Mineralogy Inspires Physics

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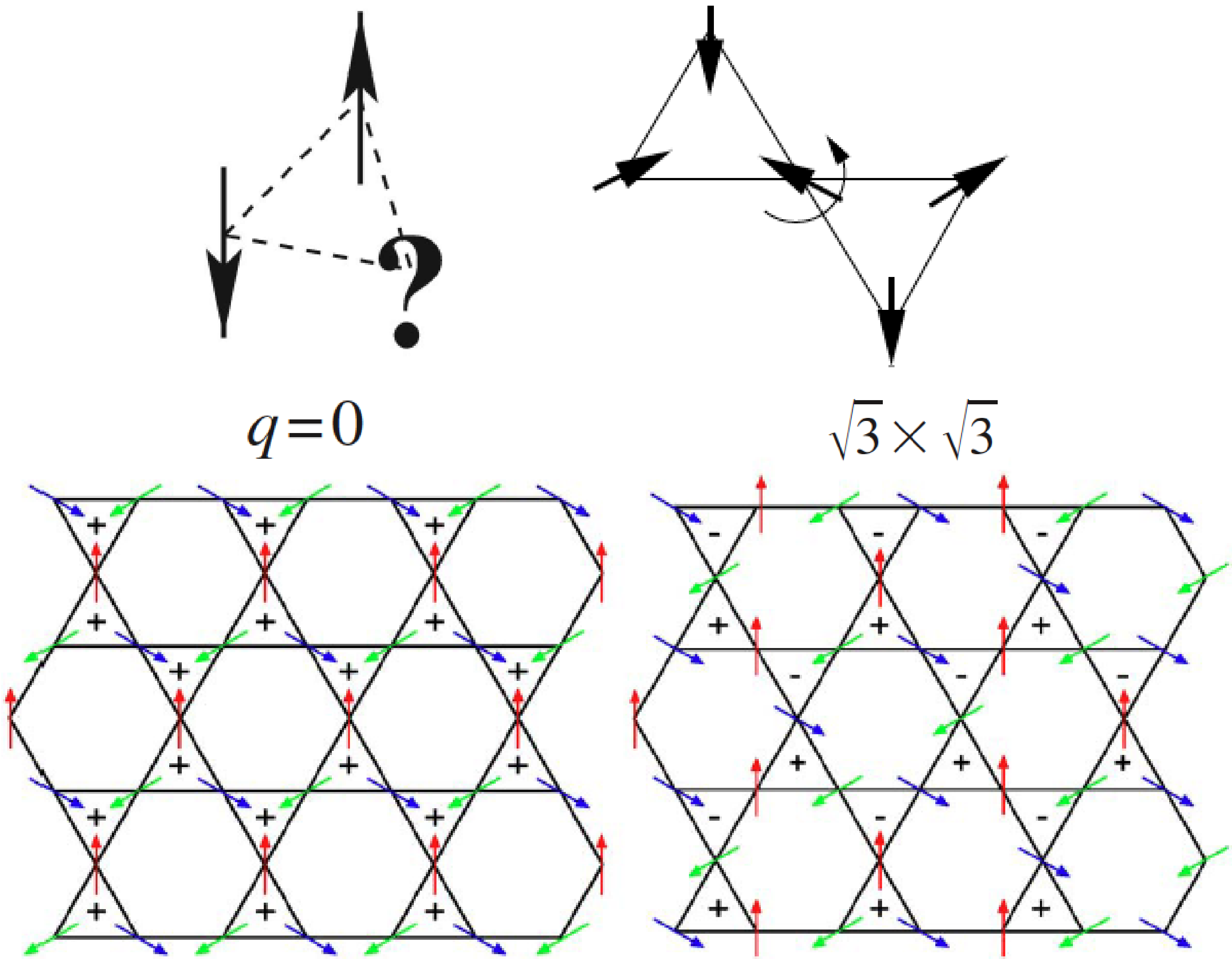
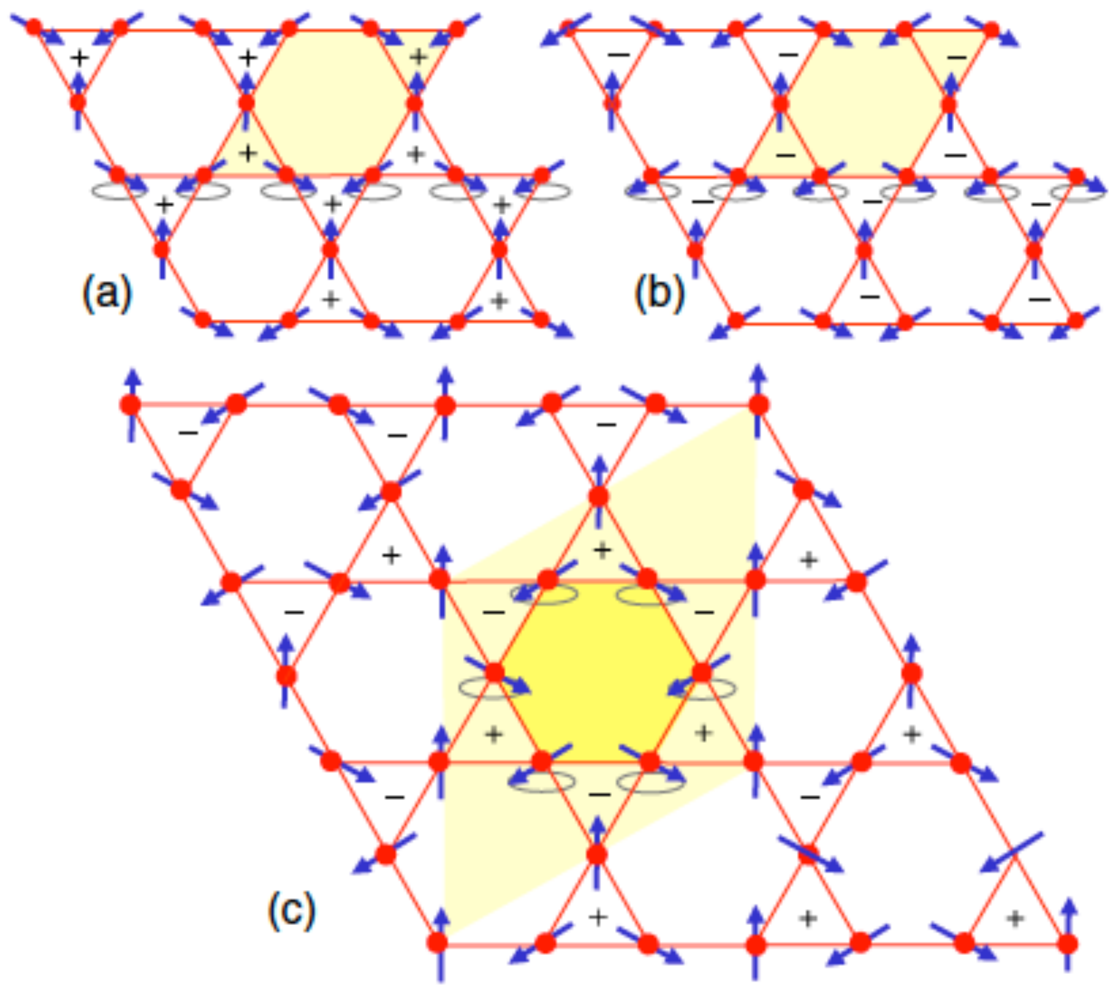
Introduction to Frustrated Magnetism and Kagome Physics



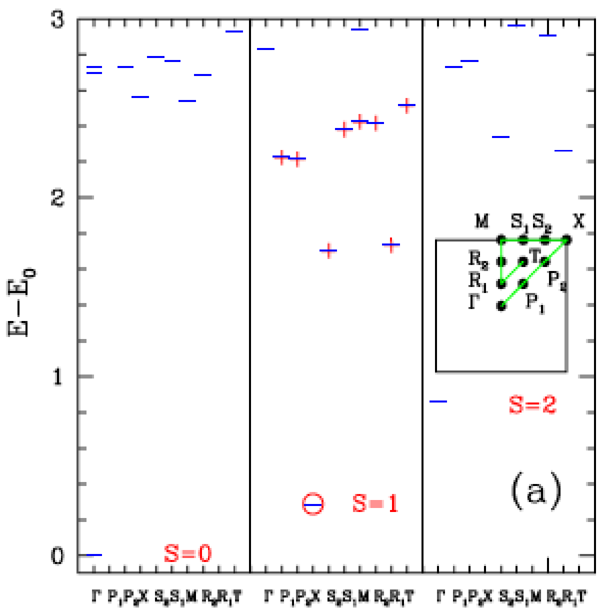
Ryu *et al.*, PRB (2007)

Near neighbor Heisenberg model on a kagome lattice
Certain rotations of spins cost no energy

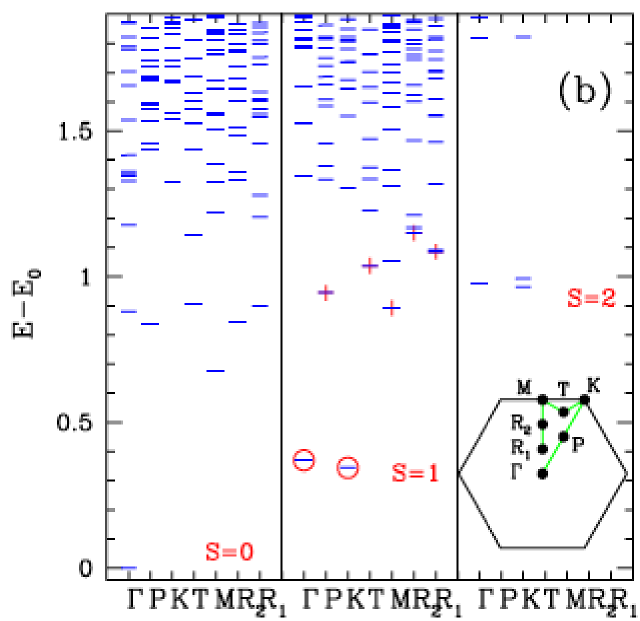


Yildirim and Harris, PRB (2007)

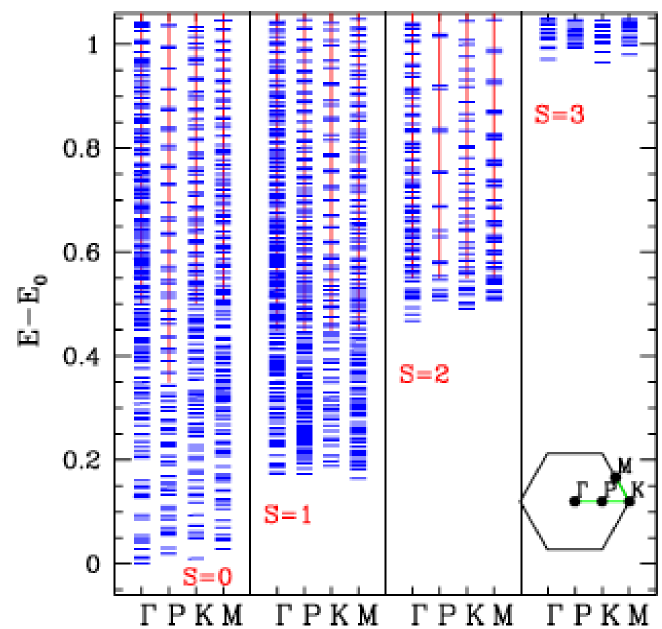
Exact diagonalization studies of NN Heisenberg model indicate a very different eigenvalue spectrum for the kagome case



square



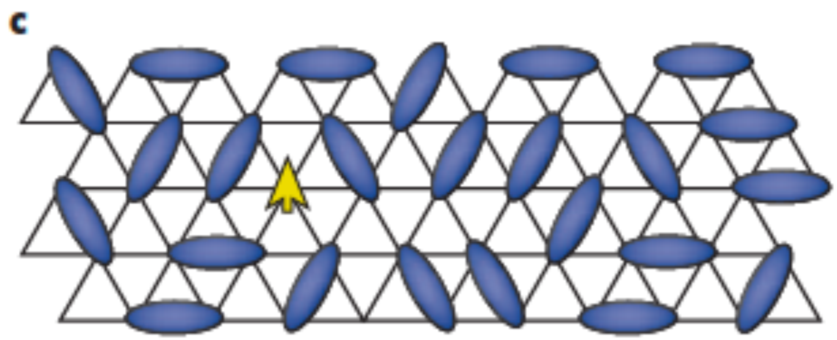
triangular



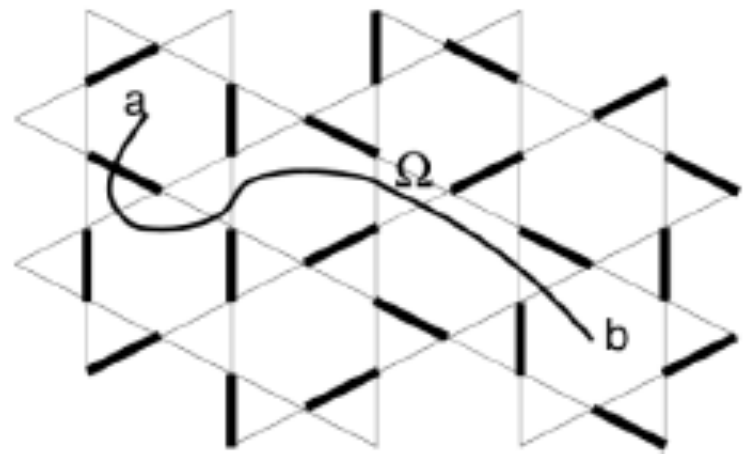
Kagome

Sindzingre & Lhuillier, EPL (2009)

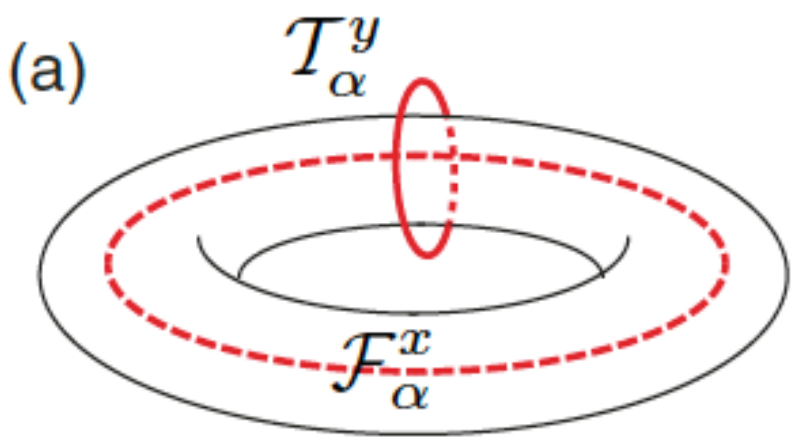
Topology and Fractionalization in Spin Liquids
Spinons and Visons



Free spinon (yellow arrow)



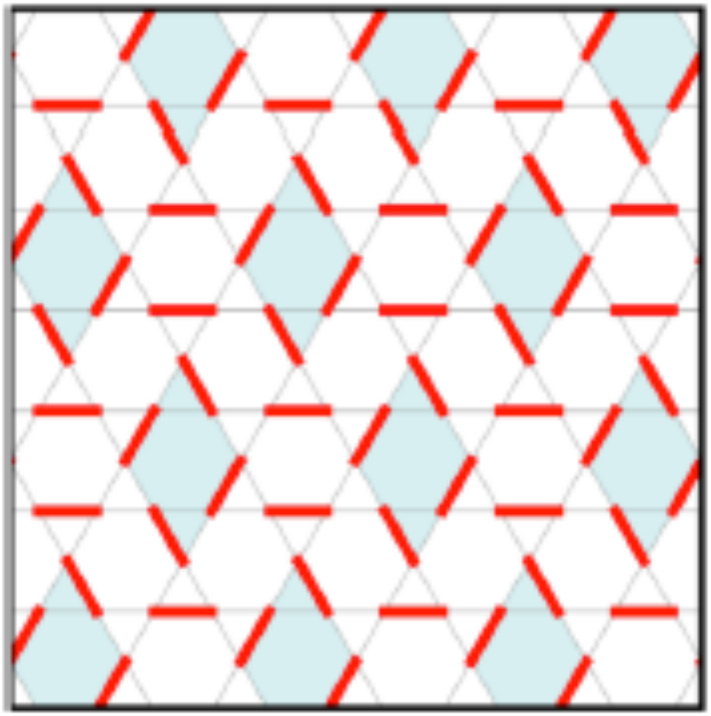
Vison pair at a and b



Ground state degeneracy
& topological sectors

Balents, Nature (2000)
Misguich & Lhuillier, arXiv (2012)
He, Sheng, Chen, PRB (2014)

DMRG studies from 2011 are consistent with a gapped Z2 spin liquid that appears to be a melted version of a diamond valence bond solid but other studies claim either a U(1) Dirac or a chiral spin liquid



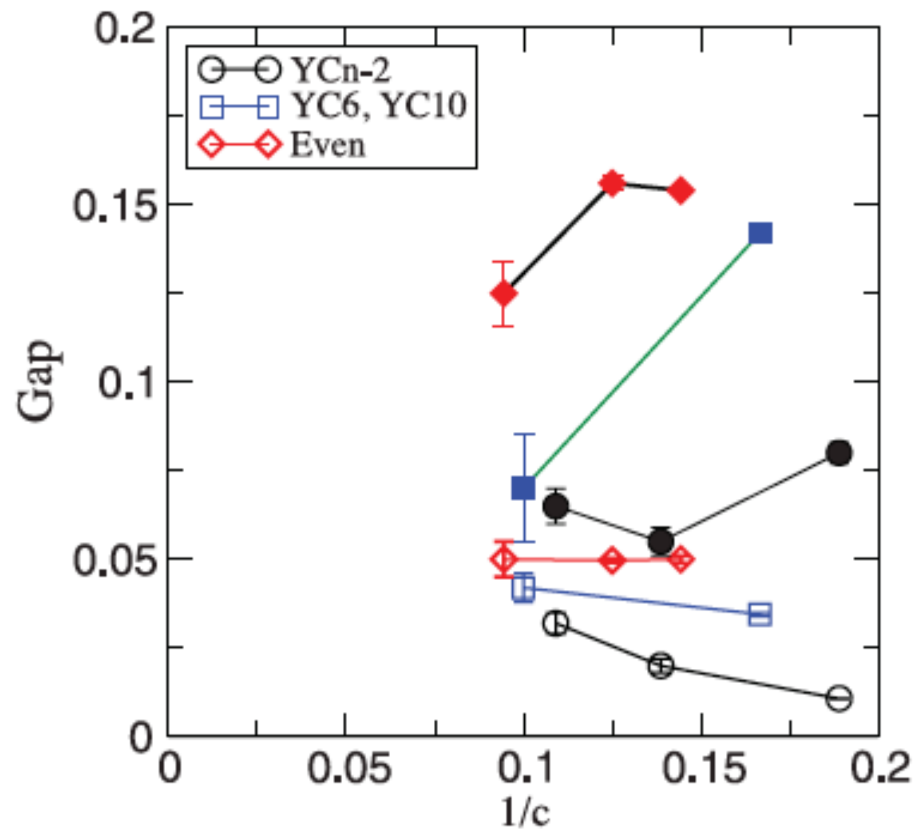


Fig. 4. Spin triplet (solid symbols) and singlet (hollow symbols) gaps for various cylinders with circumferences *c*. The type of cylinder (*15*) is indicated in the key (inset).

Yan, White, Huse, Science (2011)
Hwang, Huh, Kim, PRB (2015)

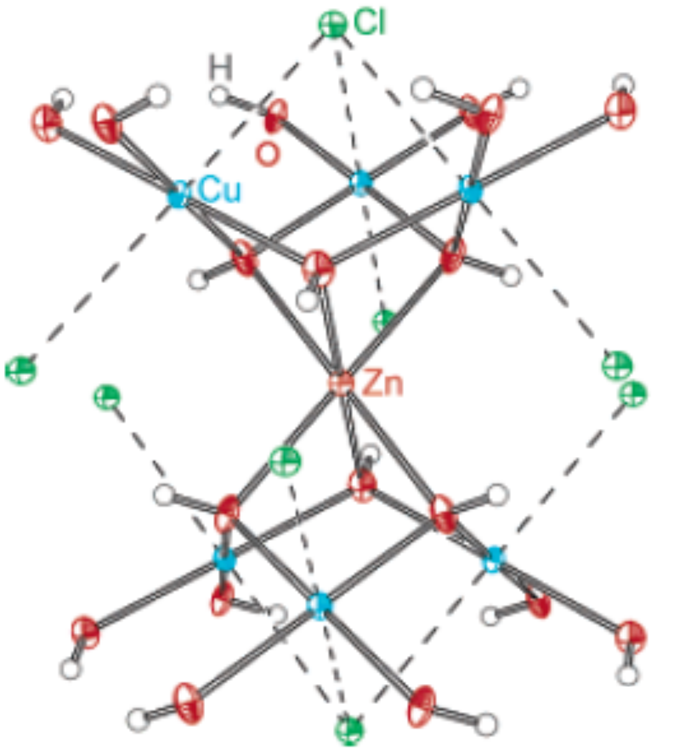
Herbertsmithite
rare mineral first identified from a mine in Chile
(hydrothermal synthesis by Dan Nocera's group ~ 180 C)

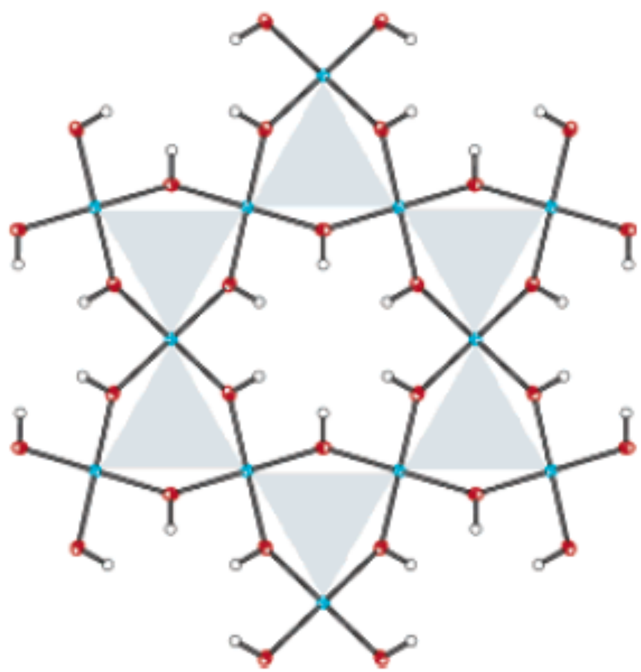
Herbertsmithite

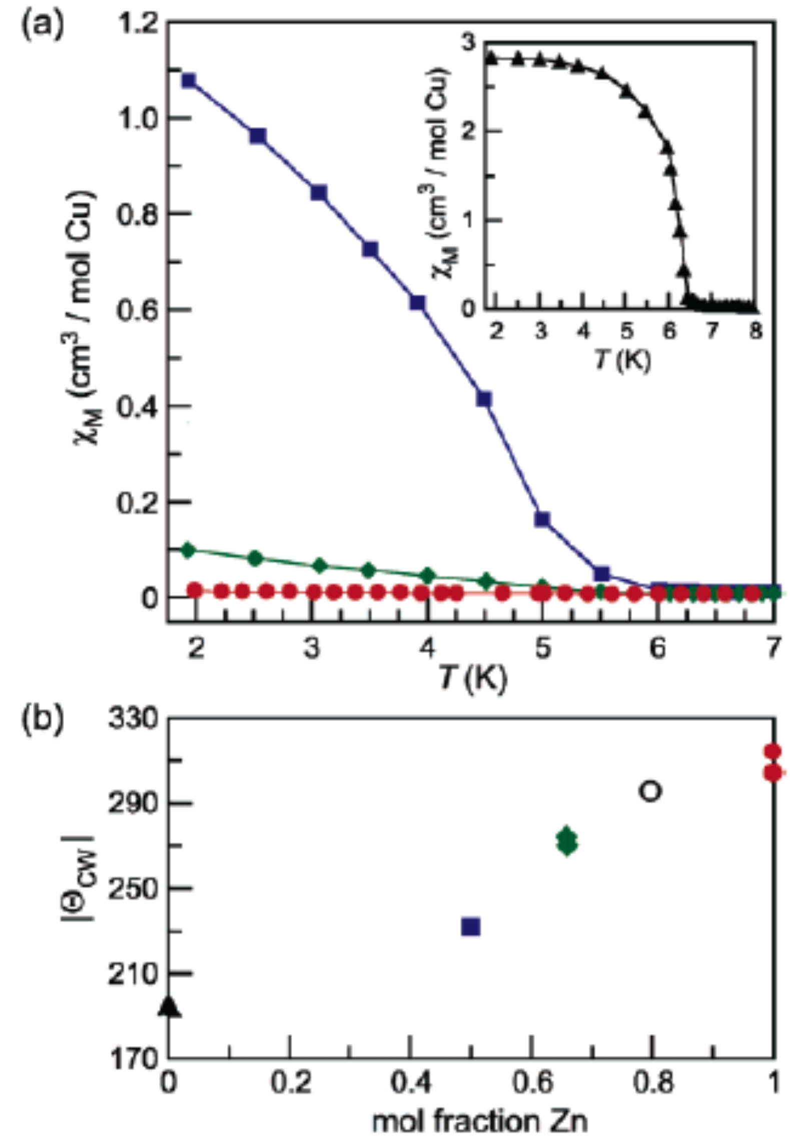
(photo courtesy of Bruce Kelley)

Shores *et al*, JACS (2005)

Herbertsmithite - $ZnCu_3(OH)_6Cl_2$ with copper on a kagome lattice



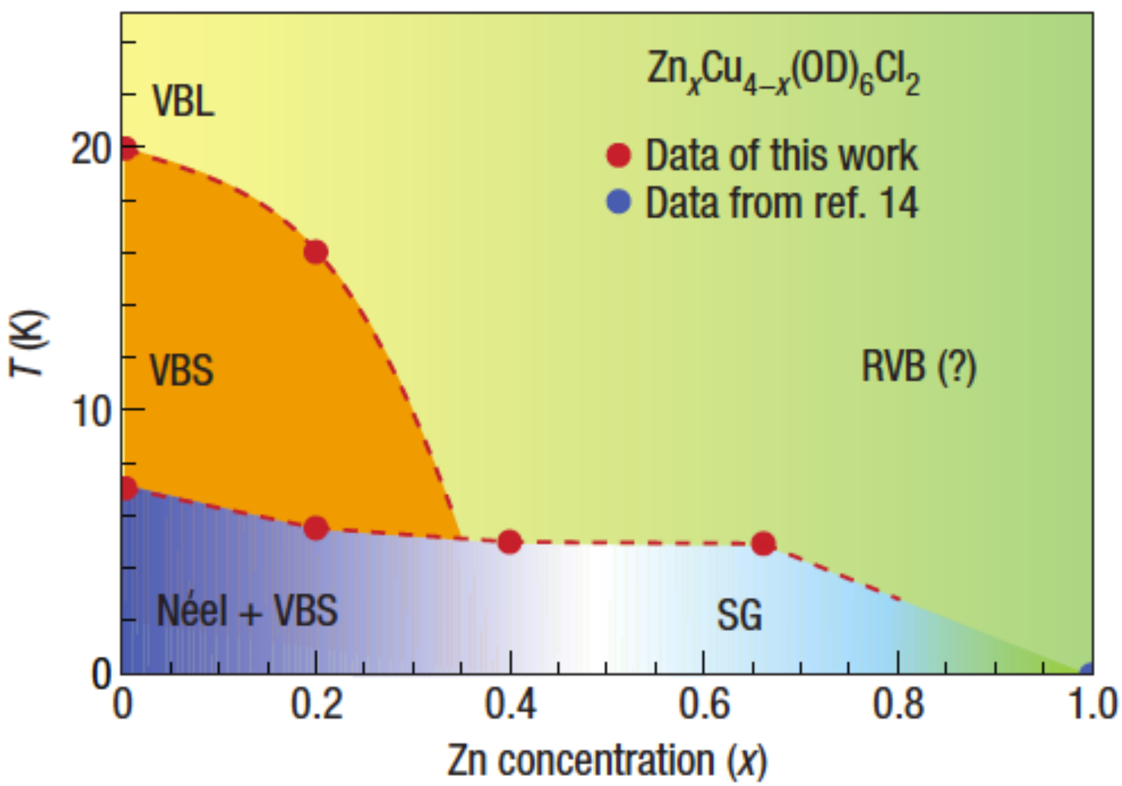


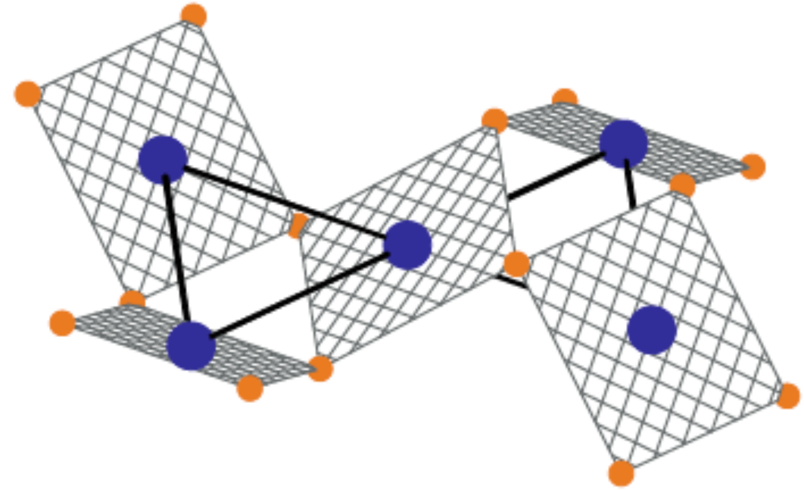


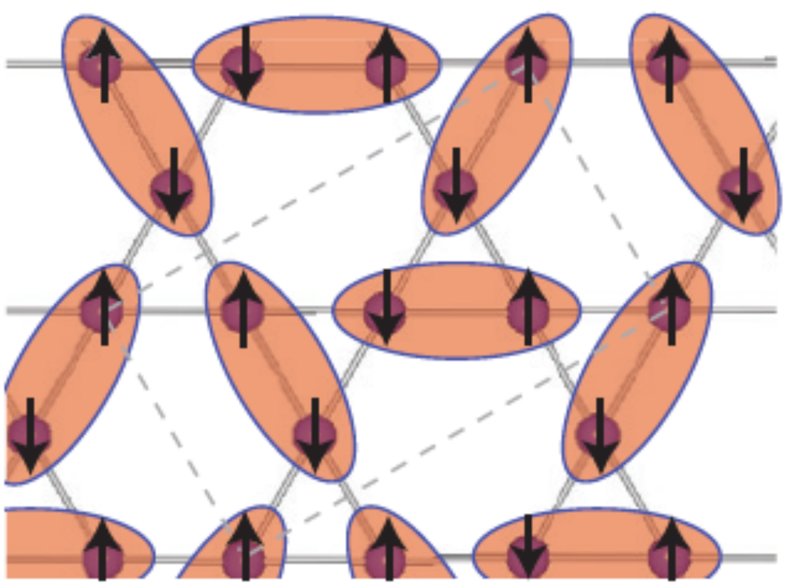
Shores *et al.*, JACS (2005)

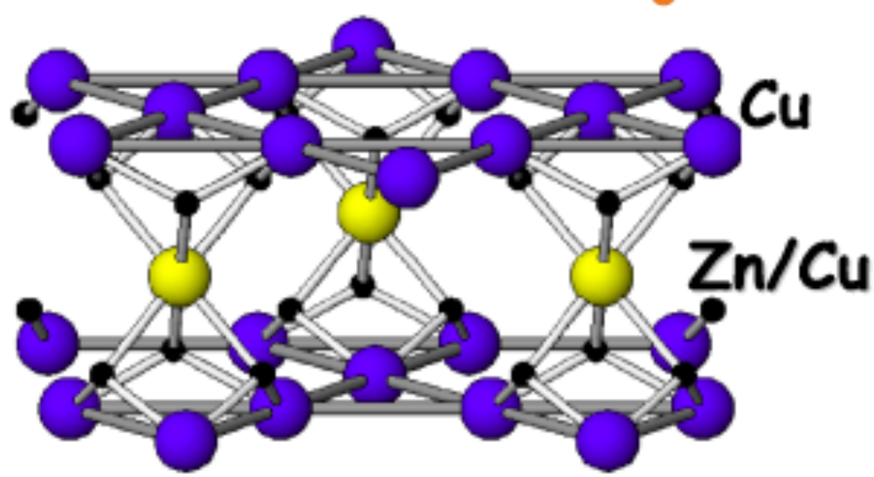
$Cu_4 \rightarrow ZnCu_3$

Canted AF $\rightarrow$ spin liquid







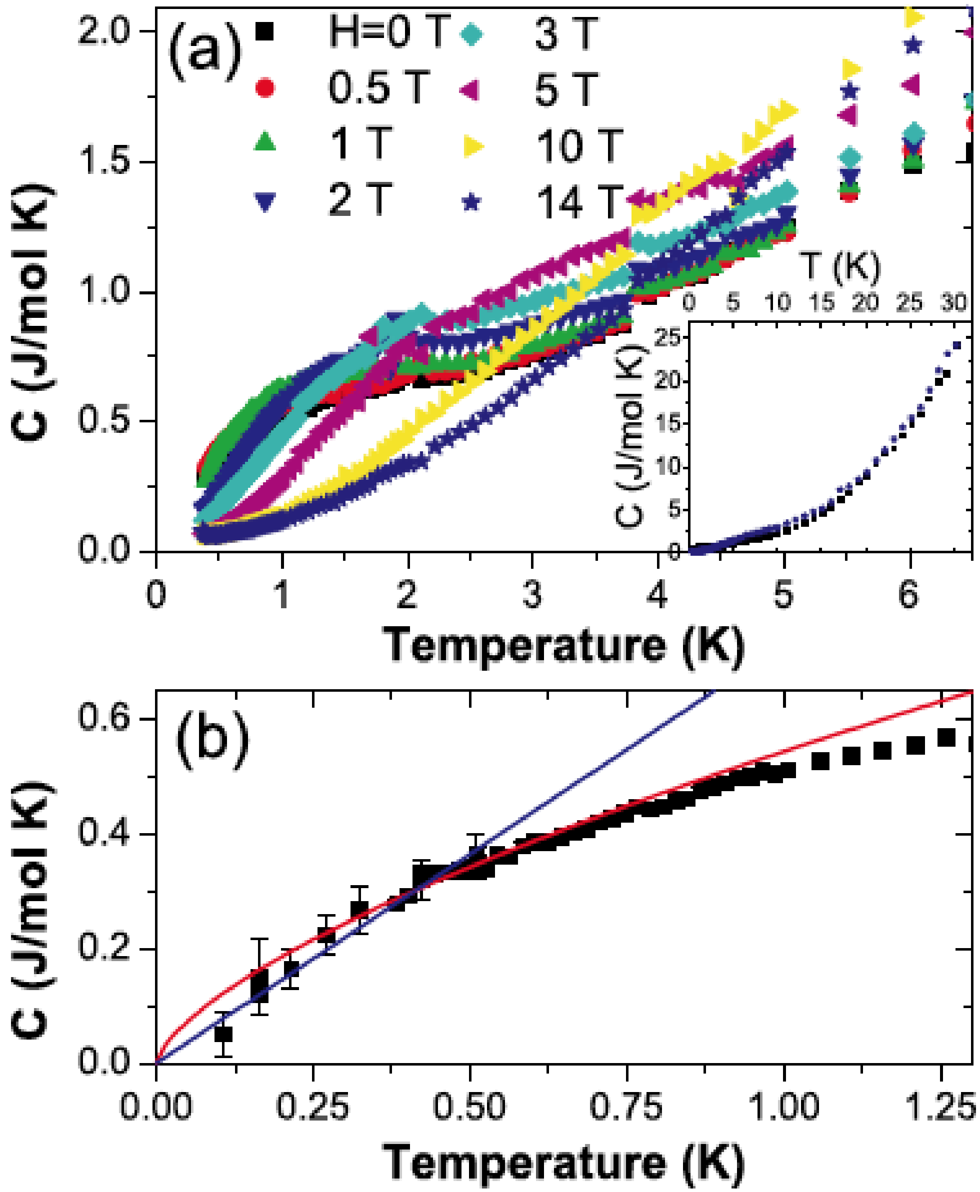


Shores *et al*, JACS (2005)

Lee *et al*, Nature Matls (2007)

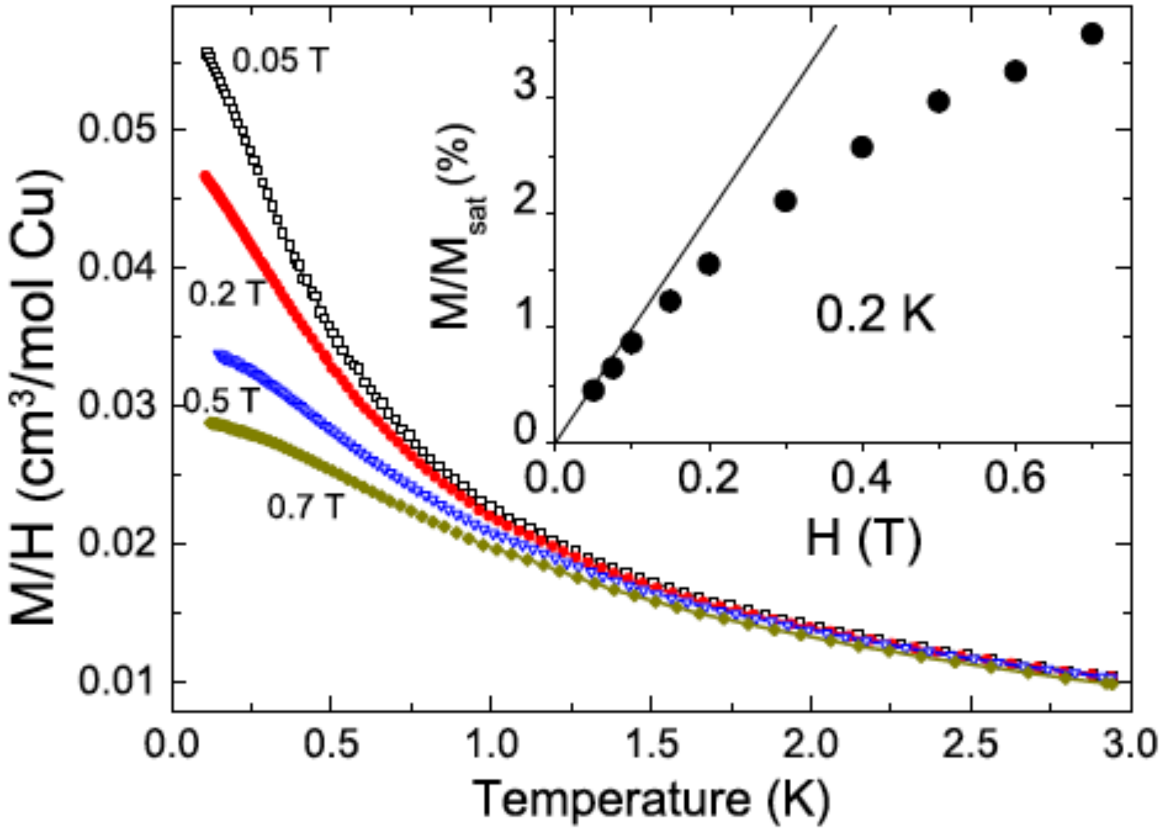
Mendels & Bert, JPSJ (2010)

Specific heat indicates gapless behavior with quasi-linear T behavior



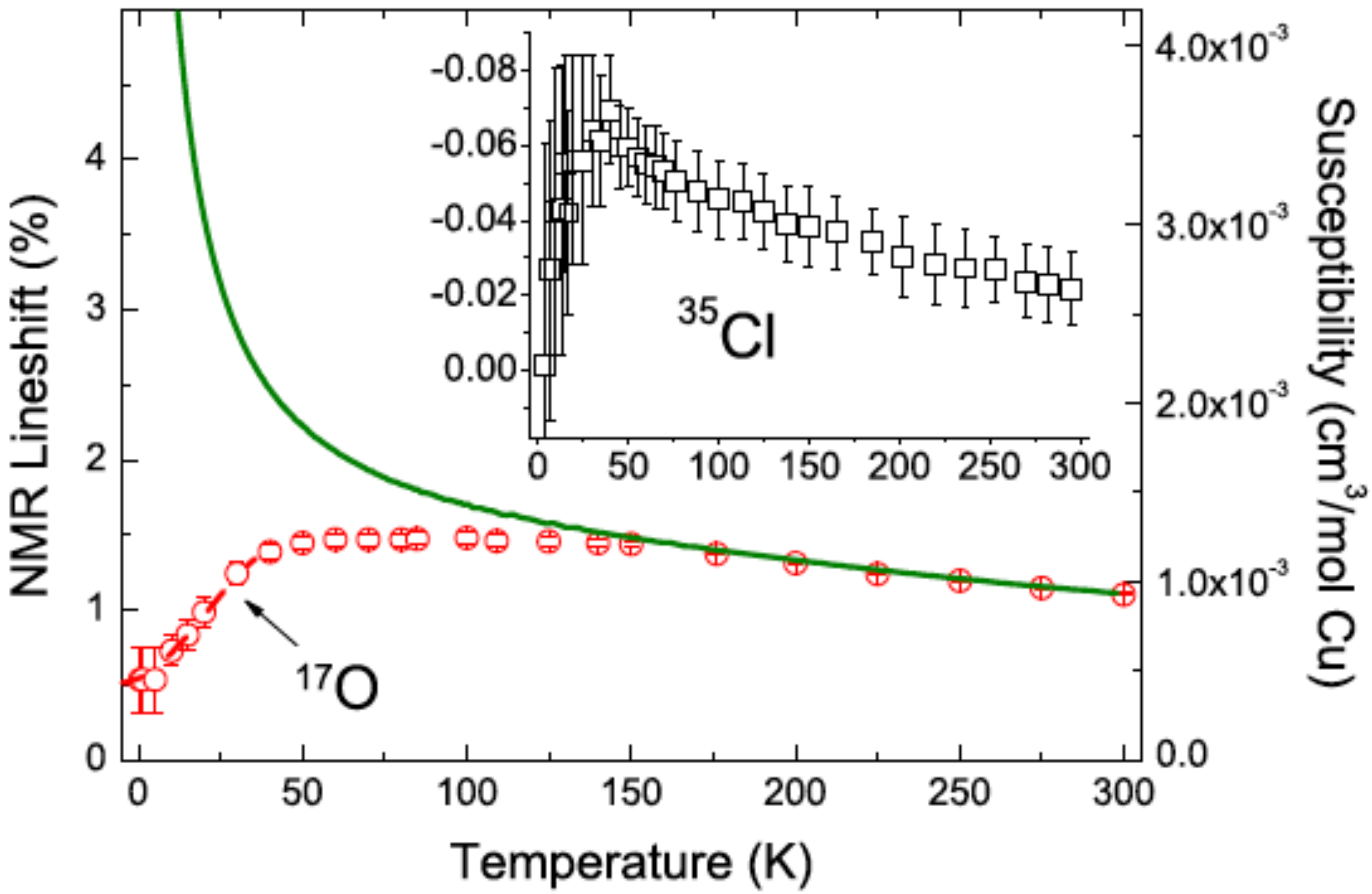
Helton *et al.*, PRL (2007)

But, there is a large spin defect concentration
Estimate is that roughly 1 in 6 Zn atoms are replaced by a Cu



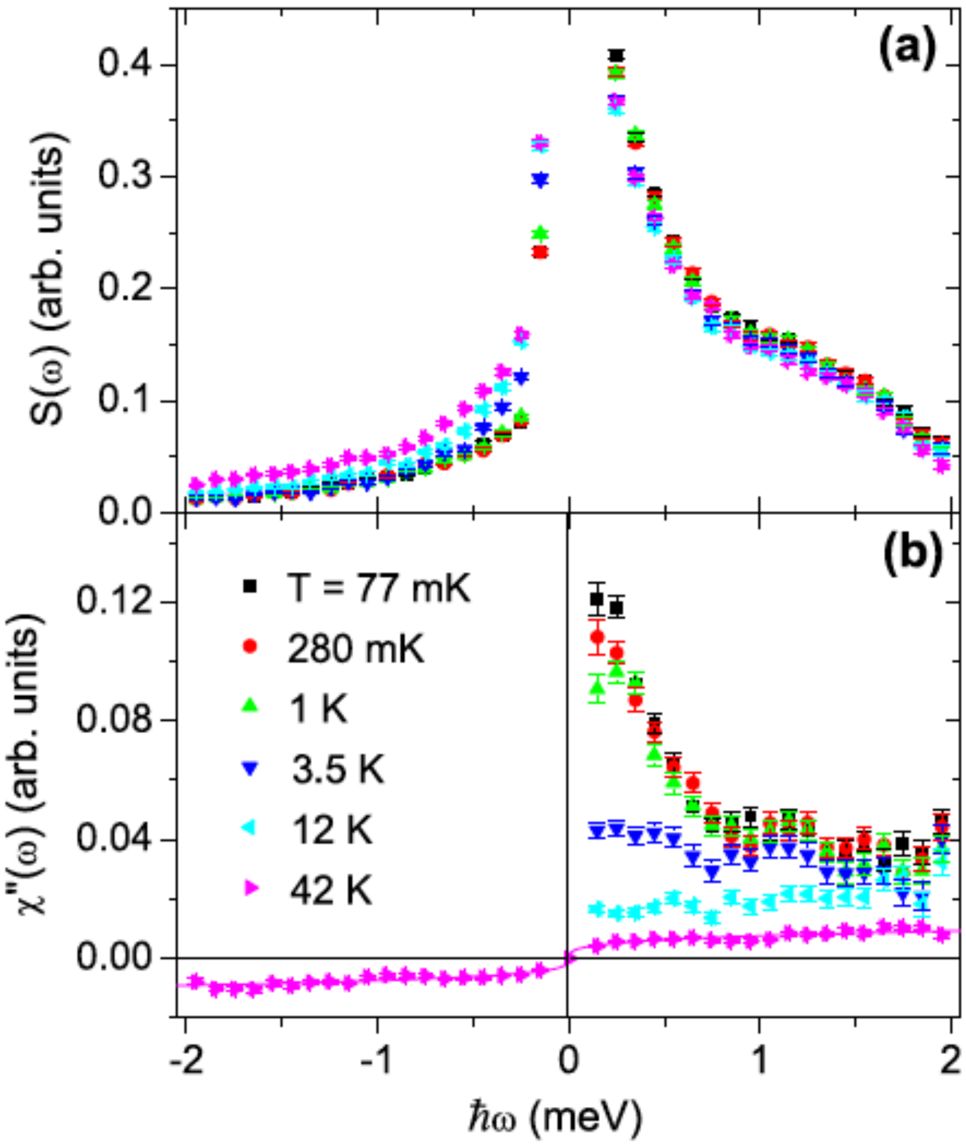
Bert *et al.*, PRB (2007)

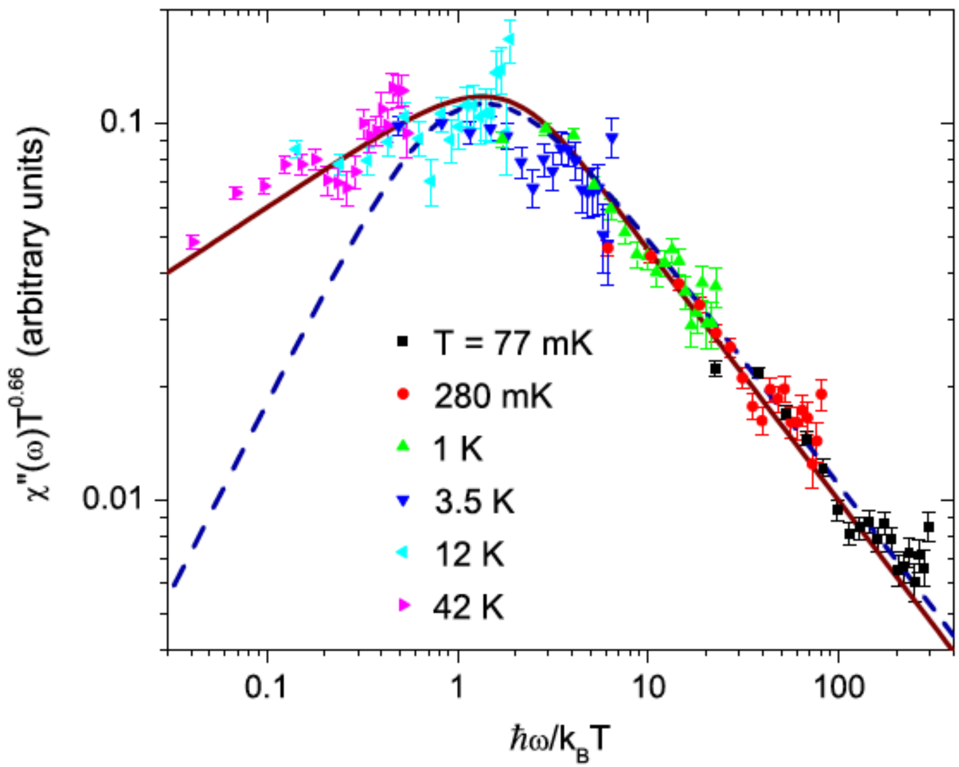
NMR indicates a decreasing χ below 50 K for the kagome spins, despite the diverging behavior of the bulk χ due to impurity interlayer spins



Mendels & Bert, JPSJ (2010)

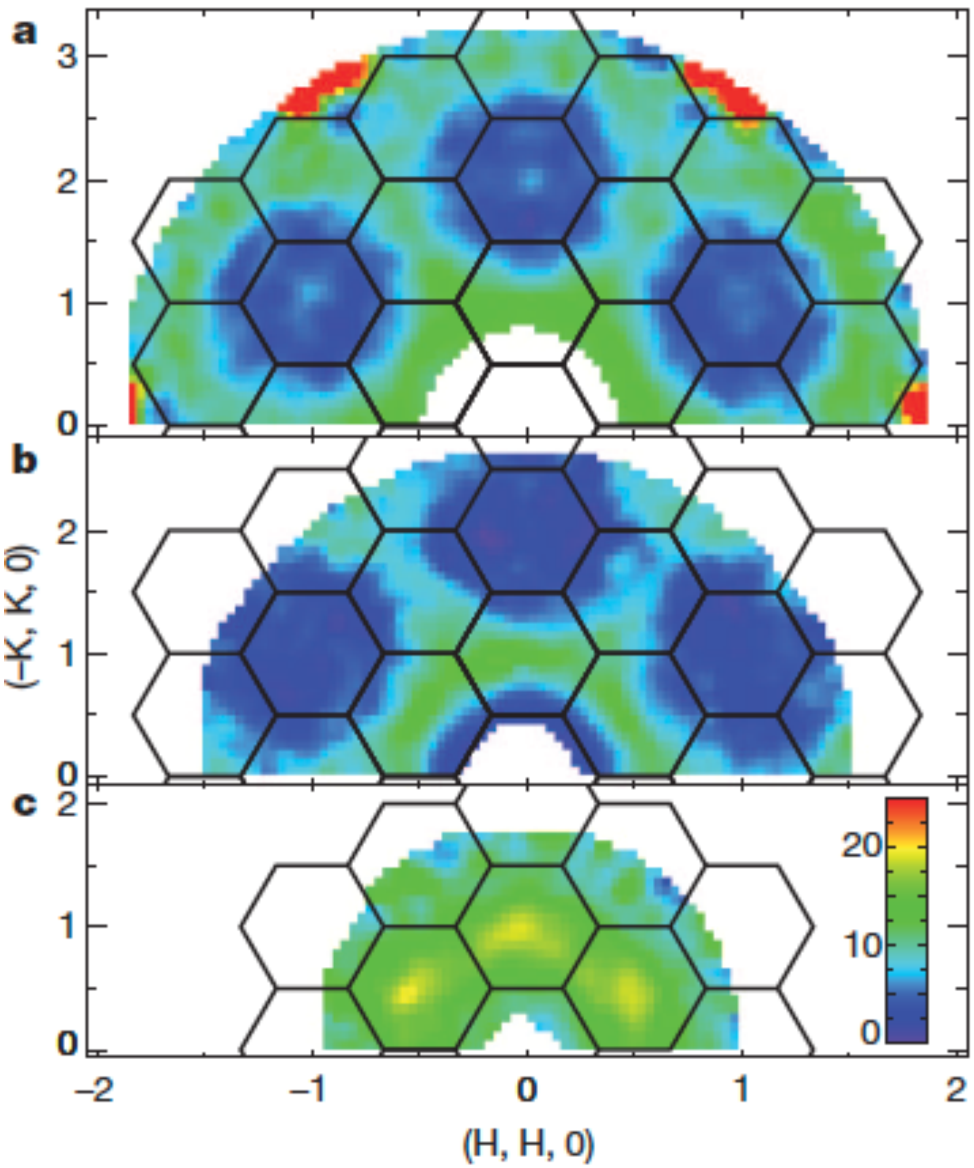
INS data indicate a divergent response below 1 meV with quantum critical scaling as also observed in heavy fermions

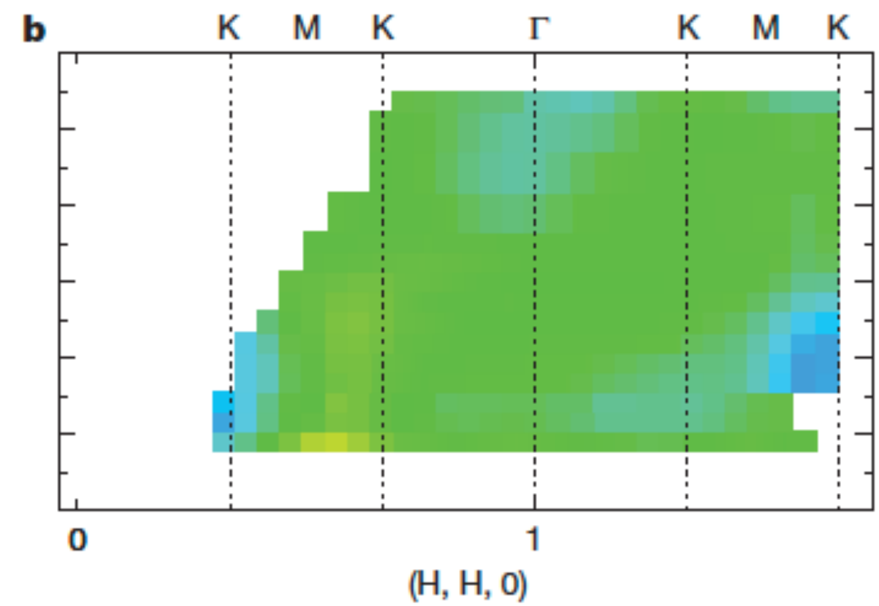


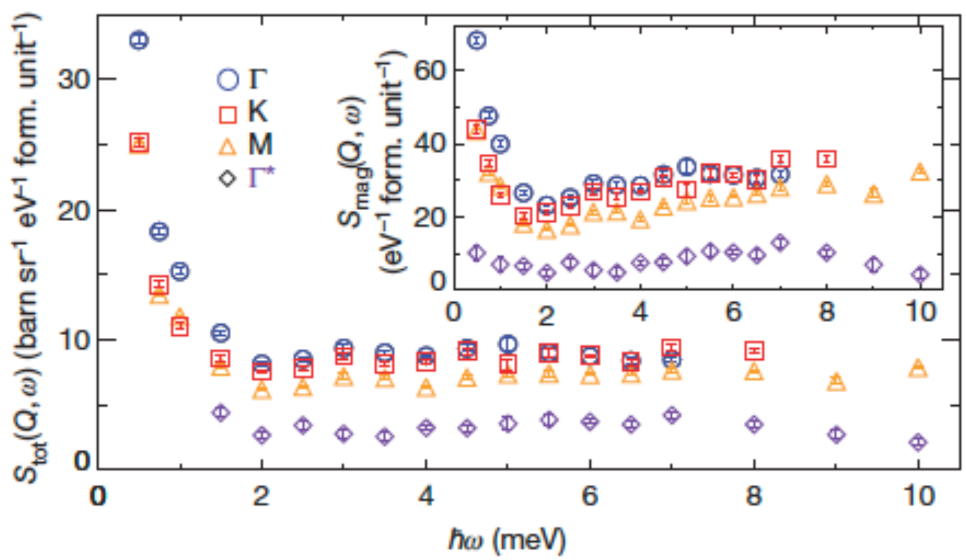


Helton *et al.*, PRL (2010)

INS data on single crystals indicate a continuum of spin excitations, with a dynamic structure factor consistent with near neighbor dimers and of the form $S(\mathbf{q},\omega) = f(\mathbf{q})\, f(\omega)$

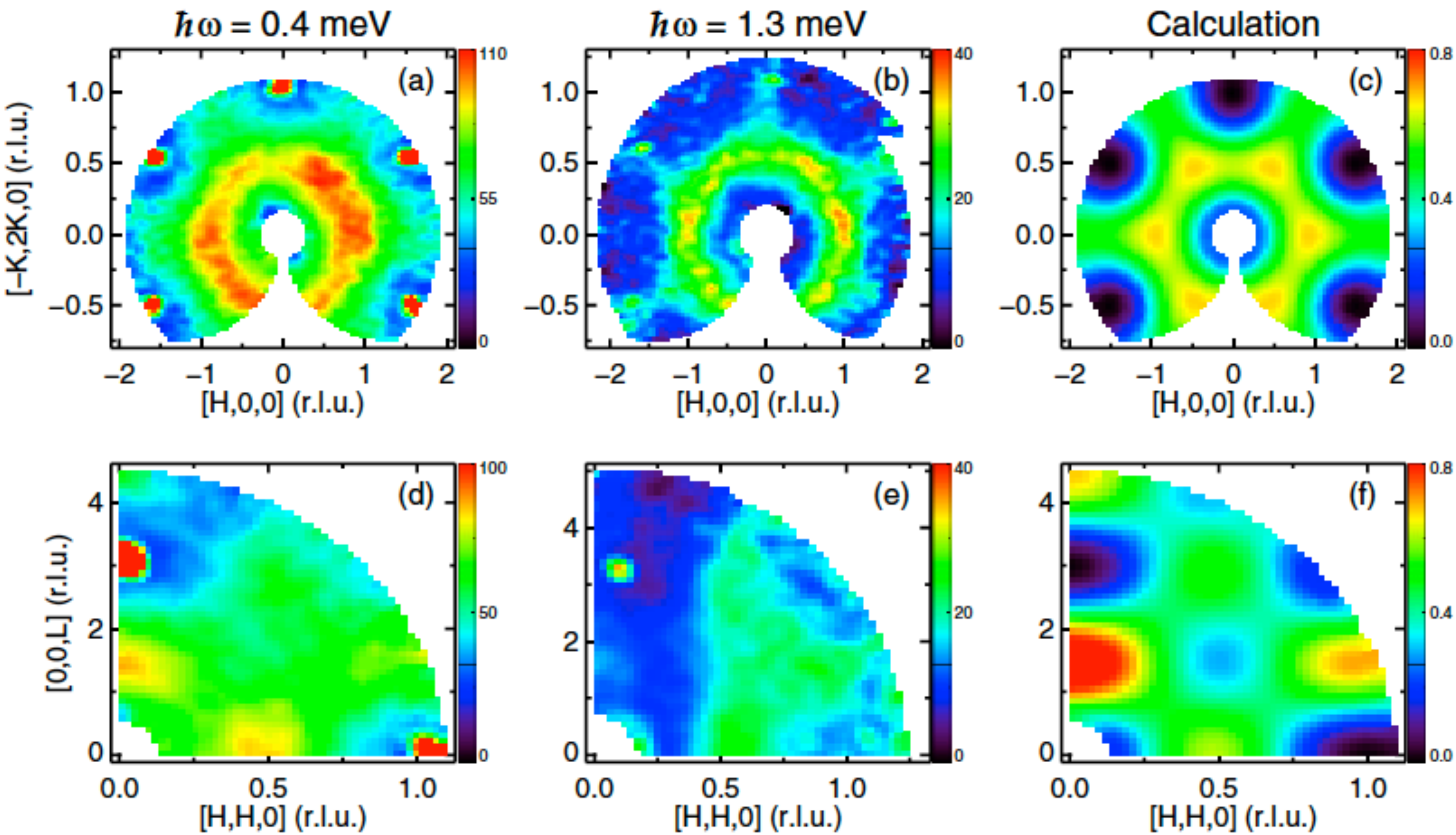






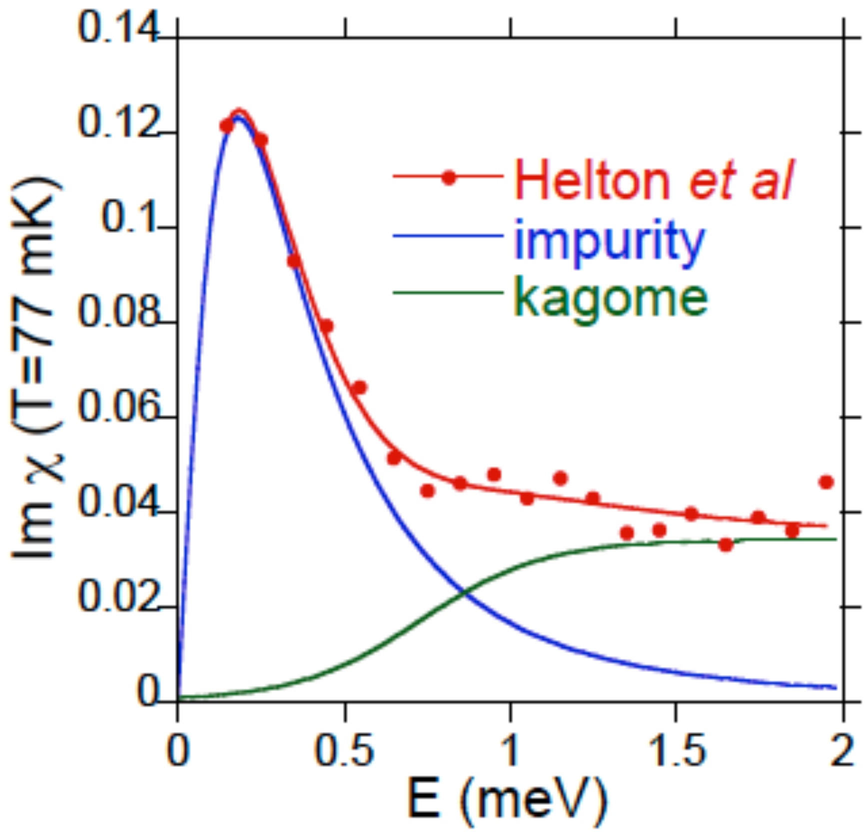
Han *et al.*, Nature (2012)

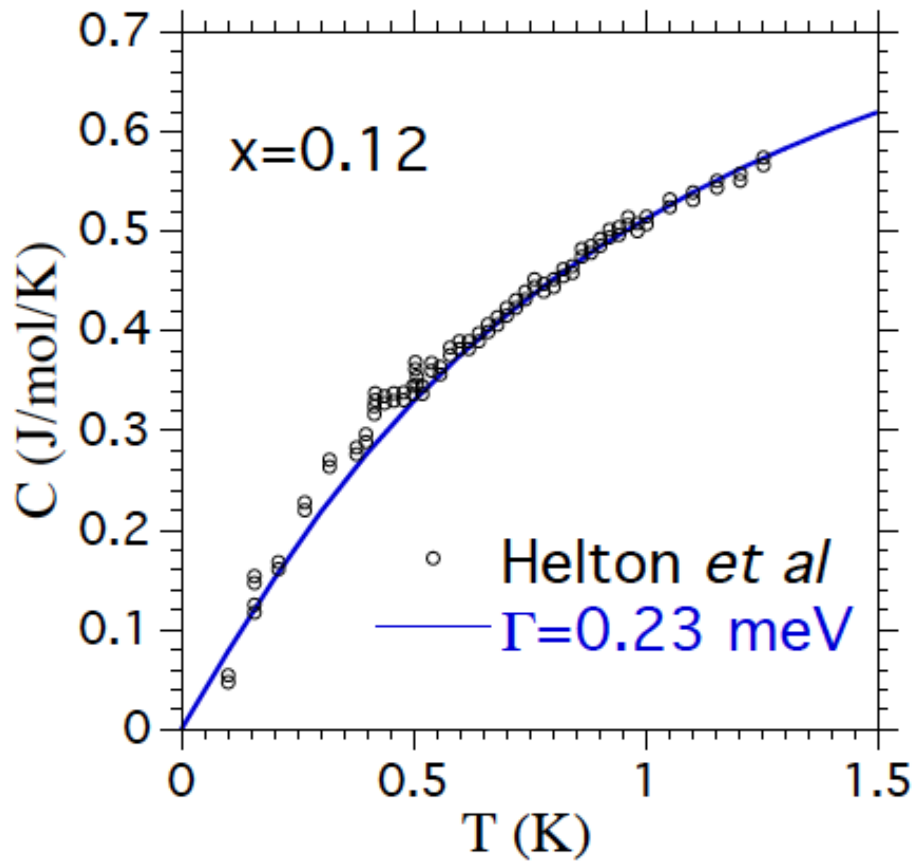
But INS data below 1 meV indicate AF interactions between defect copper spins sitting on the Zn intersites



Han *et al.*, PRB (2016)

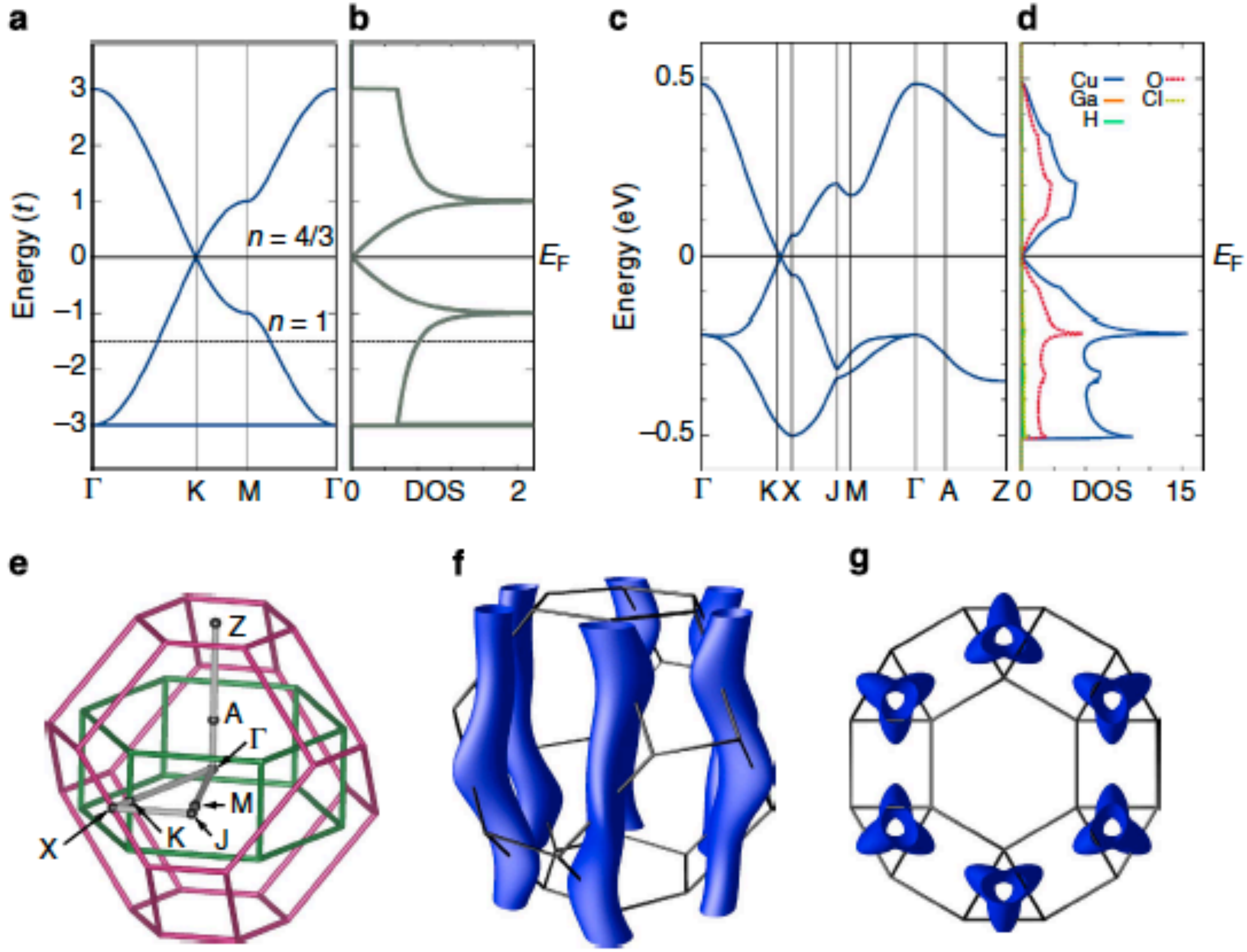
INS data are a sum of impurity and kagome spin contributions
(with the kagome spins having a spin gap)
Specific heat can be fit assuming a relaxational form for impurity $\chi(\omega)$





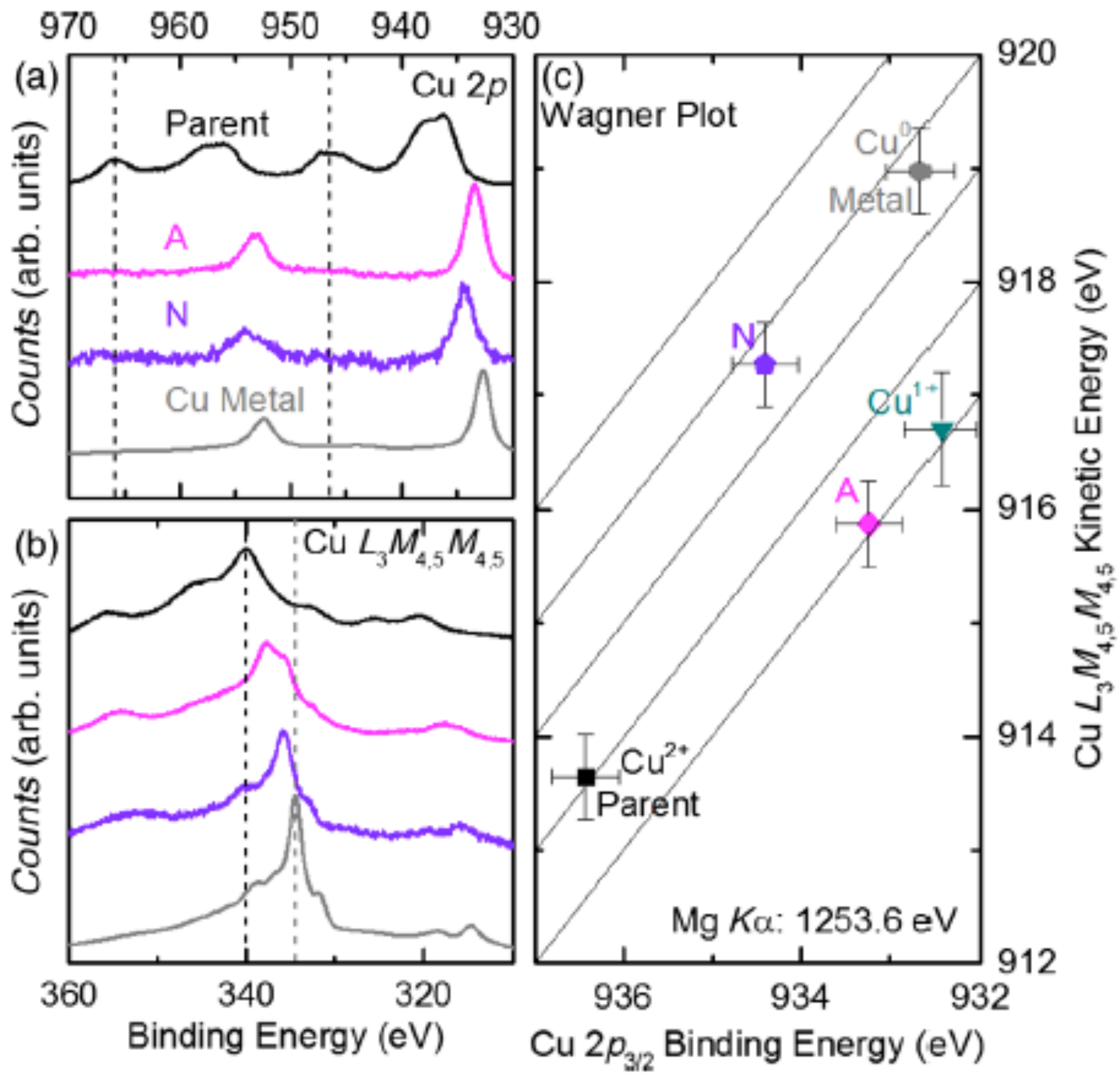
Han *et al.*, PRB (2016)

Can one “dope” herbertsmithite by replacing Zn^{2+} by 1^+ or 3^+ ions? Prediction of Dirac points (electron doping), flat bands (hole doping), and f-wave pairing



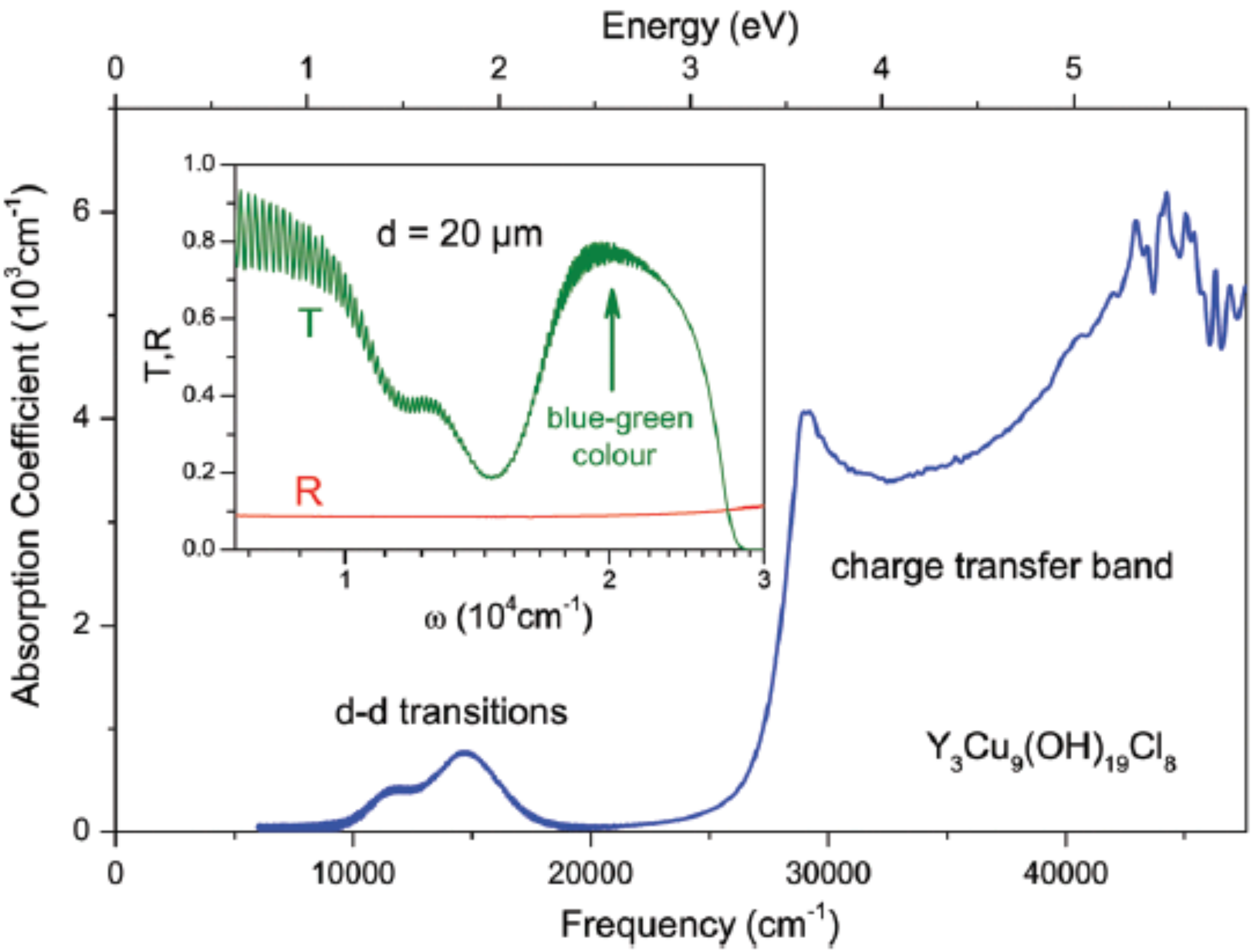
Mazin *et al.,* Nature Comm. (2014)
Guterding *et al,* Sci. Rep. (2016)

Lithium intercalated Herbertsmithite
Insulating, but with indications for a Cu non-integer valence



Kelly *et al.*, PRX (2016)

Herbertsmithite has a much larger gap than a cuprate



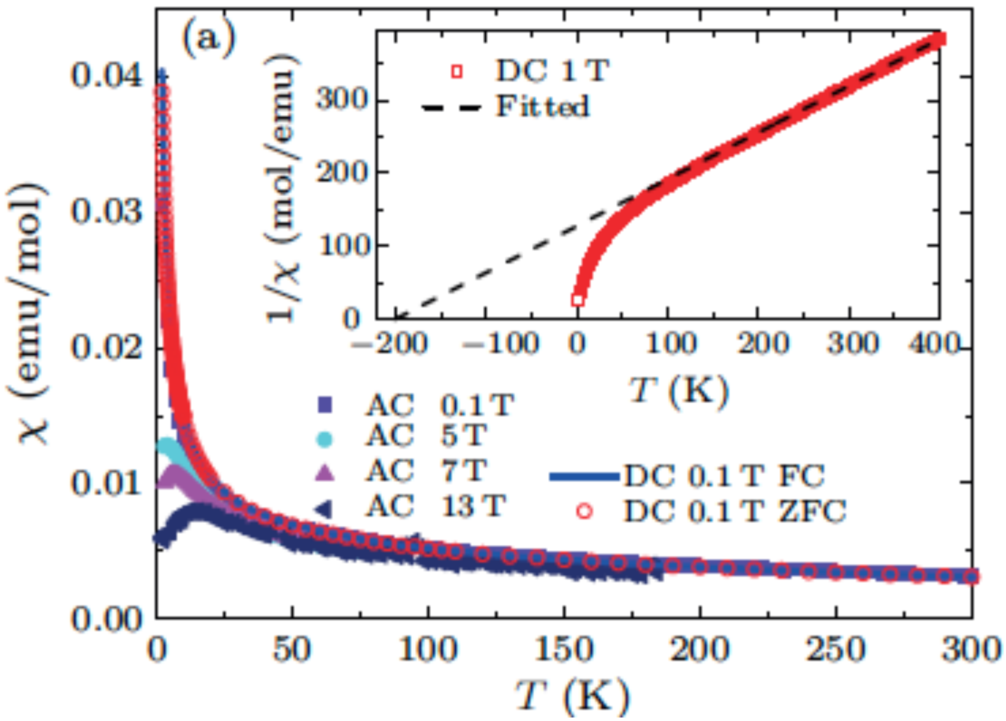
Puphal *et al.,* J Mater Chem C (2017)
Pustogow *et al*., Phys Rev B (2017)

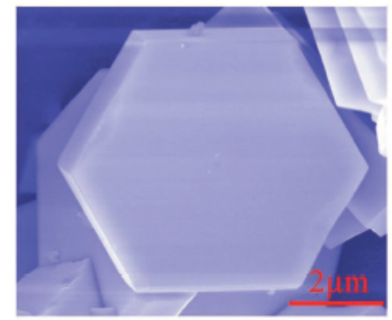
There are many relatives of herbertsmithite
Several of these are polymorphs

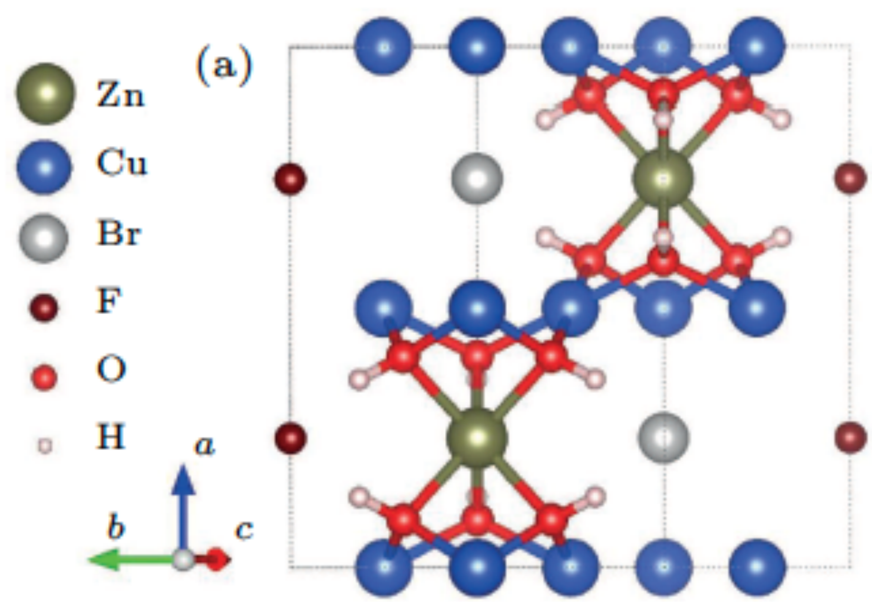
Name	Formula	Group	Lattice	Order
Botallackite	$Cu_4(OH)_6Cl_2$	$P2_1/m$	T	AF (7.2 K)
Atacamite	$Cu_4(OH)_6Cl_2$	$Pnma$	P	AF (9 K)
Clinoatacamite	$Cu_4(OH)_6Cl_2$	$P2_1/n$	P	AF (6.5 K)
Claringbullite	$Cu_4(OH)_6ClF$	$P6_3/mmc$	P	AF (17 K)
Barlowite	$Cu_4(OH)_6BrF$	$P6_3/mmc$	P	AF (15 K)
Bobkingite	$Cu_5(OH)_8Cl_2W_2$	$C2/m$	P	?
Herbertsmithite	$ZnCu_3(OH)_6Cl_2$	$R\bar{3}m$	K	AF ($\cdots$)
Tondiite	$MgCu_3(OH)_6Cl_2$	$R\bar{3}m$	K	AF ($\cdots$)
Kapellasite	$ZnCu_3(OH)_6Cl_2$	$P\bar{3}m1$	K	F ($\cdots$)
Haydeeite	$MgCu_3(OH)_6Cl_2$	$P\bar{3}m1$	K	F (4.2 K)
Zn-brochantite	$ZnCu_3(OH)_6SO_4$	$P2_1/a$	K*	AF ($\cdots$)

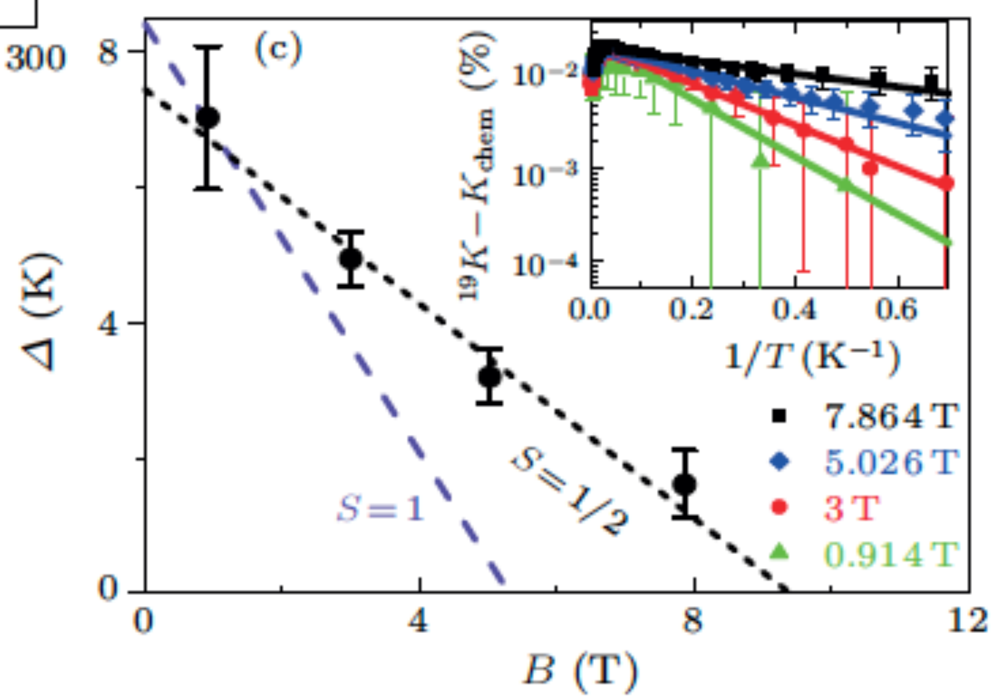
Norman, Rev Mod Phys (2016)

Zn-doped Barlowite exists, with ^{19}F NMR indicating spinons



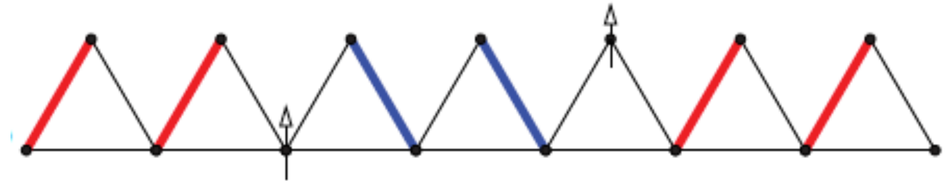


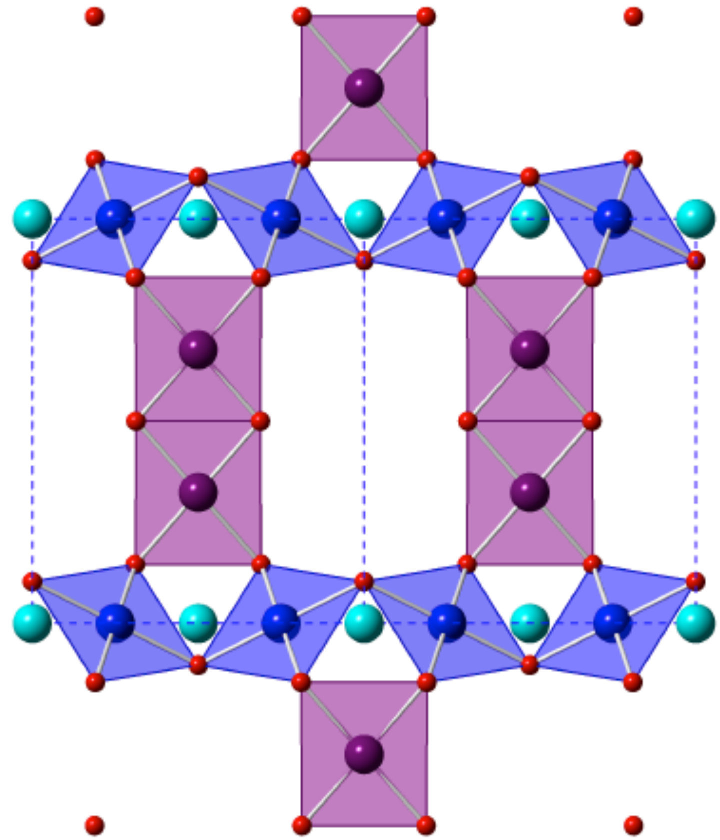


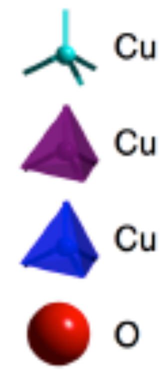


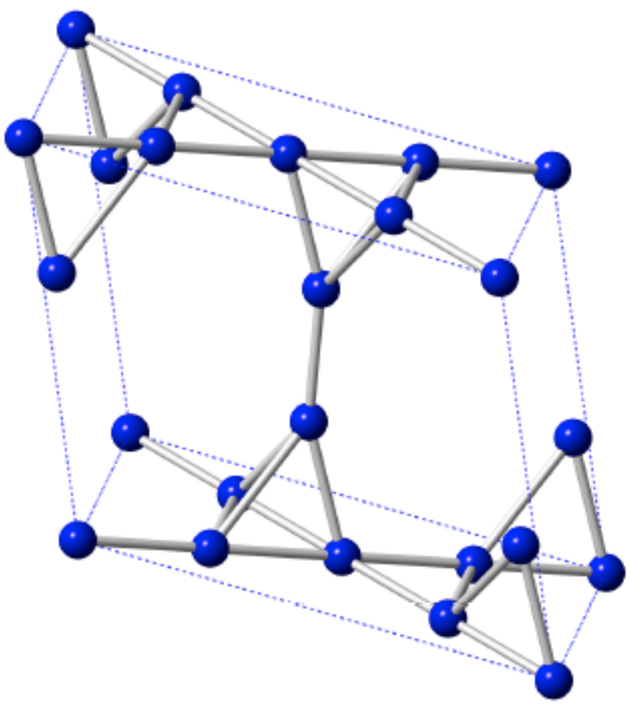
Feng *et al*, Chin Phys Lett (2017)

Bobkingite – a possible Δ chain material









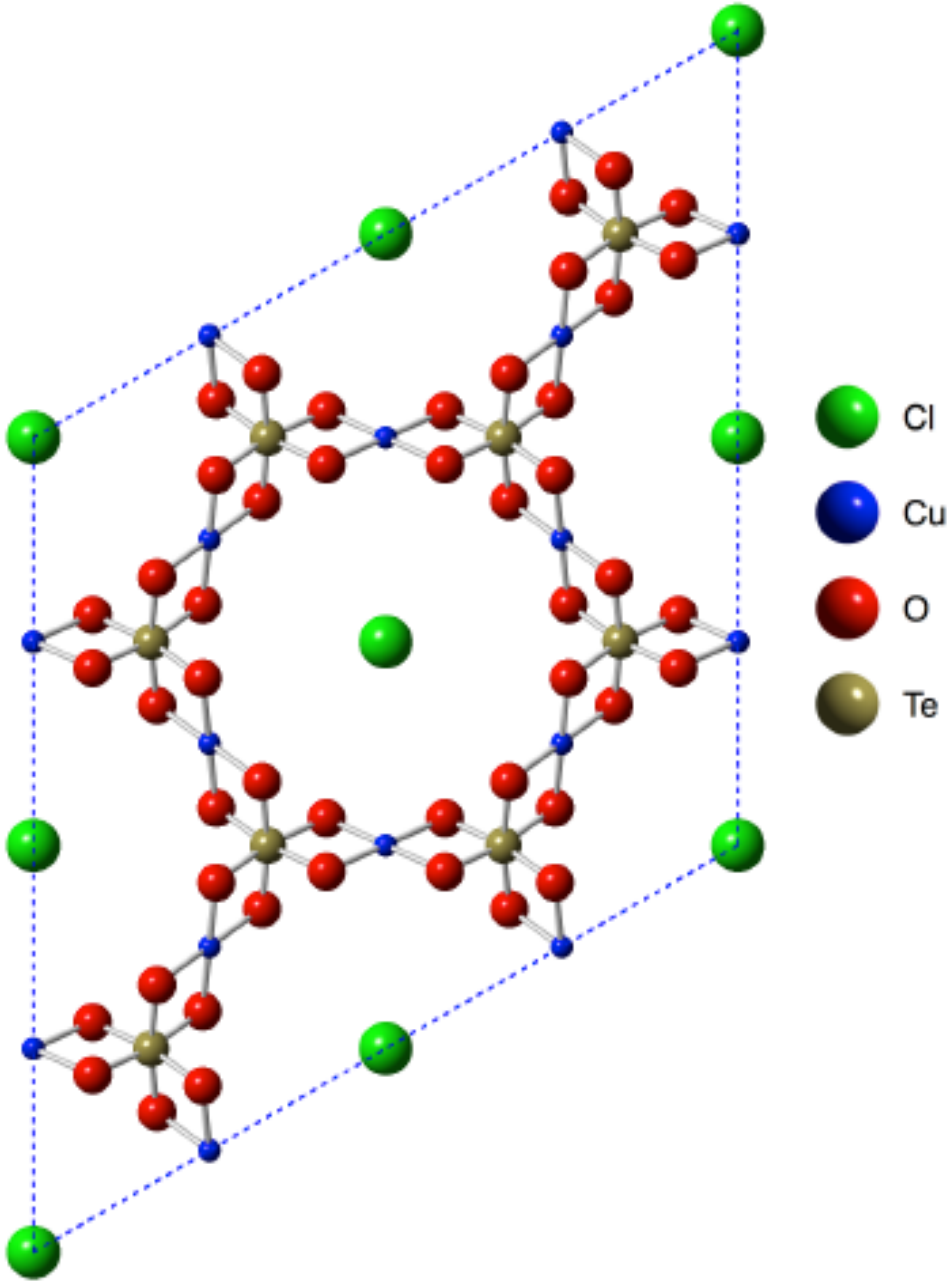
Hawthorne *et al*, Mineral. Mag. (2002)

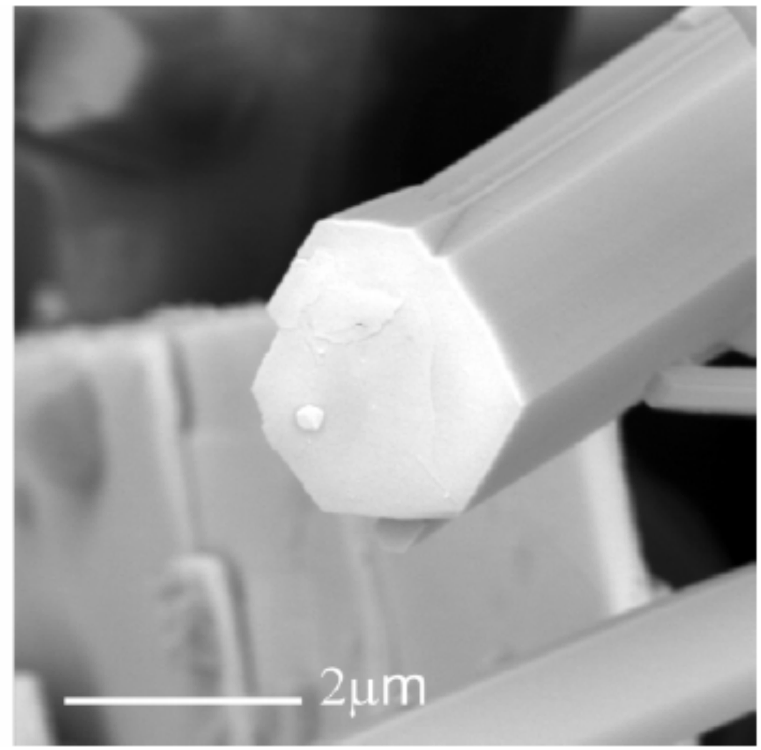
Copper Tellurium Oxides, Hydroxides, and Hydroxychlorides

Name	Formula unit	SG	copper lattice	Ref
Bluebellite	$Cu_6IO_3(OH)_{10}Cl$	R3	maple leaf	1
Mojaveite	$Cu_6TeO_4(OH)_9Cl$	R3	maple leaf	1
Fuettererite	$Pb_3Cu_6TeO_6(OH)_7Cl_5$	$R\bar{3}$	maple leaf	2
Sabelliite	$Cu_2ZnAsO_4(OH)_3$	$P\bar{3}$	maple leaf	3
Quetzalcoatlite	$Zn_6Cu_3(TeO_6)_2(OH)_6$	$P\bar{3}1m$	kagome	4
Leisingite	$MgCu_2TeO_6(H_2O)_6$	$P\bar{3}1m$	honeycomb	5
Jensenite	$Cu_3TeO_6(H_2O)_2$	$P2_1/n$	honeycomb/dimer	6
Mcalpineite	Cu_3TeO_6	$Ia\bar{3}$	hexagons	7
Choloalite	$Pb_3(Cu_5Sb)_{1/3}(TeO_3)_6Cl$	$P4_132$	hyperkagome	8
---	$PbCuTe_2O_6$	$P4_132$	hyperkagome	9
---	$CuTeO_4$	$P2_1/n$	square lattice	10
---	Sr_2CuTeO_6	I4/m	square lattice	11
---	$SrCuTe_2O_7$	Pbcm	orthorhombic	12
---	$Cu_3BiTe_2O_8Cl$	Pcmn	kagome staircase	13

Christy *et al.*, Mineral. Mag. (2016)
Norman, J. Magn. Magn. Matls. (2018)

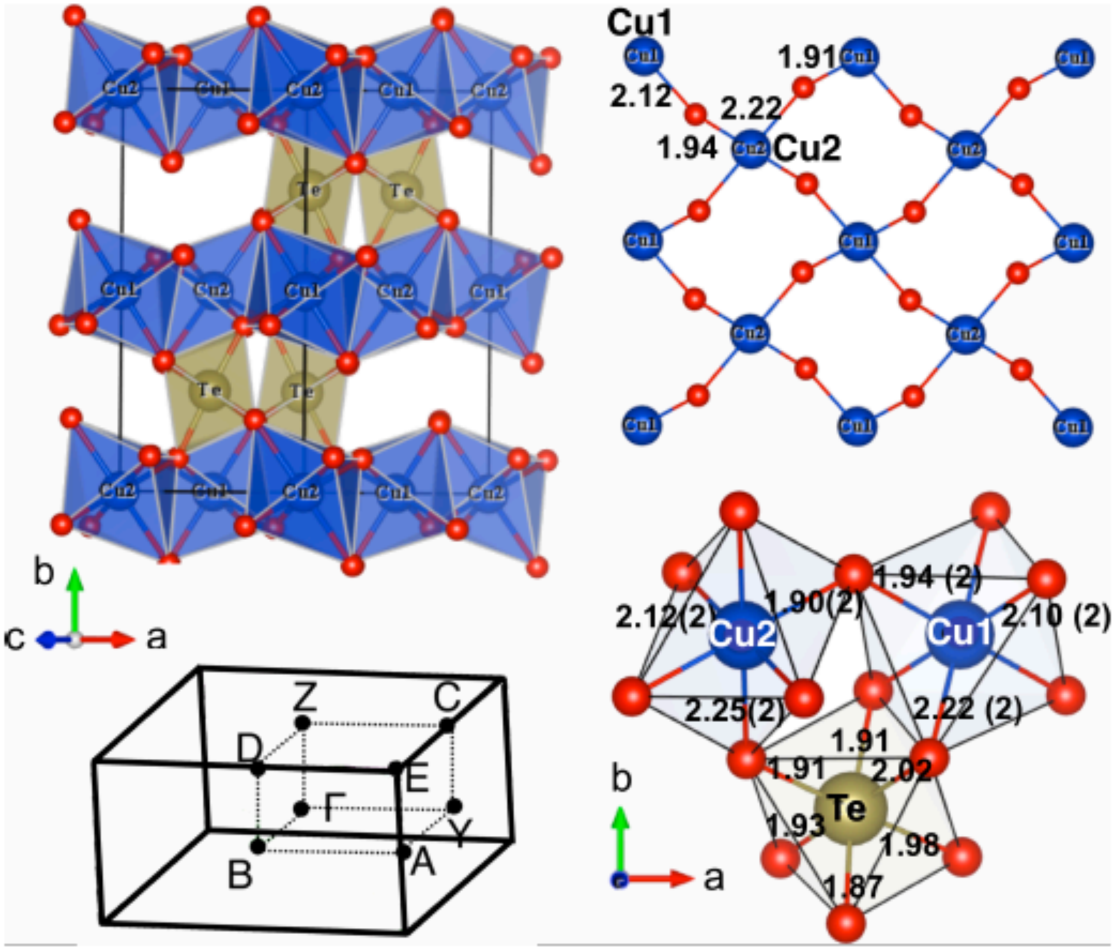
Quetzalcoatlite – a perfect Kagome lattice but with super-superexchange





Burns *et al.*, Amer. Mineral. (2000)

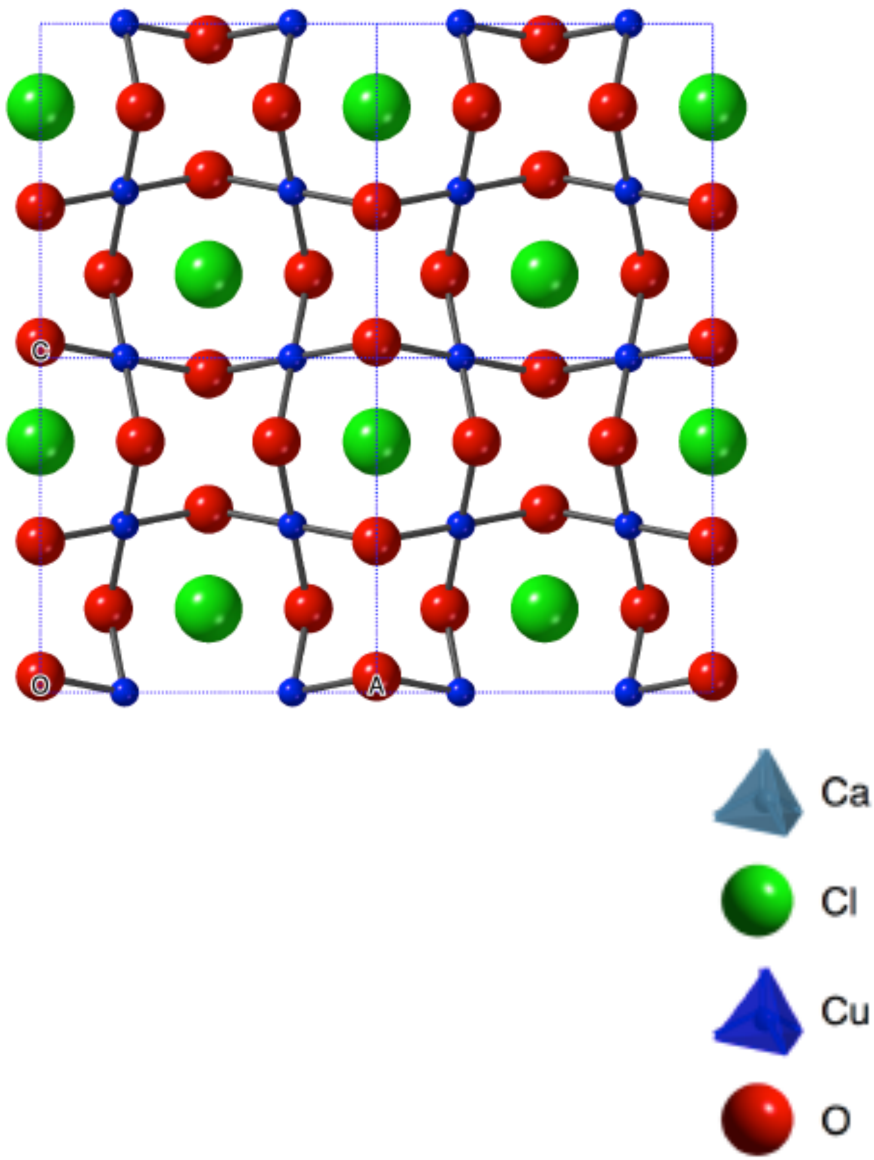
$CuTeO_4$ - Monoclinic distorted CuO_2 square net
CuO_6 quasi-octahedral, Cu-O-Cu bond angles 122.5° & 126.1°

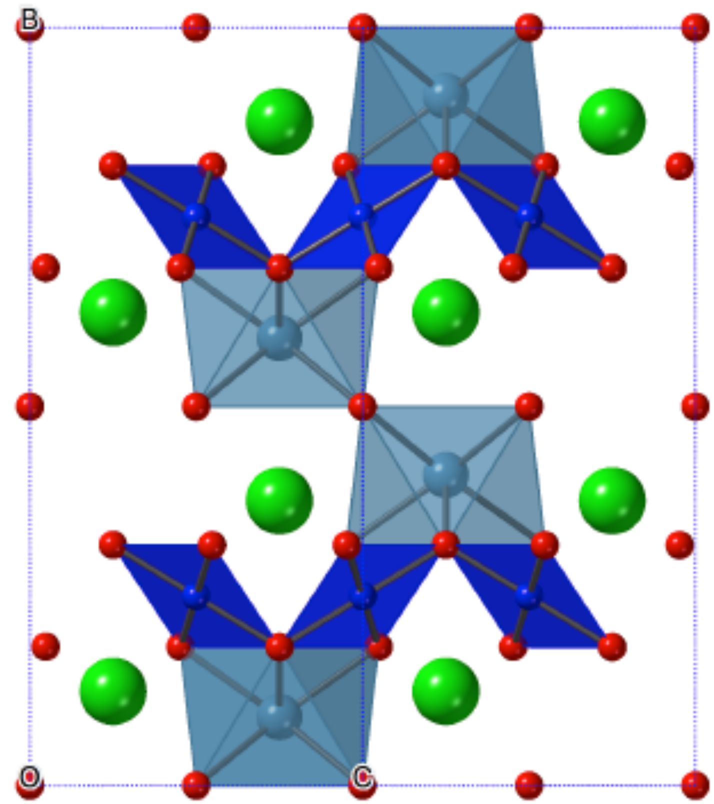


$CuTeO_4$ - Falck *et al.*, Acta Cryst. B (1978)
grown hydrothermally at 650 C
but Cu_3TeO_6 more thermodynamically stable

Botana & Norman, PRB (2017)

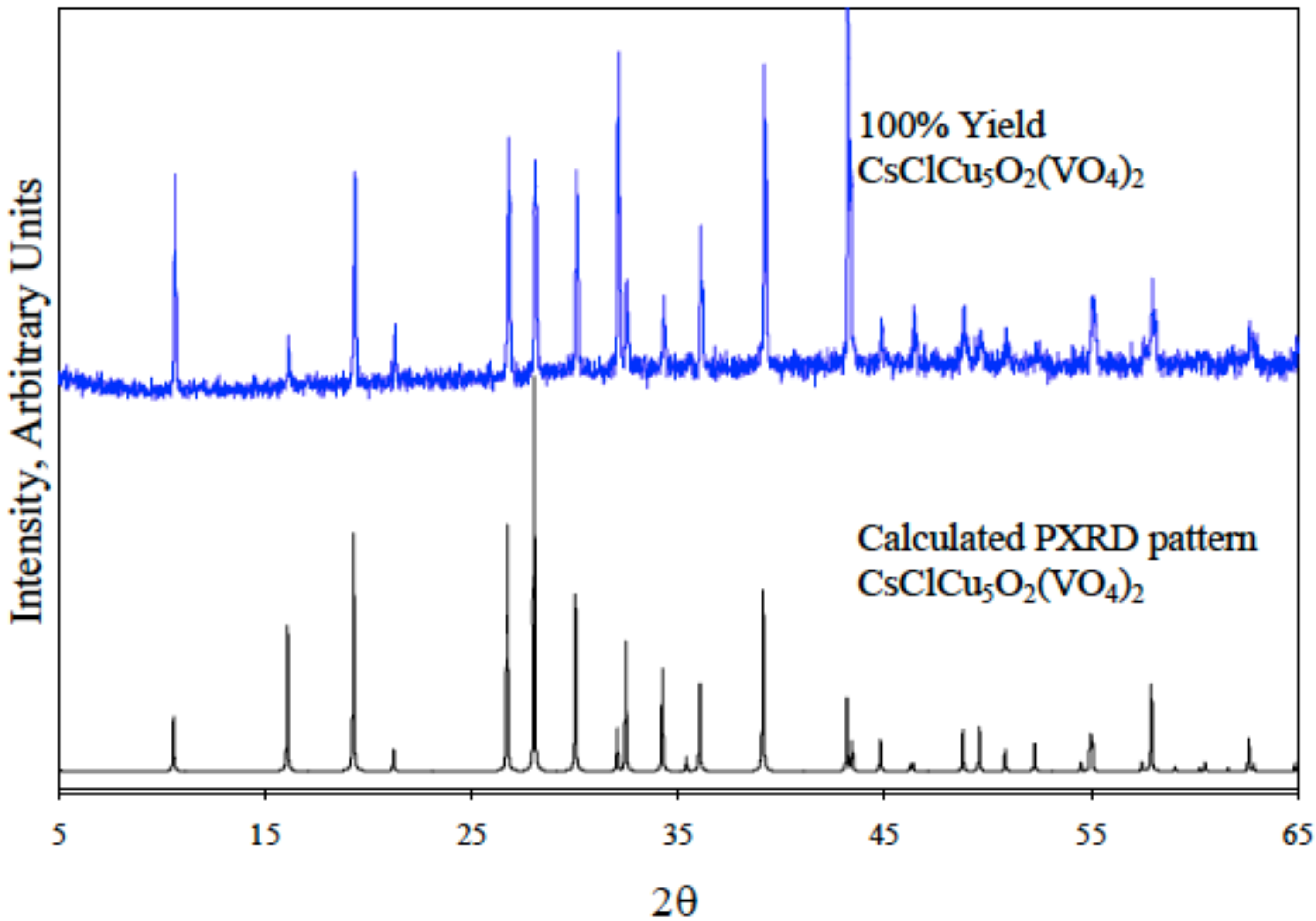
Vondechenite, $CaCu_4Cl_2(OH)_8(H_2O)_4$ - ortho distorted Cu square net
Cu-O-Cu bond angles 114.5° & 115.2°



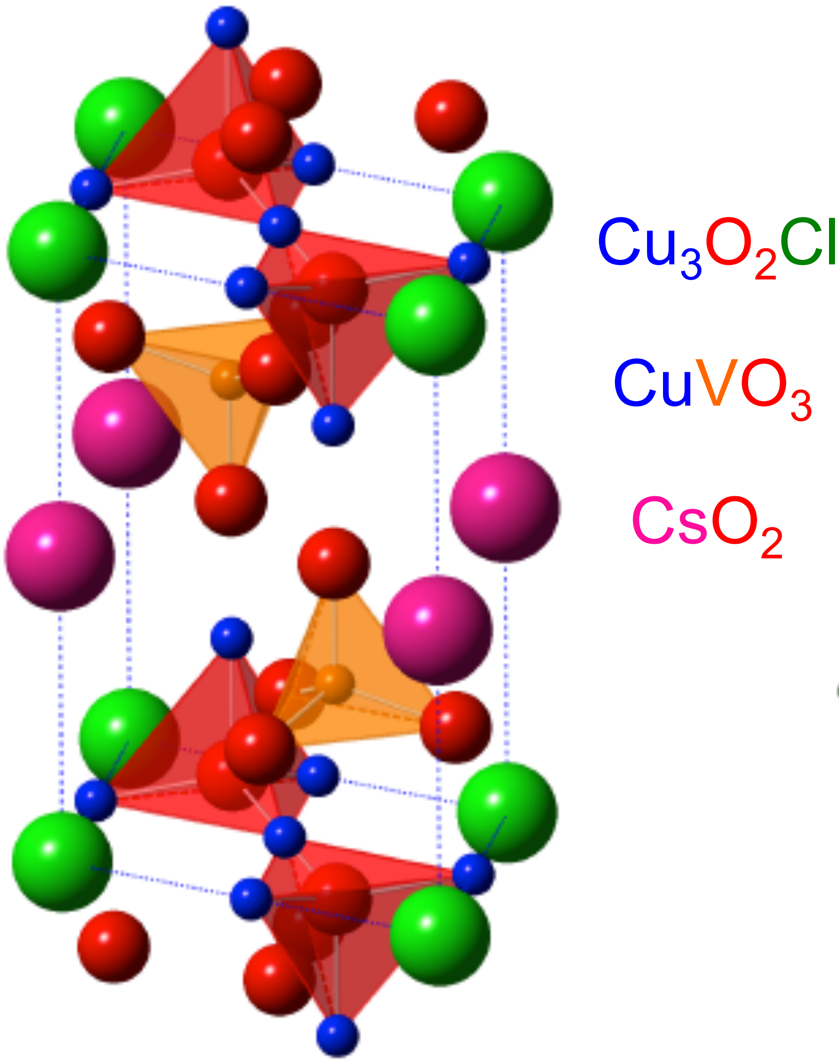


Schluter *et al*, J. Min. Geochem. (2018)

Averievite was found in a volcano in Kamchatka
It was first synthesized by Wendy Queen by solid state reaction (~ 700 C)

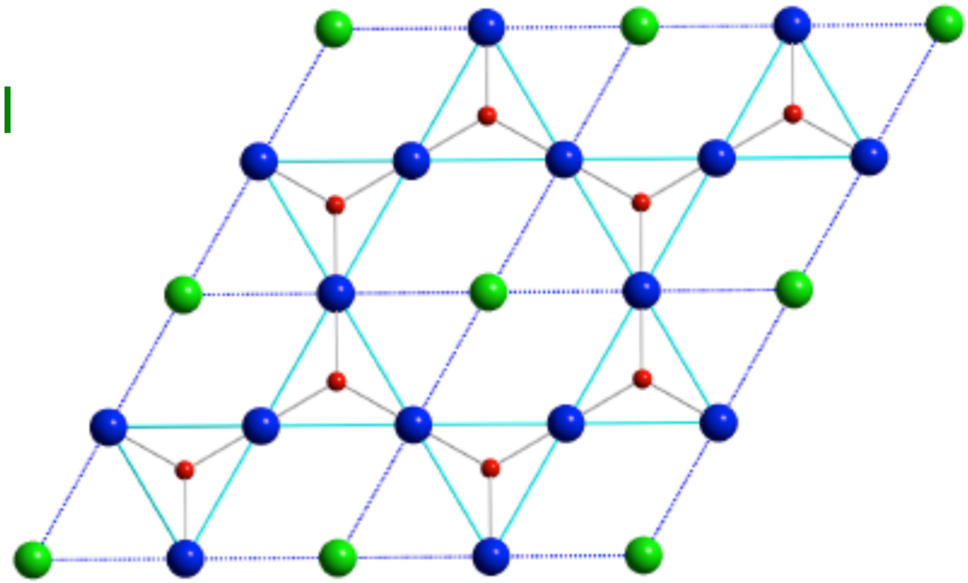


Starova *et al*, Mineral. Mag. (1997)
Wendy Queen, thesis (2009)



$Cu_5O_2(VO_4)_2(CsCl)$

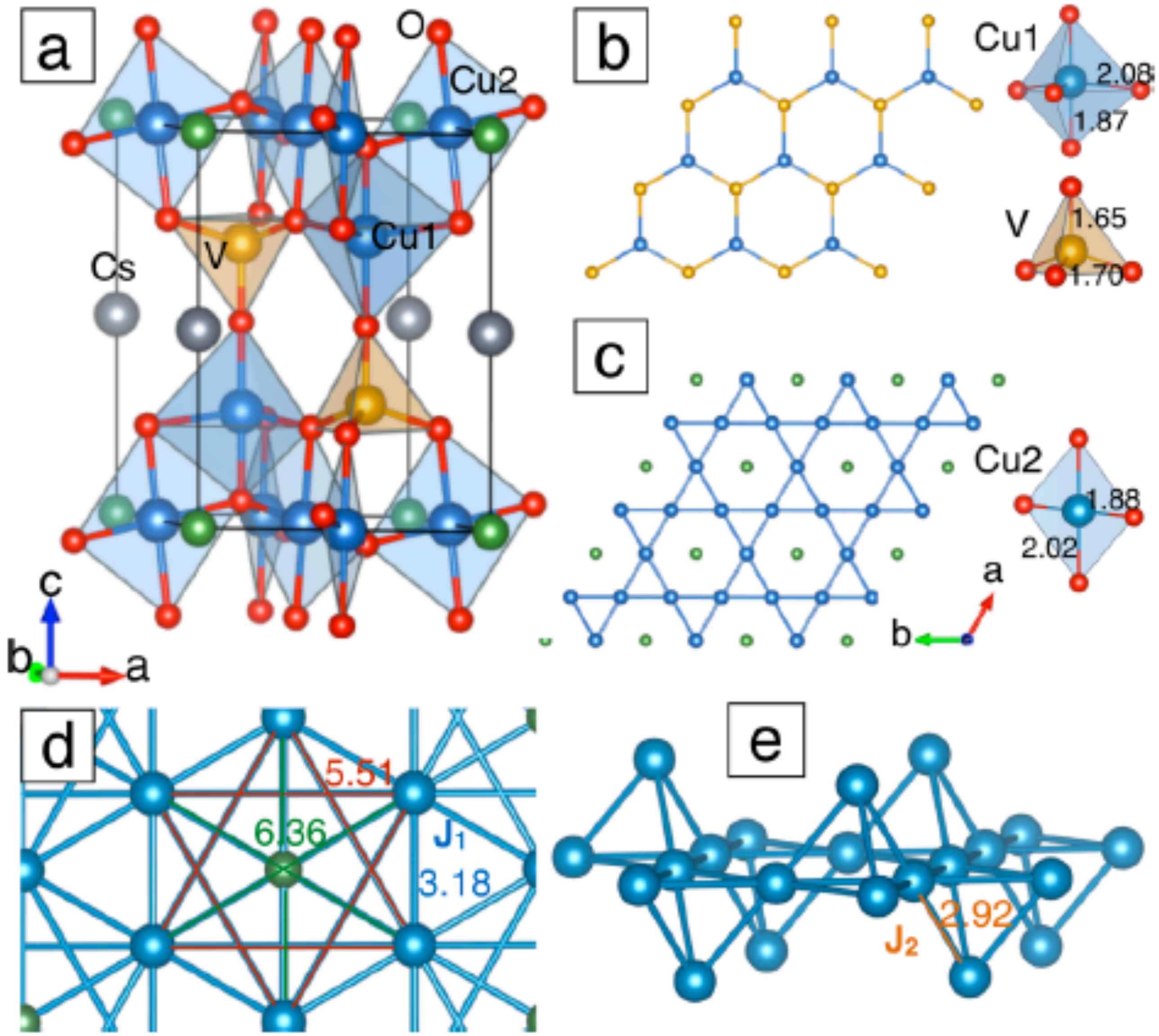
(Wendy Queen, thesis)



One kagome Cu_3O_2Cl plane

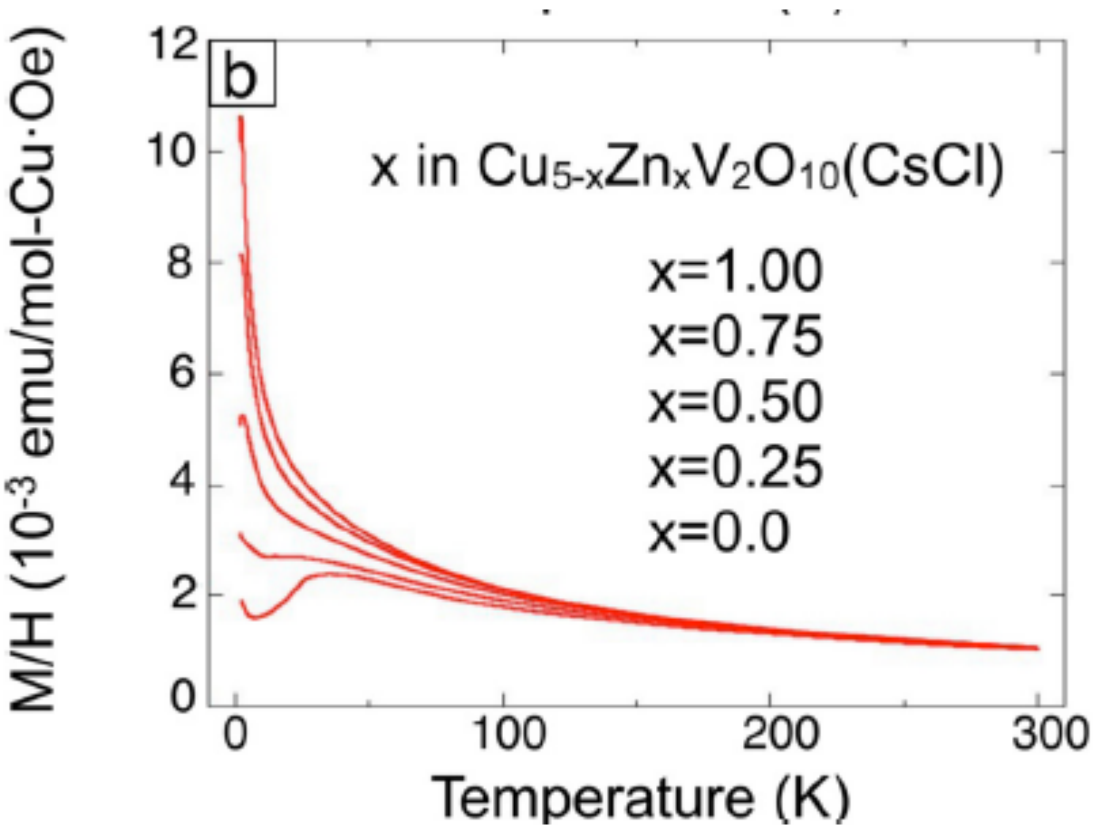
Two honeycomb $CuVO_3$ planes
One triangular CsO_2 plane

$Cu_5V_2O_{10}(CsCl)$, averievite, has a Cu kagome layer and Cu-V honeycomb layers separated by CsO_2 layers (a pyrochlore slab)



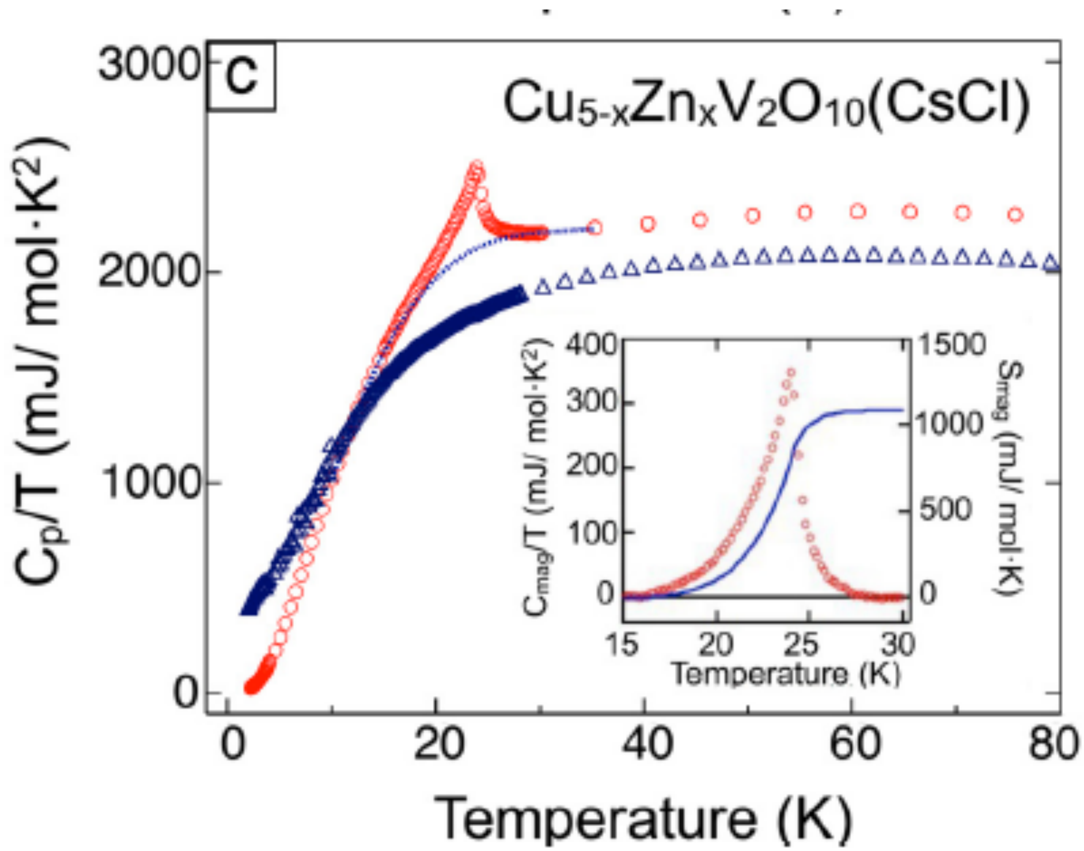
Botana *et al*, PRB (2018)

Jennifer Zheng (John Mitchell's group) has synthesized it as well
Susceptibility data indicate J ~ 200K, as predicted from LDA+U
Substitution by Zn leads to behavior similar to herbertsmithite



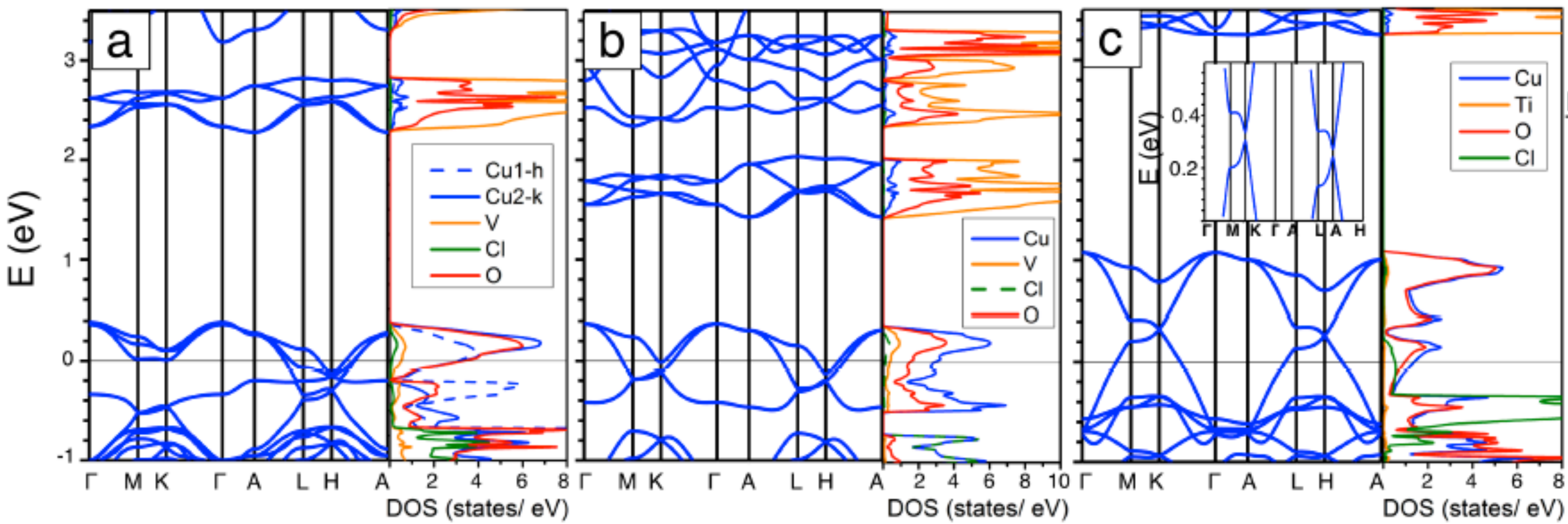
Botana *et al*, PRB (2018)

Specific heat reveals a Neel transition at 24K ($\Theta_{CW}/T_N \sim 8$)
No transition is seen in a Cu_4Zn doped version



Botana *et al*, PRB (2018)

Substitution of Cu-honeycomb in the parent phase (left) by Zn isolates the kagome planes (middle); Substitution of V^{5+} by Ti^{4+} dopes it and leads to a large increase in the bandwidth (right)



Botana *et al*, PRB (2018)

Summary

- The synthesis of herbertsmithite led to a new era in the study of quantum spin liquids
- Low energy behavior controlled by disorder (orphan spins), as also seen in other spin liquid candidates
- Attempts to dope herbertsmithite leads to insulating behavior (polarons? – recent PRL of Zunger's group)
- Several variants of herbertsmithite have been recently discovered, with others yet to be explored
- Charge transfer behavior and stability could be enhanced by looking for oxides rather than hydroxychlorides
- Averievite is a copper oxide, and a potential spin liquid
- Mineralogy space is vast, so many surprises await us