Topologically non-trivial electronic and magnetic states in doped copper Kagome lattices

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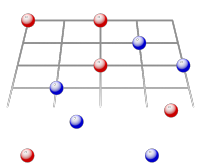

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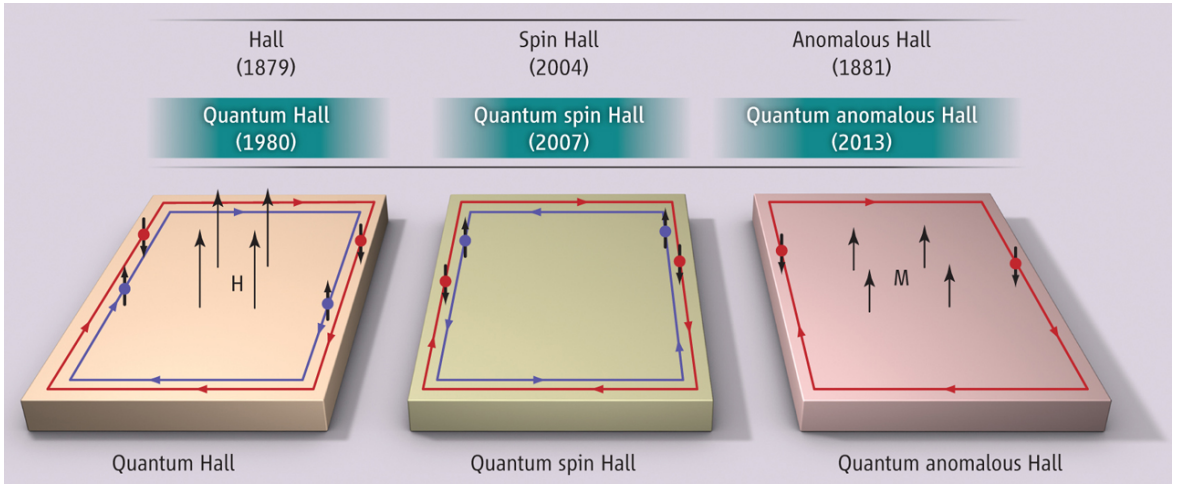
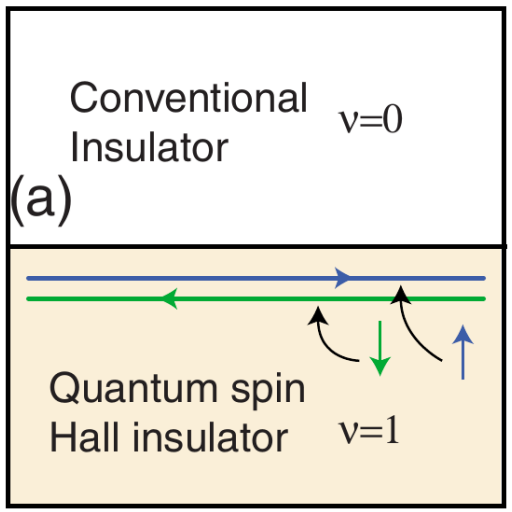
Outline

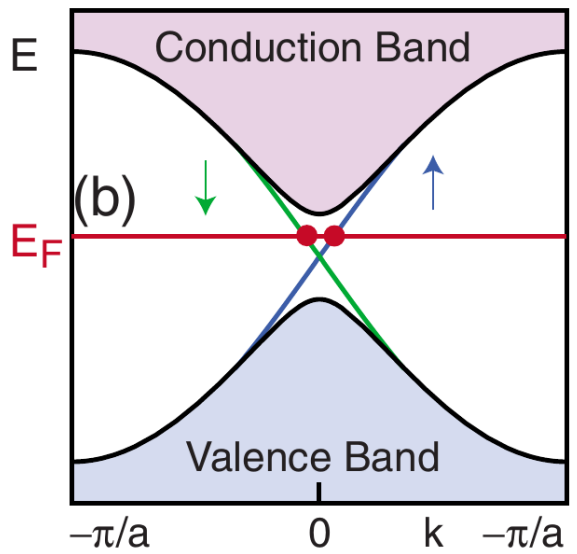
1. Introduction to Quantum Spin Hall and Quantum Anomalous Hall effect
2. Introduction to Spin-Liquids
3. Current status of copper Kagome materials
4. Suggestions for chemical modifications
5. Stability analysis for proposed crystal structures
6. Parametrization of Heisenberg Hamiltonians
7. Spin-Liquid in Barlowite
8. Quantum Spin Hall effect and Quantum Anomalous Hall effect in Herbertsmithite

Topological insulators: introduction

- topological insulator fundamentally different from trivial insulator
- insulating bulk
- gapless surface states protected by time-reversal symmetry
- robust against disorder, weak interactions, etc.
- dissipation-free transport through surface states







Hasan, Kane, RMP **82**, 3045 (2010); Oh, Science **340**, 153 (2013)

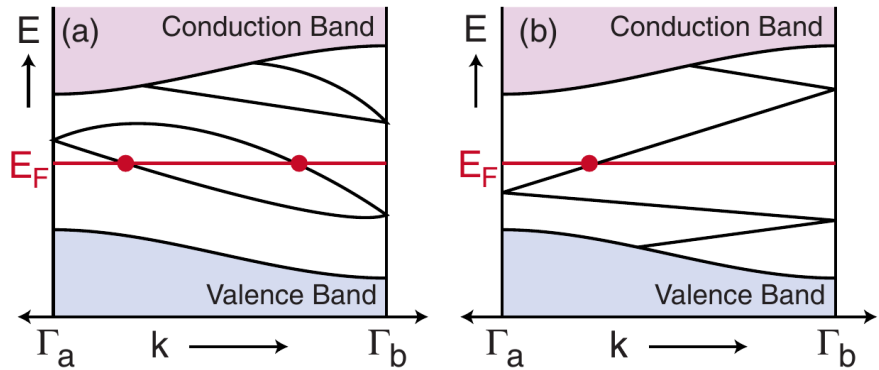
Topological insulators: computational aspects

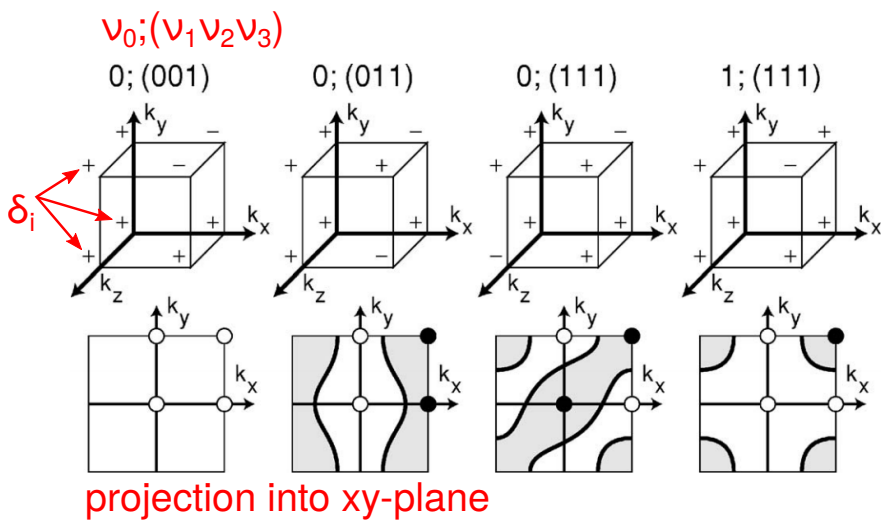
- time-reversal invariance
  $E(\vec{k}) = E(-\vec{k})$
- Kramer's theorem: time-reversal symmetry $\rightarrow$ twofold degeneracy
- connectivity between time-reversal invariant points Γ_i matters
- take product of parity eigenvalues for occupied bands

$$\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i)$$

- $(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i; \rightarrow \nu_0; (\nu_1, \nu_2, \nu_3)$

$$(-1)^{\nu_k} = \prod_{n_k=1; n_{j\neq k}=0,1} \delta_{i=(n_1 n_2 n_3)}$$

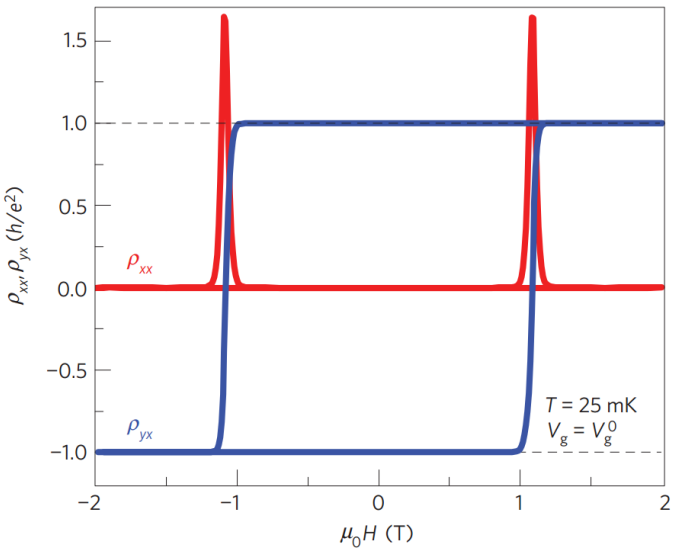


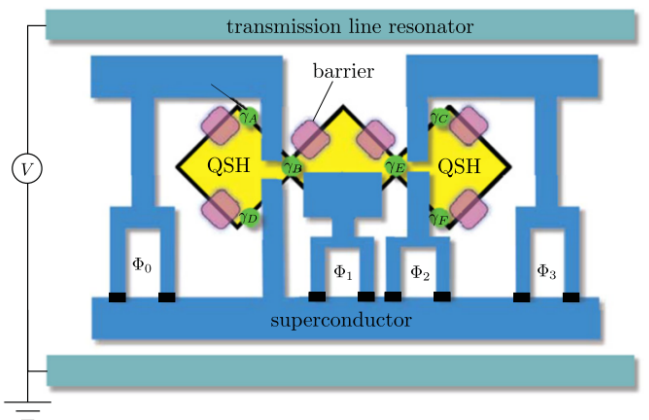


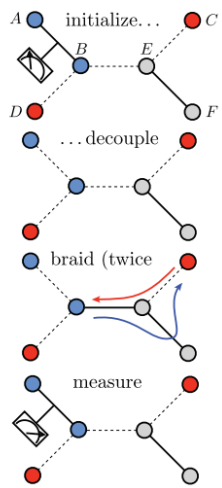
Fu, Kane, PRB **76**, 045302 (2007); Hasan, Kane, RMP **82**, 3045 (2010)

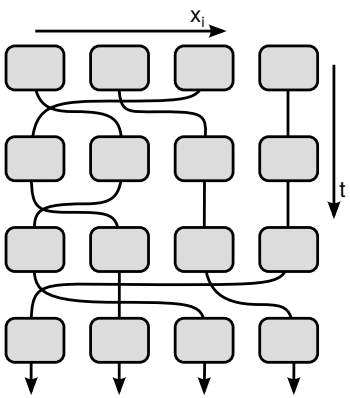
Topological insulators: application

- in QAH insulator all currents are spin-polarized → spintronics
- $\rho_{xx} = 0$ at zero field for QAHE
- Majorana zero modes (non-abelian anyons) at TI-SC interface
- braiding records history of the system
- fault-tolerant quantum computer





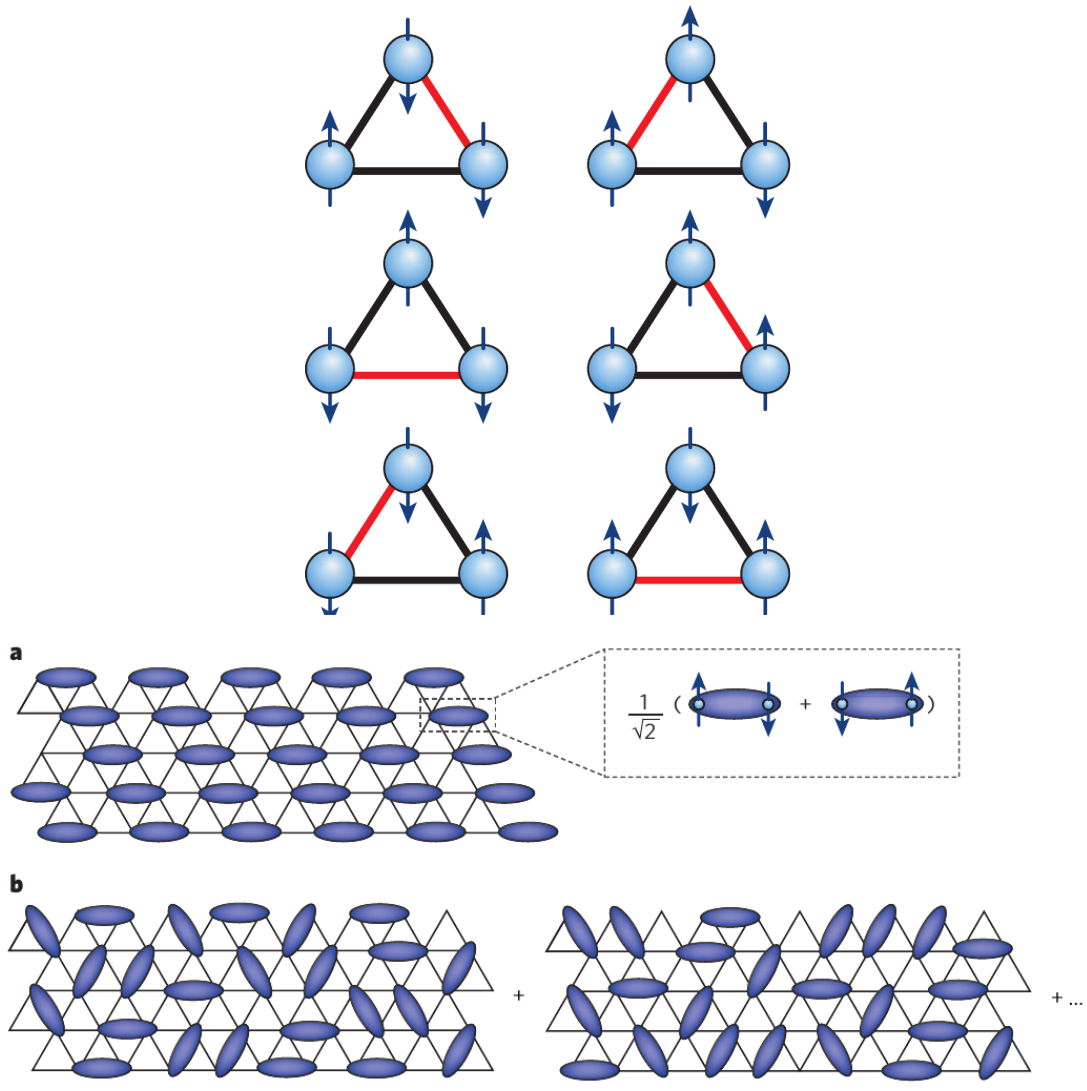




Wilczek, Nat. Phys. **5**, 614 (2009); Chang et al., Nat. Mater. **14**, 473 (2015)
Das Sarma et al., Quantum Information **1**, 15001 (2015); van Heck et al., Phys. Scr. **T164**, 014007 (2015)

Quantum spin-liquids: introduction

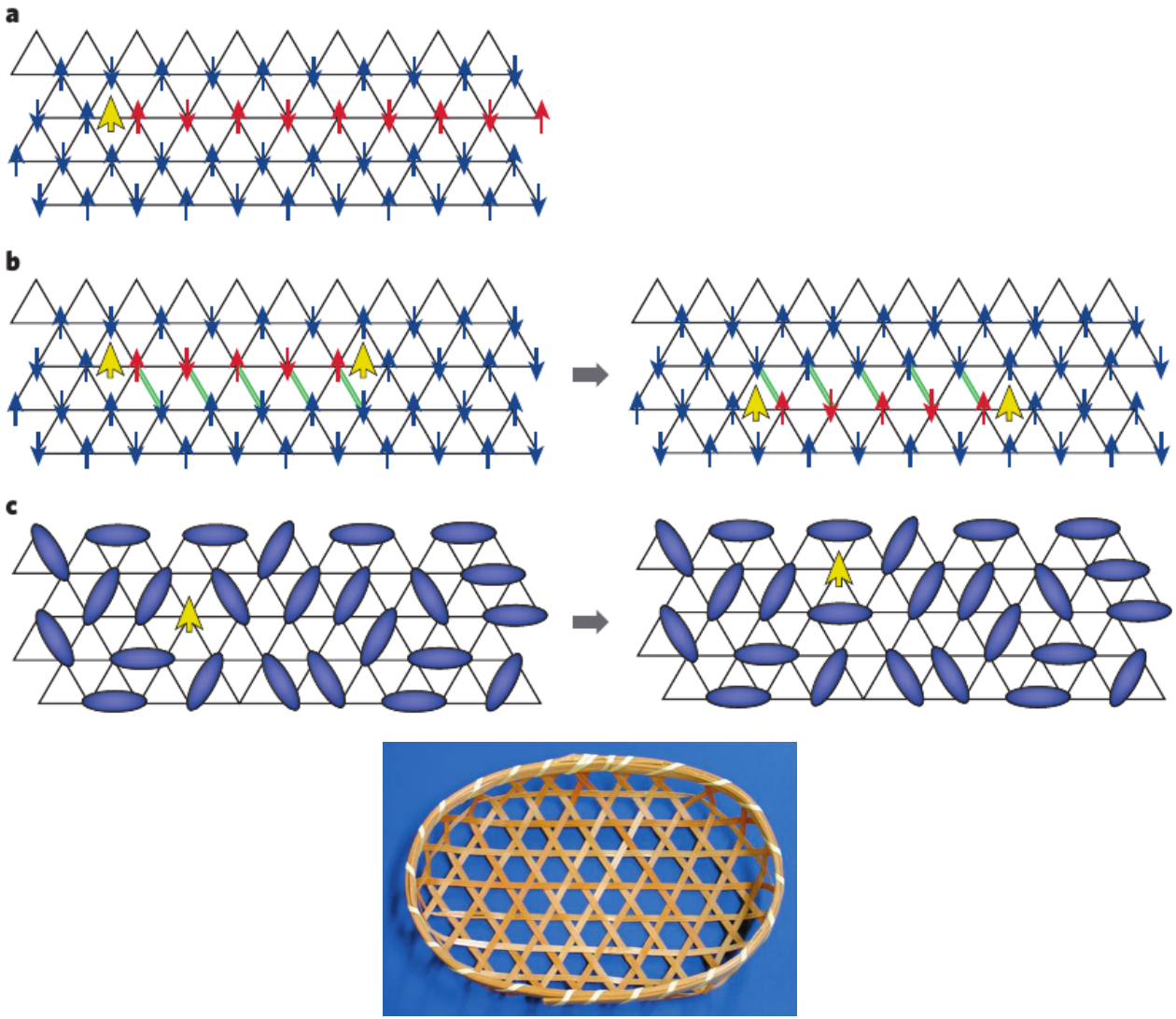
- frustration leads to degenerate ground state
- highly correlated well-formed local moments, but no static order (liquid-like)
- no spontaneous symmetry-breaking
- described by lattice covered with valence bonds
- static valence bonds give valence bond solid (VBS)
- superposition gives resonating valence bond (RVB) state → QSL



Lee, Science **321**, 1306 (2008); Balents, Nature **464**, 199 (2010)

Quantum spin-liquids: excitations

- usual excitations are electron-like ($S = 1/2,\ q = \pm e$) or magnon-like ($S = 1,\ q = 0$)
- fractionalized excitations in QSL: spinons ($S = 1/2,\ q = 0$)
- spinons can be gapped or gapless
- probe spinons with thermodynamics, neutrons, etc.



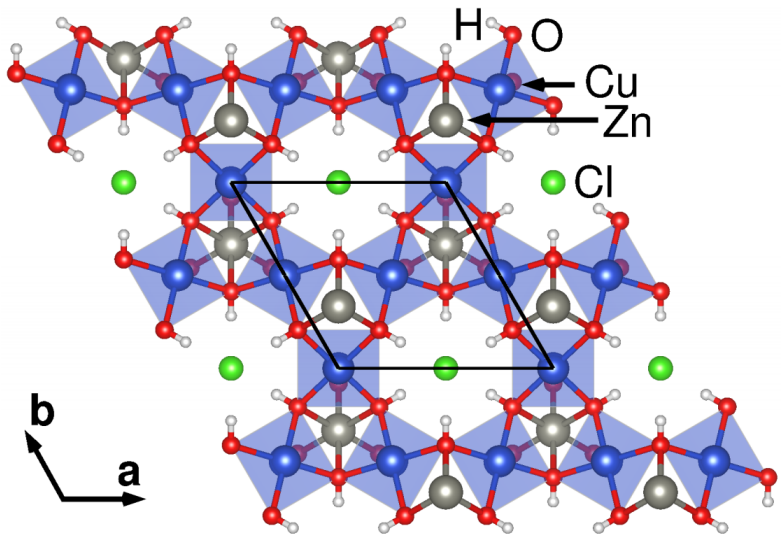
Lee, Science **321**, 1306 (2008); Balents, Nature **464**, 199 (2010)

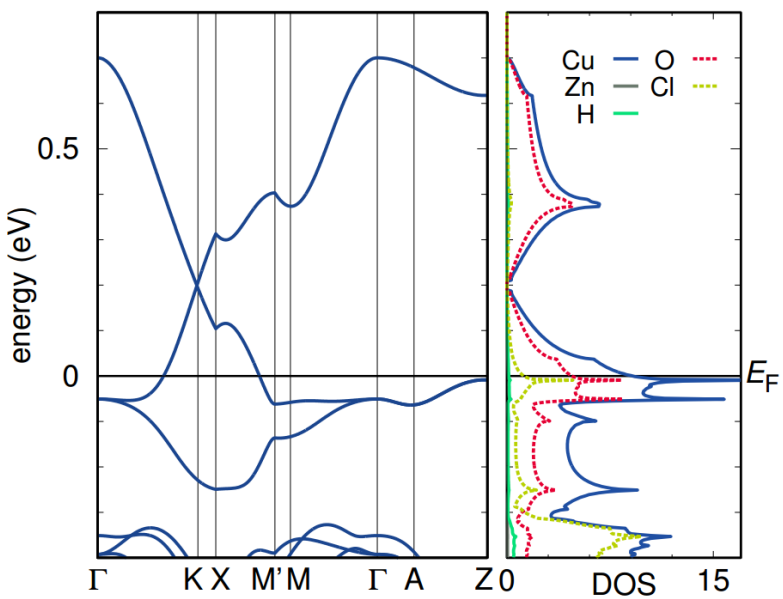
Herbertsmithite $[ZnCu_3(OH)_6Cl_2]$: spin-liquid candidate on the kagome lattice

- kagome lattice of Cu $3d^9$ (Cu^{2+}) ions
- Mott insulator
- antiferromagnetic NN exchange $J_1 = 182.4$ K
- various other couplings $J_i < 7$ K
- no magnetic order down to 50 mK

  [Helton et al., PRL **98**, 107204 (2007)]
- neutron experiments see continuum of (fractionalized) excitations

  [Han et. al, Nature **492**, 406 (2012)]
- Cu-Zn antisite-disorder of a few percent, some studies claim only Zn site disorder

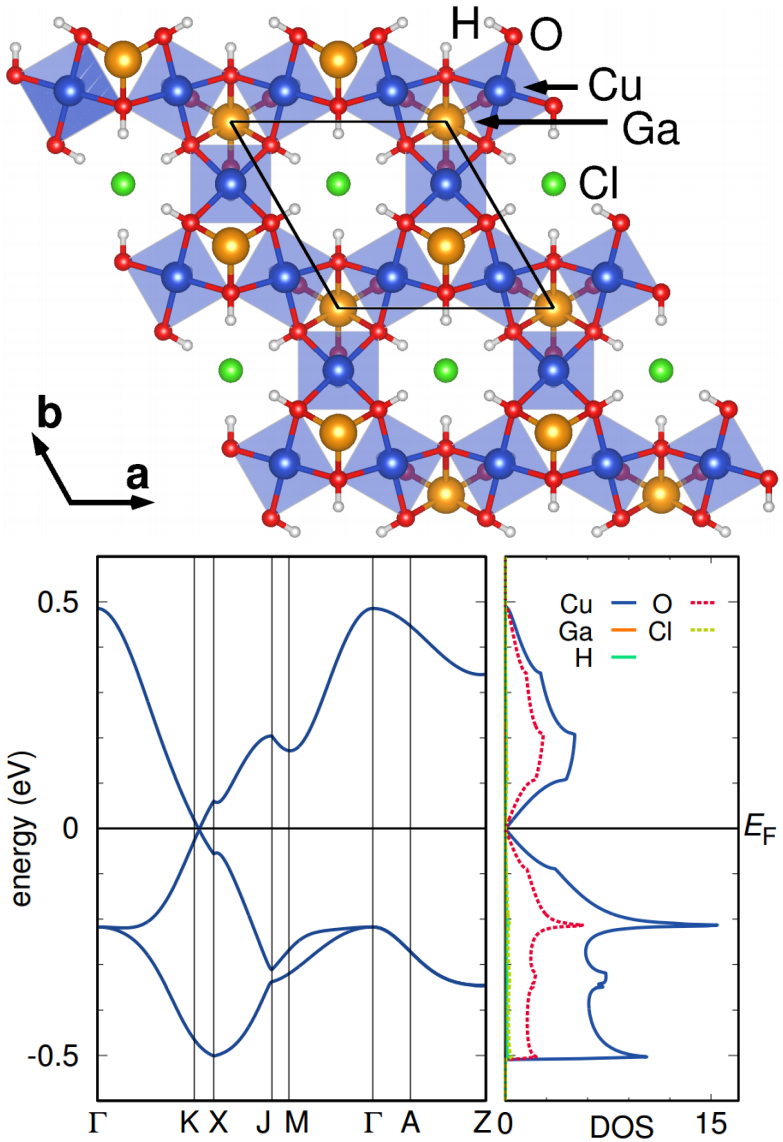




Jeschke, Salvat-Pujol, Valentí, PRB **88**, 075106 (2013)

Ga-Herbertsmithite $[GaCu_3(OH)_6Cl_2]$: predicted exotic ferromagnet or superconductor

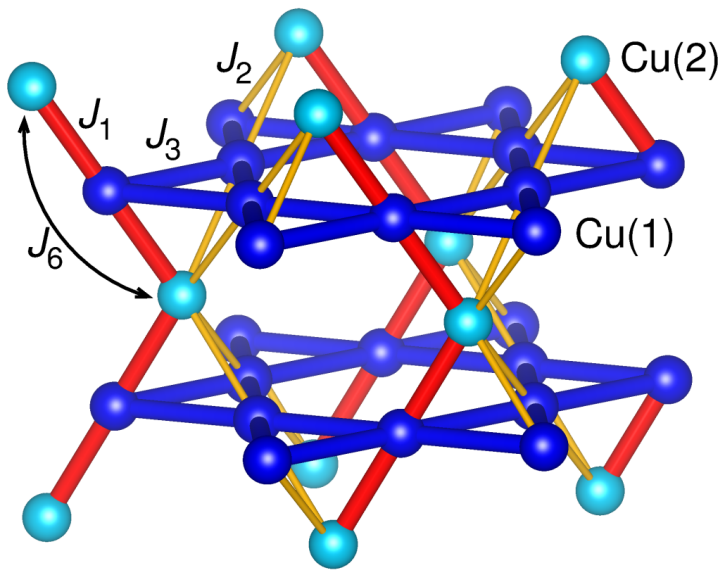
- substitute Zn^{2+} by Ga^{3+}
- electron doping moves Fermi level to Dirac point
- Dirac metal robust in presence of correlations (DCA)
- vary Zn:Ga ratio to obtain intermediate electron doping
- competition between FM and f-wave SC predicted

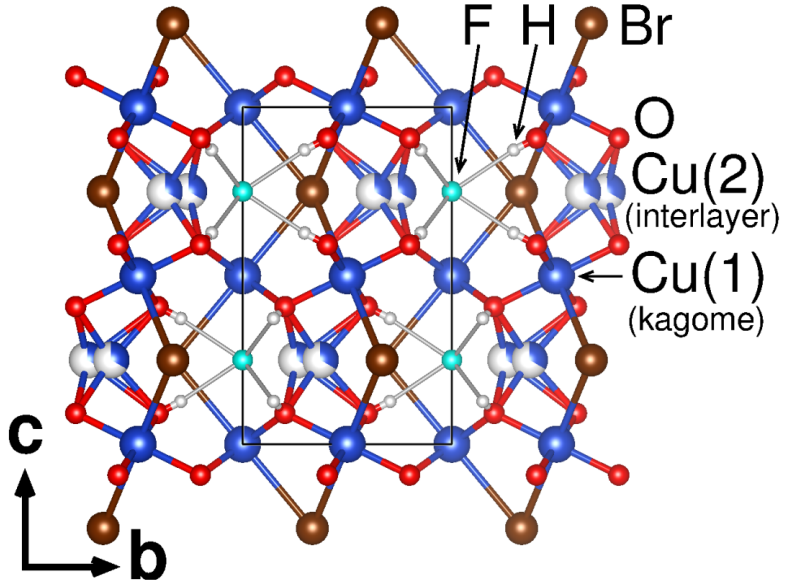


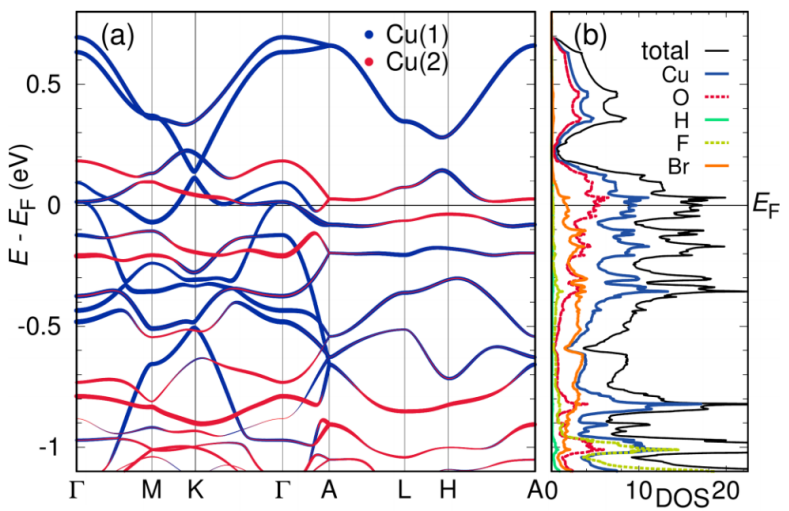
Mazin, Jeschke, Lechermann, Lee, Fink, Thomale, Valentí, Nat. Commun. **5**, 4261 (2014)

Barlowite [$Cu_4(OH)_6FBr$]: kagome lattice antiferromagnet

- kagome lattice of Cu^{2+} ions
- Cu^{2+} also between kagome layers
- antiferromagnetic Mott insulator
- AFM kagome exchange $J_3 = 178$ K
- FM interlayer exchange $J_1 = -205$ K
- remove interlayer coupling for QSL



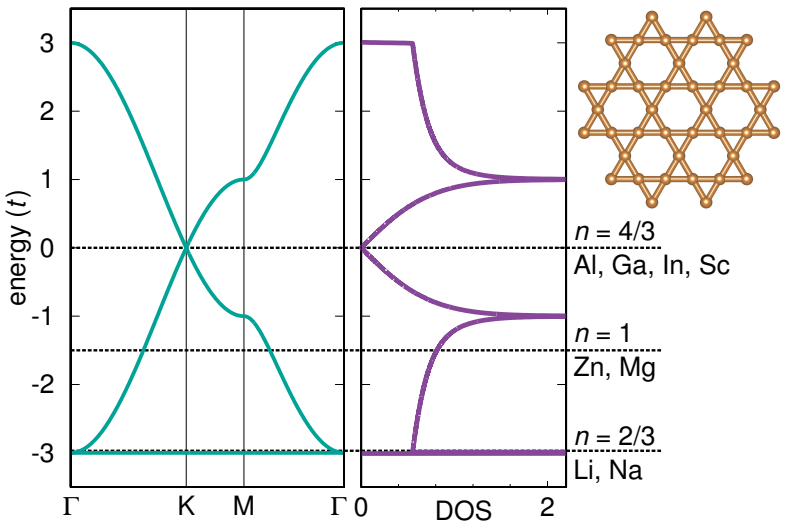


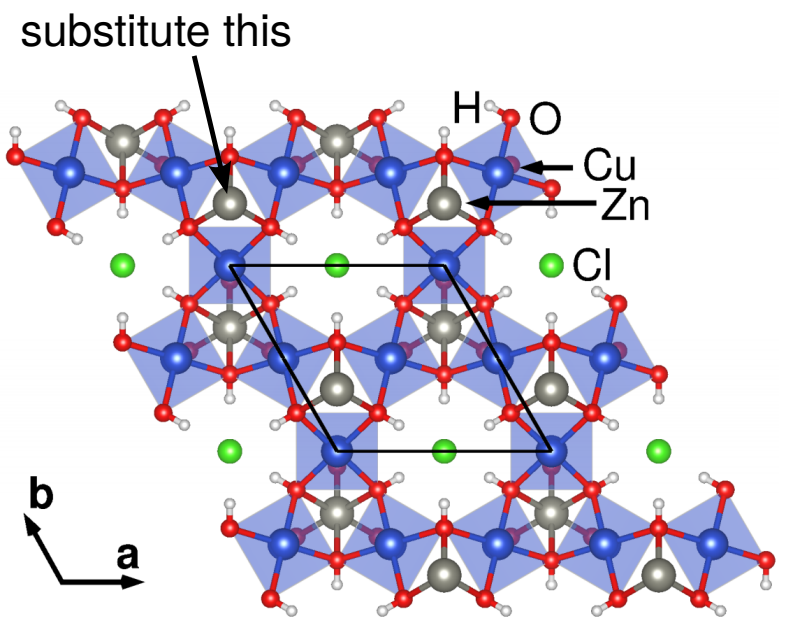


Jeschke, Salvat-Pujol, Gati, Hoang, Wolf, Lang, Schlueter, Valentí, PRB **92**, 094417 (2015)

Chemical modifications of Barlowite and Herbertsmithite

- we investigate $\mathcal{A}$-Herbertsmithite [$\mathcal{A}Cu_3(OH)_6Cl_2$] and $\mathcal{A}$-Barlowite [$\mathcal{A}Cu_3(OH)_6FBr$]
- we propose dopants for realizing QAHE, QSHE and QSL
- hole-doping (QAHE): Li^+, Na^+
- electron-doping (QSHE): Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}
- isoelectronic doping (QSL): Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}
- for all proposed compounds we analyse the stability of crystal structures
- Is kagome lattice distorted upon doping?





Guterding, Jeschke, Valentí, arXiv:1511.05686

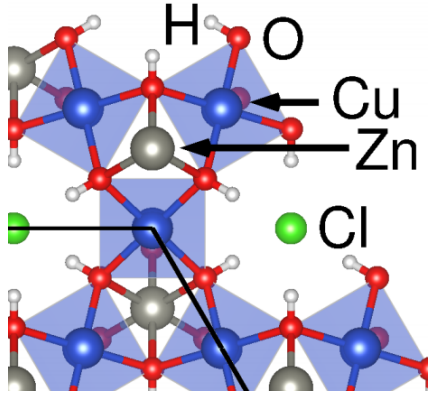
Preparation and analysis of crystal structures

structure preparation and relaxation

- replace interlayer site starting from Herbertsmithite/Barlowite
- density functional theory (DFT) calculations, GGA-PBE functional
- GPAW code, projector-augmented wave (PAW) basis, 1000 eV plane-wave cutoff
- unit cell shape and internal coordinates relaxed until forces < 10 meV/Å

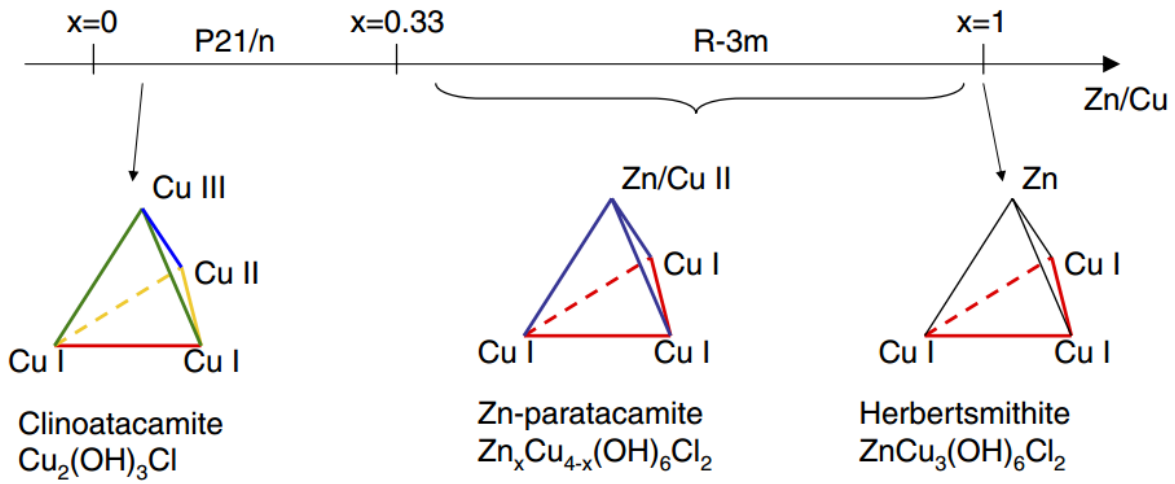
stability tests for $\mathcal{A}Cu_3(OH)_6Cl_2$ and $\mathcal{A}Cu_3(OH)_6FBr$

1. does the dopant go in at all?
2. does the dopant like the kagome environment better?
3. what about vacancies instead of $\mathcal{A}$?
4. what about Cu impurities instead of $\mathcal{A}$?



Formation energies

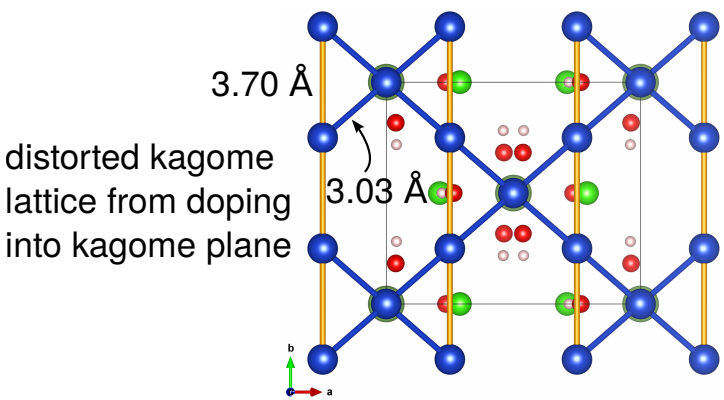
- total energies from full-potential local orbital (FPLO) code
- model growth process by solid state reaction
- compare energies of $ACu_3(OH)_6Cl_2 + Cu$ to $2\times Cu_2(OH)_3Cl + A$
- dopant metal energies from crystals, e.g. fcc-Cu
- formation energy is defined as $E_{form} = E_{AH} + E_{Cu} - (E_C + E_A)$
- negative formation energy $\rightarrow$ $ACu_3(OH)_6Cl_2$ is formed
- positive formation energy $\rightarrow$ $Cu_2(OH)_3Cl$ is formed

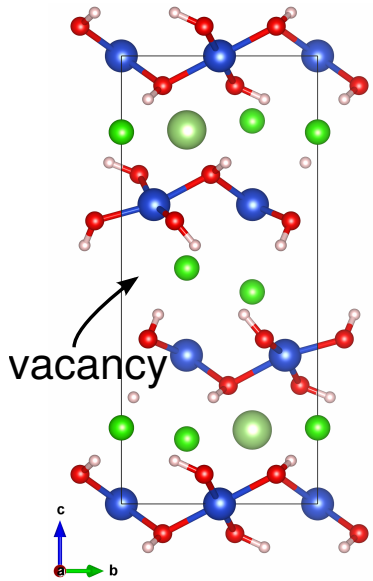


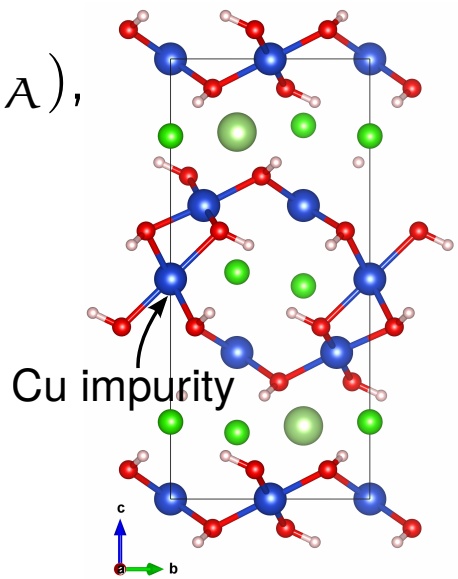
Mendels, Bert, JPSJ **79**, 011001 (2010)

Doping Energies

- evaluate energies of various defects, fully relaxed structures
- dopant A on kagome site and Cu on interlayer $Cu(ACu_2)(OH)_6Cl_2$
- compare energy directly to $ACu_3(OH)_6Cl_2$
- vacancy structure $A_{0.66}Cu_3(OH)_6Cl_2$
- impurity structure $A_{0.66}Cu_{3.33}(OH)_6Cl_2$
- doping energy: $E_{dop} = E_{AH} + y \cdot E_{Cu} - (E_{AHM} + x \cdot E_A)$, where E_{AHM} belongs to $A_{1-x}Cu_{3+y}(OH)_6Cl_2$

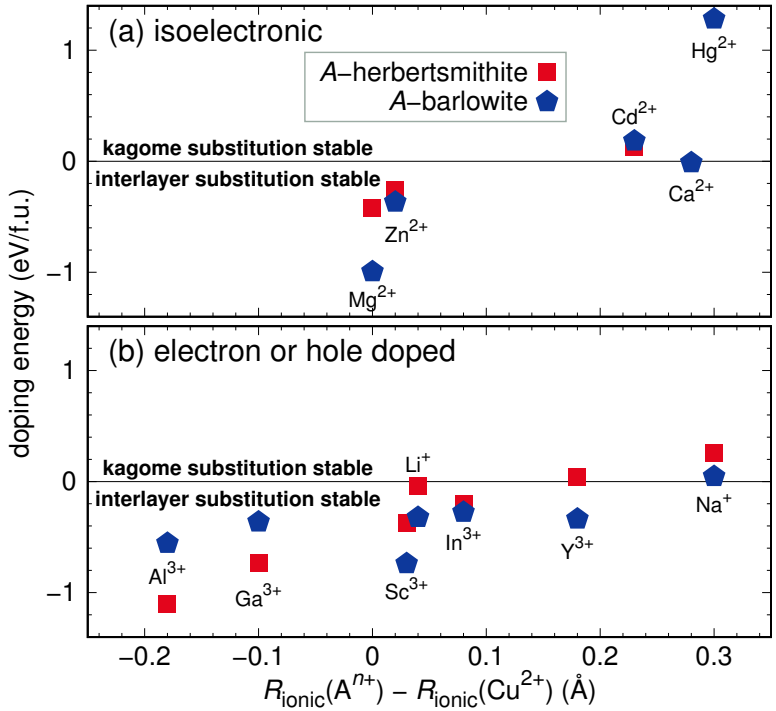






Summary of formation and doping energies

- variety of materials energetically possible
- vacancies and large fractions of Cu impurites irrelevant
- interlayer site favors small dopants
- hole-doped Li-Herbertsmithite stable
- various electron doped materials stable
- Mg-Barlowite strongly favors interlayer doping, probably reduced disorder



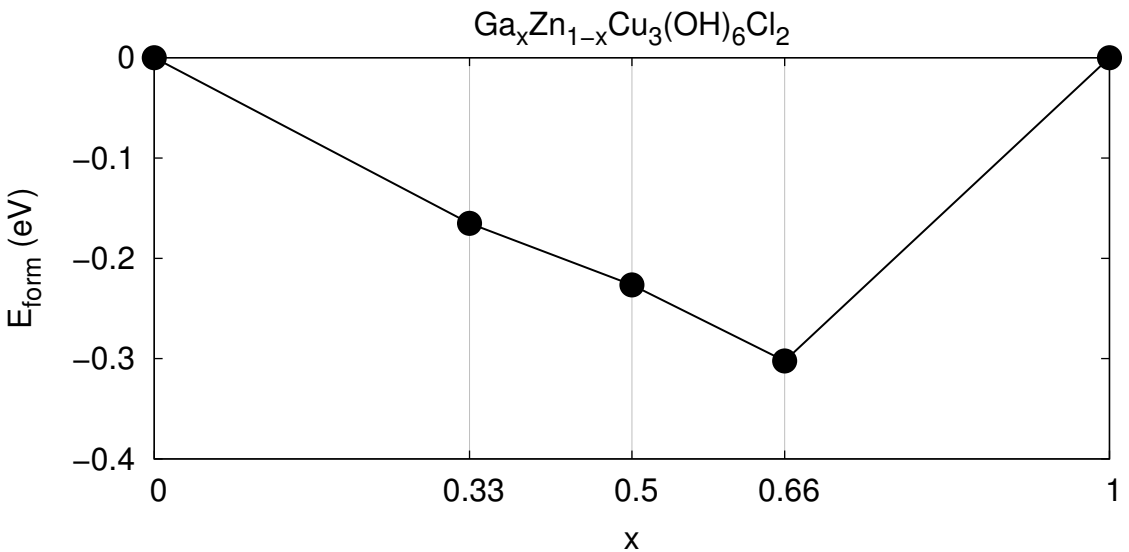
case	A-herbertsmithite, $A=$	Li^{1+}	Na^{1+}	Mg^{2+}	Ca^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Sc^{3+}	Y^{3+}	Al^{3+}	Ga^{3+}	In^{3+}
1	$ACu_3(OH)_6Cl_2$	-2.660	-2.517	-5.333	n/a	-2.082	-1.461	n/a	-7.300	-7.144	-6.257	-2.939	-3.080
2	$ACu_3(OH)_6Cl_2$	-0.041	+0.257	-0.421	n/a	-0.261	+0.128	n/a	-0.372	+0.043	-1.101	-0.736	-0.203
3	$A_{0.66}Cu_3(OH)_6Cl_2$	-0.847	-0.735	-1.689	n/a	-0.694	n/a	n/a	-2.481	-2.398	-2.141	-1.176	-1.062
4	$A_{0.66}Cu_{3.33}(OH)_6Cl_2$	-1.497	-1.350	-2.308	n/a	-1.321	n/a	n/a	-3.019	-2.878	-2.659	-1.711	-1.585
	A-barlowite, $A=$												
1	$ACu_3(OH)_6FBr$	-2.860	-2.247	-5.089	-5.808	-2.074	-1.420	+1.317	-7.498	-7.400	-5.605	-2.895	-2.919
2	$ACu_3(OH)_6FBr$	-0.322	+0.047	-0.994	-0.012	-0.367	+0.183	+1.282	-0.738	-0.336	-0.555	-0.363	-0.276
	ionic radius in pm	76	102	72	100	74	95	102	75	90	54	62	80

Guterding, Jeschke, Valentí, arXiv:1511.05686

Doping energies for small concentrations

- Herbertsmithite very stable against excess copper on interlayer site
- Herbertsmithite susceptible to excess dopants in kagome plane
- more work needed to understand impurity concentration, arrangement, etc.
- solid solution $Ga_xZn_{1-x}Cu_3(OH)_6Cl_2$ should exist

$A =$	Zn^{2+}	Mg^{2+}
$A_{0.83}Cu_{3.17}(OH)_6Cl_2$	-0.464	-0.831
$A_{1.17}Cu_{2.83}(OH)_6Cl_2$	+0.210	+0.803

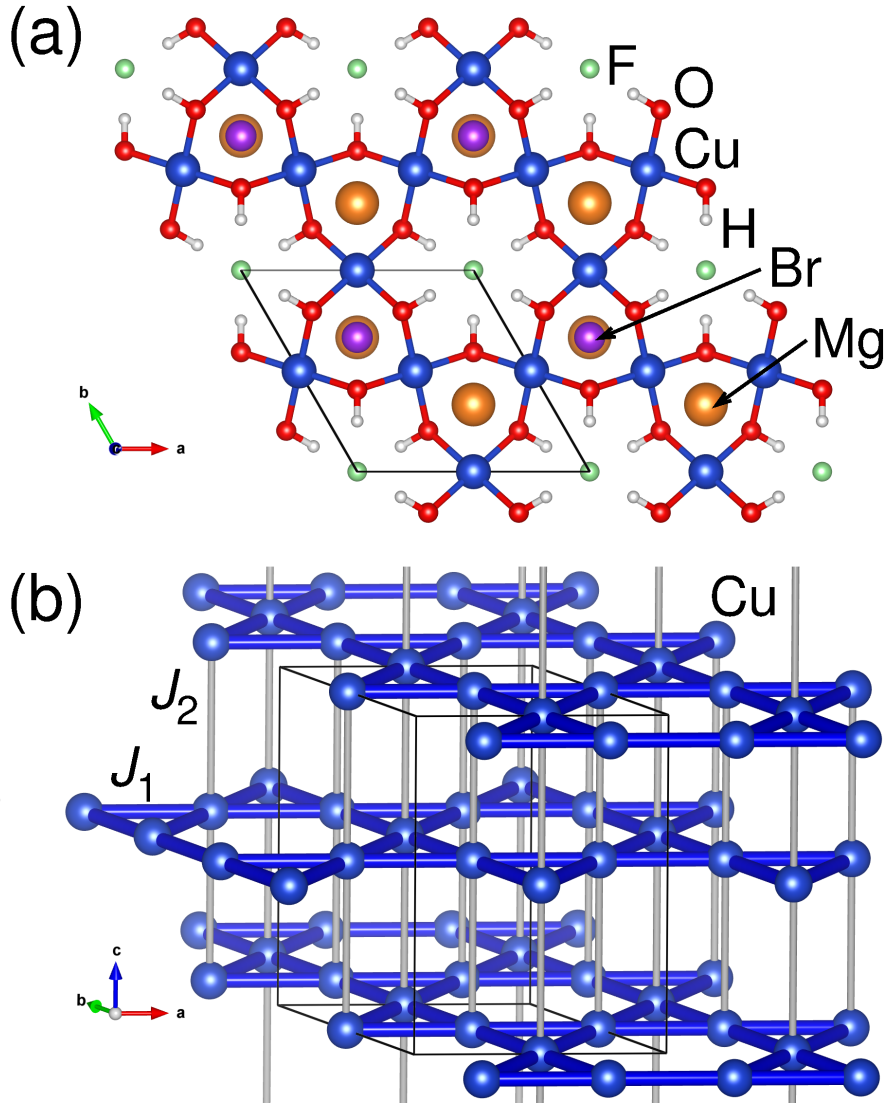


Guterding, Jeschke, Valentí, arXiv:1511.05686

Heisenberg model for Mg-Barlowite

- DFT+U calculation with $U = 6$ eV and $J_H = 1$ eV on Cu 3d
- map energies of DFT spin-configurations to Heisenberg model
- AFM kagome coupling $J_1 = 226$ K
- interlayer coupling $J_2 = 13.4$ K
- $J_2/J_1 = 0.06$
- spin-liquid predicted for $|J_2/J_1| < 0.15$

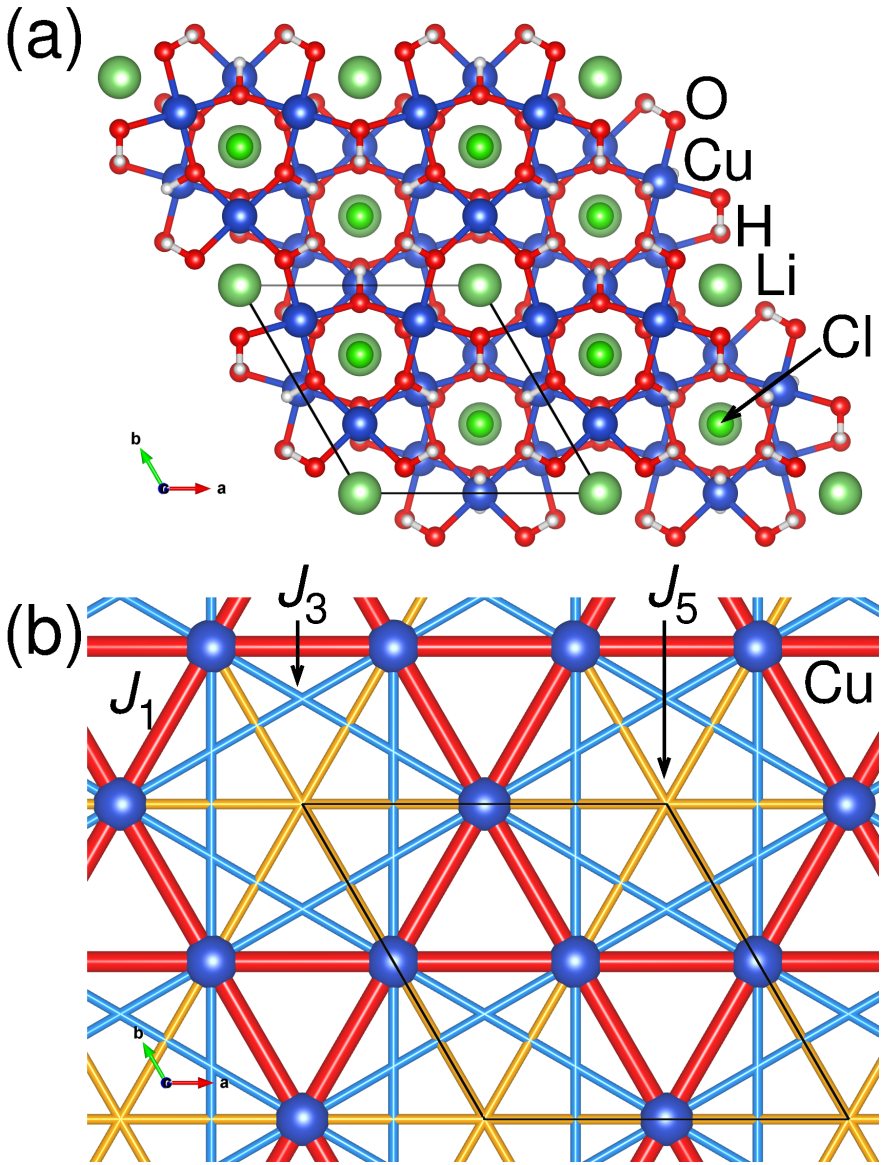
  [Götze, Richter, arXiv:1510:04898]
- Mg-Barlowite is likely a quantum spin-liquid with low anti-site disorder



Guterding, Jeschke, Valentí, arXiv:1511.05686

Heisenberg model for Li-Herbertsmithite

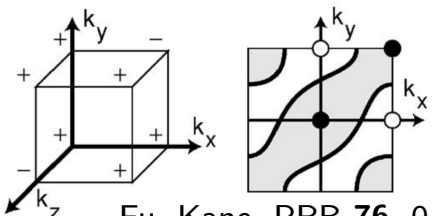
- DFT+U calculation with $U = 6$ eV and $J_H = 1$ eV on Cu 3d
- large FM kagome coupling $J_1 = -544$ K
- negligible interplane couplings
- mean-field Curie temperature $T_C = -\frac{2}{3} S(S+1) \sum_i z_i J_i$
- $J_i = \{-544, 39, -50\}$ K and $z_i = \{4, 4, 6\} \rightarrow T_C \approx 1160$ K
- Li-Herbertsmithite is a very robust ferromagnet



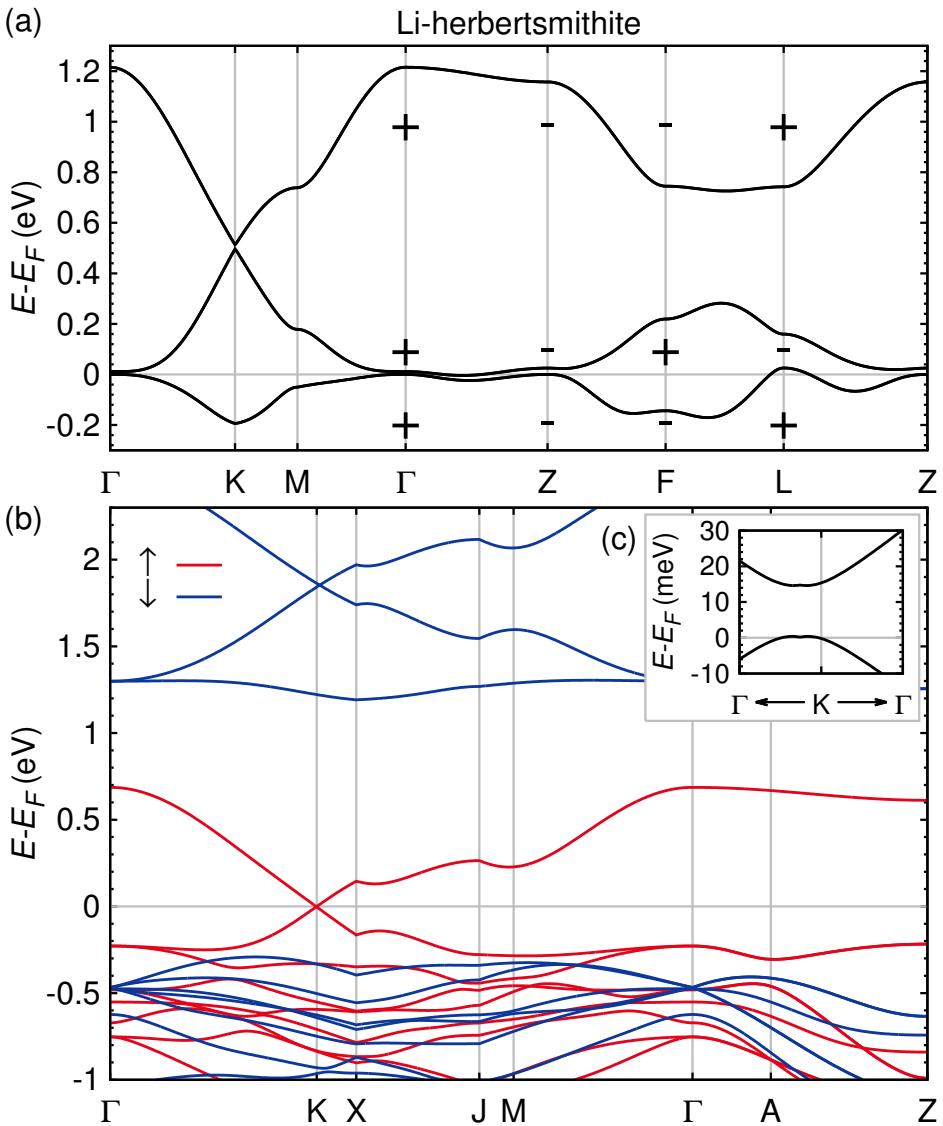
Guterding, Jeschke, Valentí, arXiv:1511.05686

Electronic properties of Li-Herbertsmithite

- Ga-Herbertsmithite is 4/3 filled, $\{\uparrow 2/3, \downarrow 2/3\}$
- Li-Herbertsmithite is 2/3 filled FM, $\{\uparrow 2/3, \downarrow 0\}$
- FM Dirac metal is suspicious of QAHE
- SOC opens gap at Dirac point
- check topological indices, parity eigenvalues from DFT
- $\nu_0; (\nu_1, \nu_2, \nu_3) = 0; (111)$
- QAHE on (001) surface



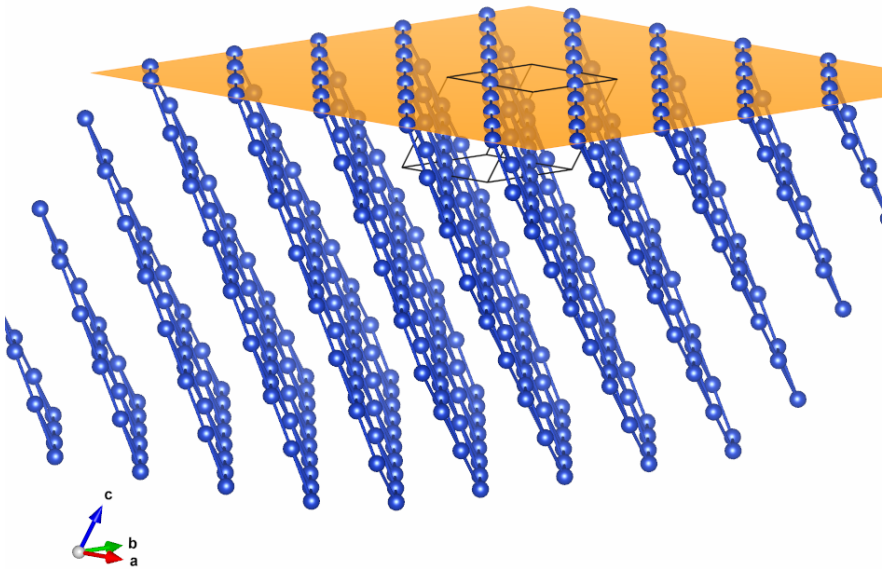
Fu, Kane, PRB **76**, 045302 (2007)

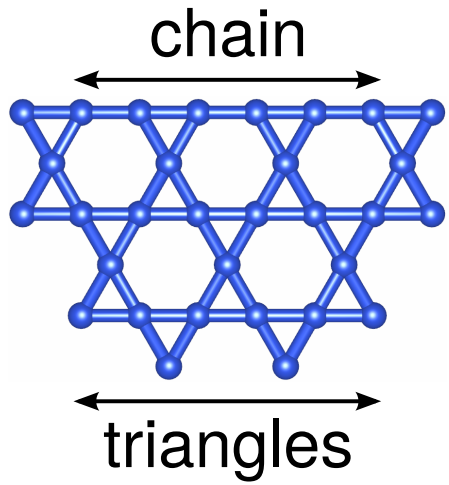


Guterding, Jeschke, Valentí, arXiv:1511.05686

Surface termination of Herbertsmithite

- $\nu_0; (\nu_1, \nu_2, \nu_3) = 0; (111)$ is stack of 2D systems
- (001) termination has edge of kagome layer at surface
- termination influences details of surface bands, not qualitative physics
- surface states are generic in Herbertsmithite system
- doping only controls Fermi level
- electron doped-materials show QSHE, two spins at Fermi level
- Barlowite bands are topologically trivial, additional band crossings

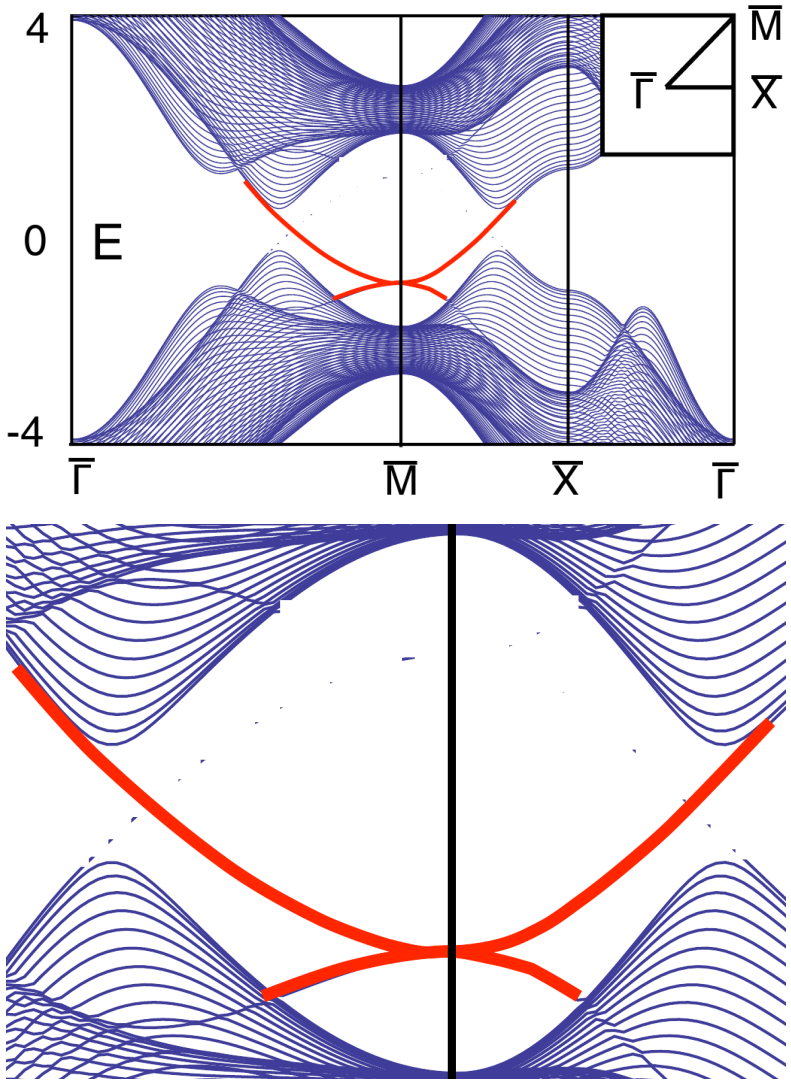




Guterding, Jeschke, Valentí, arXiv:1511.05686

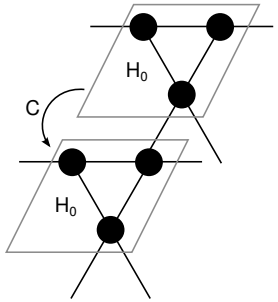
How to calculate surface states

- full-relativistic DFT calculations, projective Wannier functions
- tight binding model for Cu states $(n, j, m_j) = (3, 5/2, \pm 5/2)$
- minimum number of layers to allow bulk-surface distinction $N \sim 20$
- diagonalization effort grows with N^3
- always two surfaces in TB slab, experiment observes one at a time
- some authors just erase bands from the dual surface (justified, but ugly)
- proper way to calculate surface states: Green's functions



Fu, PRL **106**, 106802 (2011)

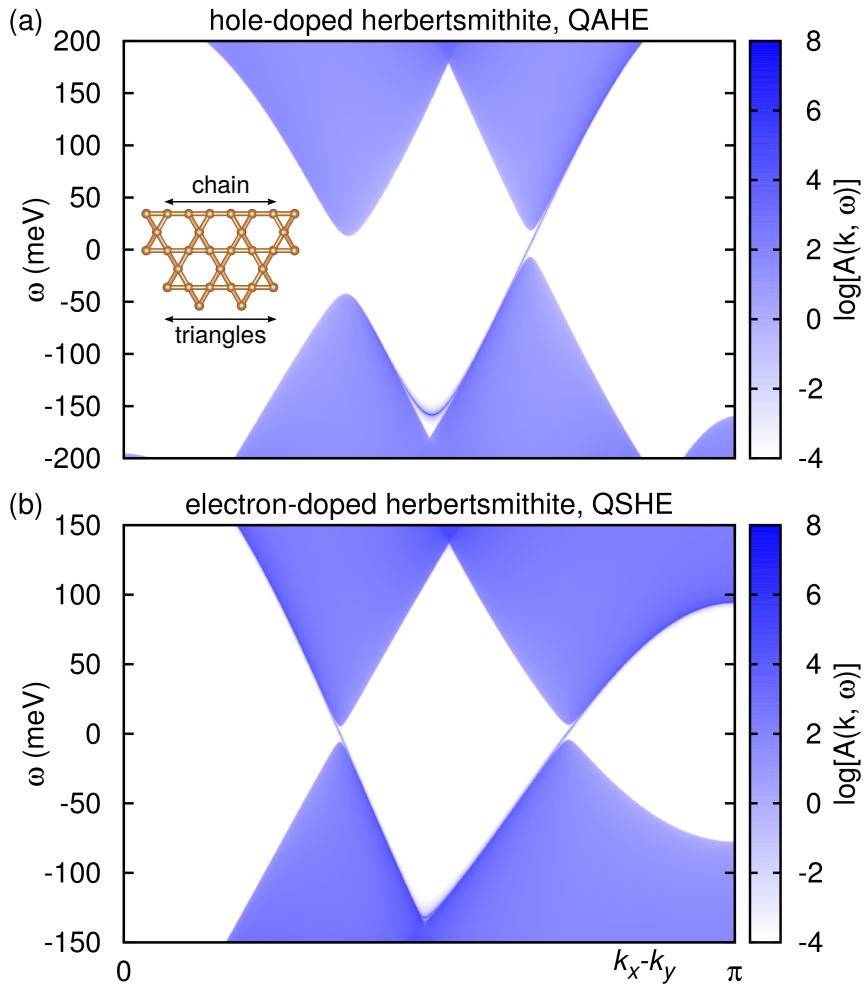
State on the surface of Herbertsmithite



- iterative Green's function method

  [Sancho et al., J. Phys. F: Met. Phys. **14**, 1205 (1984)]

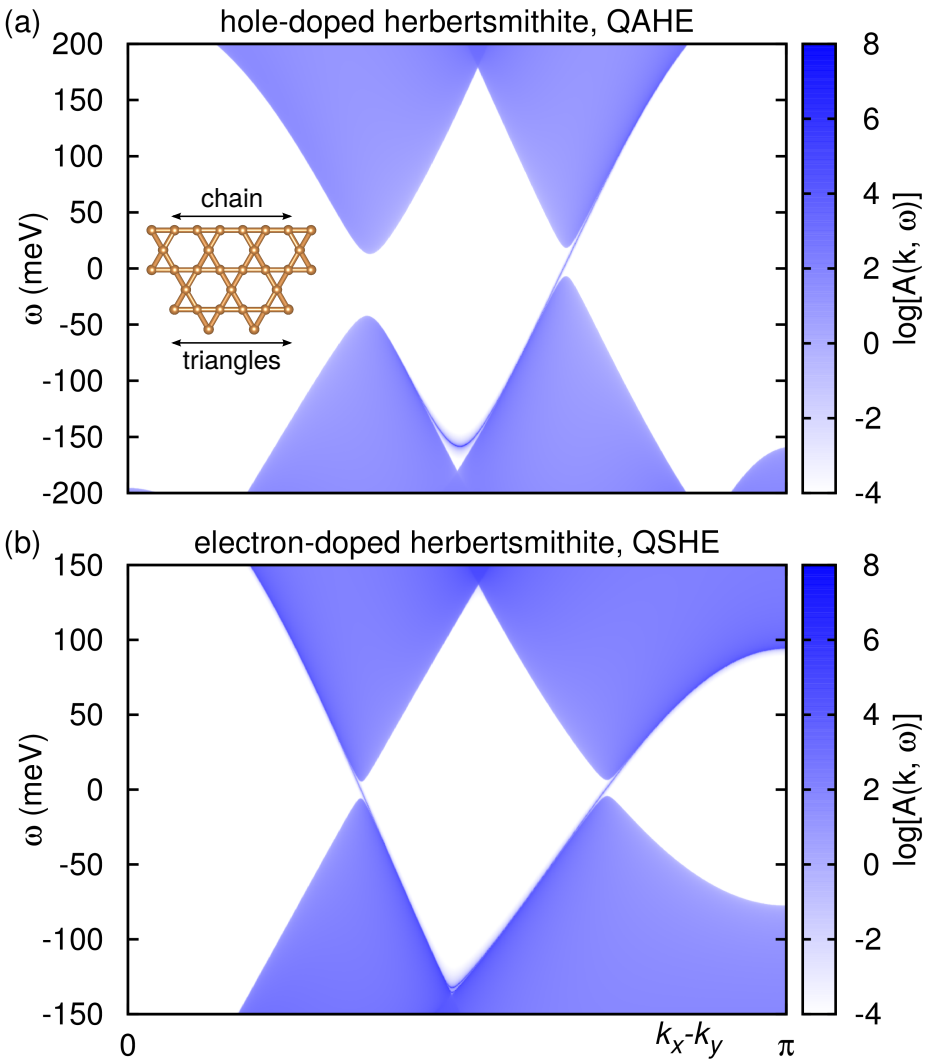
- initial condition $G_{ij}^{(1)}(\omega) = (\omega - H_0)_{ij}^{-1}$
- surface $G_{ij}^{(N)}(\omega) = \left[\left(\omega - H_0 - CG^{(N-1)}C^\dagger\right)^{-1}\right]_{ij}$
- dual surface $G_{ij}^{(N)}(\omega) = \left[\left(\omega - H_0 - C^\dagger G^{(N-1)}C\right)^{-1}\right]_{ij}$
- spectral function $A(k,\omega) = -\mathrm{Im}\ \mathrm{Tr}\left[G(k,\omega)\right]/\pi$

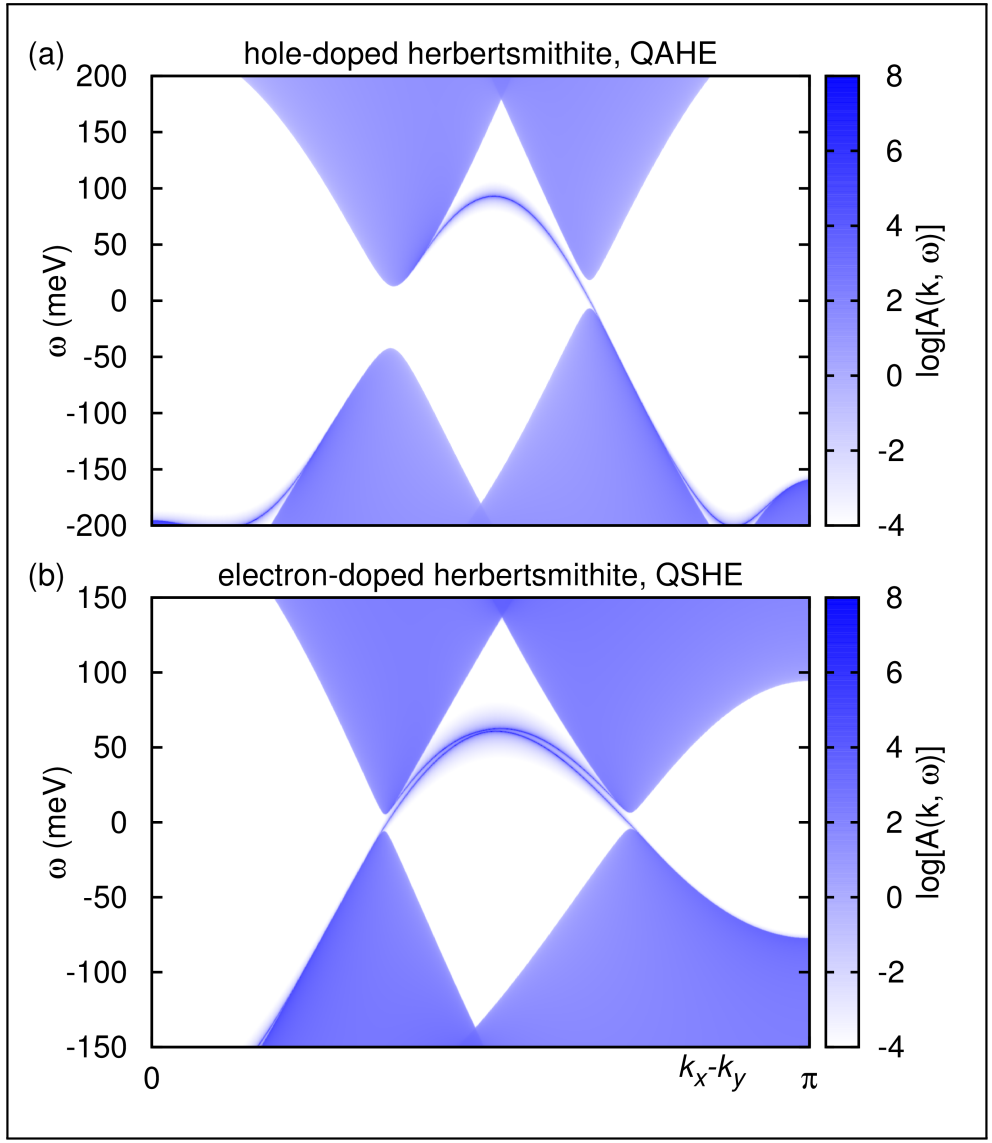


Guterding, Jeschke, Valentí, arXiv:1511.05686

- $N = 10^5$
- $\omega \to \omega + i \cdot 10^{-5}$ eV

State on the dual surface of Herbertsmithite





Guterding, Jeschke, Valentí, arXiv:1511.05686

Summary and outlook

Summary

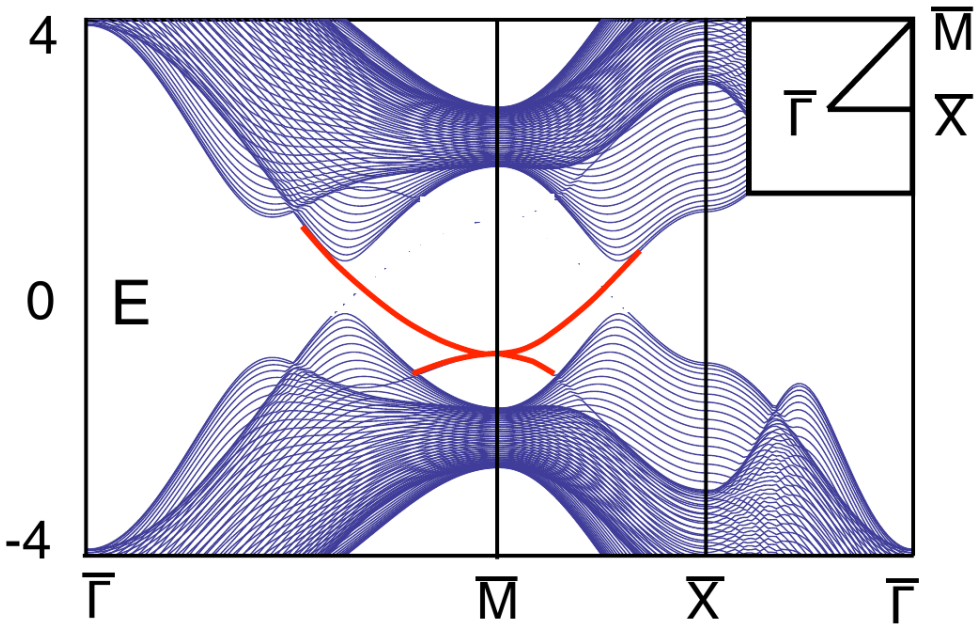
- investigated stability of a range of new copper kagome materials
- all materials feature strong electronic correlations
- substitution of interlayer ions offers tunability
- Mg-Barlowite is a new spin-liquid candidate
- Li-Herbertsmithite shows the quantum anomalous Hall effect
- (Al, Ga, In, Sc)-Herbertsmithite show the quantum spin Hall effect
- preprint available: arXiv:1511.05686

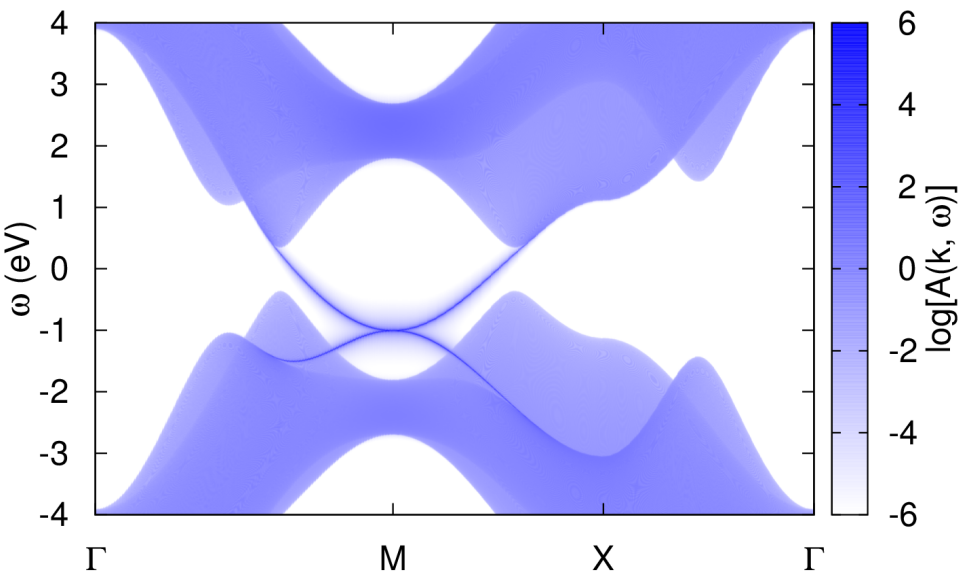
Outlook

- correlation effects beyond DFT
- material synthesis

Backup slides

Test for Green's function code: crystalline topological insulator





Fu, PRL **106**, 106802 (2011)