Layer compounds with Spin-1/2 triangular and kagome lattices

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July 12, 2017, KITS, Beijing

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Acknowledgements:

- University of Tennessee
  Zhiling Dun, Ryan Sinclair, Ryan Rawl, Cristian Batista
- University of California, Santa Cruz
  Arthur Ramirez, Jennifer Trinh, Sriram Shastry
- Oak Ridge National Lab
  Clarina R. Dela Cruz, Tao Hong, Huibo Cao,
  Adam Aczel, Massa Matsuda
- National High Magnetic Field Lab
  Minseong Lee, Eun Sang Choi, Ryan Baumbach
- University of Sherbrooke
  Jeffery Quilliam
- ShangHai JiaoTong University
  Jie Ma
- Riken
  Yoshi Kamiya
- Peking University
  Yingxia Wang, Kuo Li, Yufei Hu

NSF early career award
DMR-1350002

NHMFL VSP program

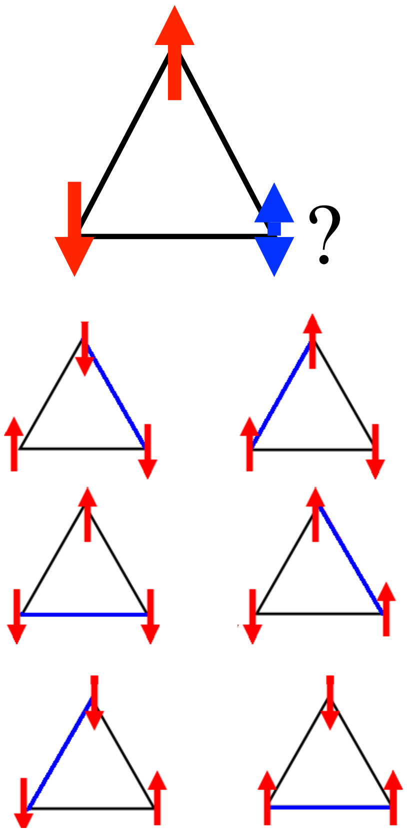
Motivation:

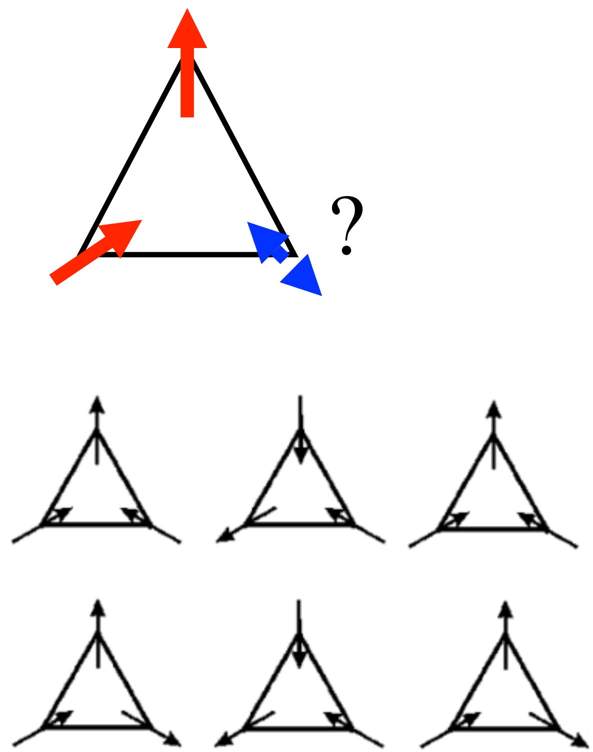
Low spin, low dimensionality, geometrically frustrated systems: strong quantum spin fluctuations

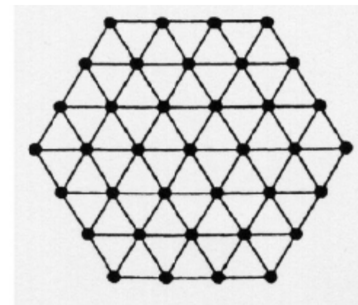
Spin 1/2, two dimensional triangular lattice and kagome lattice in layer compounds

Geometrically Frustrated Lattice

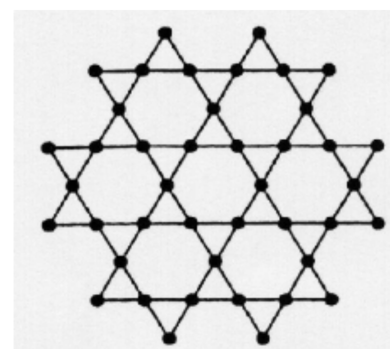
Interactions between magnetic degree of freedom in a lattice are incompatible with the underling crystal geometry ------Frustration







Triangular



Kagome

Frustration leads to degeneracy, which enhances spin fluctuations and suppresses magnetic ordering to *induce* ***exotic magnetism.***

Spin-1/2 Triangular lattice antiferromagnets

Quantum spin liquid (QSL) RARE!!

No long range order down to 0 K; No symmetry breaking; Long range entanglement; Fractional excitation

Organic molecular magnets: *k*-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

S. Yamashita et al., Nature Phys. ***4****, 459 (2008).*

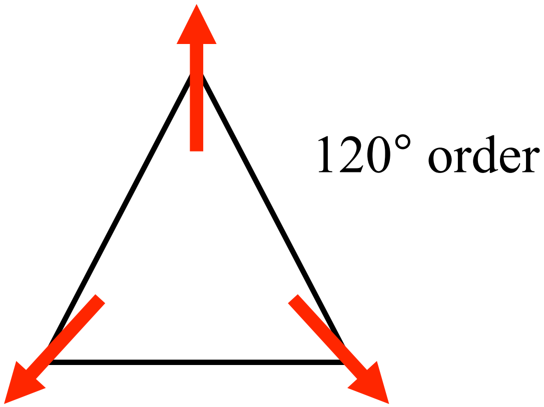
$YbMgGaO_4$ effective spin-1/2 Yb^{3+}

Y. Li et al., PRL ***115****, 167203 (2015);* ***117****, 097201 (2016)*

Y. Shen et al., Nature ***550****, 559 (2016)*

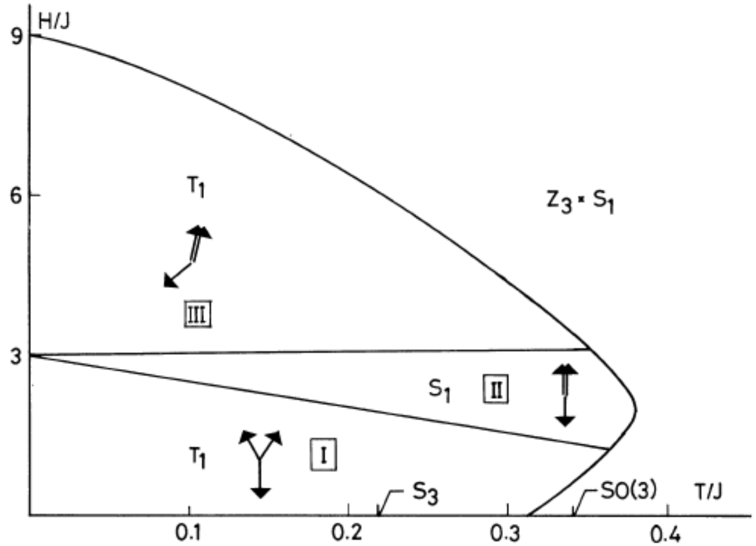
J. A. M. Paddison, H. D. Zhou et al., Nature Physics ***13****, 117 (2017)*

Spin-1/2 Triangular lattice antiferromagnets



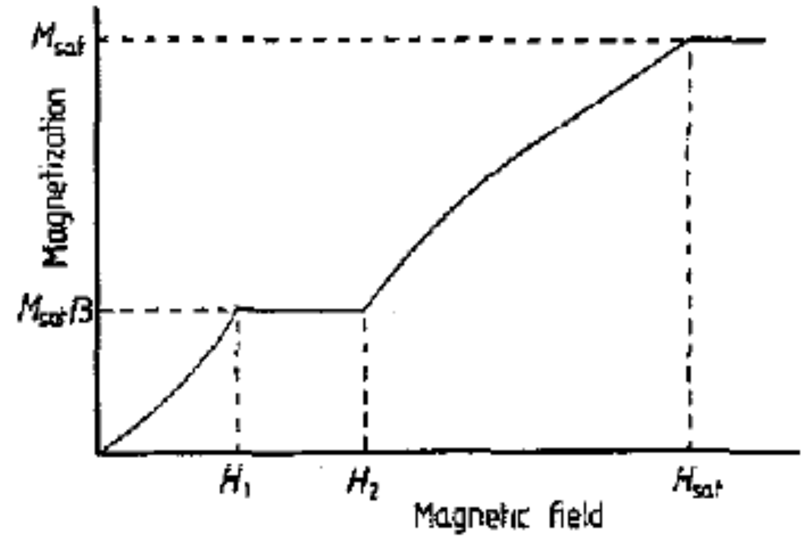
Spin anisotropy, lattice distortion (spatial anisotropy),
next nearest neighbor interactions, inter-layer interactions

Spin-1/2 Triangular lattice antiferromagnets



H. Kawamura and S. Miyashita
*JPSJ **54**, 4530 (1985)*

Spin state transitions with applied field



A. V. Chubukov and D. I. Glosov
JPCM 3, 69 (1991)

Quantum spin fluctuations (QSFs) stabilize a 1/3 magnetization plateau, which is the Up up down (UUD) phase **RARE!!**

Even with long range ordering (LRO), the QSFs still make the system approaching a "Quantum melting point" (QMP) that signals the transition into a QSL phase.

Spin-1/2 Triangular lattice antiferromagnets

In 1966, Mermin and Wagner demonstrated that thermal fluctuations prevent 2D magnets to spontaneously break their continuous spin-rotation symmetry if the interactions decay fast enough with the distance between spins. **RARE!!**

$T_N = 0$ K

N. D. Mermin and H. Wagner, PRL ***17****, 1133 (1966).*

Where to find spin 1/2 in GFMs?

Cu^{2+}, $3d^9$

$ZnCu_3(OH)_6Cl_2$, Herbertsmithite, kagome lattice, QSL

Cs_2CuBr_4, distorted triangular lattice, LRO with UUD

Ir^{4+}, $5d^5$

$Na_4Ir_3O_8$, hyper-kaogme, QSL

Co^{2+}, $3d^7$, effective spin 1/2

$Ba_3CoSb_2O_9$,

$B_3CoNb_2O_9$, $B_8CoNb_6O_{24}$,

Yb^{3+},$4f^{13}$, effective spin 1/2

$Yb_2Ti_2O_7$, pyrochlore, QSL

$MgYbGaO_4$, triangular, QSL

$Mg_2Yb_3Sb_3O_{14}$, $Mg_2Er_3Sb_3O_{14}$

Organic molecular magnets:

k-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Ru_2O_9 dimer

$Ba_3ARu_2O_9$ ($A = Y^{3+}$, In^{3+}, Lu^{3+})

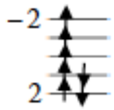
Mo_3O_{13} clusters

$LiZn_2Mo_3O_8$, triangular QSL?

$Li_2In_{1-x}Sc_xMo_3O_8$

Co^{2+}

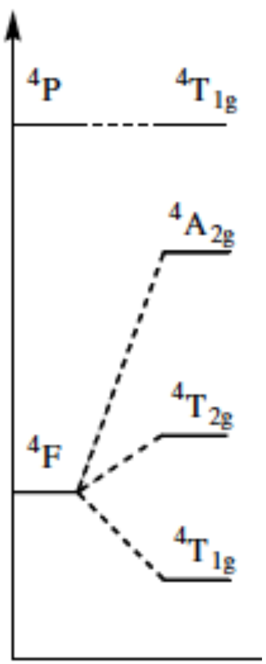
Co^{2+} : $3d^7$



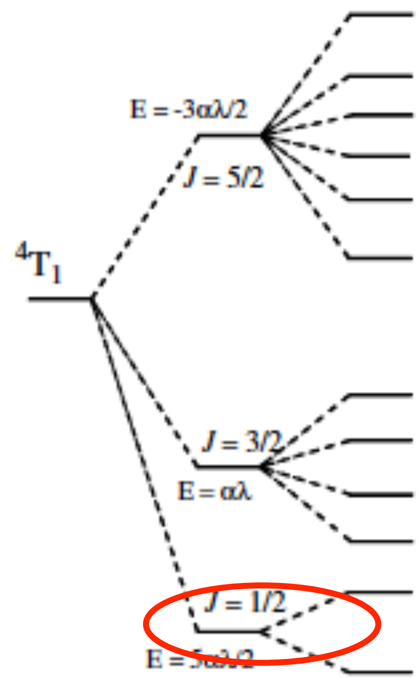
$$\begin{cases} S = 3/2 \\ L = 4 + 2 - 1 - 2 = 3 \\ J = L + S = 9/2 \end{cases} \Rightarrow {}^4F_{9/2}$$

Co^{2+} on octahedron site

F. Lloret et al., Inorganica Chimica Acta ***361****, 3432 (2008)*

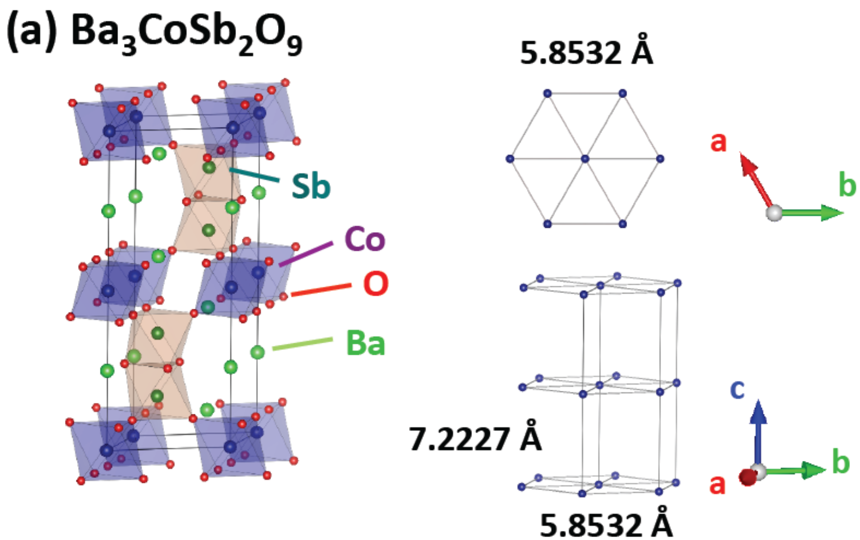


Crystal field



Spin orbital coupling

$Ba_3CoSb_2O_9$ triple perovskite



Ba^{2+}: non magnetic
Co^{2+}: magnetic
Sb^{5+}: non magnetic

Single crystal grown by using floating zone technique

Equilateral triangles with Co^{2+} effective spin 1/2

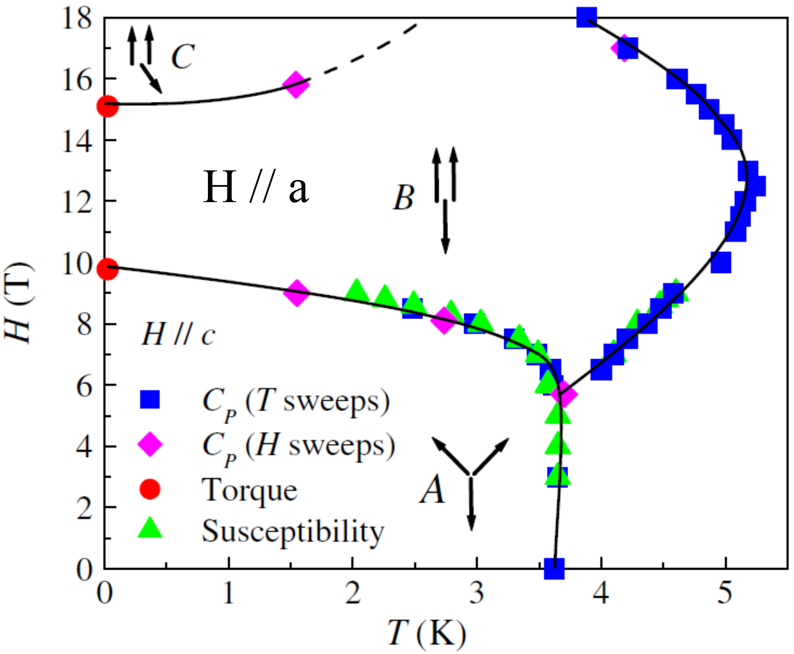
crystal structure: P63 /mmc

$T_N = 3.7$ K

Weak XXZ anisotropy (easy-plane)

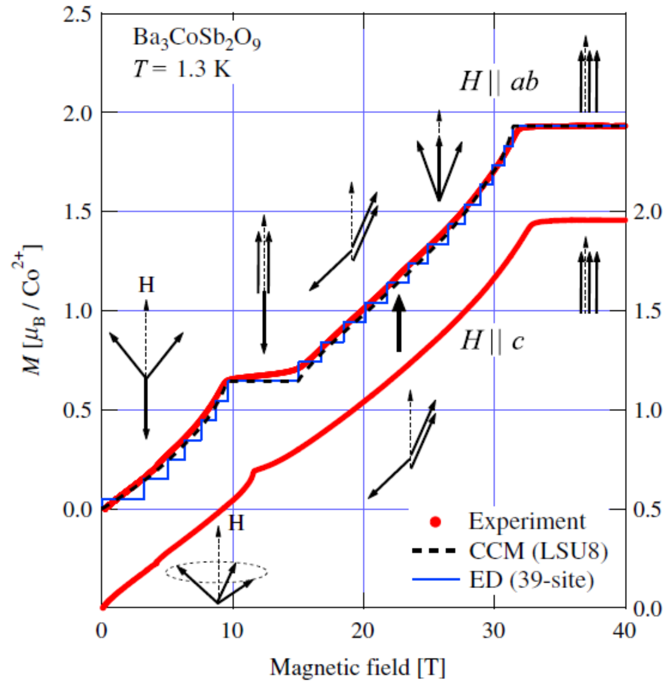
Small inter-layer coupling (antiferromagnetic)

$Ba_3CoSb_2O_9$ phase diagram



UUD phase: 10 – 15 T approaching zero temperature

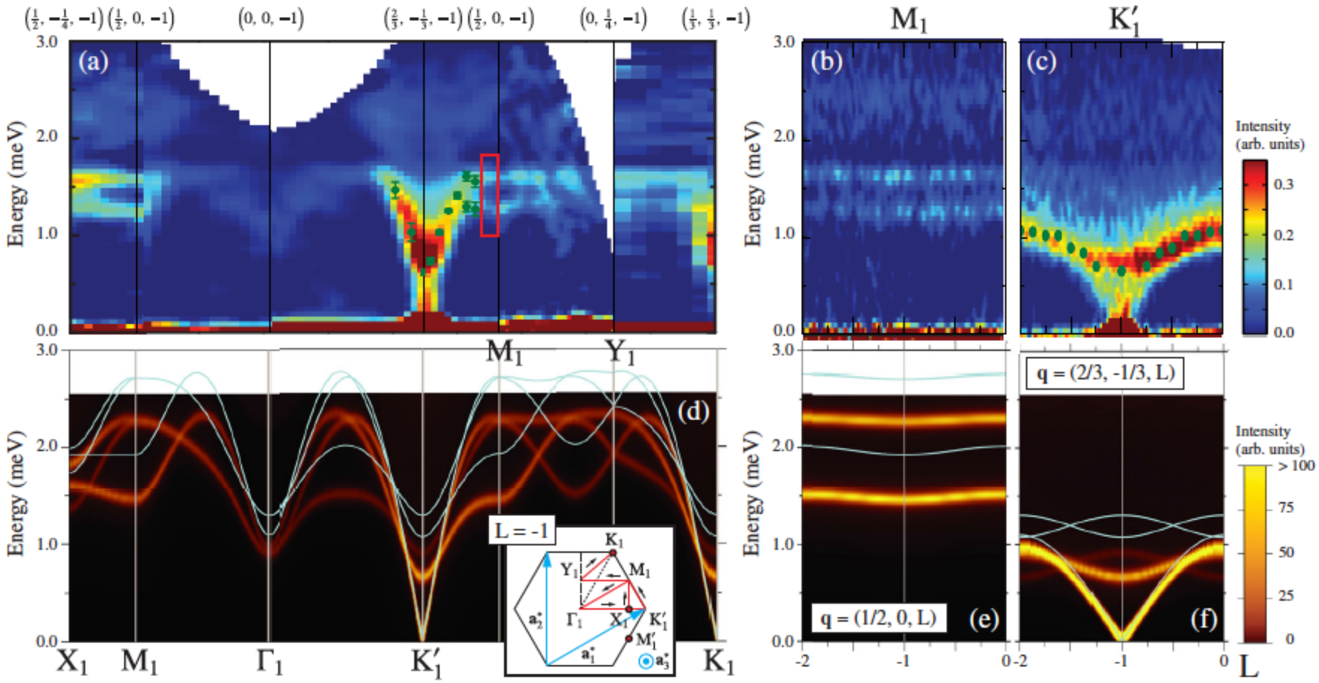
H. D. Zhou, et al. PRL ***109****, 267206 (2012)*

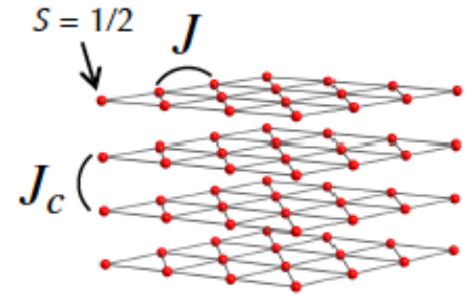


Saturation moment is around 1.9 μ_B, meaning S = 1/2, g = 3.8.

T. Susuki, et al. PRL ***110*** *267201 (2013)*

$Ba_3CoSb_2O_9$ zero field spin wave





$$\mathcal{H} = \sum_{\langle jk \rangle} J_{jk} \left(S_j^x S_k^x + S_j^y S_k^y + \Delta S_j^z S_k^z \right) - g_{\alpha\alpha} \mu_B H^\alpha \sum_j S_j^\alpha$$

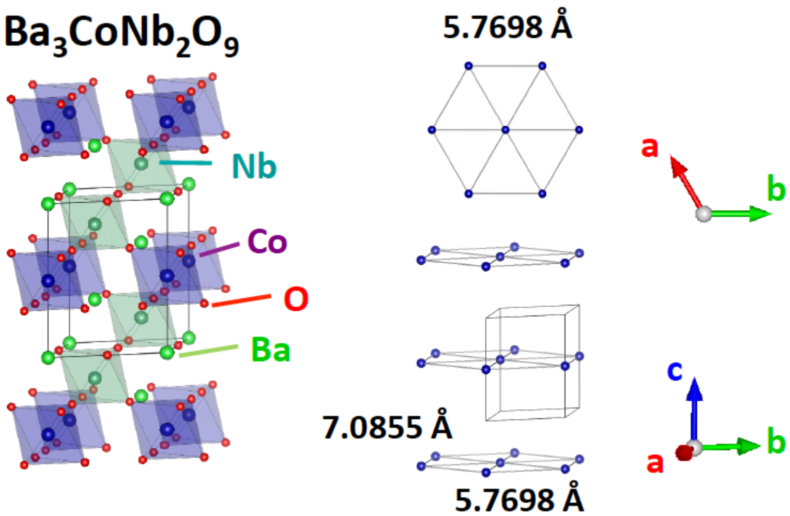
$$J_{jk} = \begin{cases} J & \text{for intra-layer nearest neighbors (NNs)} \\ J_c & \text{for inter-layer NNs} \end{cases}$$

$$\Delta = 0.89, \quad J_c/J = 0.05, \quad J = 1.7\ \text{meV}$$

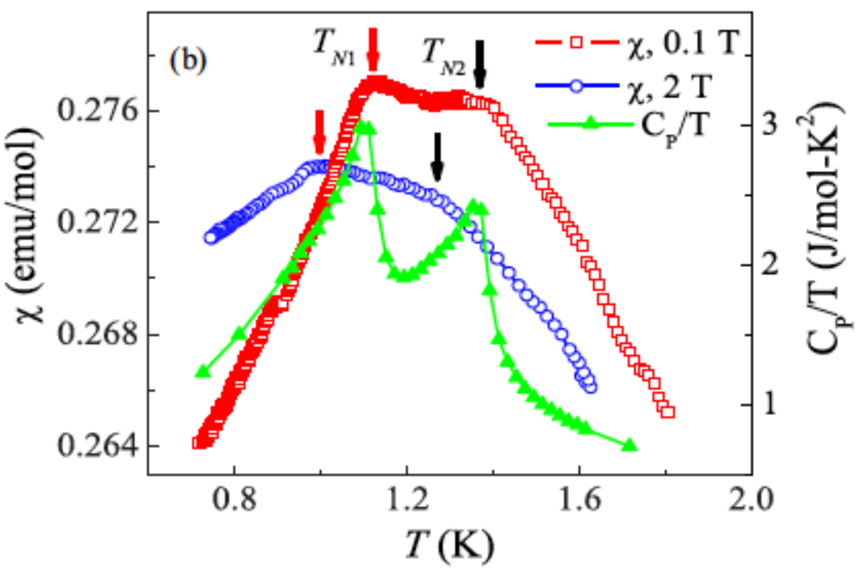
*J. Ma and H. D. Zhou et al. PRL **116** 087201 (2016)*

The linear and nonlinear spin-wave theories (SWTs) are inadequate to explain magnon decay with intrinsic line broadening. The system is approaching QMP with strong QSFs.

$Ba_3CoNb_2O_9$



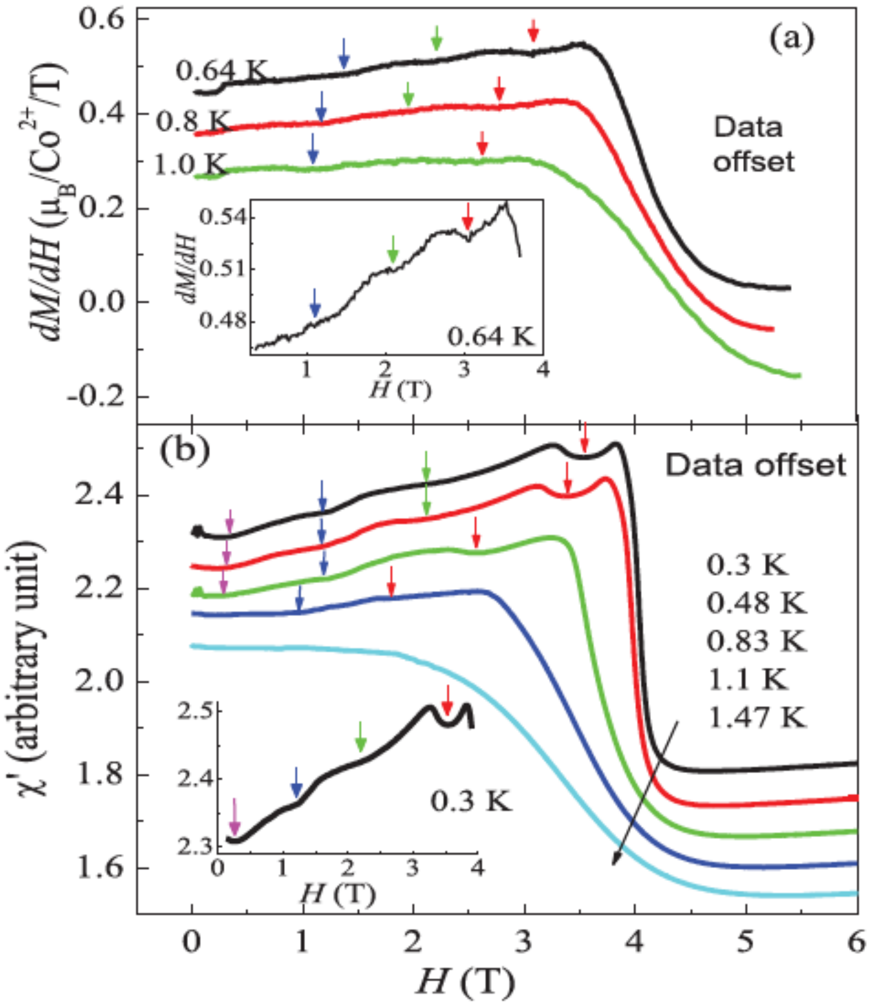
Ba^{2+}: non magnetic
Co^{2+}: magnetic
Nb^{5+}: non magnetic

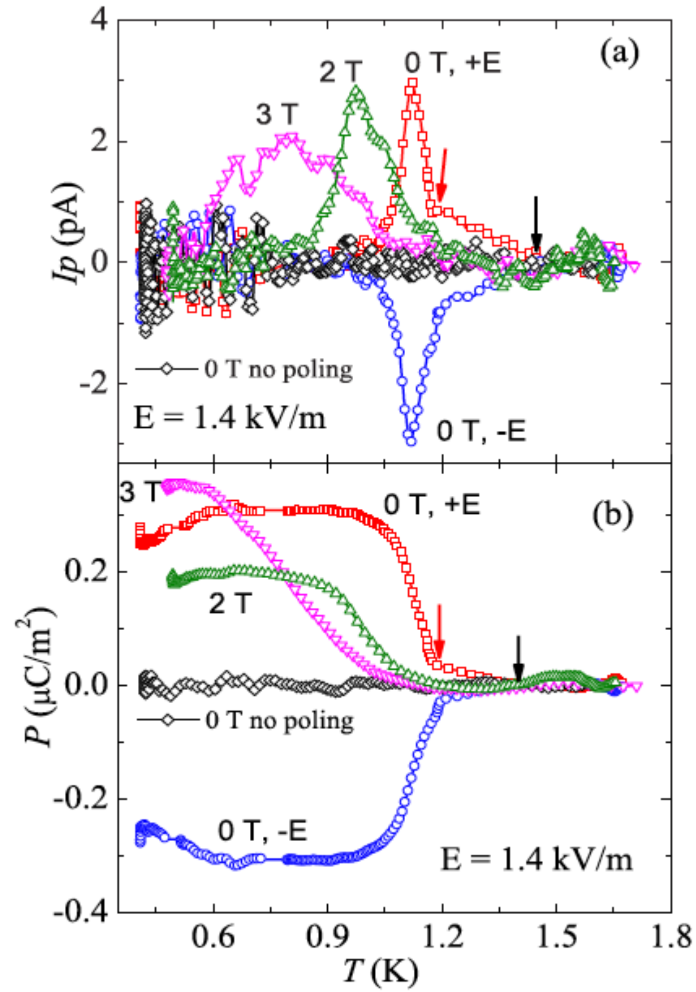


Two step transitions
T_{N1} = 1.36 K, T_{N2} = 1.31 K ,
indicating easy axis anisotropy

*M. Lee and H. D. Zhou, et al. PRB **89**, 104420 (2014)*

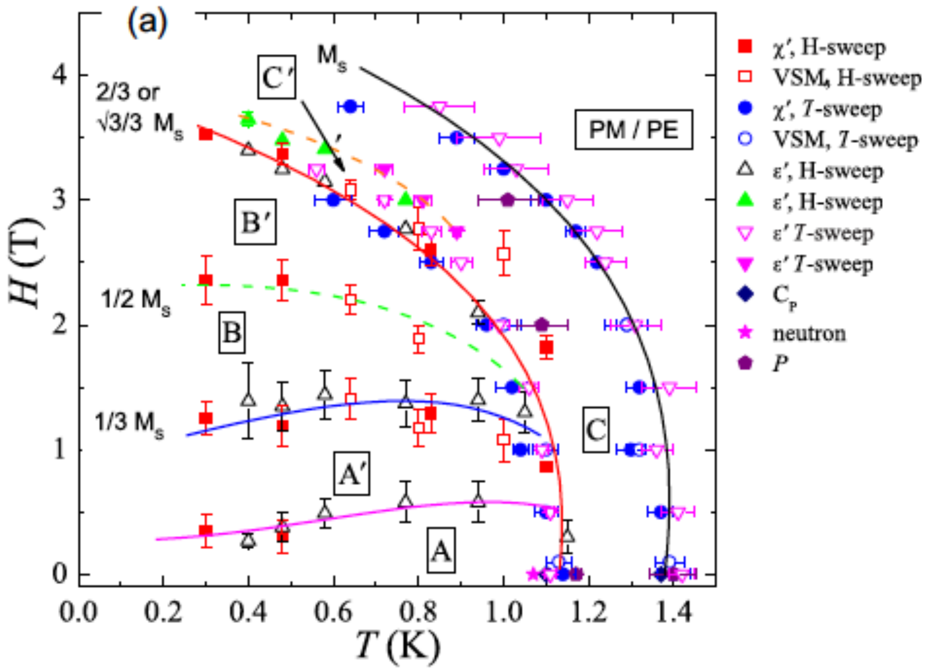
$Ba_3CoNb_2O_9$

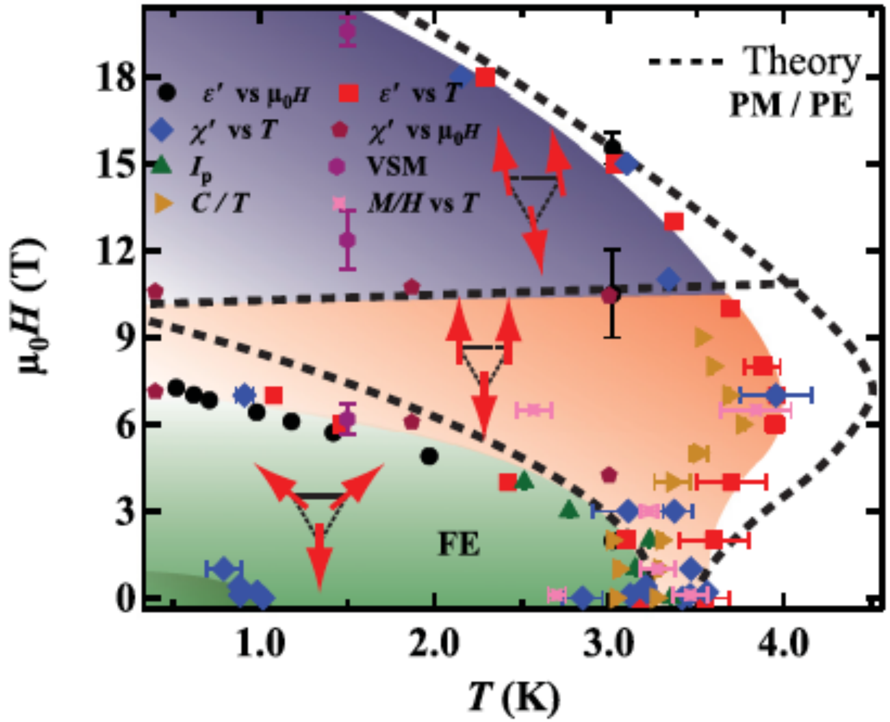




Series magnetic phase transitions and multiferroicity

$Ba_3CoNb_2O_9$ phase diagram





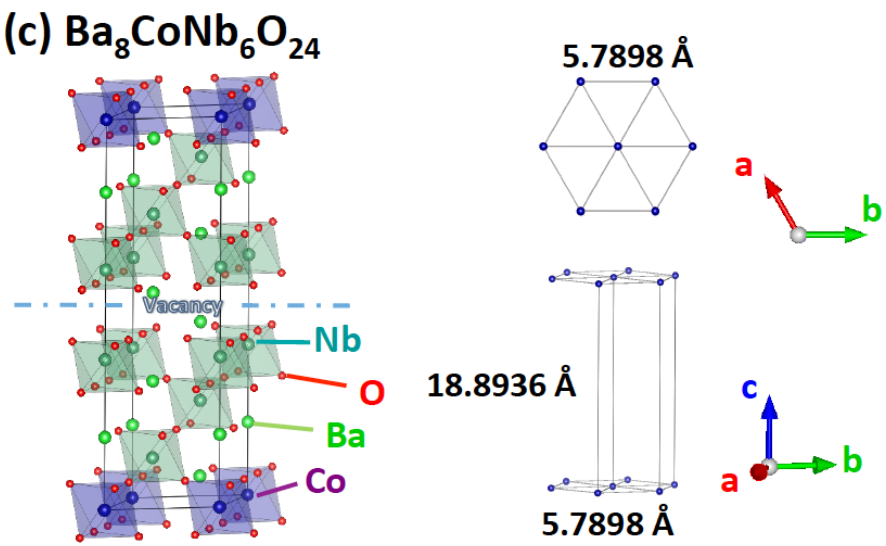
$Ba_3CoNb_2O_9$

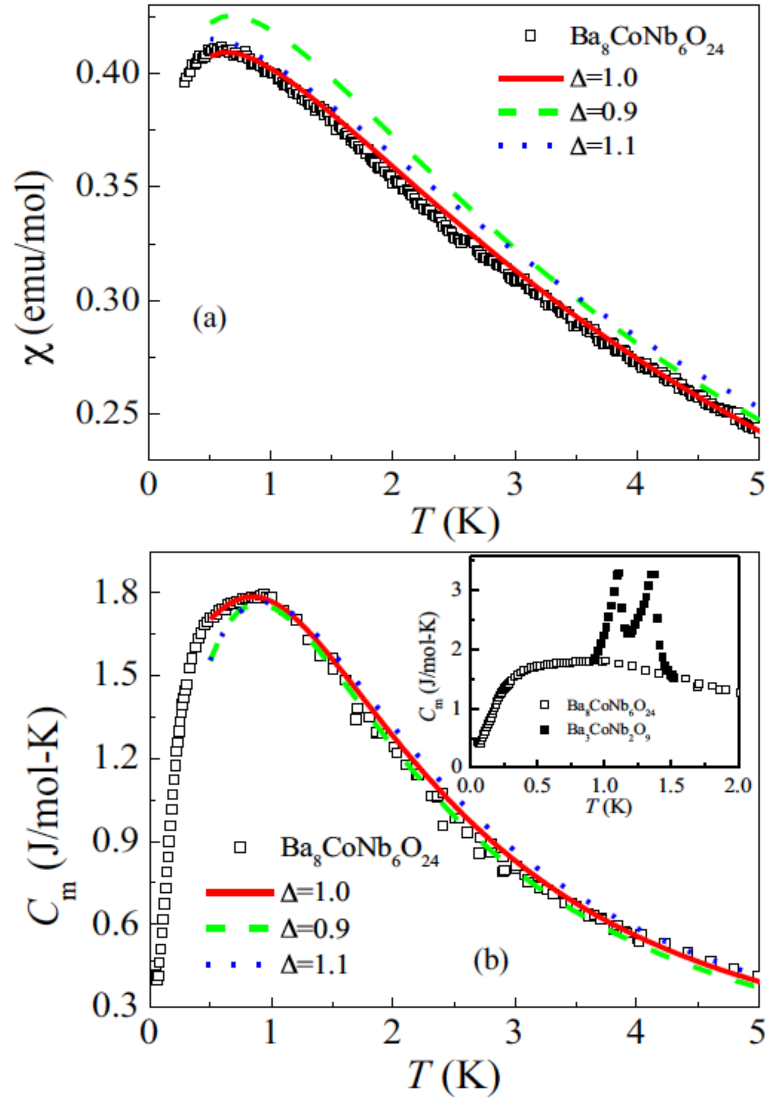
$Ba_3MnNb_2O_9$ (Mn^{2+}: S = 5/2)
the UUD phase closes at zero temperature

M. Lee and H. D. Zhou, et al. PRB ***90****, 224402 (2014)*

The dashed line is a theoretical calculation from
L. Seabra, T.Momoi, P. Sindzingre, and N. Shannon,
Phys. Rev. B ***84****, 214418 (2011).*

$Ba_8CoNb_6O_{24}$





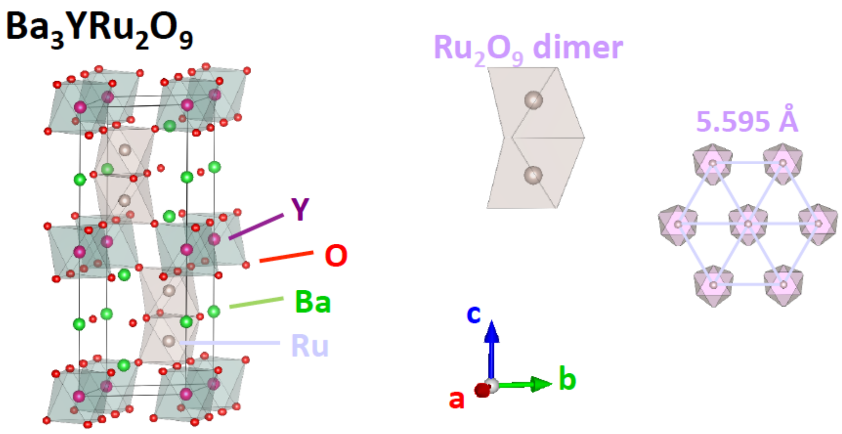
Approaching 2D Spin-1/2 triangular lattice without inter-layer interaction and anisotropy

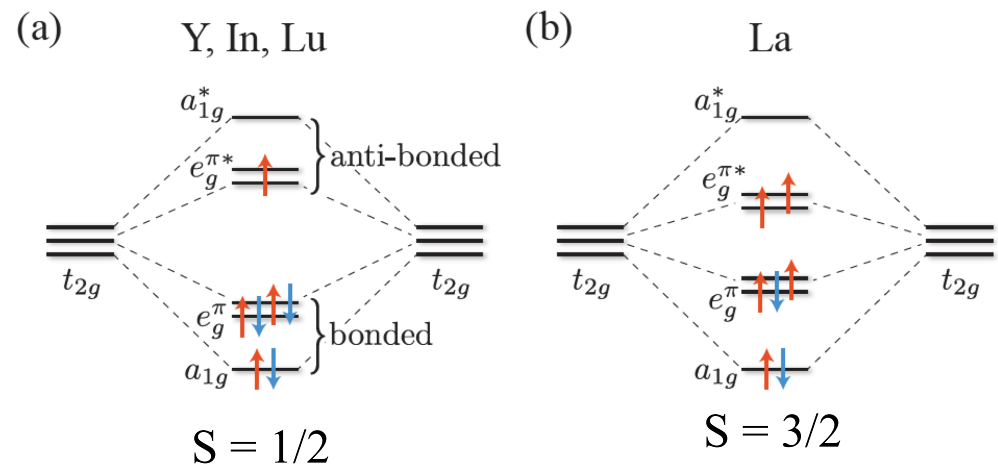
No ordering down to 0.06K

Demenstration of MW theory

*R. Rawl and H. D. Zhou, et al., PRB **95**, 060412(R) (2017)*

$Ba_3ARu_2O_9$ (A = Y^{3+}, In^{3+}, Lu^{3+})





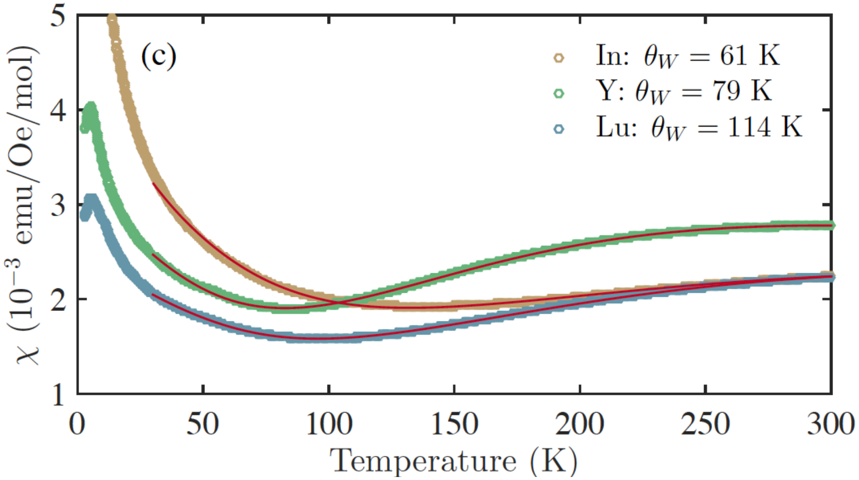
Ba^{2+}: non magnetic

Y^{3+}: non magnetic

$Ru^{4.5+}$-$Ru^{4.5+}$ dimer 7 electrons (Ru:$4d^7 5s^1$): magnetic

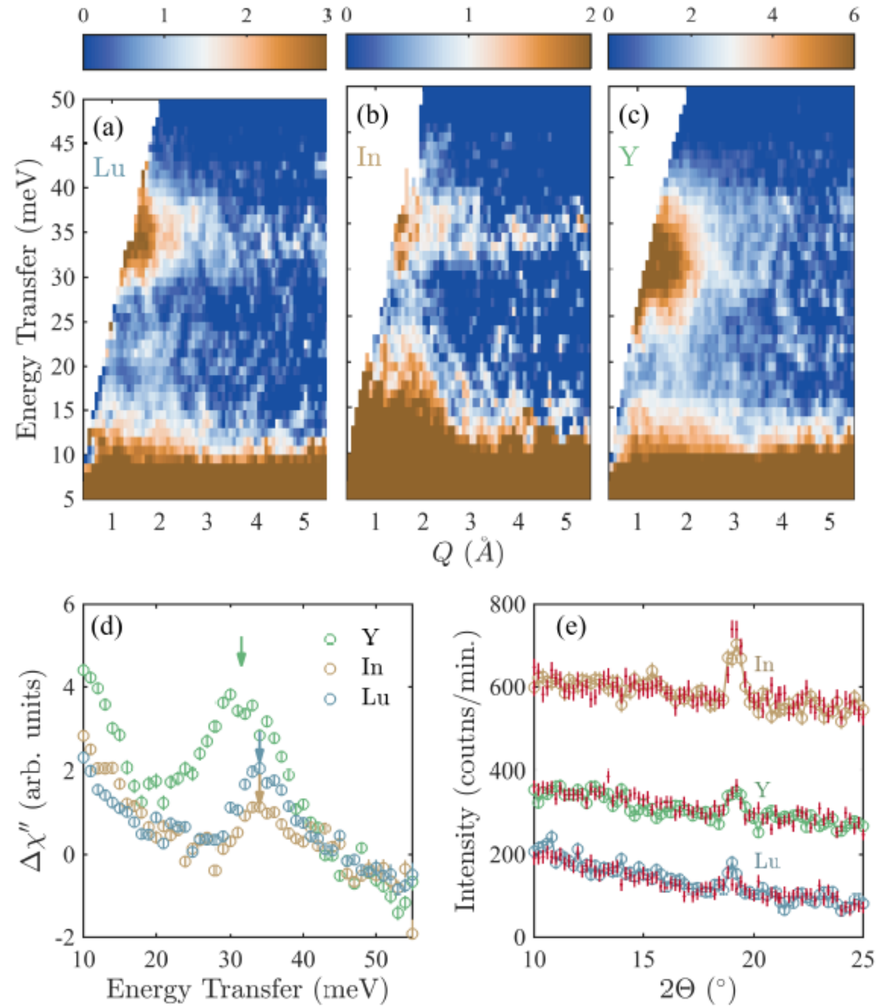
The Ru_2O_9 dimers are better described as molecular units due to significant orbital hybridization, resulting in one spin-1/2 moment distributed equally over the two Ru sites.

$Ba_3ARu_2O_9$ ($A = Y^{3+}, In^{3+}, Lu^{3+}$), spin 1/2

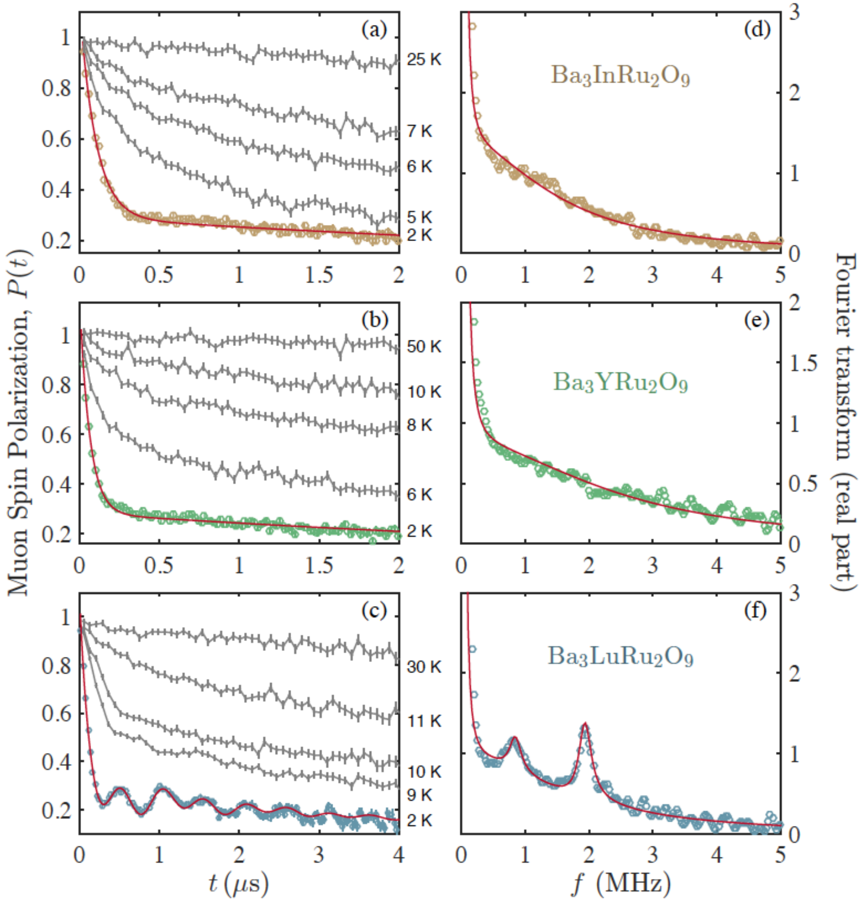


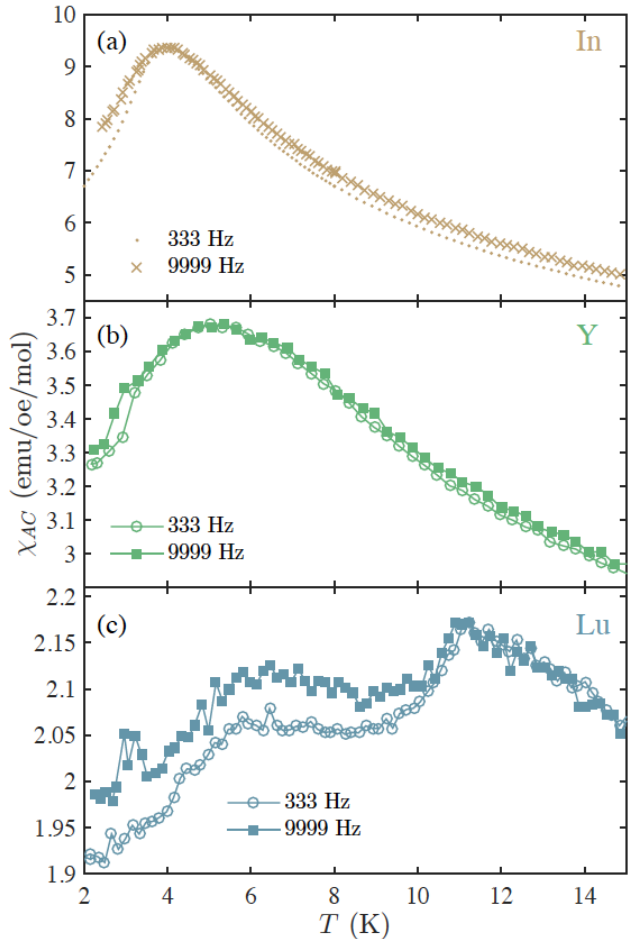
$$\chi(T) = \frac{C}{T+\Theta_W} \cdot \frac{1+10e^{-\Delta_1/k_BT}+35e^{-\Delta_2/k_BT}}{1+2e^{-\Delta_1/Tk_B}+3e^{-\Delta_2/k_BT}} \quad (1)$$

$\Delta_1 \sim 30$ meV, the excitation between S = 1/2 and S = 3/2



$Ba_3ARu_2O_9$ ($A = Y^{3+}, In^{3+}, Lu^{3+}$)

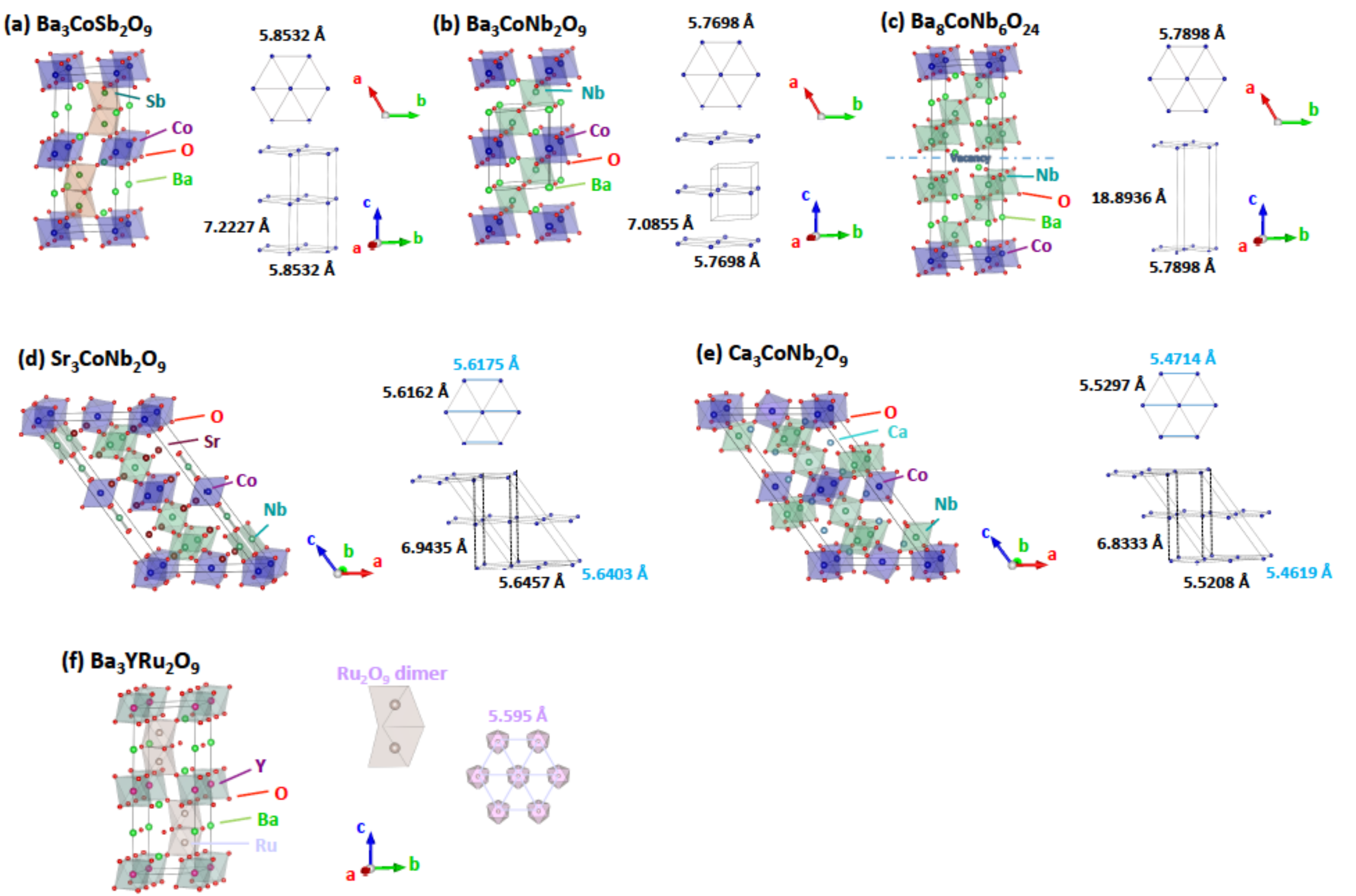




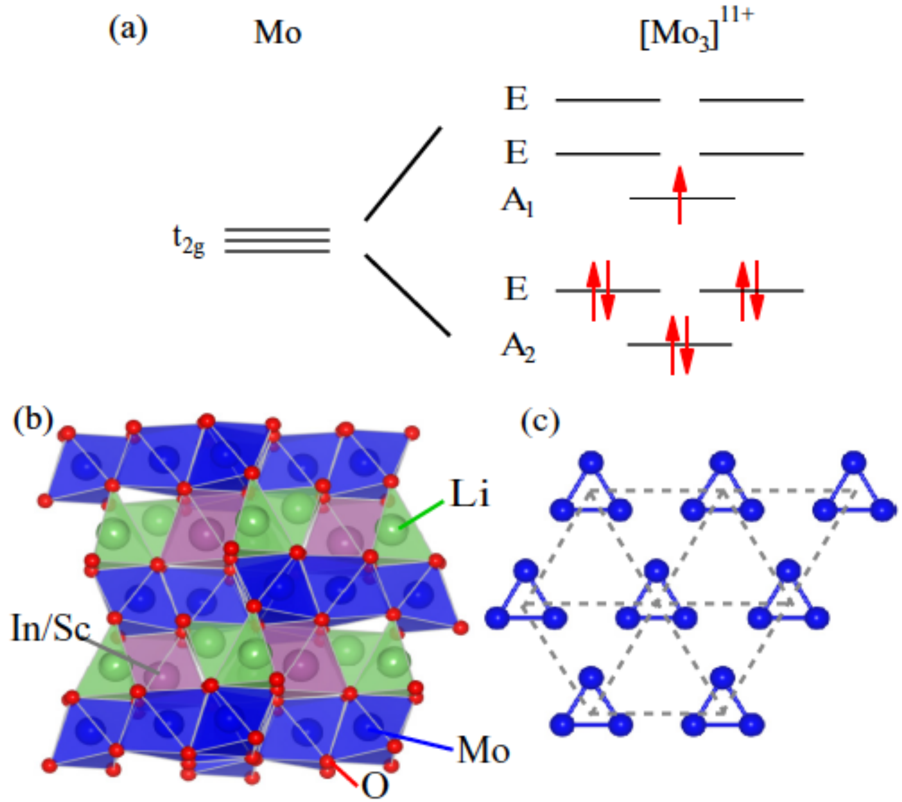
*D. Ziat and H. D. Zhou, et al. PRB **95,** 184424 (2017).*

SRO in Y and In samples, but not normal spin glass. LRO in Lu sample

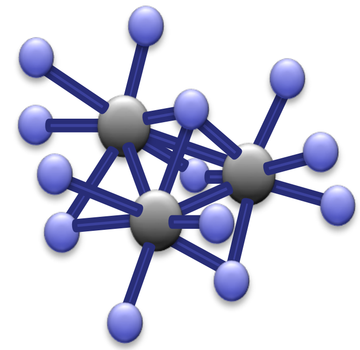
Triple perovskites

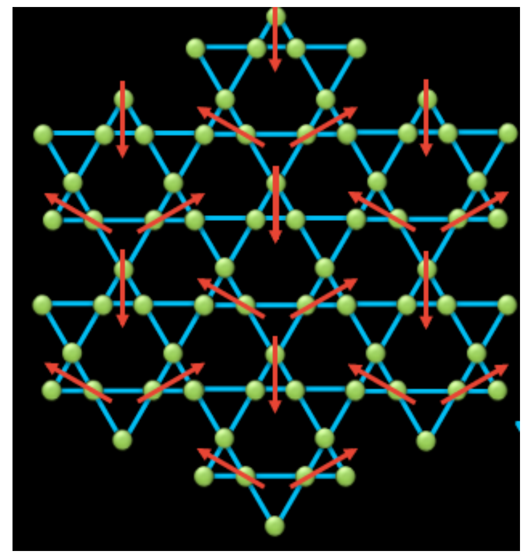


Tunable quantum spin liquidity in Mo_3O_{13} cluster $Li_2In_{1-x}Sc_xMo_3O_8$



Y. Haraguchi, et al., PRB ***92****, 014409 (2015)*

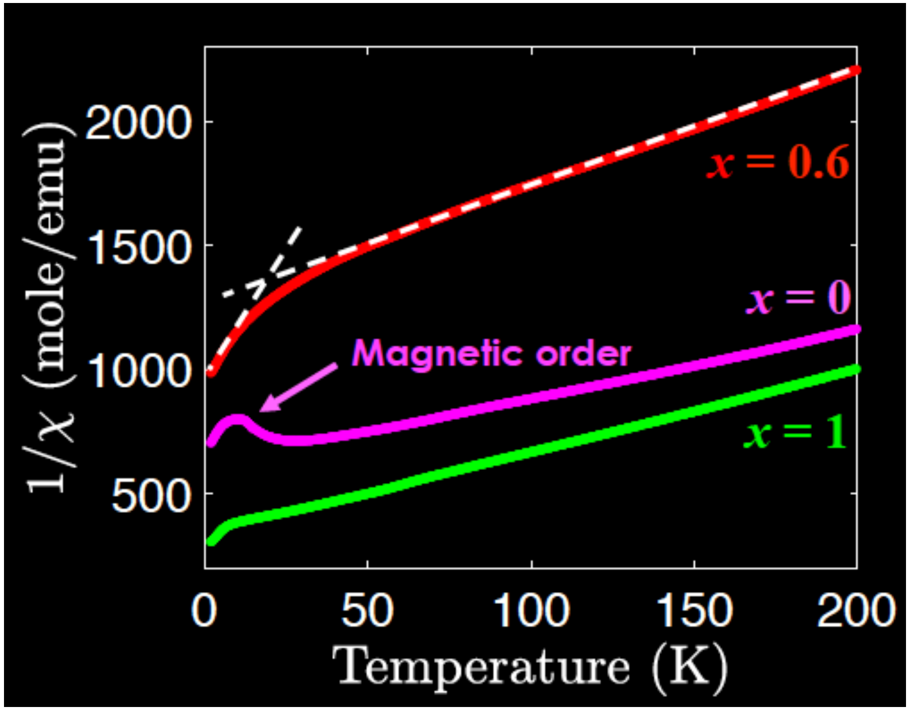


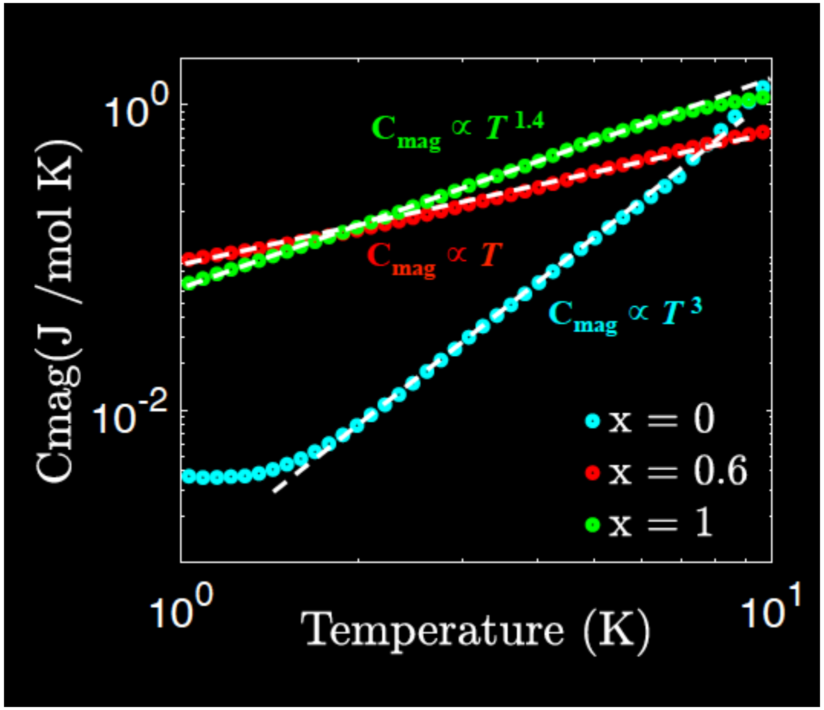


Li^{+}, In^{3+}, and Sc^{3+}: non magnetic

Magnetic Mo_3O_{13} (7 electrons) with spin-1/2 forms triangular lattice in *ab* plane

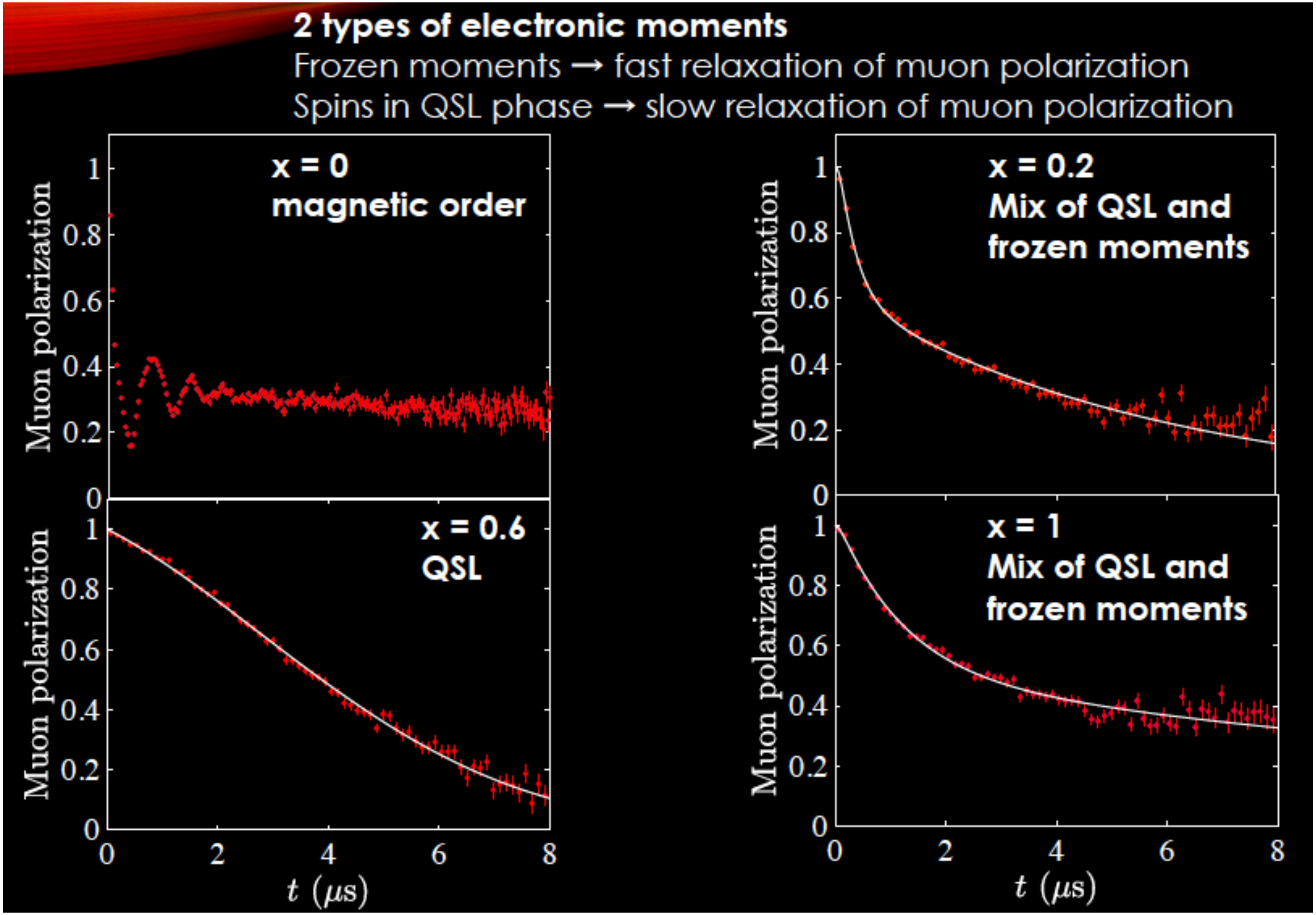
Tunable quantum spin liquidity in Mo_3O_{13} cluster $Li_2In_{1-x}Sc_xMo_3O_8$





$x = 0.6$ sample shows no ordering down to 0.5 K with a linear T specific heat

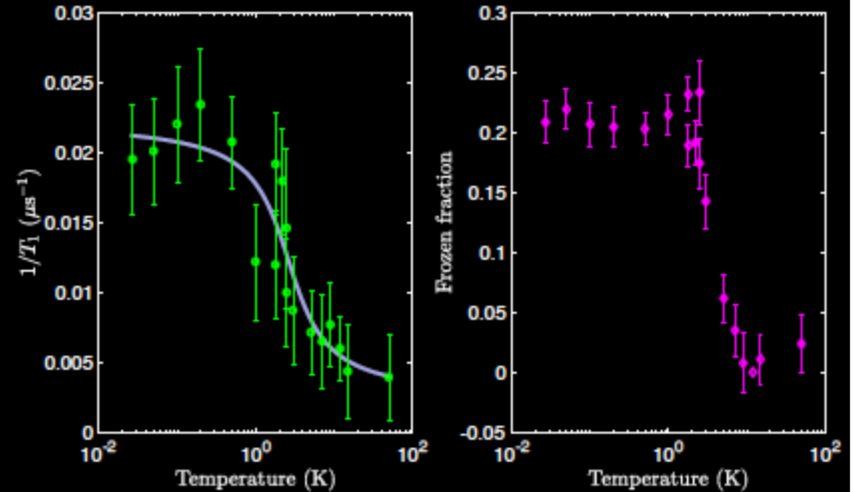
Zero field muon spectra of $Li_2In_{1-x}Sc_xMo_3O_8$



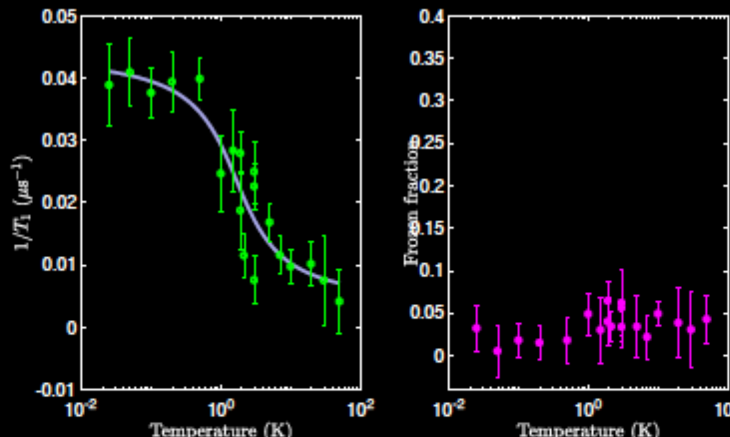
Longitudinal field muon spin relaxation

- Measurements at 55G longitudinal field (quench nuclear moments)
- Frozen fraction extracted from fits
- The relaxation rate for slow relaxing component plateaus at low temperature consistent with QSL phase

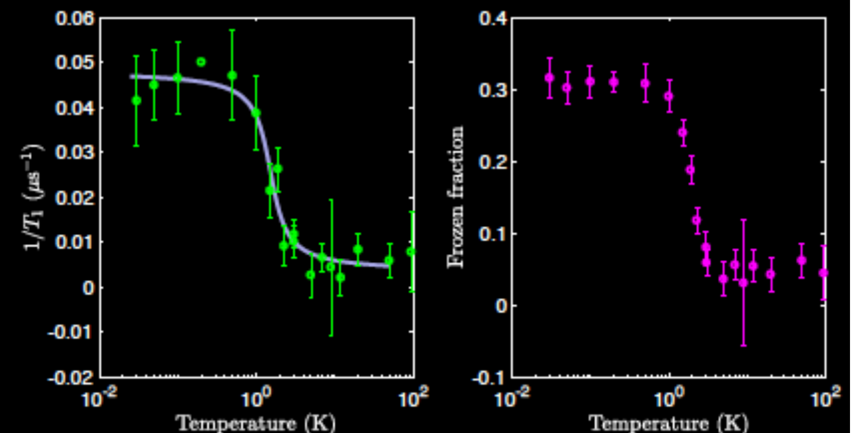
x = 0.2 (frozen fraction ~ 20%)



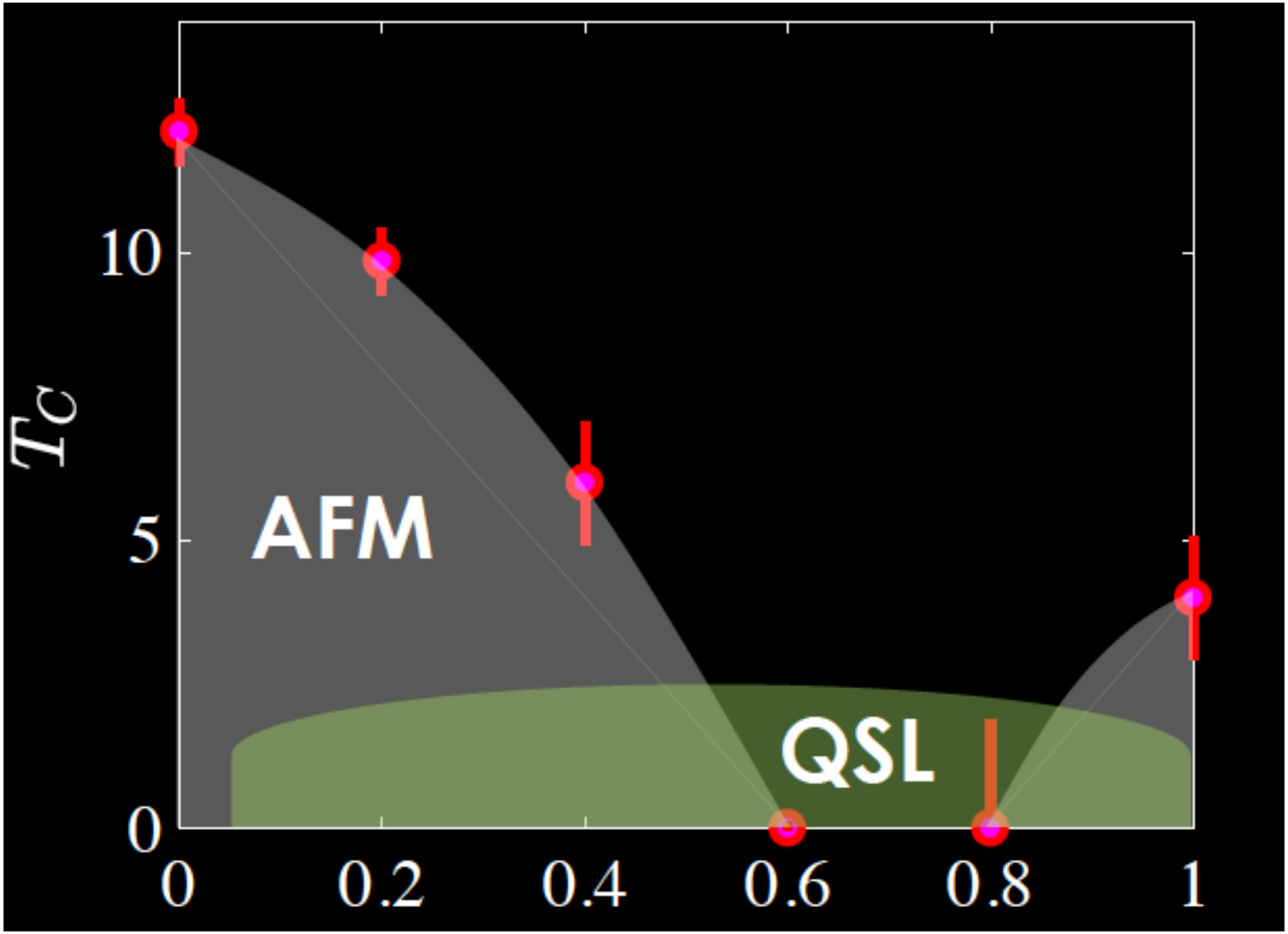
x = 0.6 (frozen fraction ~ 0%)



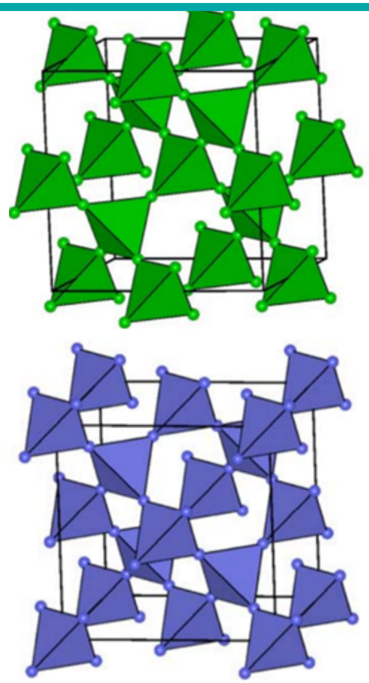
x = 1 (frozen fraction ~ 30%)

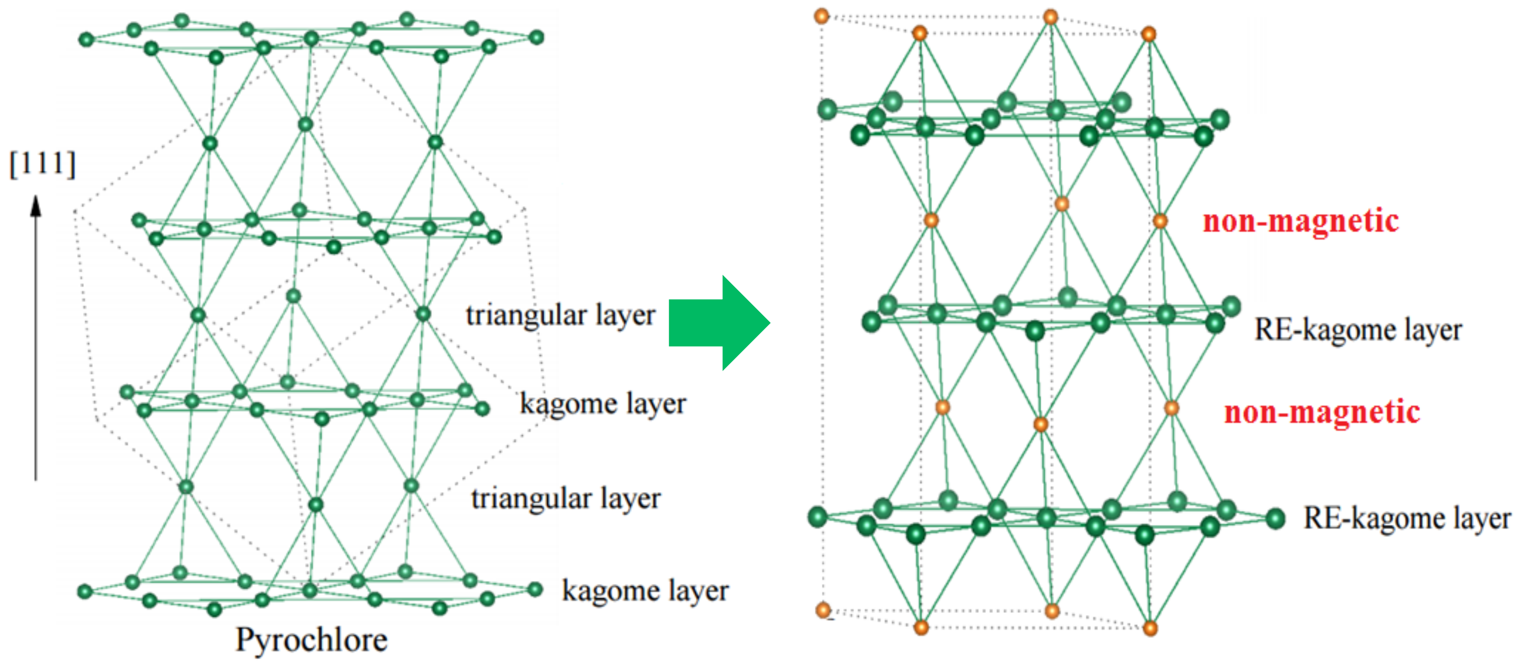


Phase diagram of $Li_2In_{1-x}Sc_xMo_3O_8$



From pyrochlore to Kagome



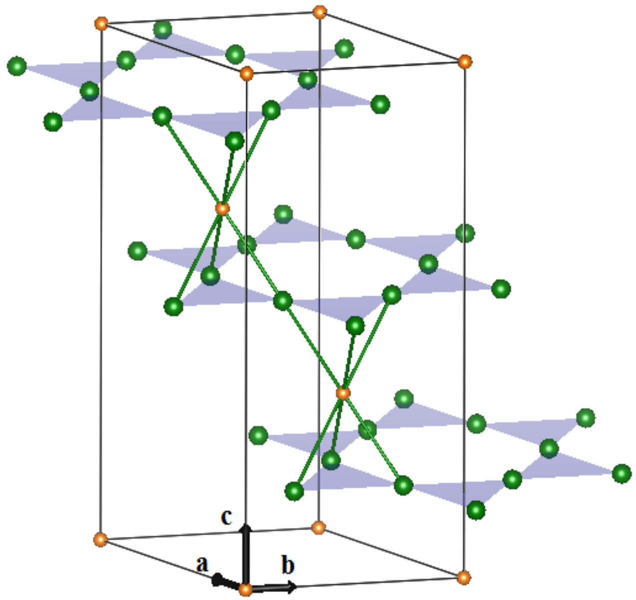


$R_2Ti_2O_7$

Advantages

- ❑ A large family
- ❑ Heisenberg + Ising + XY (based on RE^{3+})
- ❑ Structural perfect Kagome lattice

The Tripod Kagome Lattice $Mg_2R_3Sb_3O_{14}$



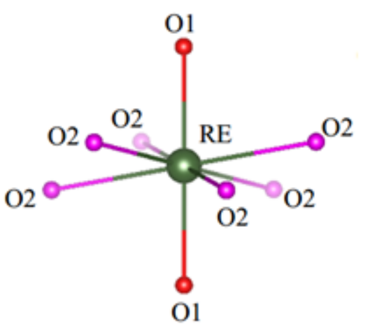
Overall structure

$\quad\quad\quad +2 \quad +3 \quad +5 \quad -2$

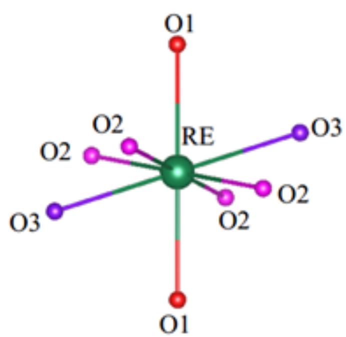
- ½ $A_2RE_3Sb_3O_{14}$ = $2(RE_{0.75}A_{0.25})_2(Sb_{0.75}A_{0.25})_2O_7$
- A = Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}
  RE = La^{3+} …. Lu^{3+}
- Space group: R-3m (Hex)
  $a=b\approx a_p/\sqrt{2}$, $c\approx\sqrt{3}\,/a_p$
- A-B-C stacking, similar to Herbertsmithite
- d_{nn} (inter-plane) ~ $2d_{nn}$(intra-plane)

Local environment

- Similarity: 8-oxygen, 2 shortest O1, O-ring
  same spin anisotropy as their pyrochlore parents
- Difference: 6-O2 splits into two sets
  additional point group symmetry reduction



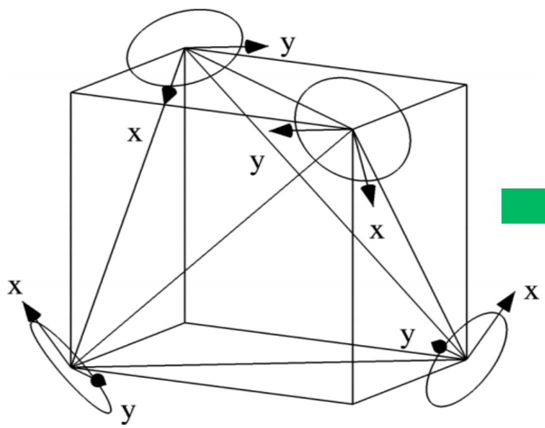
Pyrochlore

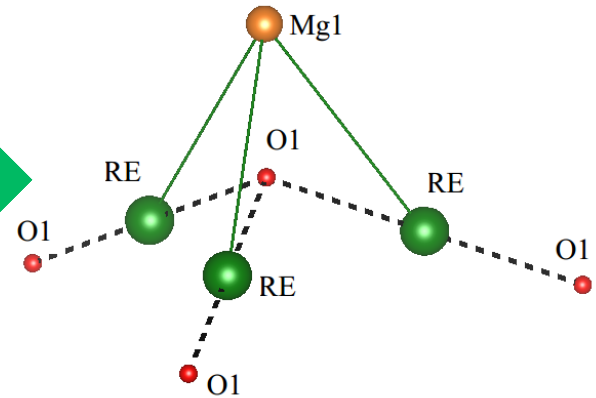


Tripod Kagome

*Z. Dun and H. D. Zhou, et al. PRL **116**, 157201 (2016).*

The Tripod Kagome lattice — anisotropies

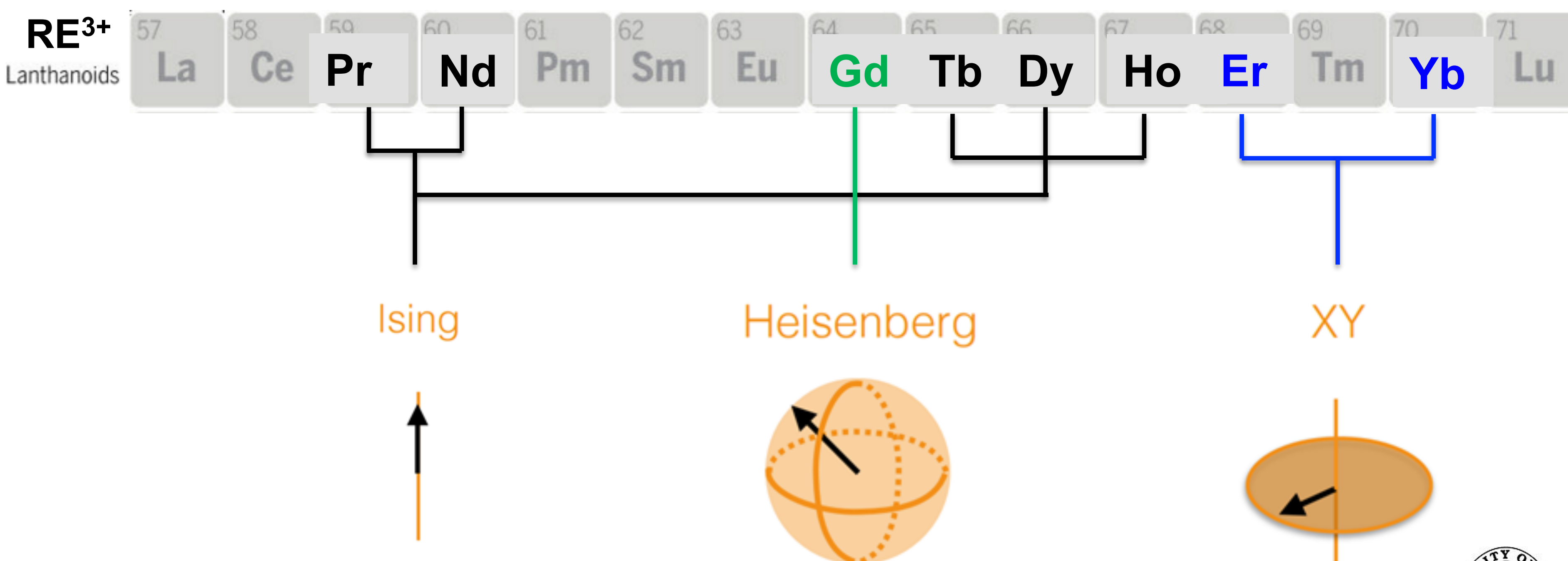




Three Ising axes:
non-uniaxial

Three XY planes:
non-coplanar

Tripod



The Tripod Kagome lattice — Hamiltonian

$$H = H_{CEF} + H_{dip} + H_{ex}$$

Crystal electric field (CEF)

$$\widehat{H}_{cf}(J) = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q O_k^q$$

- Dominating term
- Due to O^{2+} charge
- $|J, Jz\rangle$ as basis
- Define spin anisotropy
- Doublet: Effective spin-1/2

Dipolar interaction

$$D r_{nn}^3 \sum_{i>j} \frac{S_i^{\hat{z}_i} \cdot S_j^{\hat{z}_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{\hat{z}_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{\hat{z}_j} \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}$$

- Long range
- FM at 1st n. n.
- $\propto \langle m \rangle^2$
- Columbic like $\propto 1/r^3$

Exchange interaction

$$-\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \bullet \mathbf{S}_j$$

- Short-ranged
- In principle 1st n. n. for 4f electron
- Anisotropic J_{ex}

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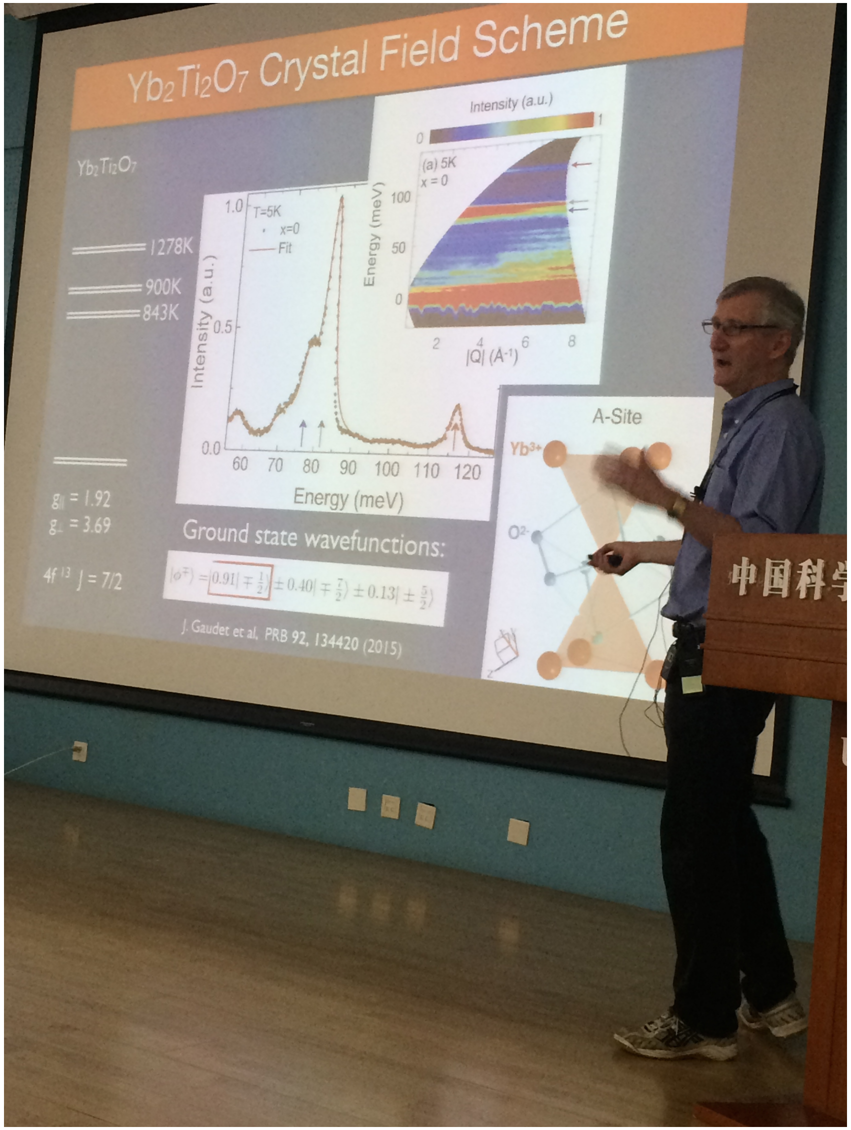
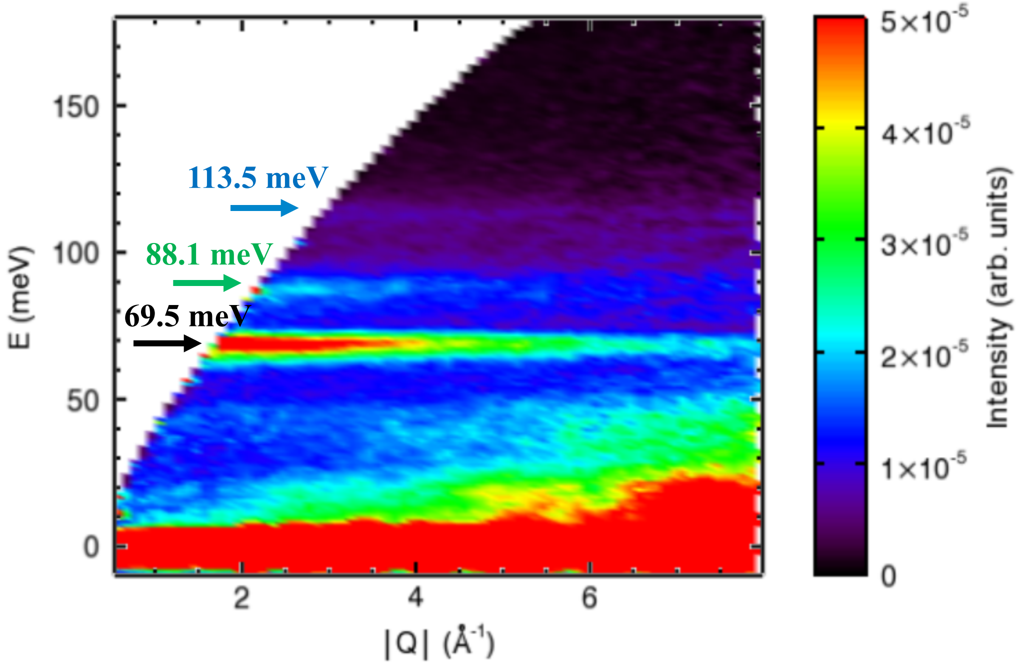
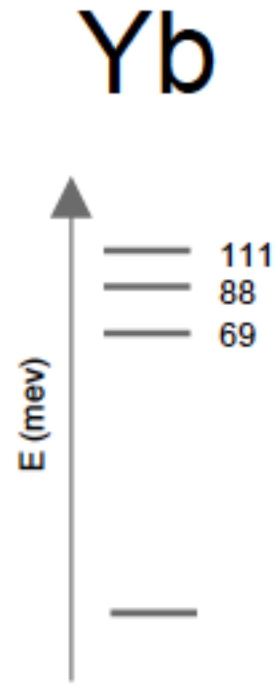
Yb^{3+}



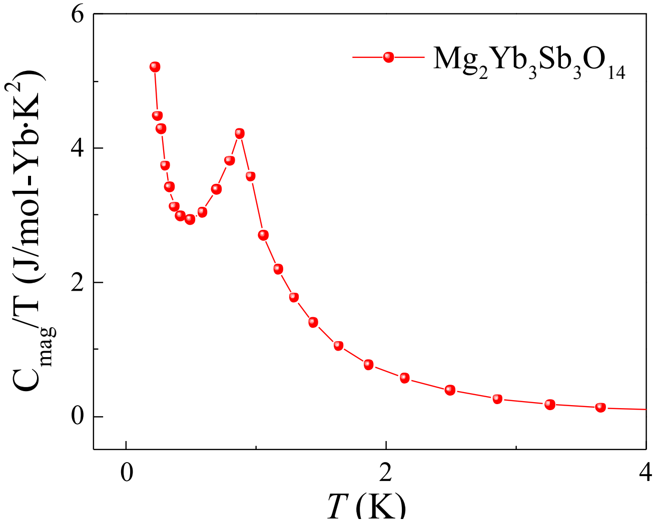
Yb2Ti2O7 Crystal Field Scheme
Yb2Ti2O7
1278K
900K
843K
g|| = 1.92
g⊥ = 3.69
4f 13 J = 7/2
Intensity (a.u.)
T=5K
x=0
Fit
Energy (meV)
(a) 5K
x = 0
|Q| (A-1)
Ground state wavefunctions:
J. Gaudet et al, PRB 92, 134420 (2015)
A-Site
Yb3+
O2-
中国科学

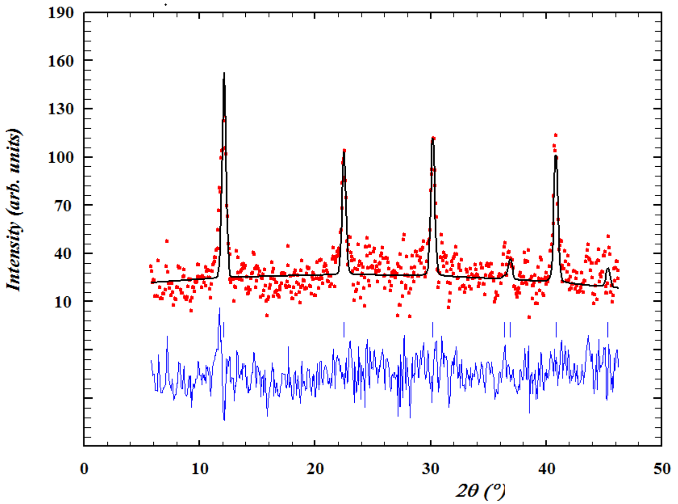
$Mg_2Yb_3Sb_3O_{14}$



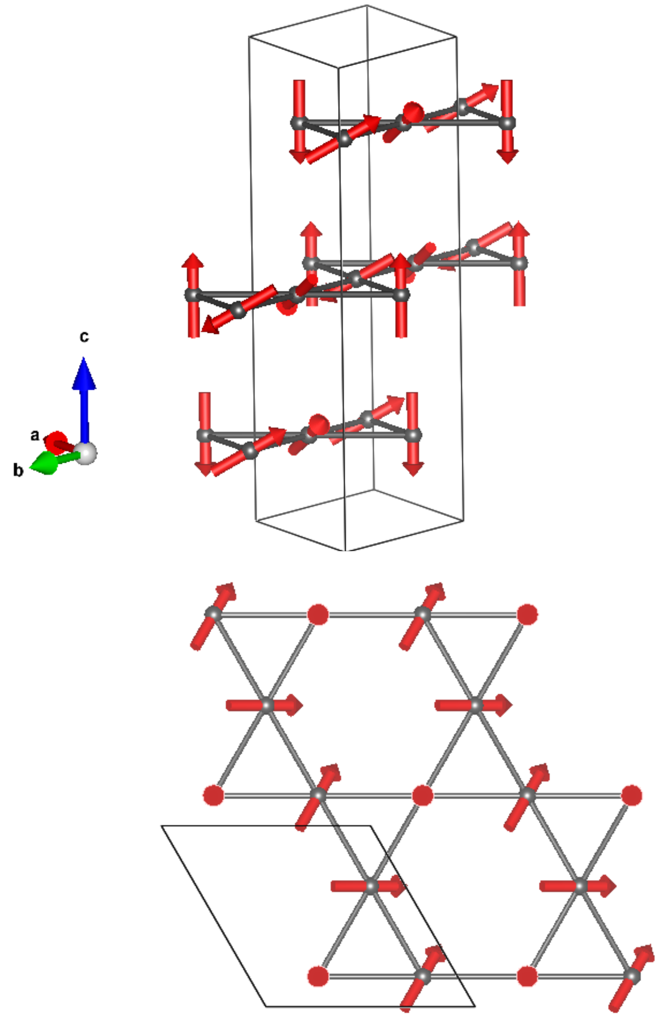


$Mg_2Yb_3Sb_3O_{14}$





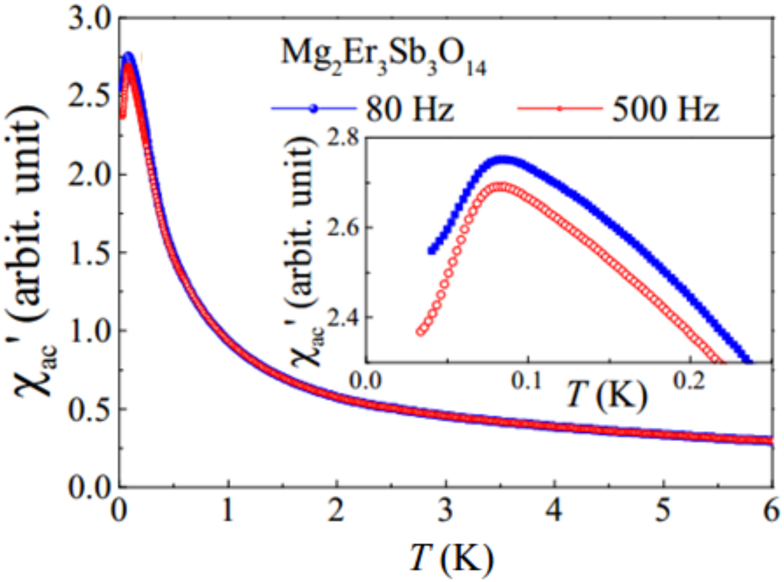
$T_N = 0.88$ K, $k = (0, 0, 3/2)$



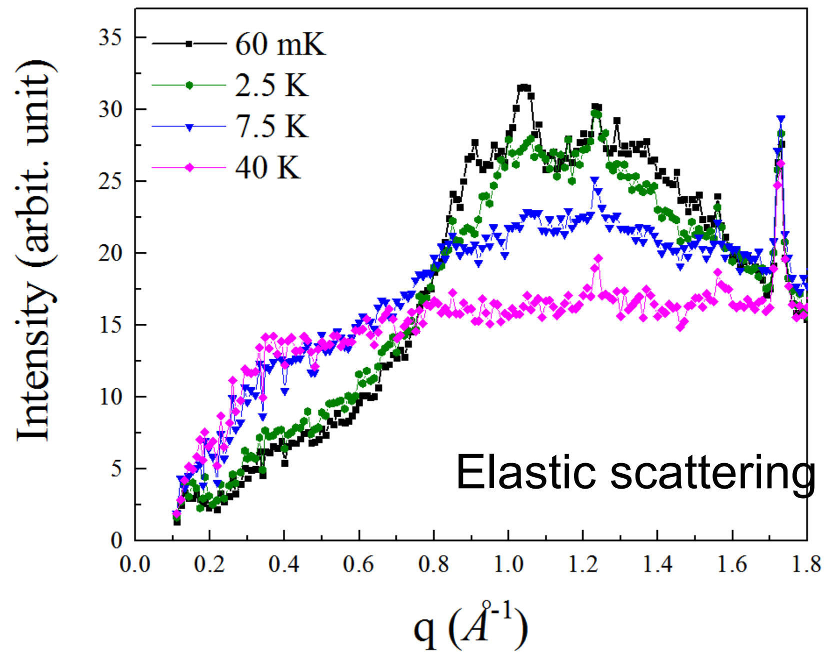
Refined moment 0.95 μ_B

Canting angle 30 degree

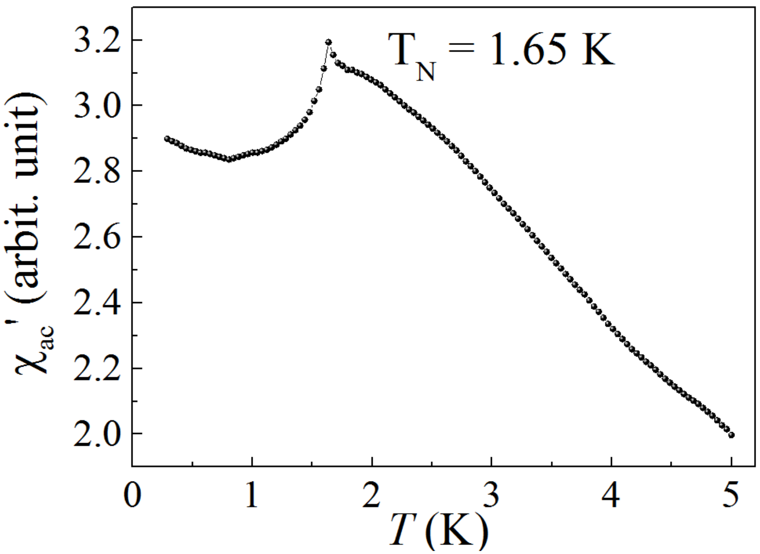
$Mg_2Er_3Sb_3O_{14}$

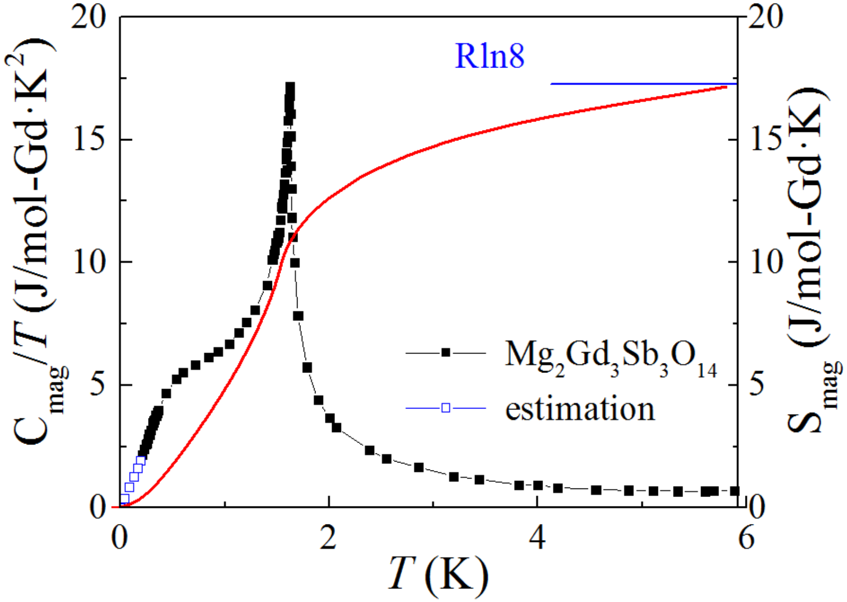


A spin liquid?



Heisenberg spin: $Mg_2Gd_3Sb_3O_{14}$ Gd^{3+} ($4f^7$): J=7/2, S = 7/2, L = 0

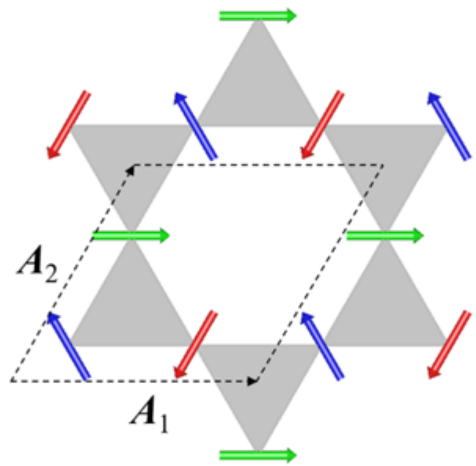




What defeat the Mermin-Wagner theorem?

- μ_{eff} = 7.9 μ_B, D_{nn} = 0.79 K
- θ_w = -7.35 K, J_{ex} = 6.1 K

$$H = \frac{1}{2} \sum_{k,\alpha,\beta,a,b} S^{\alpha,a}(k)\, S^{\beta,b}(-k)\, V_{ab}^{\alpha\beta}(k)$$



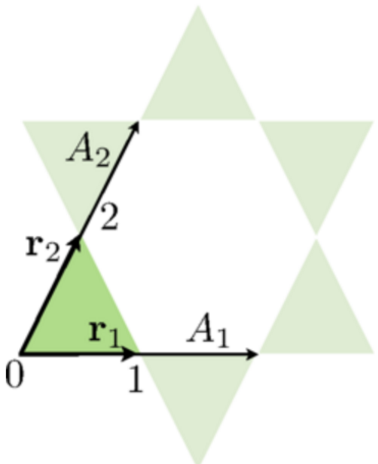
k = 0, 120 degree coplanar order

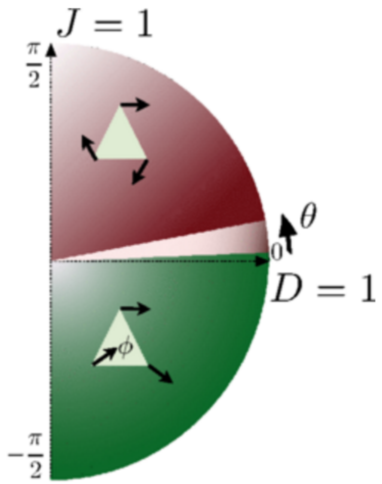
Z. L. Dun and H. D. Zhou et. al., PRL 116, 157201 (2016).

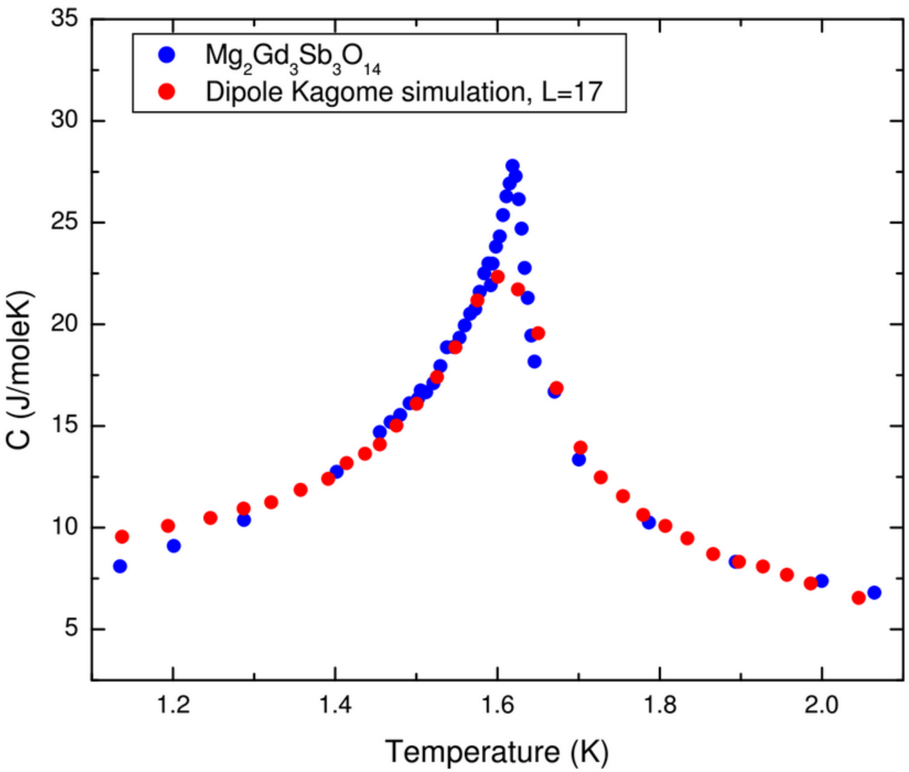
Realization of dipolar interaction mandated spin order

$$H = \sum_{k,i,l,j} \sum_{\alpha,\beta} J_{ij}^{\alpha\beta}(\mathbf{R}_{ij}^{kl}) S_i^{\alpha}(\mathbf{R}^k) S_j^{\beta}(\mathbf{R}^l),$$

$$J_{ij}^{\alpha\beta}(\mathbf{R}) = \frac{1}{2}\left[J\delta_{\alpha\beta,|\mathbf{R}|=R_{nn}} + D R_{nn}^3 \left(\frac{\delta_{\alpha\beta}}{|\mathbf{R}|^3} - 3\frac{R^\alpha R^\beta}{|\mathbf{R}|^5} \right) \right].$$

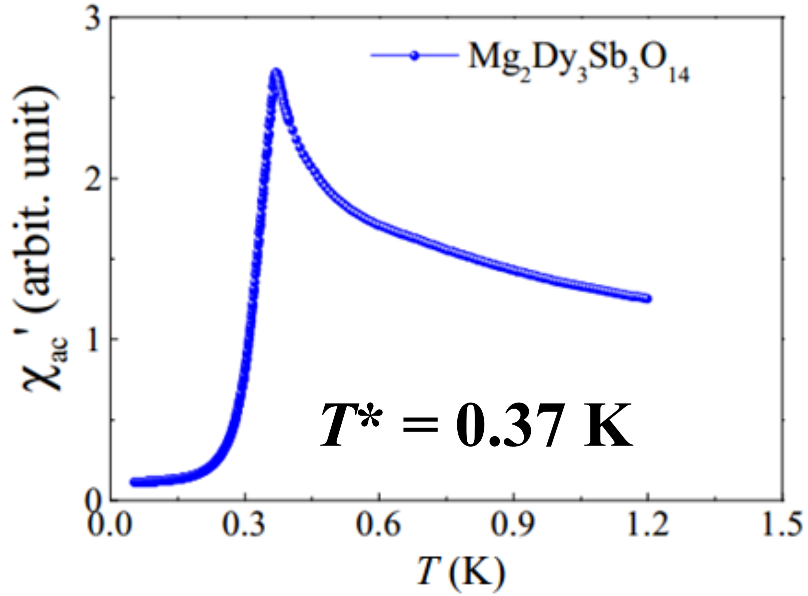


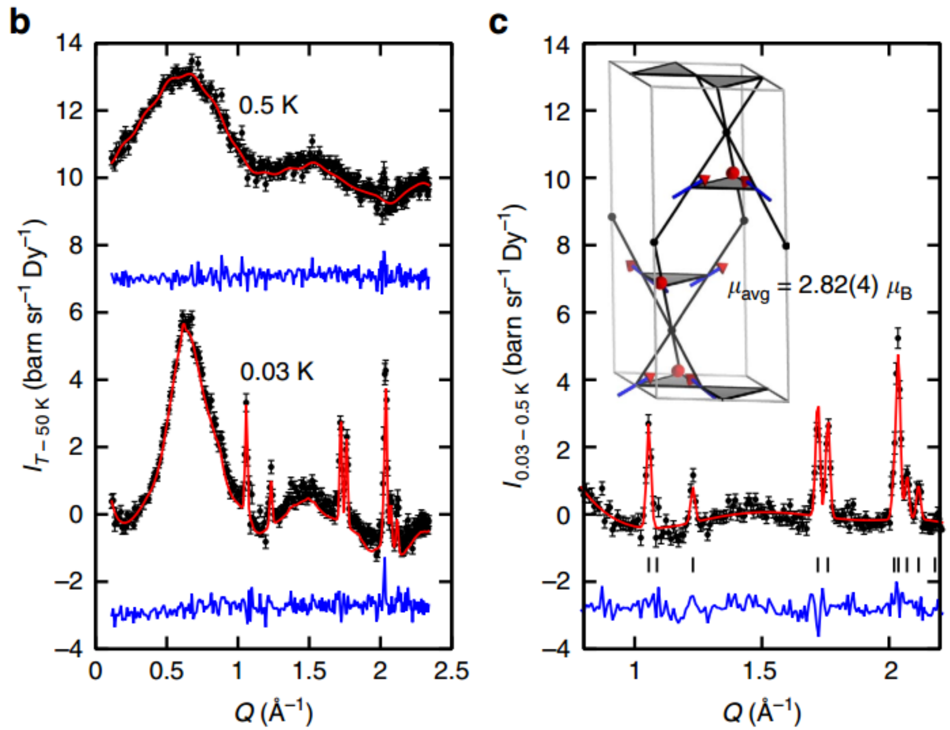




M. Maksymenko, etc. al.
Phys. Rev. B, ***91***, *184407 (2015).*

Ising spin : $Mg_2Dy_3Sb_3O_{14}$ Dy^{3+} ($4f^9$): J=15/2, S = 5/2, L = 5

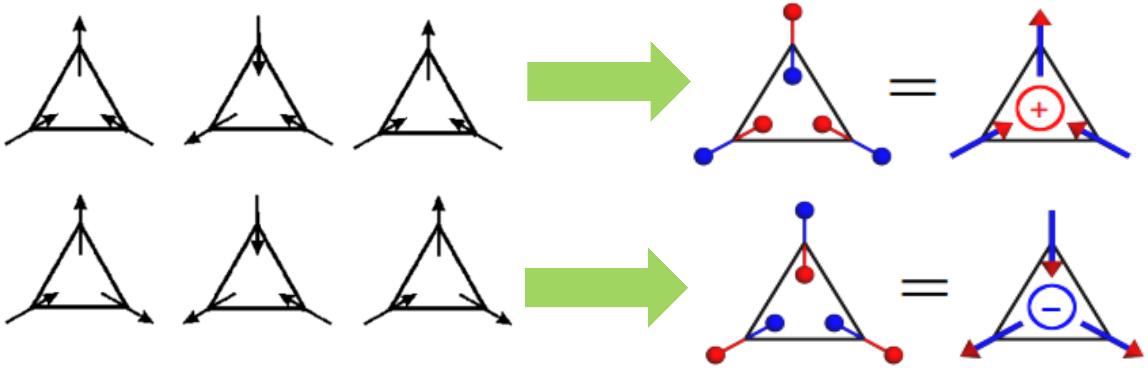


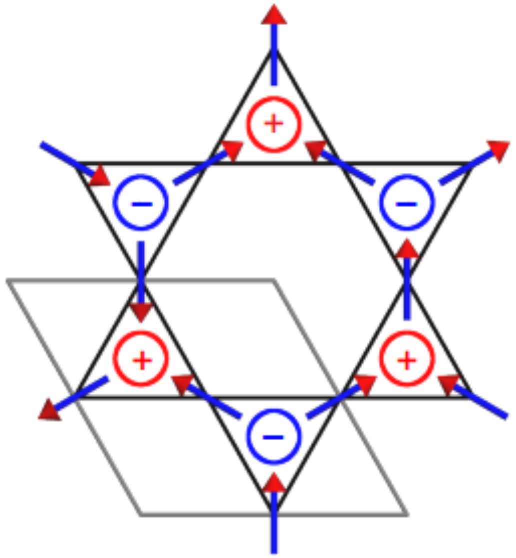


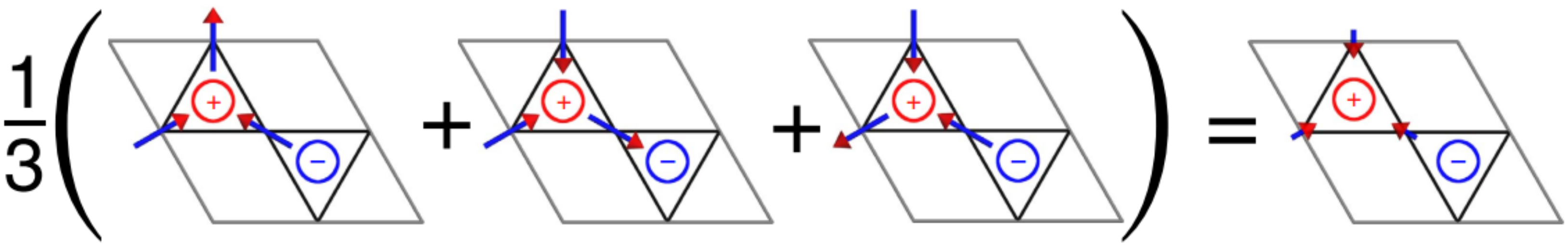
The measured Dy^{3+} moment (2.82 μ_B) is 1/3 of the full moment

J. M. Paddison et. al., Nature Comm. (2016)

Magnetic charge order in MgDy







J. M. Paddison et. al., Nature Comm. (2016)

$Mg_2R_2Sb_3O_{14}$ and $Zn_2R_2Sb_3O_{14}$

		Pr	Nd	Gd	Tb	Dy	Ho	Er	Yb
	f electron (RE^{3+})	$4f^2$	$4f^3$	$4f^7$	$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{13}$
	Kramers ion (?)	No	Yes	Yes	No	Yes	No	Yes	Yes
	Putative anisotropy	~	Ising	Heisenberg	Ising	Ising	Ising	XY	XY
A = Mg	θ_W (K)	-46.18	-0.05	-6.70	-13.70	-0.18	-0.27	-14.52	-0.45
	μ_{eff} (μ_B)	3.4	2.49	8.06	9.88	10.2	10.54	9.45	3.24
	Possible Ground state	non-mag.	LRO	LRO	QSL(?)	LRO(ECO)	SRO(KSI)	QSL(?)	LRO
	$T_{N,f,SG}$ (K)	~	0.56	1.65	~	0.37	0.4	0.08, 2.1	0.88
A = Zn	θ_W (K)	-68.43	-0.11	-6.85	-13.41	-0.72	-2.49	-16.08	-0.39
	μ_{eff} (μ_B)	3.61	2.28	8.09	9.86	10.2	10.22	9.67	3.18
	Possible Ground state	non-mag.	LRO	LRO	QSL(?)	LRO(ECO)	SG(?)	SG	SG(?)
	$T_{N,f,SG}$ (K)	~	0.47	1.69	~	0.39	0.45	0.35	~(?)

*Z. Dun and H. D. Zhou, et al., PRB **95**, 104439 (2017)*

Summary

- Layer compounds are ideal materials to explore 2D GFMs with exotic spin states

- $Ba_3CoSb_2O_9$: LRO with strong QSFs, approaching QMP.
  Its spin wave spectrum demands more advanced theory.

- $Ba_3CoNb_2O_9$: an example of coexistence of quantum spin state transitions and multiferroicity.

- $Ba_8CoNb_6O_{24}$: an example of MW theory

- $Ba_3ARu_2O_9$: spin-1/2 molecular building blocks on a triangular lattice.

- $Li_2In_{1-x}Sc_xMo_3O_8$: unique example of QSL on triangular lattice.

- $Mg_2R_3Sb_3O_{14}$: a new family of kagome lattice magnets. The various spin sets of rare earth elements lead to different exotic spin states. Waiting for exploration.