Strongly correlated Dirac electrons in electron doped herbertsmithite

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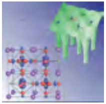
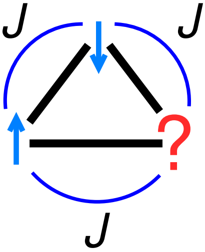
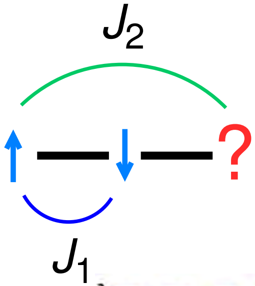
• DFG FOR 1346 “Dynamical Mean Field Approach with Predictive Power for Strongly Correlated Materials”



• DFG TR 49 “Condensed Matter Systems with Variable Many-Body Interactions”

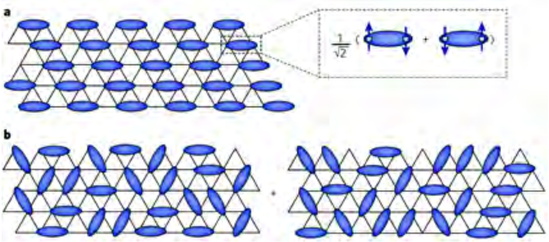
Frustrated magnetism





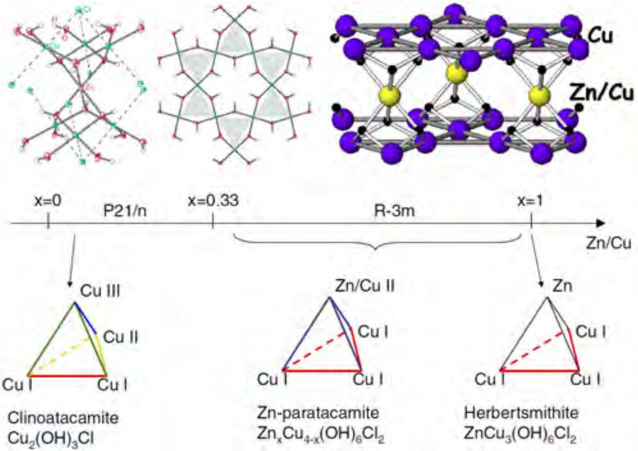
- geometrical frustration
- competition between exchange couplings

- large degeneracy of ground states
- quantum fluctuations
- spin liquid (cooperative paramagnet) as exotic state of matter



Balents, Nature **464**, 199 (2010).

An end to the drought of quantum spin liquids (P. A. Lee)

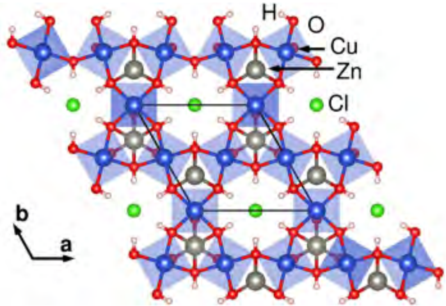


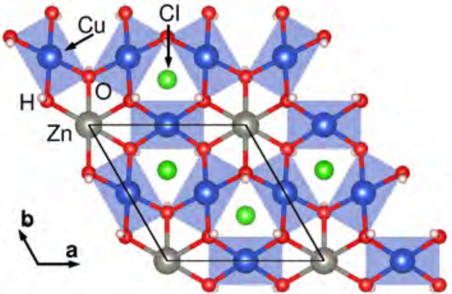
Mendels, Bert, JPSJ **79**, 011001 (2010)

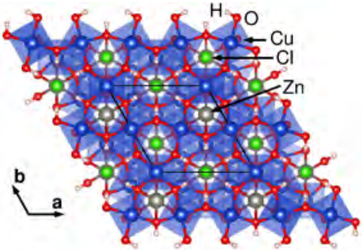
- Herbertsmithite $ZnCu_3(OH)_6Cl_2$ reported to be very good realization of a quantum spin liquid (Shores *et al.*, JACS **127**, 13462 (2005)).
- part of a family with tunable properties

Topic 1: Barlowite $Cu_4(OH)_6FBr$ **Topic 2: Ga-Herbertsmithite**

Herbertsmithite and kapellasite: different kagome systems





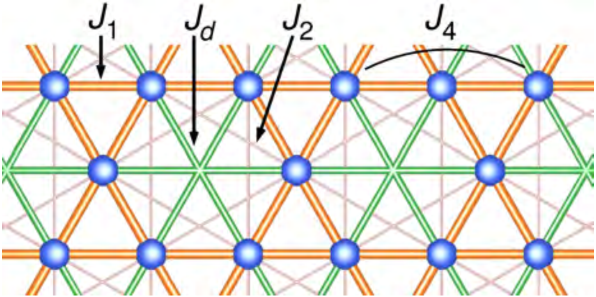


- same stoichiometry $ZnCu_3(OH)_6Cl_2$
- different Zn positions, different stacking

➜ very different properties!

H. O. Jeschke, F. Salvat-Pujol, R. Valentí, Phys. Rev. B **88**, 075106 (2013).

Kapellasite as test case: competing interactions

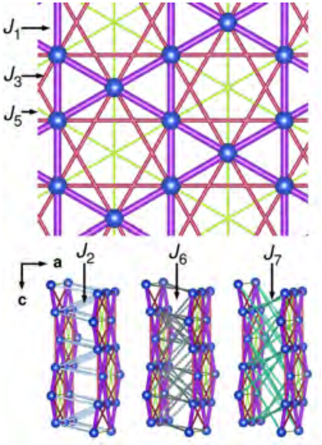


name	d_{Cu-Cu}	type	J_i (K) $U=6$ eV
J_1	3.15	kagome nn	−14.2
J_2	5.45596	kagome 2nd nn	−0.7
J_4	6.3	kagome 3rd nn	−0.3
J_d	6.3	kagome 3rd nn	24.0

- Janson *et al.*, PRL **101**, 106403 (2008) values $J_1 = 29$ K and $J_d = 10$ K **in contrast** to experiment Fåk *et al.*, PRL **109**, 037208 (2012).
- Latest exp./series expansion yields $J_1 = -12$ K, $J_2 = -4$ K, $J_d = 15.6$ K (Bernu *et al.*, Phys. Rev. B **87**, 155107 (2013)).

Herbertsmithite: beyond simple kagome antiferromagnet

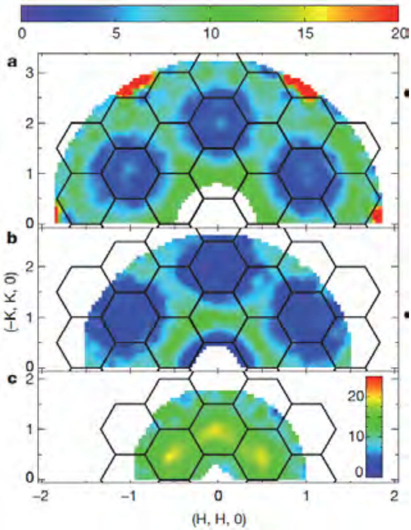
name	d_{Cu-Cu}	type	J_i (K) $U=6$ eV
kagome layer couplings			
J_1	3.4171	kagome nn	182.4
J_3	5.91859	kagome 2nd nn	3.4
J_5	6.8342	kagome 3rd nn	−0.4
interlayer couplings			
J_2	5.07638	interlayer 1st nn	5.3
J_4	6.11933	interlayer 2nd nn	−1.5
J_6	7.00876	interlayer 3rd nn	−6.4
J_7	8.51328	interlayer 4th nn	3.0
J_9	9.17347	interlayer 6th nn	2.5



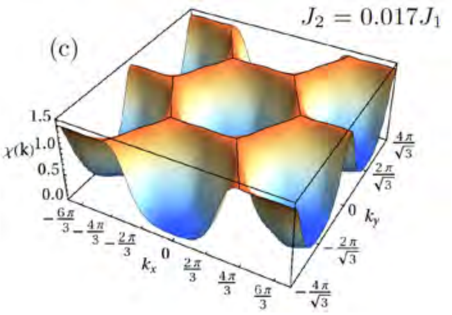
- J_1 agrees very well with literature values ($\sim$ 190 K)
- new aspects: (i) inplane $J_3/J_1 = 0.019$, and (ii) interplane couplings

Jeschke, Salvat-Pujol, Valentí, Phys. Rev. B **88**, 075106 (2013).

Herbertsmithite: J_3/J_1 ratio



Han *et al.*, Nature **492**, 406 (2012).



Suttner *et al.*, PRB **89**, 020408(R) (2014).

- **our result**: $\mathbf{J_3/J_1 = 0.019}$
- Functional renormalization group (Suttner *et al.*, PRB **89**, 020408(R) (2014)) needs $\mathbf{J_3/J_1 = 0.017}$ to explain inelastic neutron scattering experiment Han *et al.*, Nature **492**, 406 (2012).

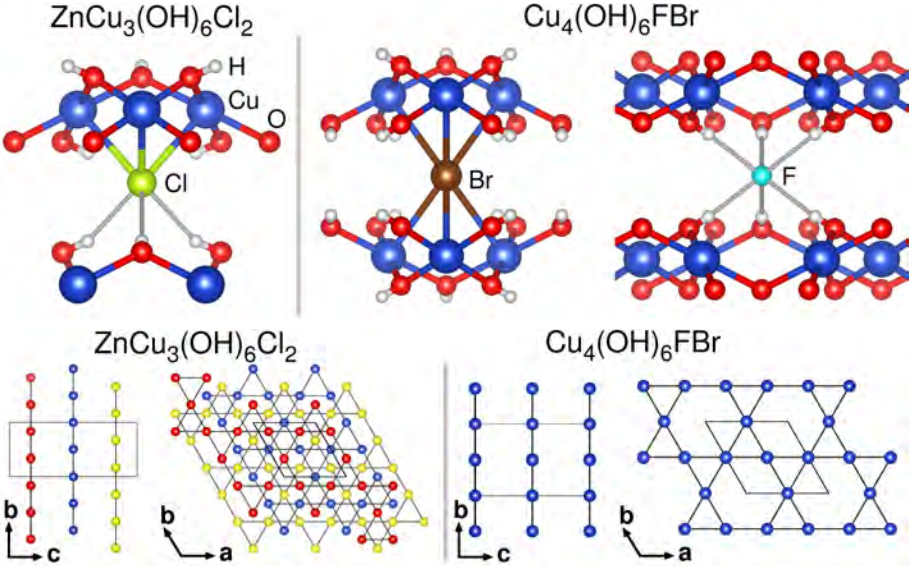
Herbertsmithite summary

- Heisenberg Hamiltonians for herbertsmithite and other kagome systems
- DFT yields insight into subleading couplings
- Role of corrections to perfect kagome Hamiltonian needs to be worked out using manybody techniques
- Role of Zn/Cu disorder? (a) diluted kagome, and (b) interplane Cu?
- Potential for materials design:

1. Can we have a disorder free kagome system?
2. Can we electron dope the kagome layer?

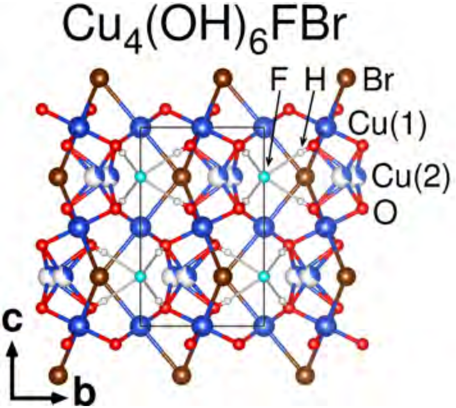
Improving on herbertsmithite: A road towards new spin liquids?

Barlowite: fixing the halogen environment



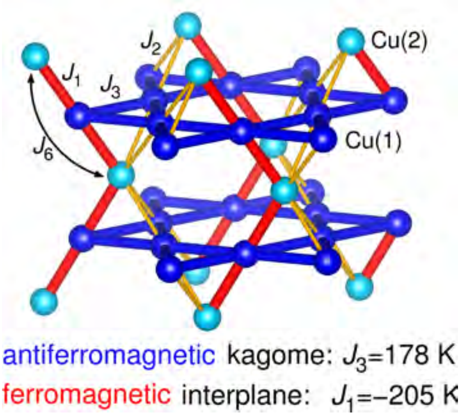
Jeschke, Salvat-Pujol, Jeschke, Gati, Hoang, Wolf, Lang, Schlueter, Valentí, arXiv:1412.4668

Barlowite: Structure and exchange couplings



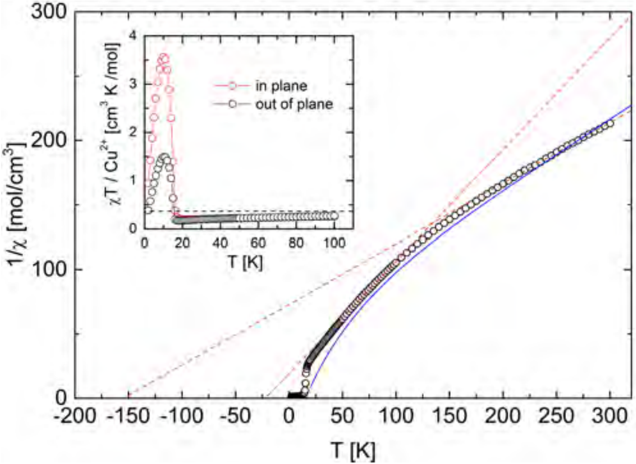
Cavity at Cu(2) site: room for large nonmagnetic metal ion

All electron full potential local orbital (FPLO) calculation of spin configurations



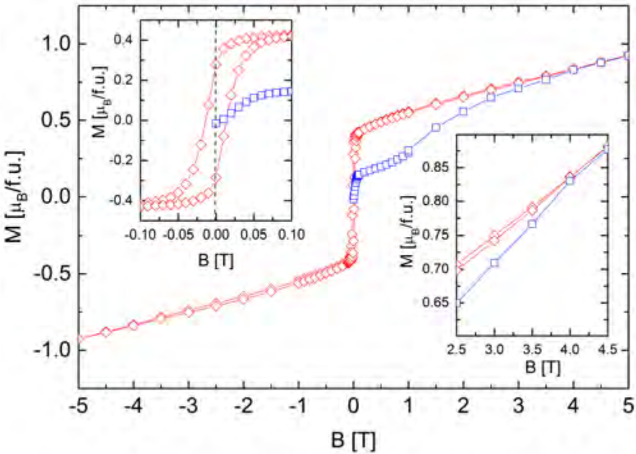
Jeschke, Salvat-Pujol, Jeschke, Gati, Hoang, Wolf, Lang, Schlueter, Valentí, arXiv:1412.4668

Barlowite: Magnetic properties



Circles: Single crystal inverse molar susceptibility (at $B = 0.1$ T, $B \parallel c$).
Blue: high temperature series expansion (10th order code written by Lohmann *et al.*, PRB **89**, 014415 (2014)).

Barlowite: Evidence for canted antiferromagnetism



Magnetization as function of magnetic field at $T = 2$ K. Remanent magnetization of 0.3 μ_B/f.u. indicates **canted antiferromagnet** with 4.5° canting angle. DM coupling estimate: $|\mathbf{D}|/J_3 \approx \Delta g/g = 0.1$.

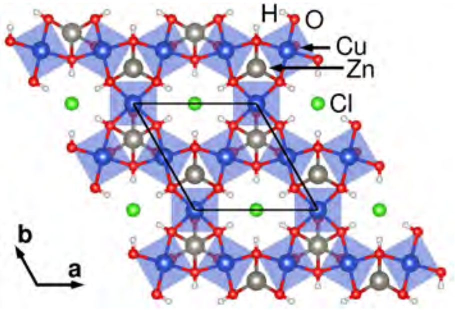
Barlowite conclusions

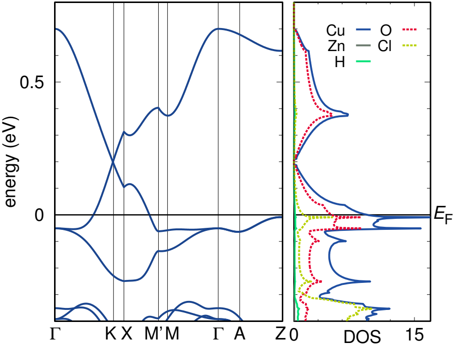
- Crystallization of barlowite $Cu_4(OH)_6FBr$ leads to a perfect kagome lattice system
- Replacement of Cu(2) in large cavity as design path for new spin liquid compounds
- Material promises to have less disorder problems than herbertsmithite

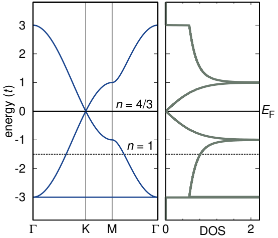
Jeschke, Salvat-Pujol, Jeschke, Gati, Hoang, Wolf, Lang, Schlueter, Valentí, arXiv:1412.4668

Doping the spin liquid: Theoretical prediction of a strongly correlated Dirac metal

How about electron doping Herbertsmithite?



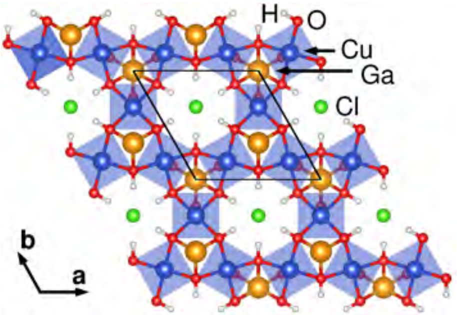


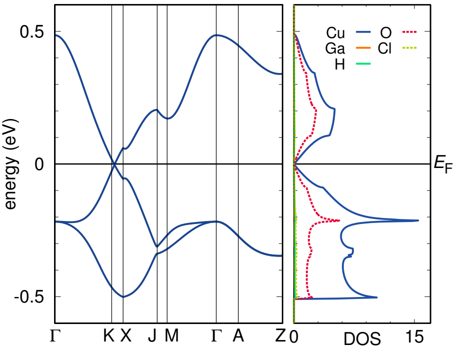


- $ZnCu_3(OH)_6Cl_2$ at half filling of Cu $3d_{x^2-y^2}$ bands
- Doping to 4/3 filling to reach Dirac point?
- $Zn^{2+} \rightarrow$ some M^{3+} ion?

Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).

Ga-Herbertsmithite: a Dirac metal?

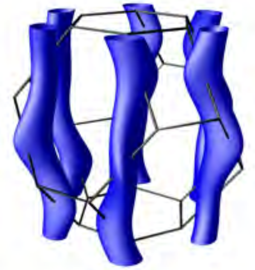


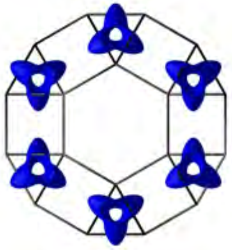


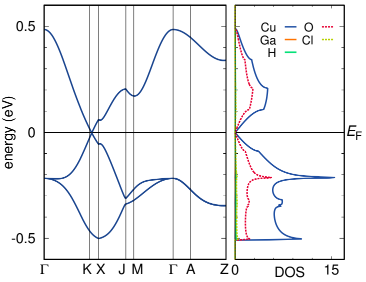
- $GaCu_3(OH)_6Cl_2$ predicted using projector augmented wave basis (VASP) relaxation; tested for dynamical stability
- Filling is 4/3!
- DFT electronic structure shows Dirac points exacly at the Fermi level

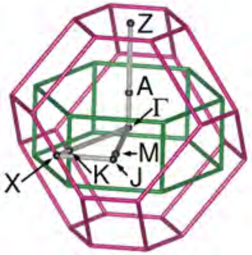
Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).

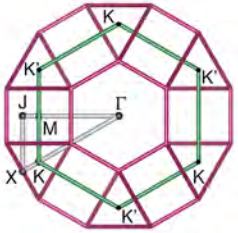
Ga-Herbertsmithite Fermi surface







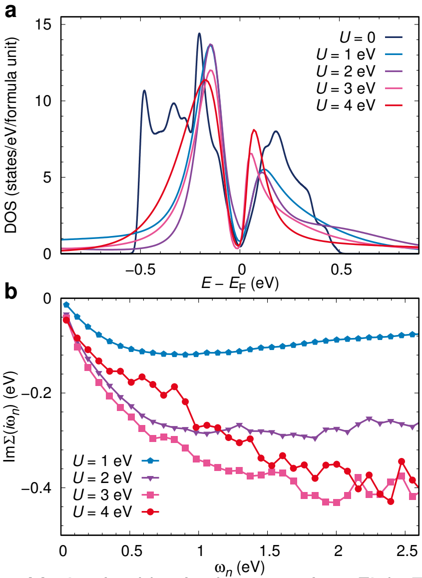




- Fermi surface at $E = -60$ meV
- Dirac points at E_F twist around K point
- rhombohedral $R\bar{3}m$ space group

→ **Need to check stability of metallic state!**

Mott-Hubbard instability? Dynamical cluster approximation



Dynamical mean field theory test for instability against large onsite interaction U

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm int}$$

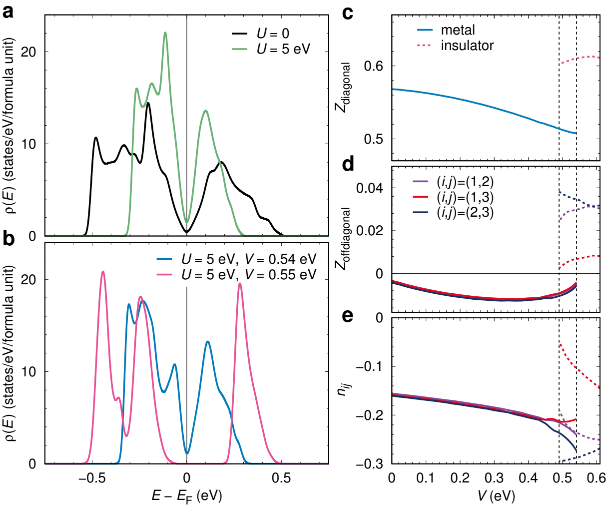
$$\mathcal{H}_0 = \sum_{i,j}\sum_{\sigma} t_{ij} c^\dagger_{i,\sigma} c_{j,\sigma} + \mu \sum_{i,\sigma} c^\dagger_{i,\sigma} c_{i,\sigma}$$

$$\mathcal{H}_{\rm int} = U \sum_i n_{i,\uparrow} n_{i,\downarrow} + \frac{V}{2} \sum_{<i,j>} \sum_{\sigma,\sigma'} n_{i,\sigma} n_{j,\sigma'}$$

- DCA solved with interaction expansion continuous time QMC impurity solver
- cluster size $N_c = 3$, $T = 150$ K
- system remains metallic for all U values

Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).

Mott-Hubbard instability? Rotationally invariant slave boson approximation



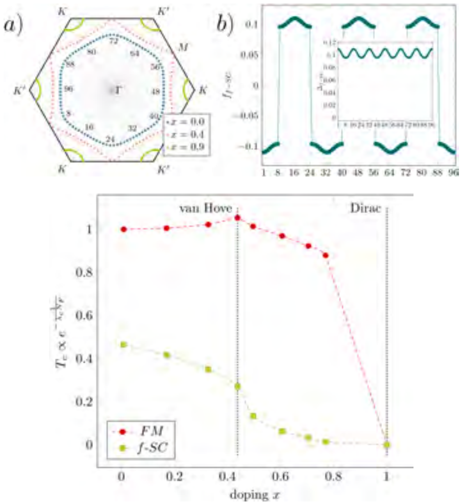
- LMTO estimate of $U = 5 - 7$ eV; Thomas-Fermi theory estimate of $V = 0.11$ eV for $GaCu_3(OH)_6Cl_2$.
- Strongly correlated Dirac metal stable up to $V \approx 0.48$ eV
- Instability to charge order at large V

Robust metallic state!

Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).

Possible ferromagnetic and superconducting instabilities

- $GaCu_3(OH)_6Cl_2$ is far from the regime of Nagaoka ferromagnetism
- DFT sees tendency to ferromagnetism
- DCA(RISB) stabilizes FM state for $n > 4/3$
- weak coupling functional renormalization group (fRG) for effective $2D$ Hamiltonian sees FM instability at all n
- fRG predicts a nodeless f-wave superconducting ground state



Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).

Electron doped herbertsmithite conclusions

- Electron doped herbertsmithite ($Zn_{1-x}Ga_xCu_3(OH)_6Cl_2$) would interpolate between frustrated magnetism at $x = 0$ and a strongly correlated Dirac metal at $x = 1$
- Solid solution at finite x and near $x = 1$ promises phases with unconventional physics like f-wave superconductivity
- Challenge to solid state chemists and crystal growers
- There is hope for more unusual compounds in the paratacamite family of materials

Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nature Commun. **5**, 4261 (2014).