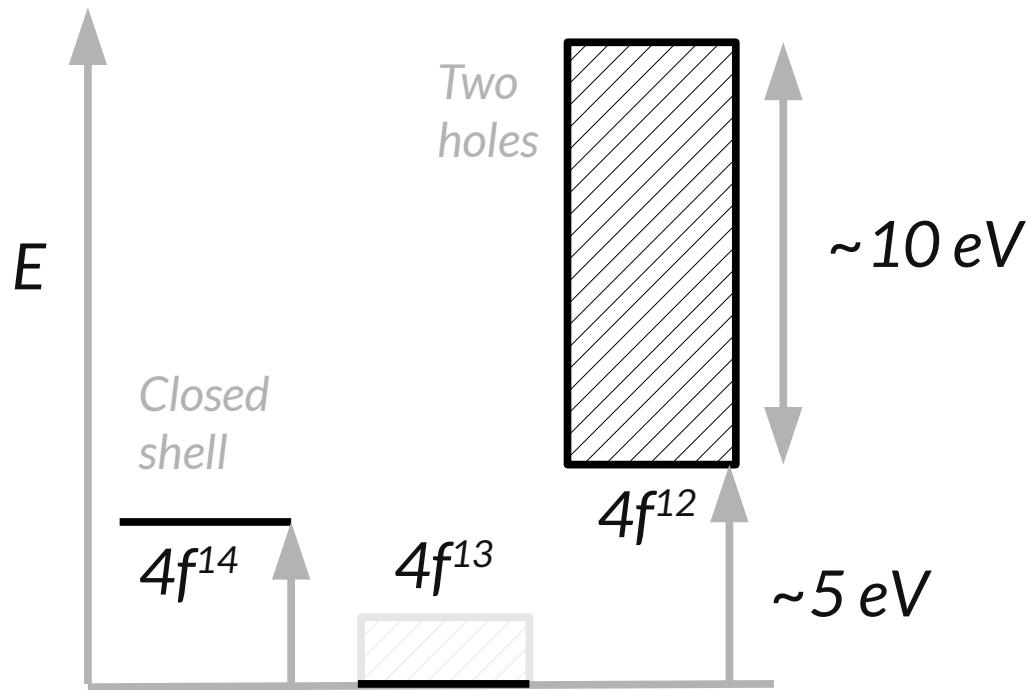
Example:
Charge transfer process
 $Tb^{3+} - Tb^{3+}$
 $\xleftarrow{\hspace{1cm}}$
 $Tb^{2+} - Tb^{4+}$
 $\xrightarrow{\hspace{1cm}}$
 $Tb^{3+} - Tb^{3+}$



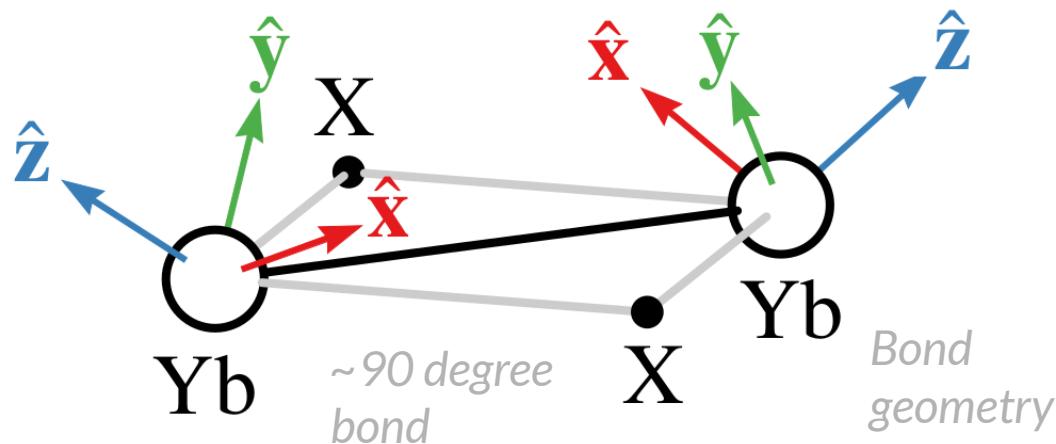
In ytterbium?

Exchange physics (cont.)

Still ~ 100 states



Yb^{2+} Yb^{3+} Yb^{4+}



- Charge-transfer to and from ligand
- Excited states include $4f^{12}, 4f^{14}$ manifolds
 - Closed shell trivial
- Compute using **full rare-earth free-ion virtual states**
- Project into ground doublet \rightarrow exchanges

Super-exchange calculation

Schematically:

- Overlap integrals evaluated in Slater-Koster approximation
 - 2nd order degenerate perturbation theory
 - Use *full, free-ion* atomic states for $4f^{12}, 4f^{14}$
 - Project in crystal-field ground doublet
-
- Need:
 - Bond angle → *Crystal structure*
 - Composition of ground doublet → *INS or g-factors*
 - *Unknown* parameters: Slater-Koster overlaps, charge-transfer energies, ...

What comes out?

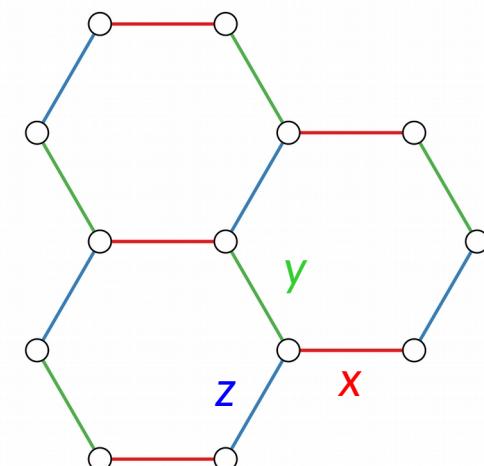
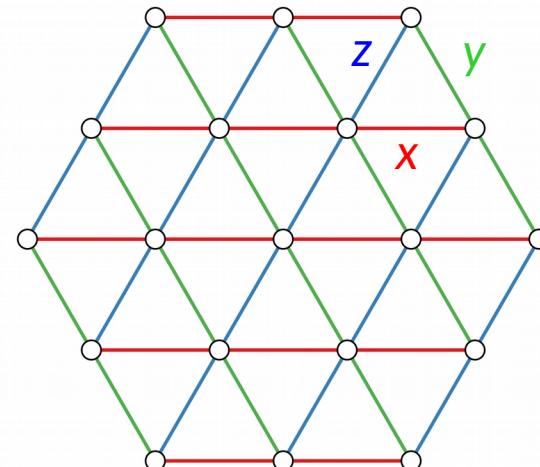
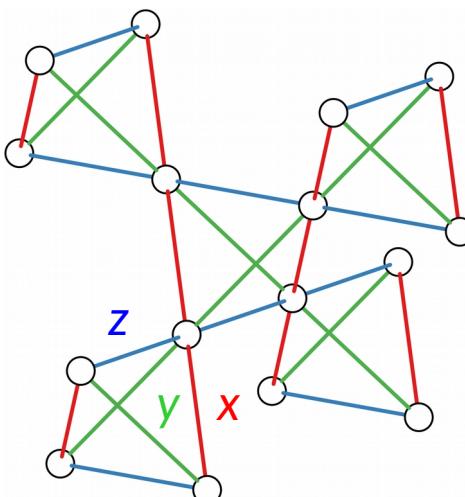
Exchange models

- In all cases of interest: four exchanges:

$$\sum_{\langle ij \rangle} [J_{zz} S_i^z S_j^z - J_{\pm} (S_i^+ S_j^- + S_i^- S_j^+) + J_{\pm\pm} (\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-) + J_{z\pm} (\zeta_{ij} [S_i^z S_j^+ + S_i^+ S_j^z] + \zeta_{ij}^* [S_i^z S_j^- + S_i^- S_j^z])]$$

Bond-dependent phases

- Three bond types: $\gamma_x = 1, \gamma_y = e^{2\pi i/3}, \gamma_z = e^{-2\pi i/3}$ $\zeta_{ij} = -\gamma_{ij}^*$



Exchange models (cont.)

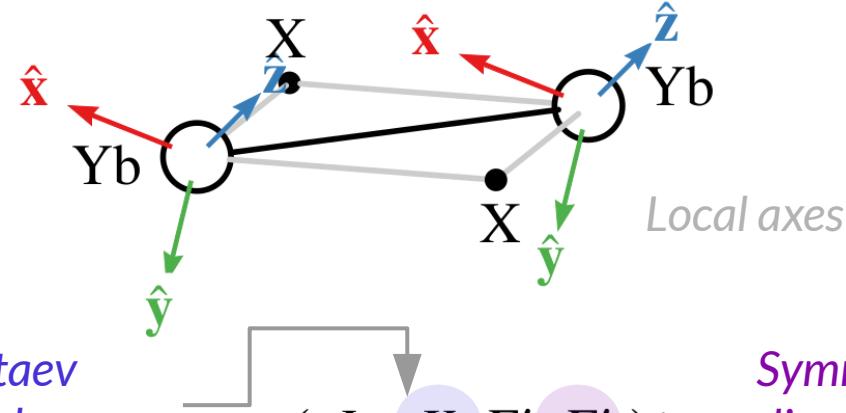
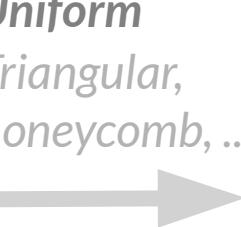
- Global frame:

$$\sum_{\langle ij \rangle} \bar{\mathbf{S}}_i^\top \bar{\mathbf{J}}_{ij} \bar{\mathbf{S}}_j$$

Equivalent to local exchanges

Non-uniform
Pyrochlore,
breathing
pyrochlore

Uniform
Triangular,
honeycomb, ...

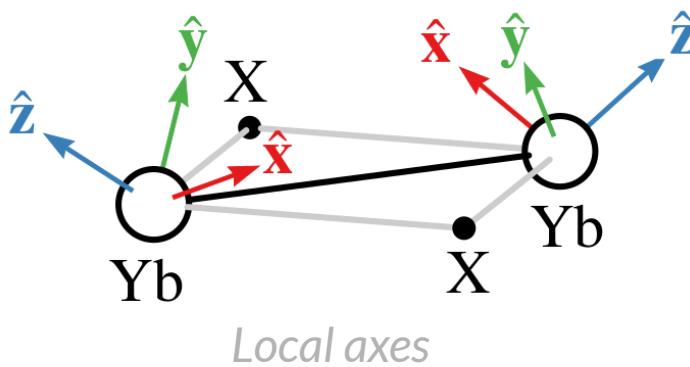


Kitaev exchange

Symmetric off-diagonal

Symmetric off-diagonal
Heisenberg exchange

$$\begin{aligned} \sum_{\langle ij \rangle} [J_{zz} S_i^z S_j^z - J_\pm (S_i^+ S_j^- + S_i^- S_j^+) + J_{\pm\pm} (\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-)] \\ + J_{z\pm} (\zeta_{ij} [S_i^z S_j^+ + S_i^+ S_j^z] + \zeta_{ij}^* [S_i^z S_j^- + S_i^- S_j^z]) \end{aligned}$$



Kitaev exchange

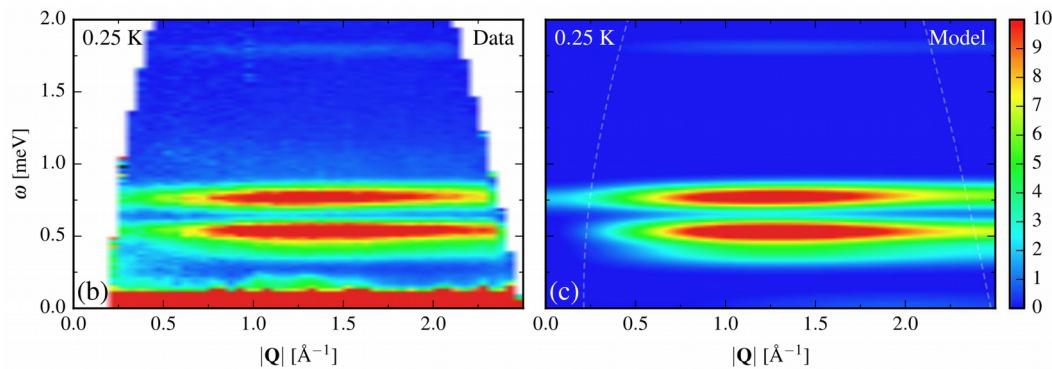
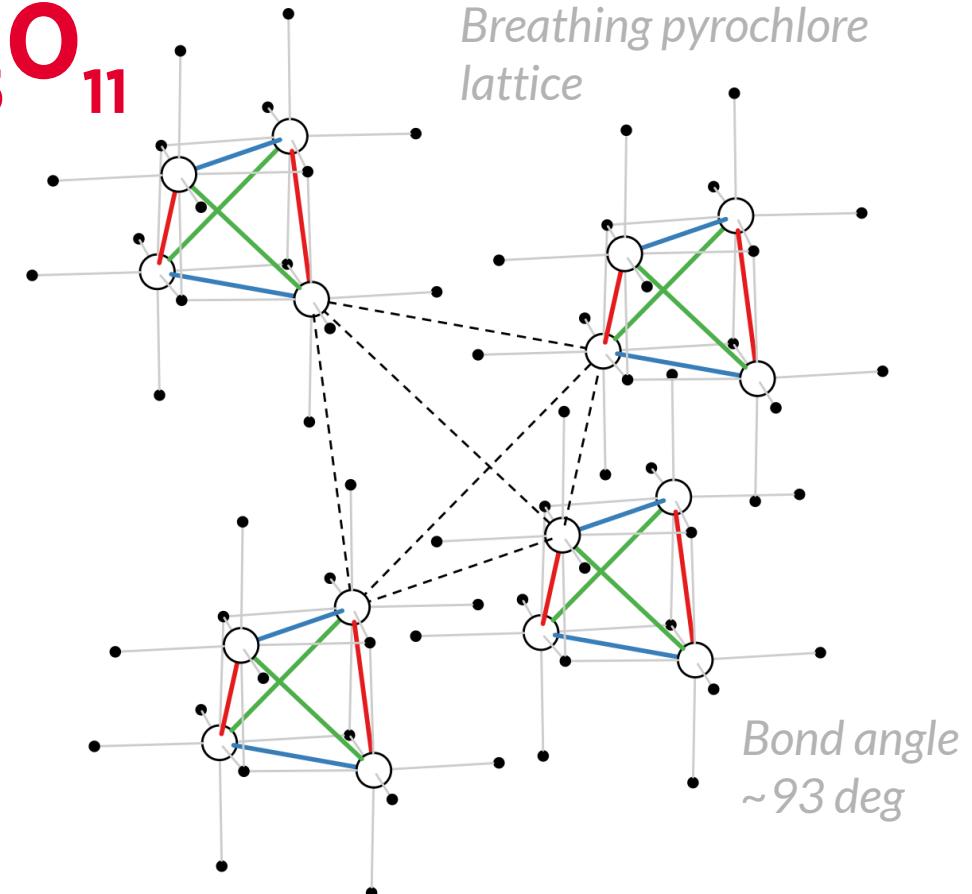
Symmetric off-diagonal

Dzyaloshinskii-Moriya (DM)
Heisenberg exchange

Does it work?

Validation: $\text{Ba}_3\text{Yb}_2\text{Zn}_5\text{O}_{11}$

- *Nearly decoupled* tetrahedra \rightarrow theoretically controlled
- Simple geometry – two *equivalent* exchange paths
- **Known:** g-factors and exchange constants
- *Robust* to details

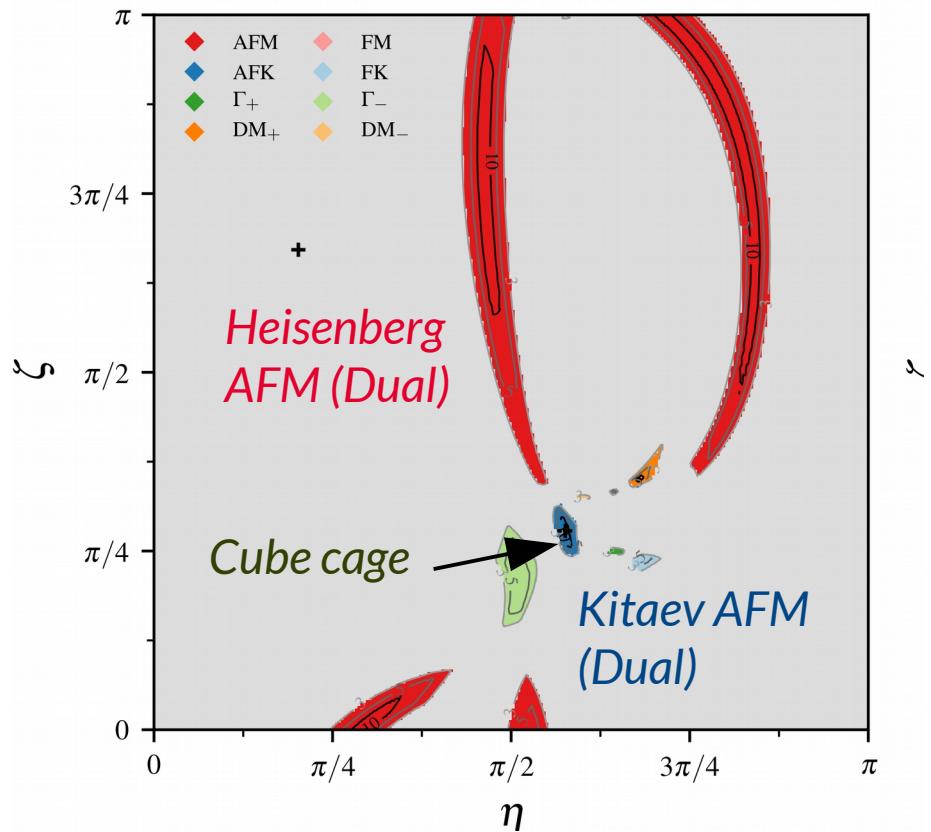
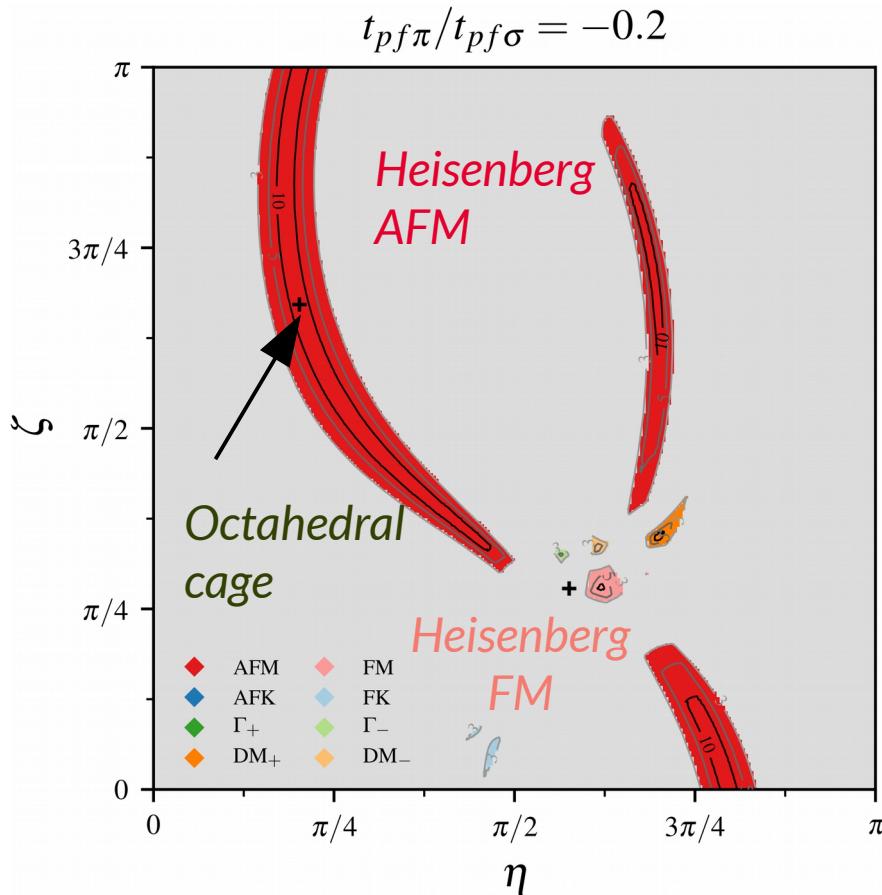


Computed from g-factors:
 $D/J \sim -0.23, K/J \sim \Gamma/J \sim -0.01$

Fitted from experiment:
 $D/J \sim -0.28, K/J \sim \Gamma/J \sim -0.01$

Exchange diagram (pyrochlore)

- Crystal field composition (η, ζ) \rightarrow exchange parameters
- Contains: Heisenberg AFM, Heisenberg FM, Kitaev, ...

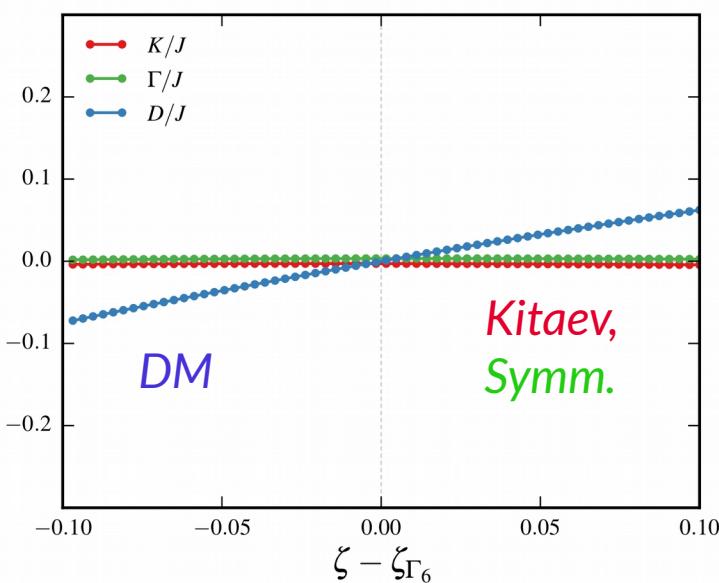
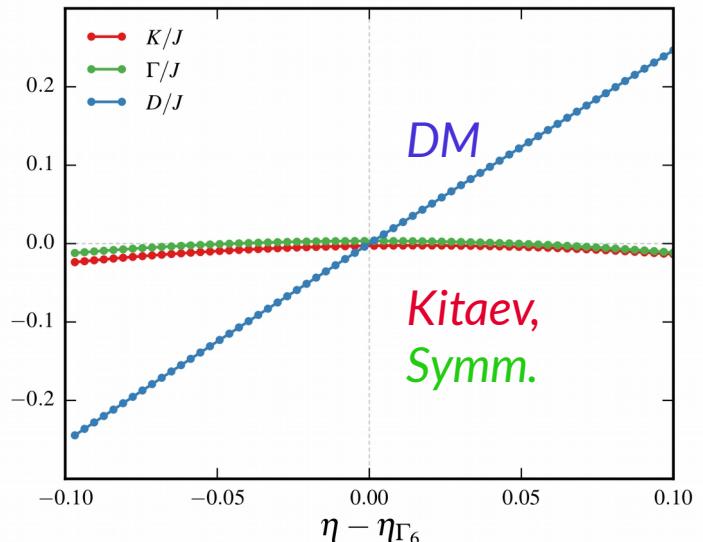
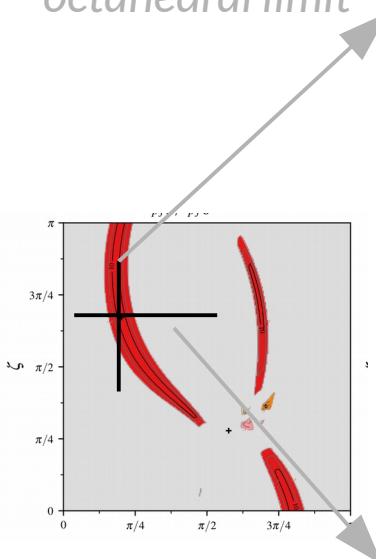


- Sensitive near cube limit

Non-generic regime?

Emergent weak anisotropy

Cuts near
octahedral limit

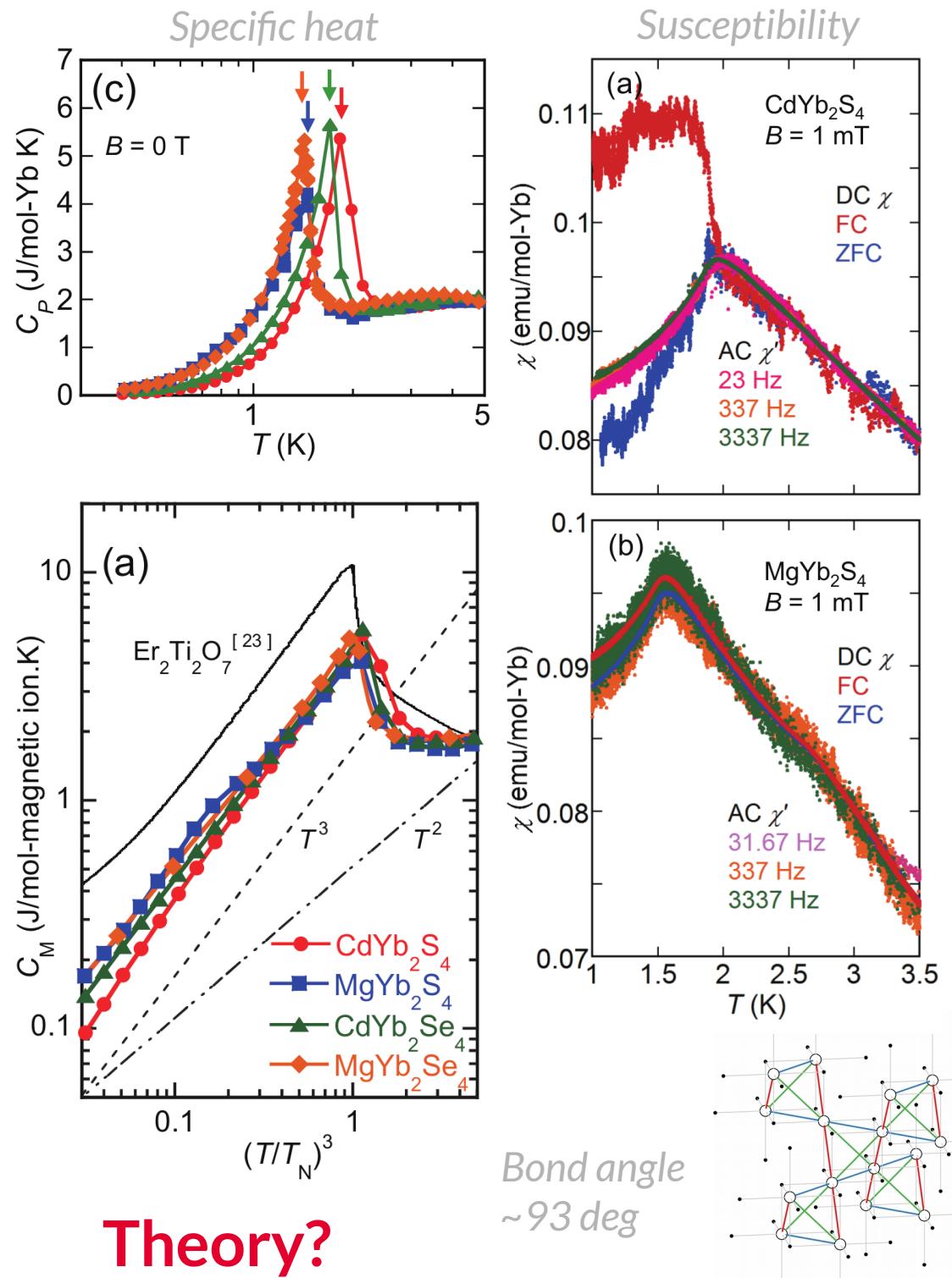


- Octahedral limit
- Not Γ_7 ($J_{\text{eff}}=1/2$) – ground doublet is Γ_6 doublet
- “Single orbital picture” → No cancellation
- Robust Heisenberg AFM with leading DM
- Near Γ_7 limit: cancellation → sensitive to details

Implications for rare-earth spinels?

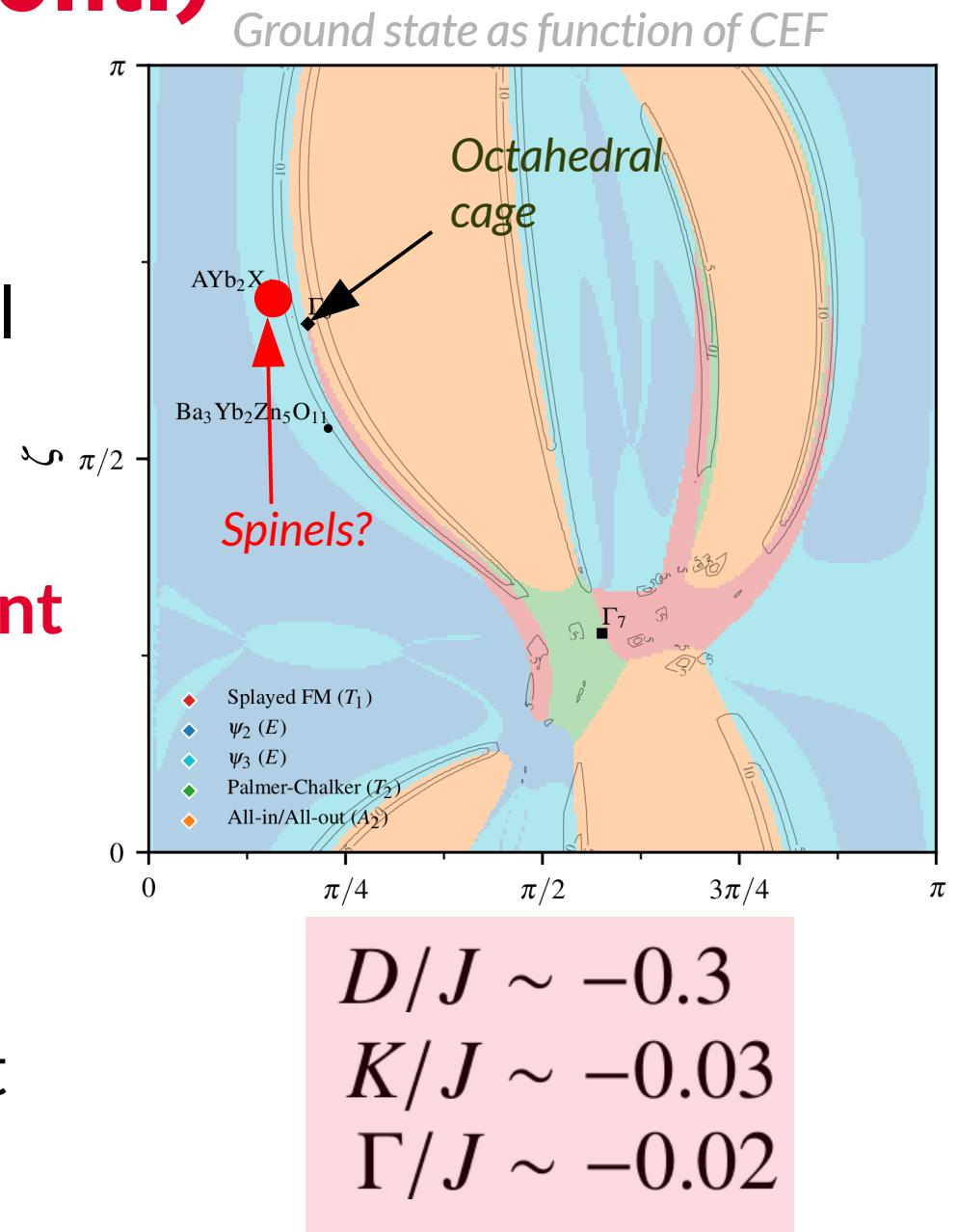
Ytterbium Spinels

- AYb_2X_4
 - A = Mg, Cd
 - X = S, Se
- Pyrochlore lattice
- Highly frustrated with T_N much smaller than exchange scale
- Ordered state appears to have **gapless excitations**
- μ -SR hard to interpret



Ytterbium Spinels (cont.)

- Estimate crystal field by rescaling related MgEr_2Se_4
[D. Reig-i-Plessis et al, arxiv:1703.04267]
- Not too far from octahedral limit
- Dominant **AF Heisenberg** exchange with **sub-dominant (indirect) DM interactions**
- Classical ground state?
 - Local XY FM (Γ_5)
- Observed directly in recent neutron scattering experiments



[P. Dalmas de Reotier et al, Phys. Rev. B. 96, 134403 (2017)]

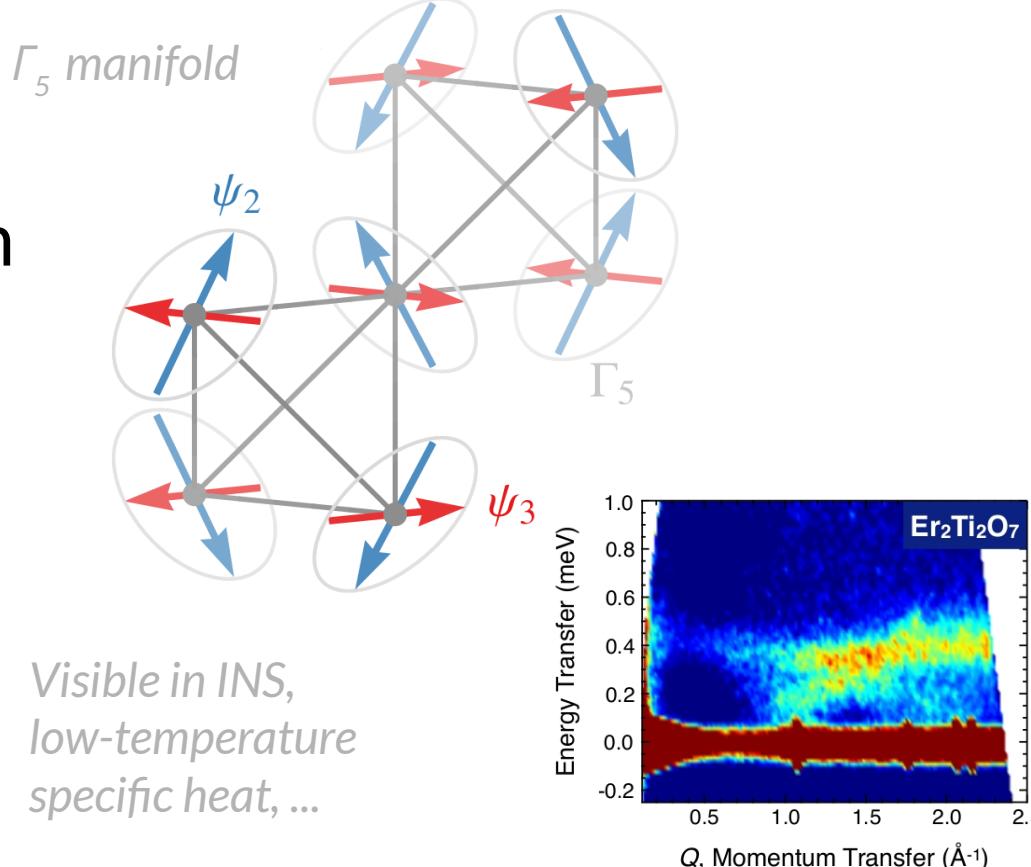
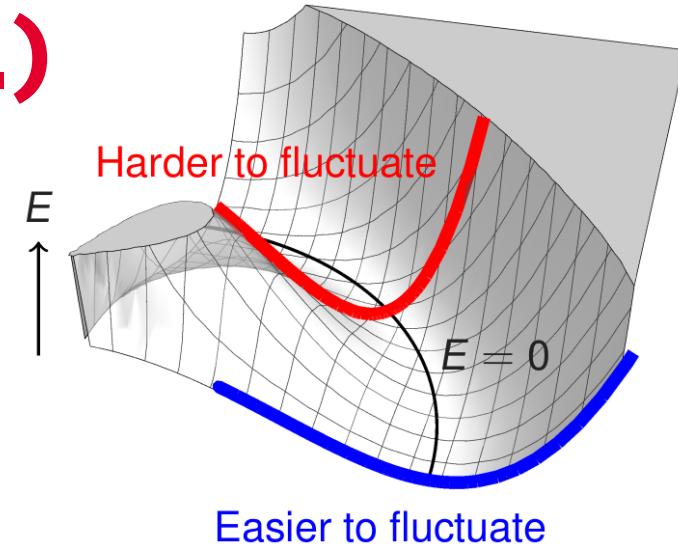
What does it look like?

Ytterbium Spinels (cont.)

Possibility #1: Similar to physics in $\text{Er}_2\text{Ti}_2\text{O}_7$

- Clean “order-by-disorder”
 - Quantum selection should dominate
- For calculated parameters: quantum zero-point motion selects a ψ_3 state
- Well-defined magnons
- Expect pseudo-Goldstone gap of $\sim \mathcal{O}(90 \mu\text{eV})$ or so

Taking $J \sim 1 \text{ meV}$



Visible in INS,
low-temperature
specific heat, ...

Ytterbium Spinels (cont.)

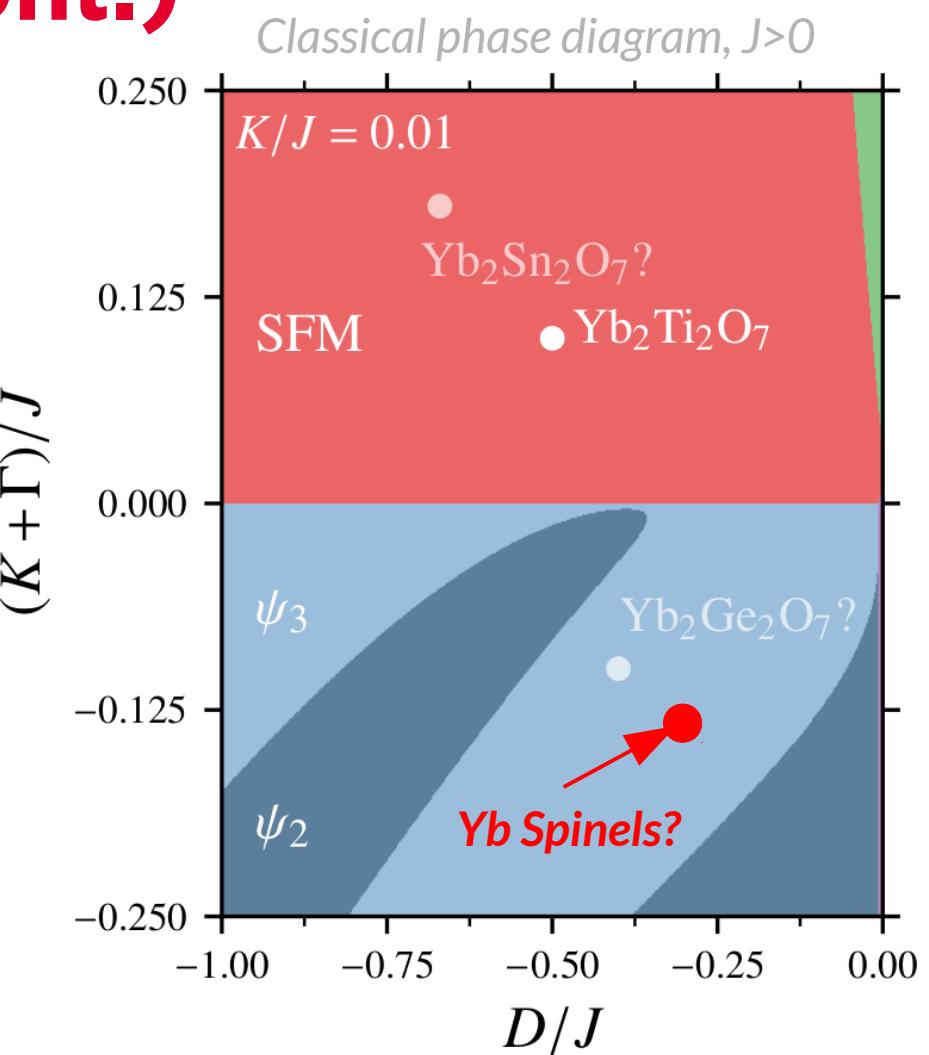
Possibility #2: Similar to physics in $\text{Yb}_2\text{Ti}_2\text{O}_7$

- Sits near **phase boundary**

[Canals et al, Phys. Rev. B 78, 214431 (2008)
Chern, arXiv:1008.3038]

- Boundary between Γ_5 and splayed-FM order
- **Same boundary** (modulo a duality) thought to be responsible for rich physics in $\text{Yb}_2\text{M}_2\text{O}_7$

Estimated exchanges
for $\text{Yb}_2\text{Ti}_2\text{O}_7$

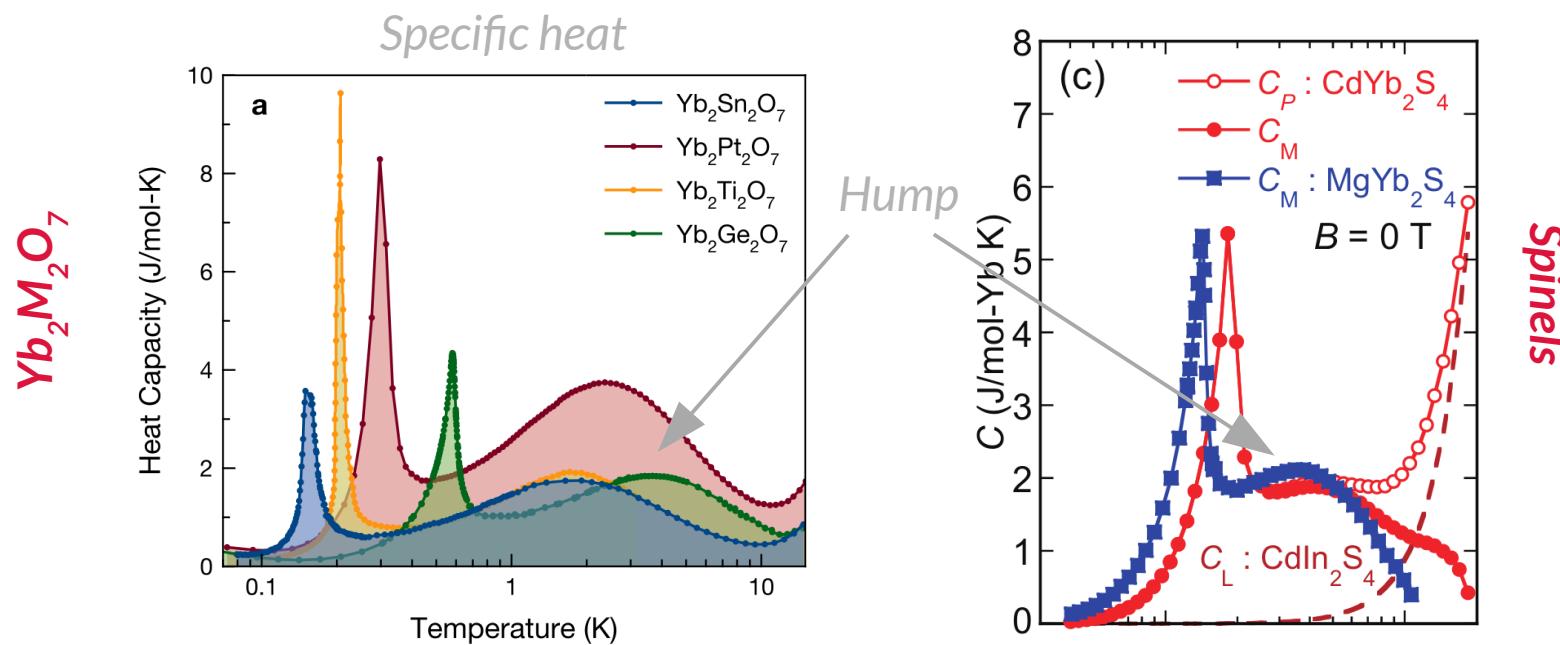
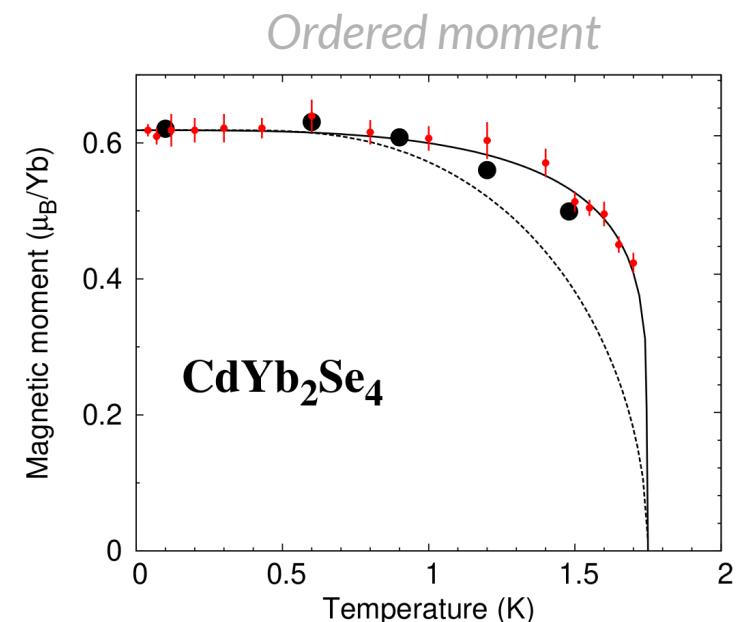


Jaubert et al, Phys. Rev. Lett. 115, 267208 (2015)
Thompson et al, Phys. Rev. Lett. 119, 057203 (2017)

$\tilde{D}/\tilde{J} = -0.5$
 $\tilde{K}/\tilde{J} = 0.01$
 $\tilde{\Gamma}/\tilde{J} = +0.1$

Ytterbium Spinels (cont.)

- Indirect evidence for #2
- Similar high temperature “hump” in specific heat above ordering temperature
- Similar small ordered moment



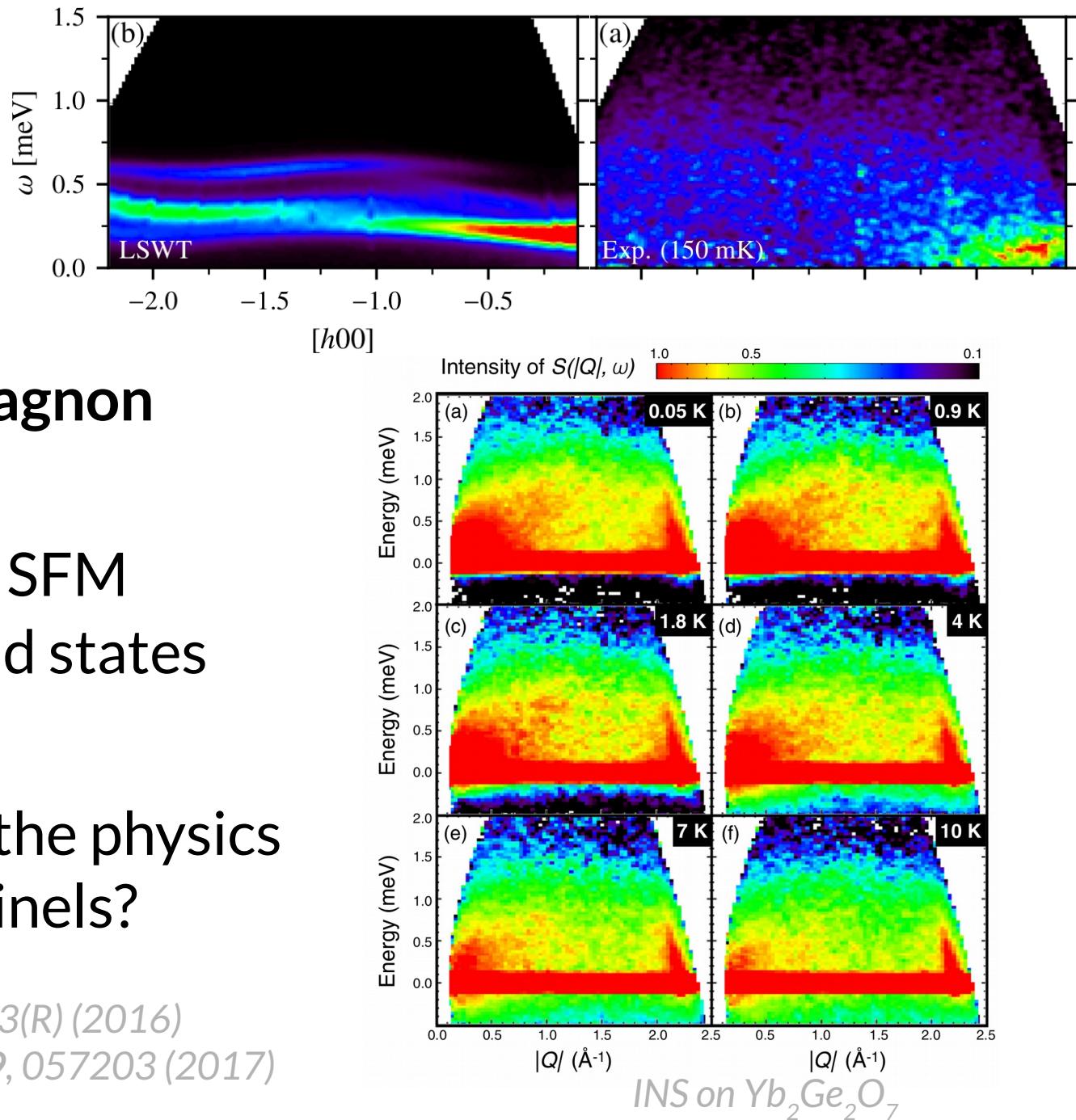
Ytterbium Spinels (cont.)

Highly unusual dynamics in $\text{Yb}_2\text{M}_2\text{O}_7$

- No well-defined magnon modes
- In compounds with SFM (Ti, Sn) and Γ_5 ground states (Ge)
- New realization of the physics in the ytterbium spinels?

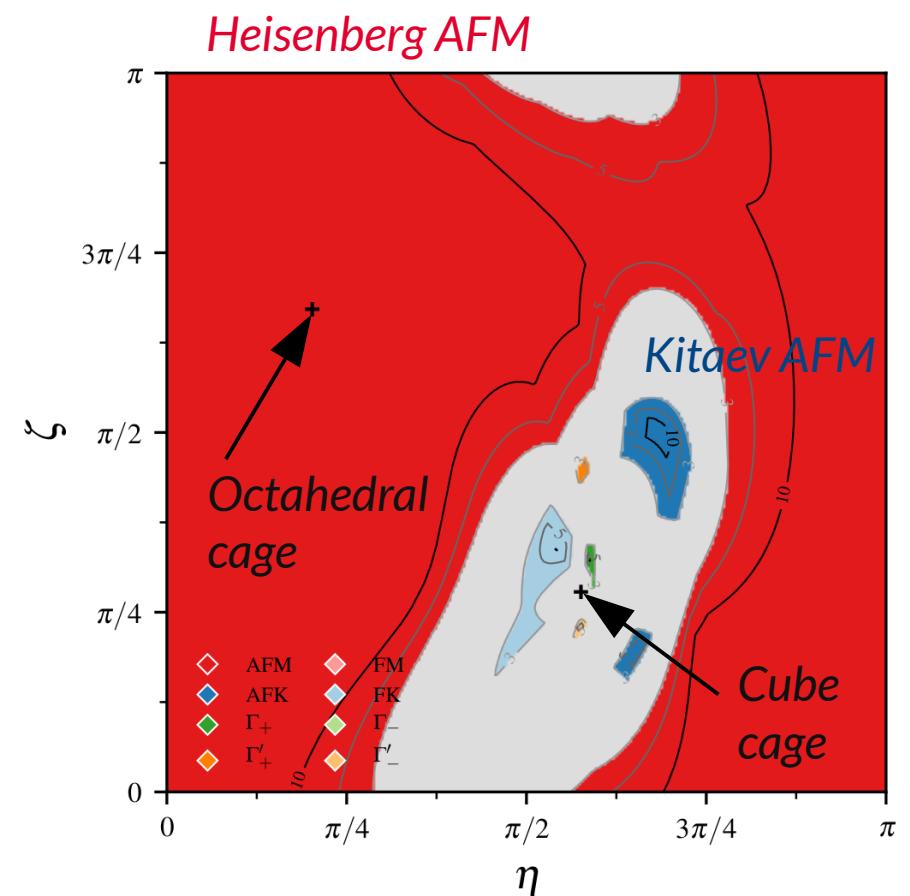
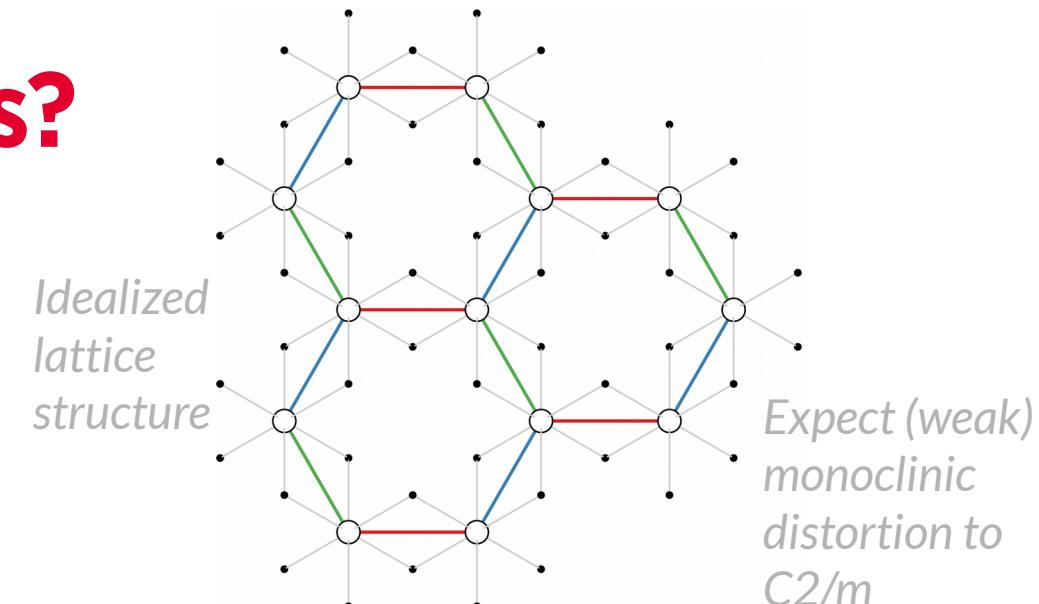
Hallas *et al*, Phys. Rev. B 93, 100403(R) (2016)

Thompson *et al*, Phys. Rev. Lett. 119, 057203 (2017)



Honeycomb magnets?

- Connect directly back to Kitaev materials
- Possible example: YbCl_3
 - Limited information
- Appears to have same structure as RuCl_3
- Kitaev physics?
- Bond angle looks fairly non-ideal
- Speculative; role of monoclinic disorder, etc



Conclusions

- There are corners of rare-earth exchange that is understandable → **non-generic**

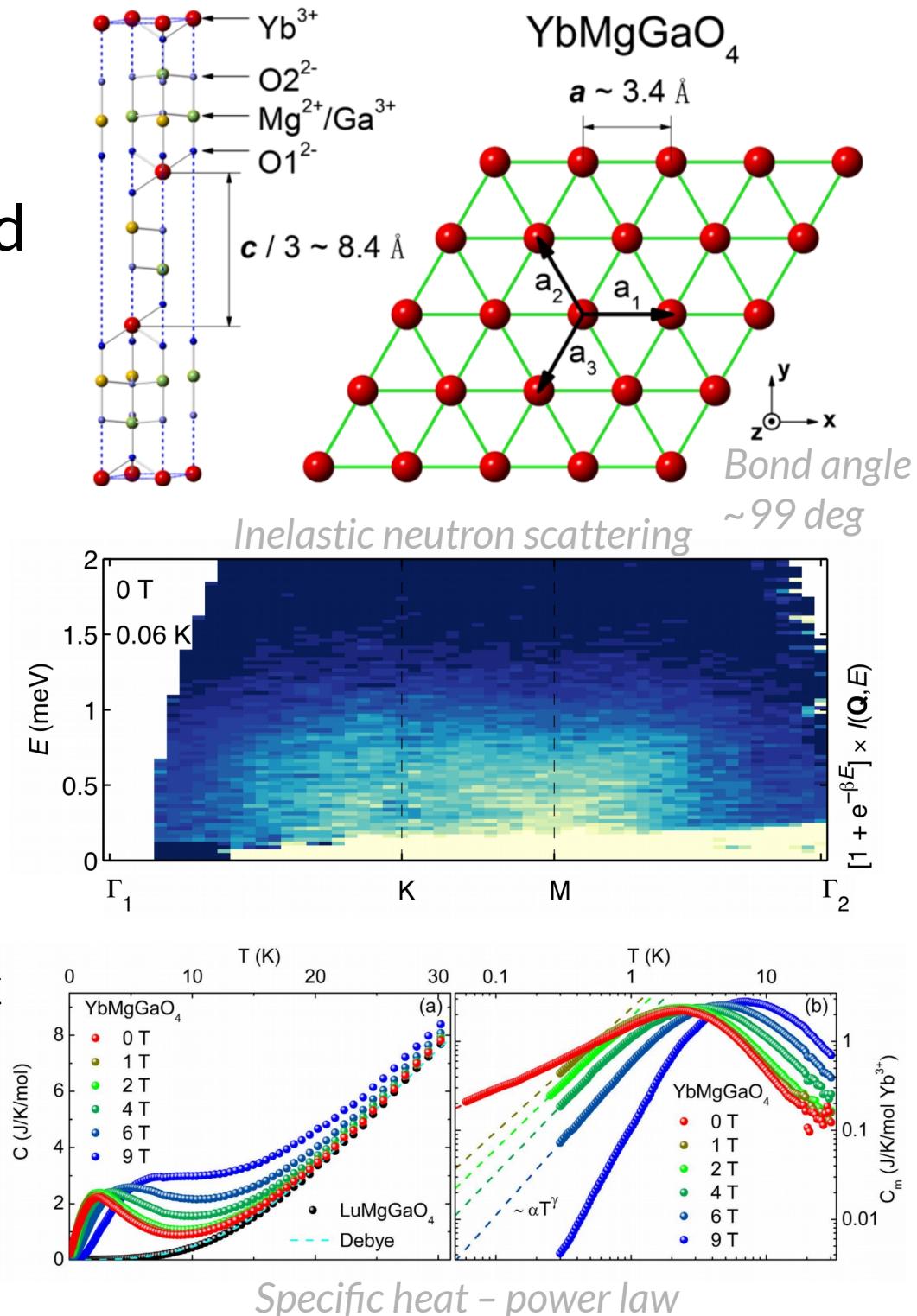
Emergent “weak” spin-orbit limit: robust H-AFM with subdominant DM near octahedral limit (Γ_6)

- Applications to $(\text{Cd},\text{Mg})\text{Yb}_2(\text{S},\text{Se})_4$?
- Applications to YbMgGaO_4 (**exchange disorder**), possibly YbCl_3, \dots (**new materials?**)
- Sensitive regime near “cube” (Γ_7) limit
 - Relevant for pyrochlores (distorted cube, not 90°)
 - **Highly** anisotropic regimes (Kitaev, etc)
 - Possible reason why so rich

**Thank you for your
attention**

YbMgGaO_4

- Recent quantum spin liquid candidate
- Triangular lattice of edge-shared YbO_6 octahedra
- **No phase transition** down to low temperature
- Power-law specific heat
- **Broad continuum** of scattering seen in inelastic neutron scattering



Li et al, Sci. Rep. 5, 16419 (2015)

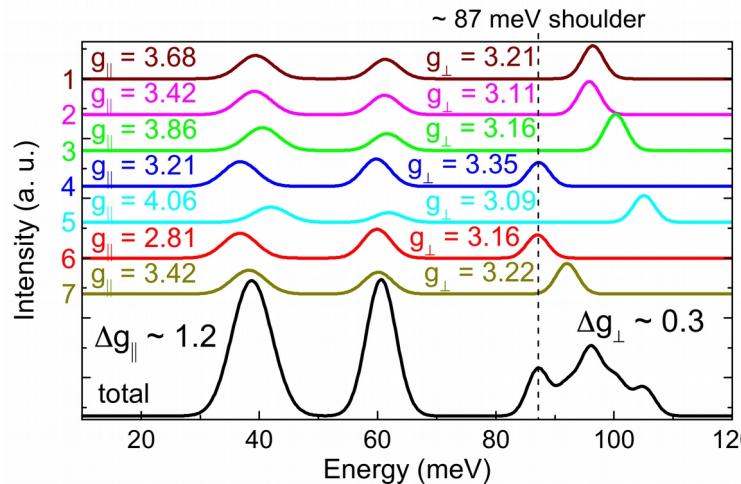
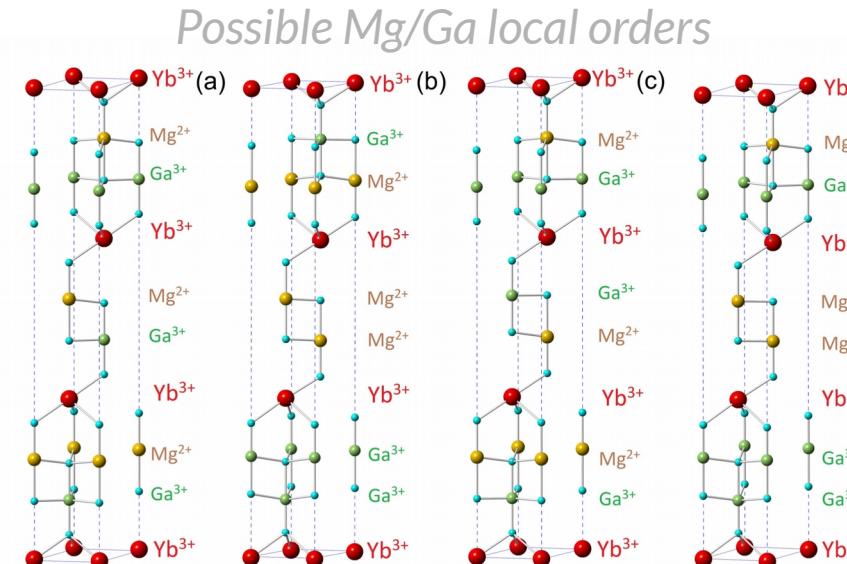
Li et al, Phys. Rev. Lett. 115, 167203 (2016)

Shen et al, Nature 540, 559–562 (2016)

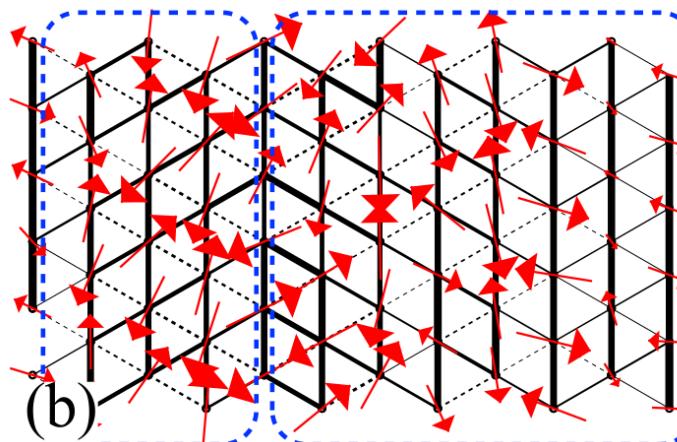
Paddison et al, Nat. Phys. 13, 117–122 (2017)

YbMgGaO_4 (cont.)

- Some wrinkles
- $\text{Mg}^{2+}/\text{Ga}^{3+}$ ions are **structurally disordered**
- Effects on magnetic properties?
 - Single-ion?
 - Exchange?
- Expected thermal conductivity due to “spinons” not observed
- **Disorder in disguise?**



Evidence for several CEF environments in INS



Disordered “stripe” ground state

YbMgGaO₄ (cont.)

- Compute exchange within our approach
- Use estimate single-ion/structural details from Li et al.
 - Seven local envs.
- Strong variation in magnitude of exchange and anisotropy
- Supports picture that **strong exchange disorder should be present**

Variation in ground doublet composition

Env.	η	ζ	g_z	g_{\pm}
1	1.197	2.440	+3.697	-3.221
2	1.195	2.439	+3.670	-3.229
3	1.218	2.444	+3.873	-3.163
4	1.147	2.423	+3.213	-3.352
5	1.242	2.449	+4.066	-3.092
6	1.144	2.422	+3.182	-3.359
7	1.179	2.434	+3.530	-3.270

Different Mg/
Ga positions

Variation
Strong variation as function of bond angle in scale

θ	Env.	J_{\pm}/J_{zz}	$J_{\pm\pm}/J_{zz}$	$J_{z\pm}/J_{zz}$	J_{zz}/J_{zz}^0
97°	1	-0.44	-0.06	0.03	1.63
	2	-0.44	-0.06	0.03	1.65
	3	-0.44	-0.07	0.04	1.49
	4	-0.44	-0.06	0.02	2.0
	5	-0.44	-0.07	0.04	1.34
	6	-0.44	-0.06	0.02	2.02
	7	-0.44	-0.06	0.03	1.76
99°	1	-0.36	-0.14	0.04	1.0
	2	-0.36	-0.13	0.04	1.02
	3	-0.36	-0.15	0.05	0.89
	4	-0.38	-0.11	0.02	1.29
	5	-0.35	-0.16	0.07	0.78
	6	-0.38	-0.11	0.02	1.31
	7	-0.37	-0.13	0.03	1.1
101°	1	-0.19	-0.3	0.05	0.56
	2	-0.2	-0.29	0.05	0.57
	3	-0.17	-0.32	0.08	0.49
	4	-0.25	-0.24	0.01	0.76
	5	-0.13	-0.36	0.11	0.42
	6	-0.25	-0.23	0.01	0.78
	7	-0.21	-0.27	0.04	0.63

Weak variation
as function of
CEF