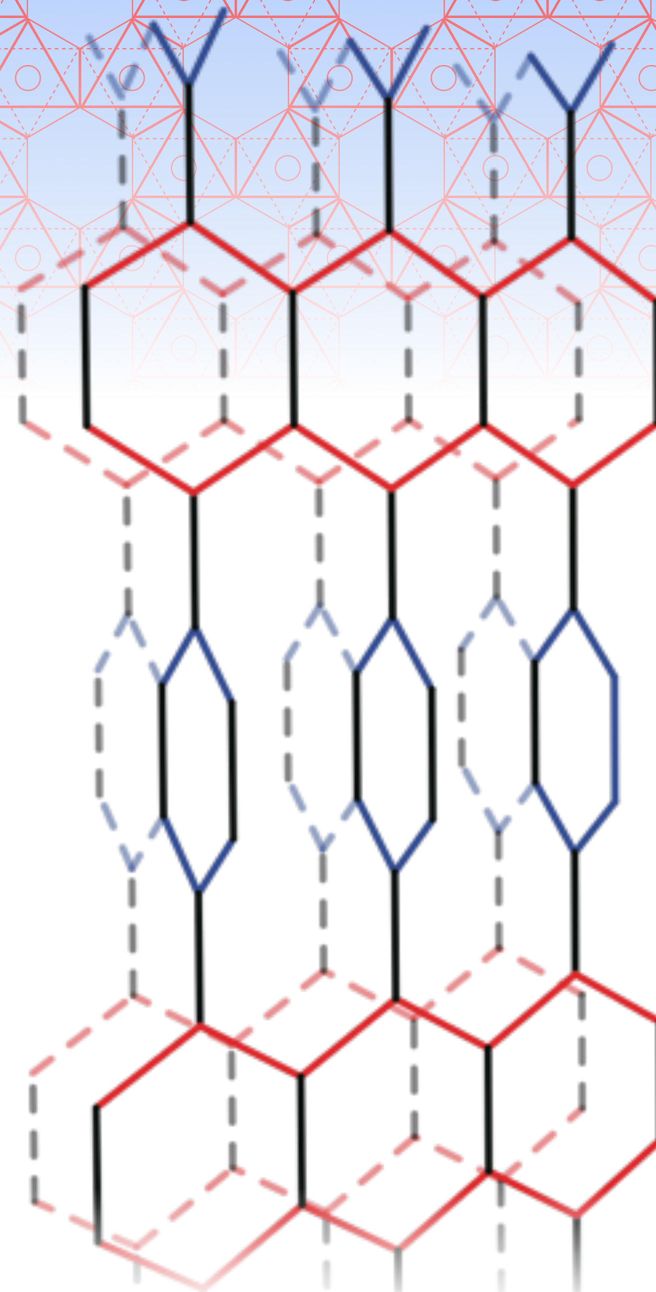
A New Spin-anisotropic Harmonic Honeycomb Iridate



Tess Smidt

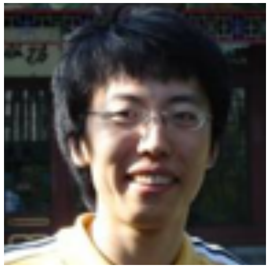
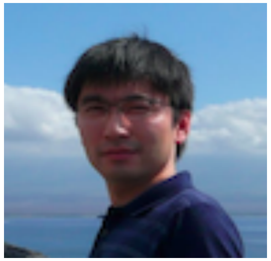
Analytis and Neaton Groups

Molecular Foundry Theory Seminar

2014.04.16

Collaborators



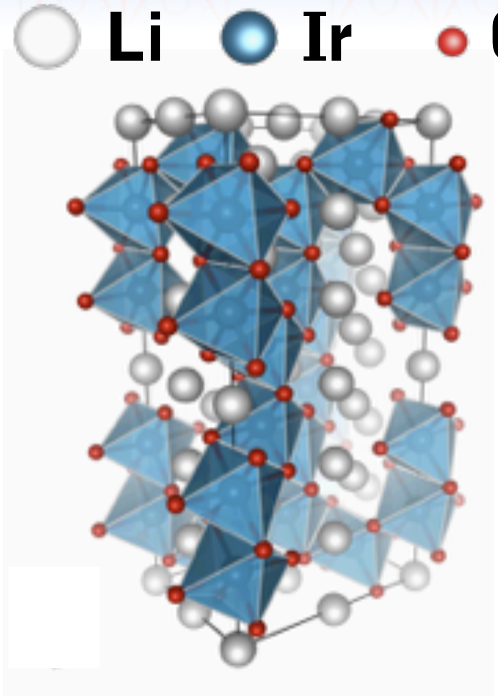

(UCB & LBL) James Analytis, Nicholas Breznay, Jeff Neaton, Qimin Yan, Zhenfei Liu, Ashvin Vishwanath, Itamar Kimchi, (Argonne APS) Zahir Islam, (Los Alamos NL) Ross MacDonald, and Kim Modic

Not pictured but very important! – A. Biffin, S.K. Choi, P. Watkins-Curry, G. T. McCandless, Felipe Gandara, R. D. Johnson, J. Y. Chan, R. Coldea, Arkady Shekhter, Alejandro Ruiz, and Xue Fan

An Introduction

Iridates are an exciting frontier of Mott physic and spin-orbit coupling where new physics may emerge.

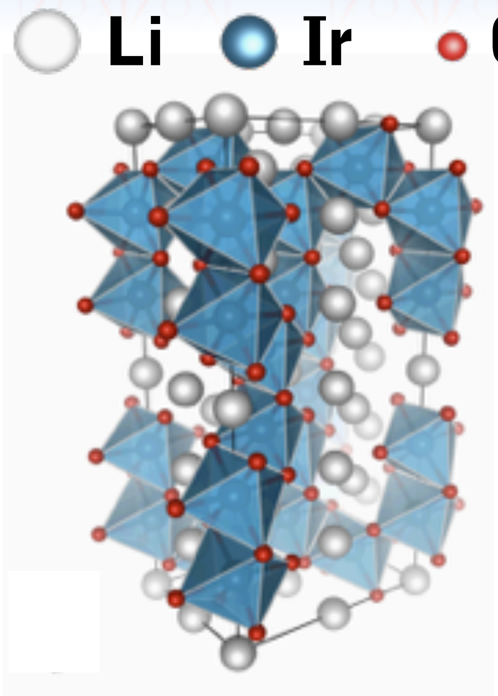
Li_2IrO_3 Mott physics, spin-orbit coupling and the quest to find a quantum spin liquid



- Iridum in magnetic oxidation
- Mott Insulator
- Strong Spin-Orbit Coupling
- Octahedrally coordinated Ir and Li
- Ir octahedra edge-share with 3 n.n.

Li_2IrO_3

Mott physics, spin-orbit coupling and the quest to find a quantum spin liquid



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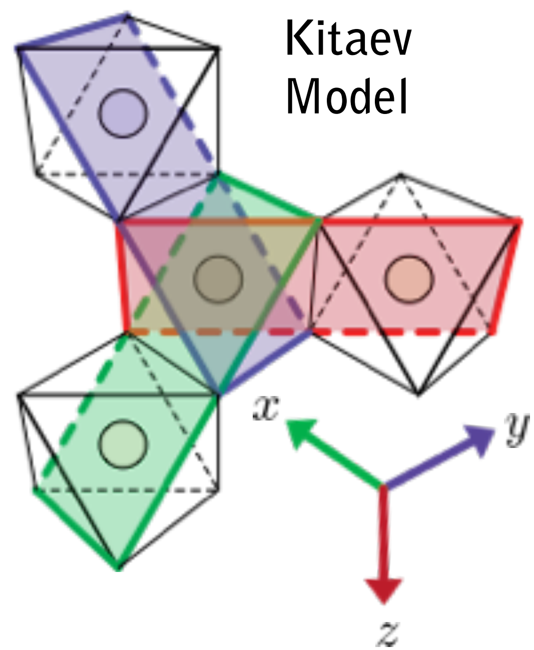
Kitaev Model



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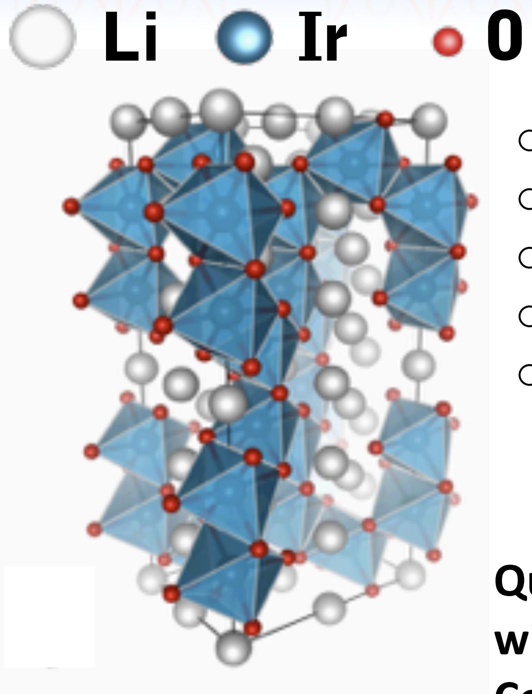

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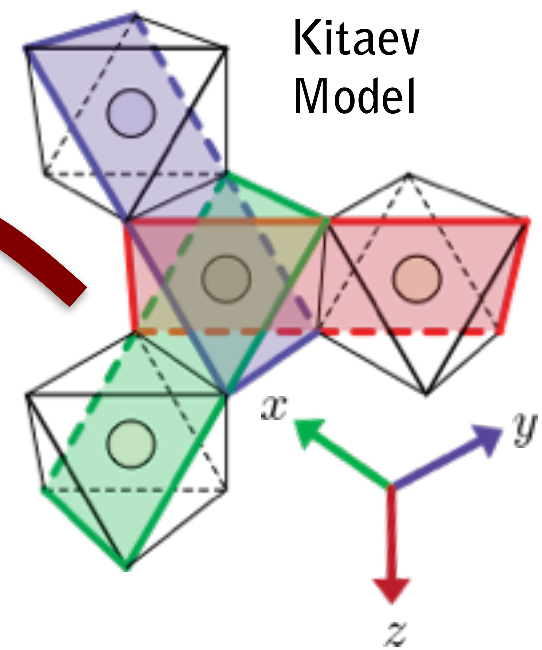
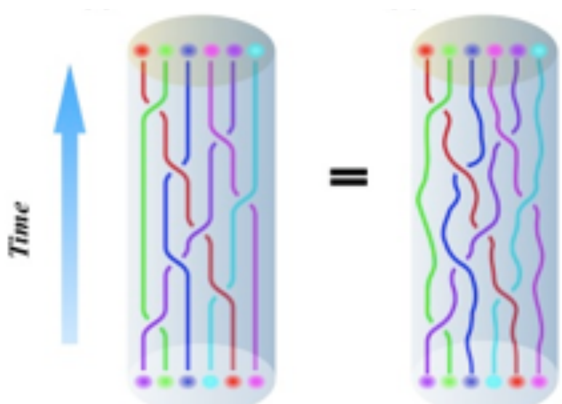
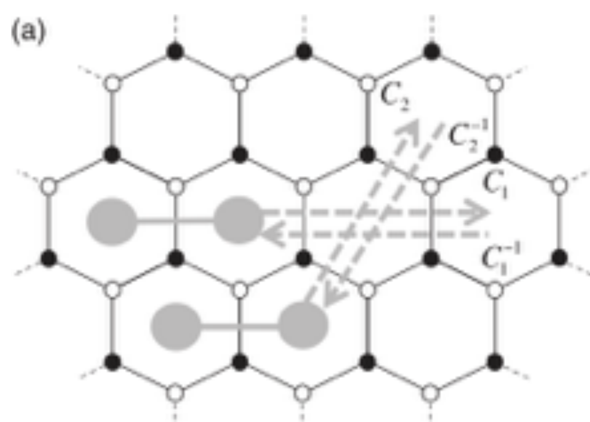


Quantum Spin Liquid
with Exotic Excitations and
Computational Possibilities



Graphic by Layla Hormozi



This Talk

Mapping the Kitaev Model to Li_2IrO_3

Ideal octahedral geometry is crucial for the model.

Only hexagonal lattices have been studied,
but we propose a series of new structural candidates
– the "harmonic honeycomb iridates.

Magnetic Measurements 1st Harmonic Honeycomb Li_2IrO_3

Magnetism is spin-anisotropic at low temperature.
Magnetization deviates expected linear behavior in high field.

Ongoing studies on Harmonic Honeycomb Iridates

DFT Relaxations of series members may help determine which members are most energetically favorable – thus guide synthesis and explain why we have only synthesized particular members.

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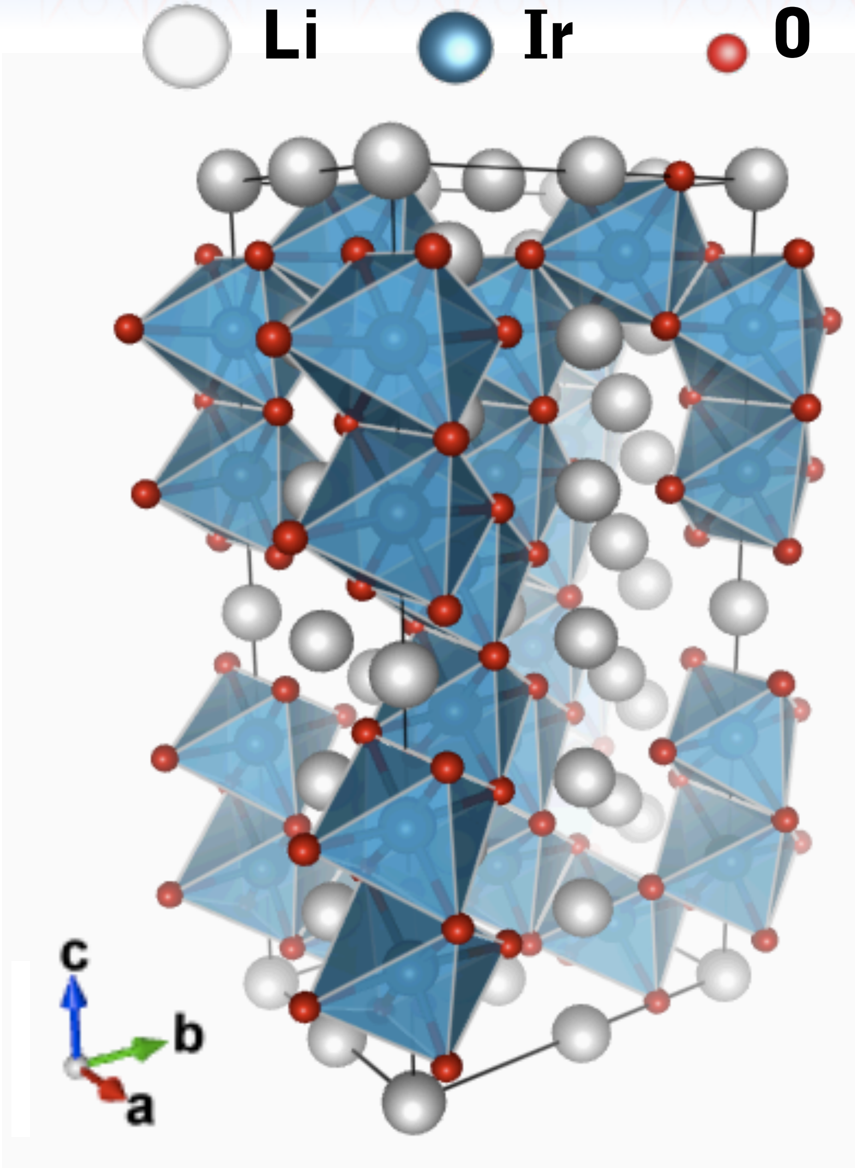
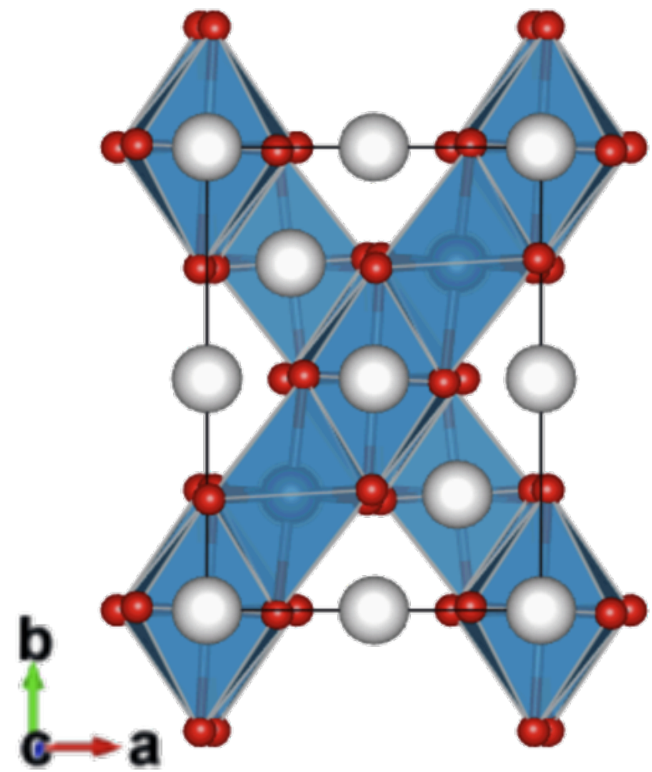
STRUCTURE: 1ST HARMONIC HONEYCOMB LITHIUM IRIDATE (Li_2IrO_3)

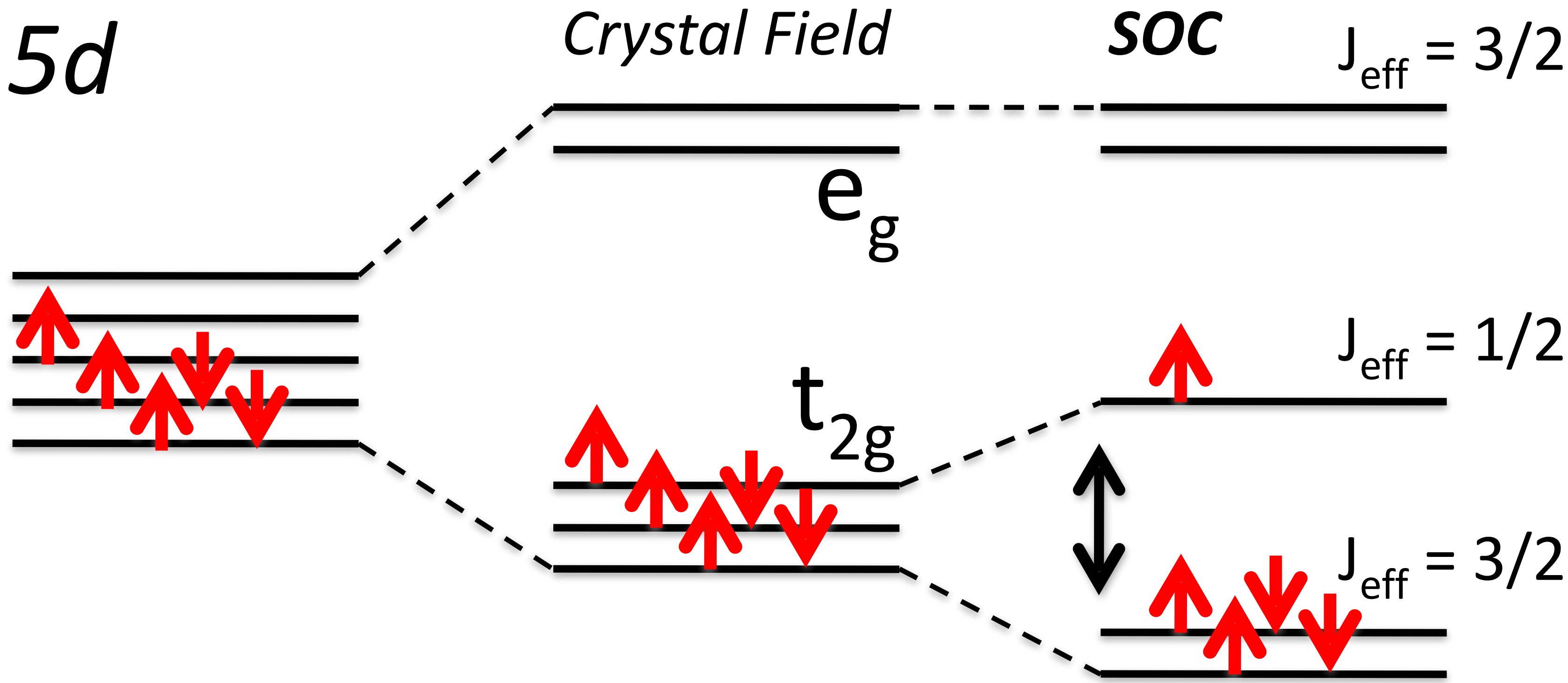




Ir in an Octahedral Environment

Ir^{3+} Ir^{4+} Ir^{5+}

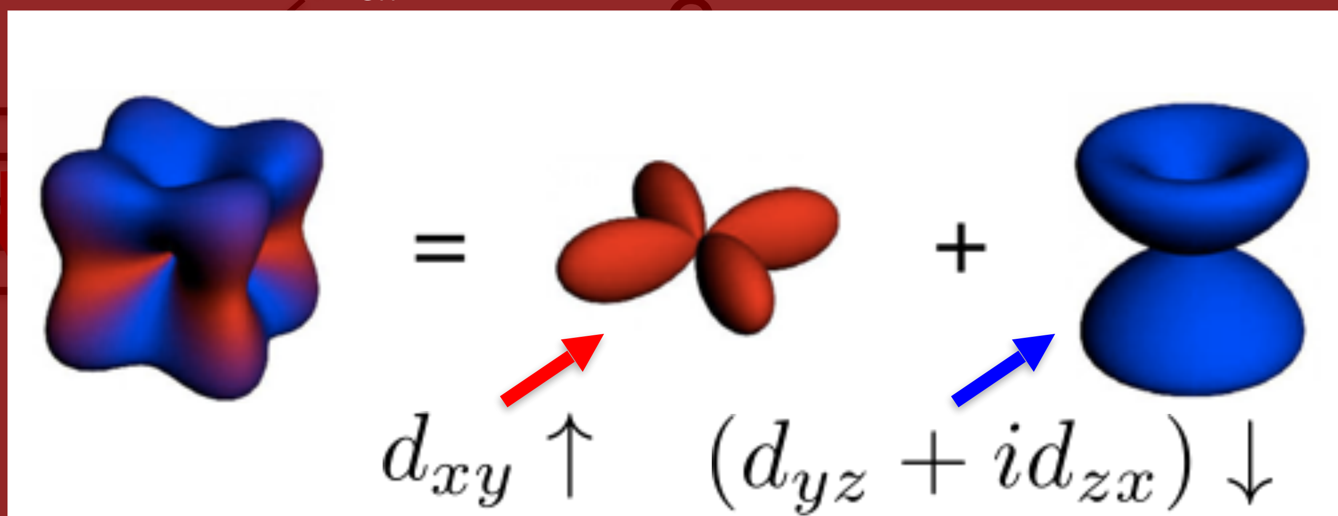
5 electrons



Ir in an Octahedral Environment

J_{eff} states are complex superposition of the d_{xy}, d_{yz}, and d_{zx} orbitals

For example: J_{eff} = ½, m=½



Ir in an Octahedral Environment

Ir3+ Ir4+ Ir5+

5 electrons

5d

Crystal Field SOC $J_{eff} = 3/2$ 1/2 $J_{eff} = 3/2$

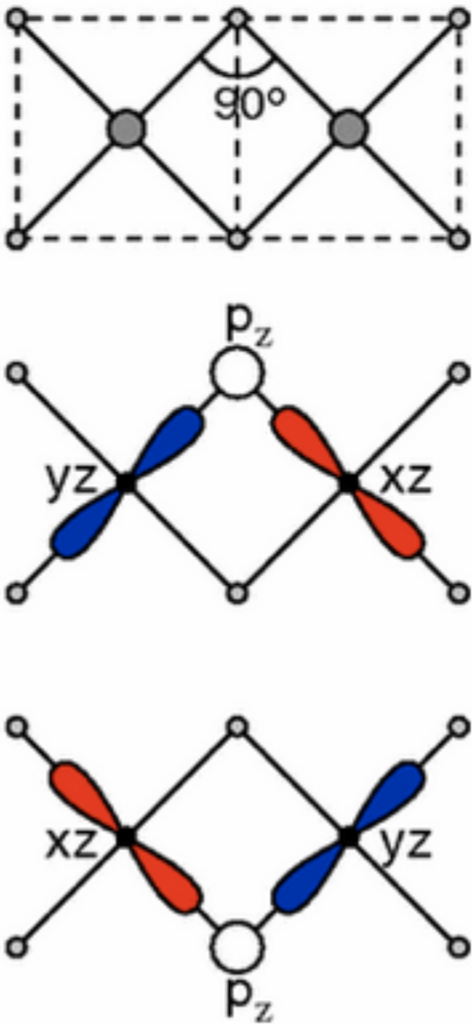
J_{eff} states are complex superposition of the d_{xy}, d_{yz}, and d_{zx} orbitals

For example:

$$|J_{eff} = 1/2, m = 1/2\rangle$$

Destructive Interference in the Quantum Compass Model

Superexchange



Ir in octahedra interact through shared oxygen.

Two exchange paths destructively interfere due to "imaginary" orbital component of the J_{eff} states.

In-plane interactions cancel. Only interactions perpendicular to bonding plane survive.

G. Jackeli and G. Khaliullin, Phys. Rev. Lett. 102, 017205

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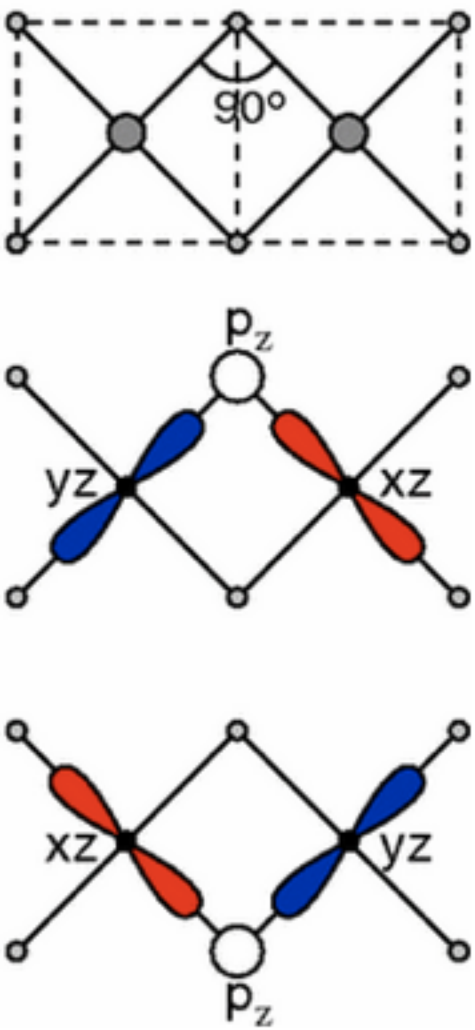

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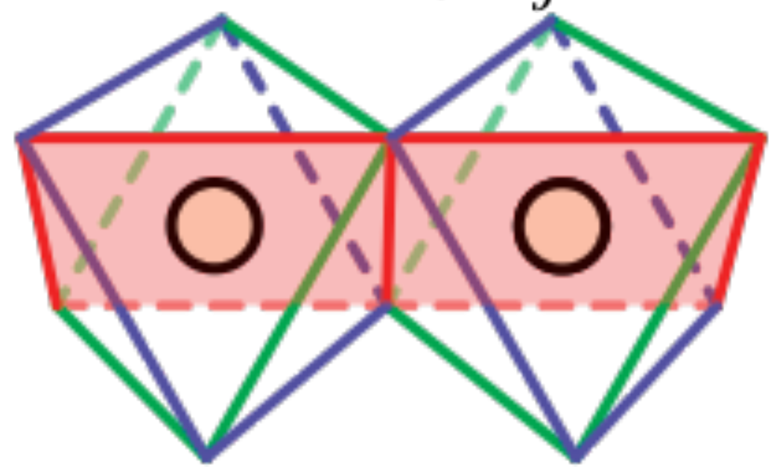
Typical Heisenberg isotropic spin interaction

$$H = J S_i \cdot S_j$$

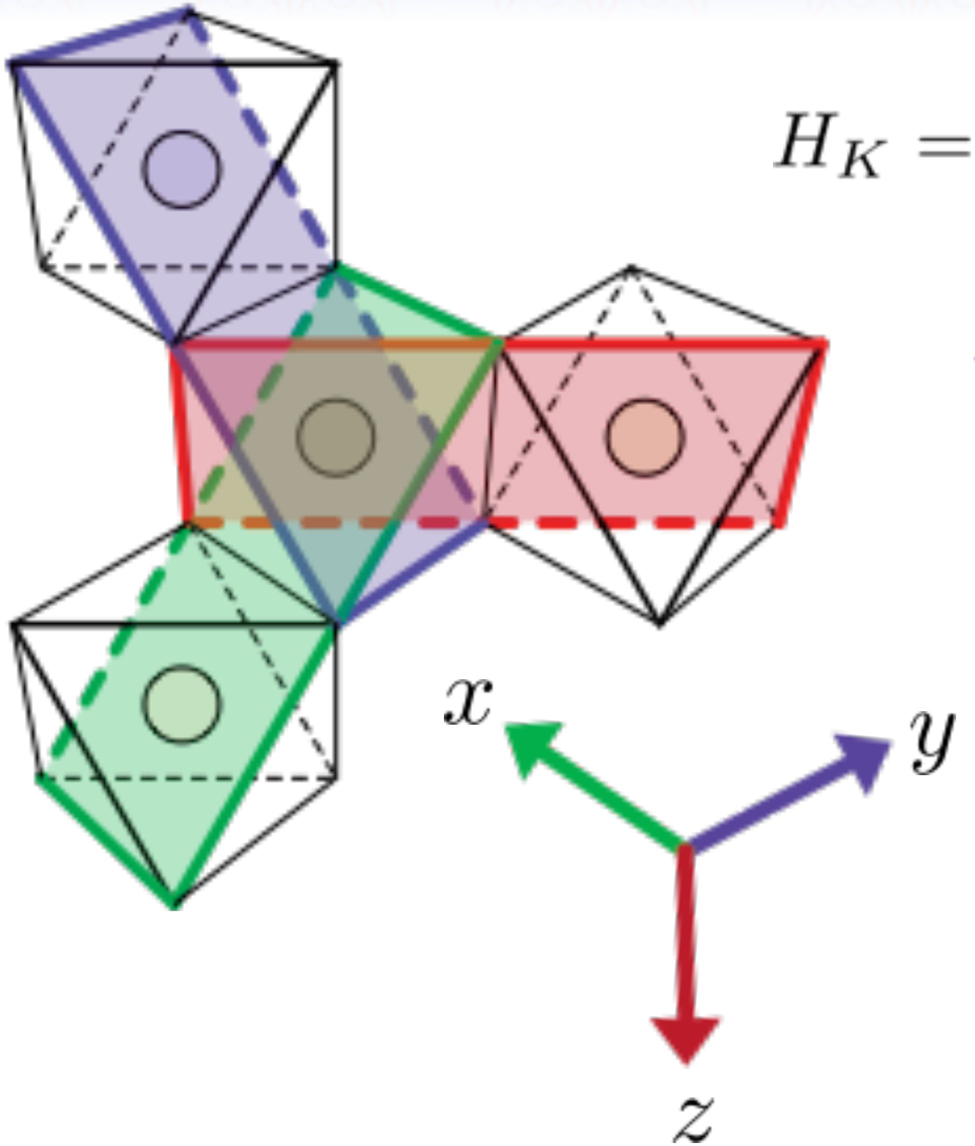
Reduce to a spin-anisotropic interaction

$$H = J S_i^z S_j^z$$



G. Jackeli and G. Khaliullin, Phys. Rev. Lett. 102, 017205

The Kitaev Model is made of three Orthogonal Compass Models



$$H_K = \sum_{\langle ij \rangle \in x} K^x S_i^x S_j^x + \sum_{\langle ij \rangle \in y} K^y S_i^y S_j^y + \sum_{\langle ij \rangle \in z} K^z S_i^z S_j^z$$

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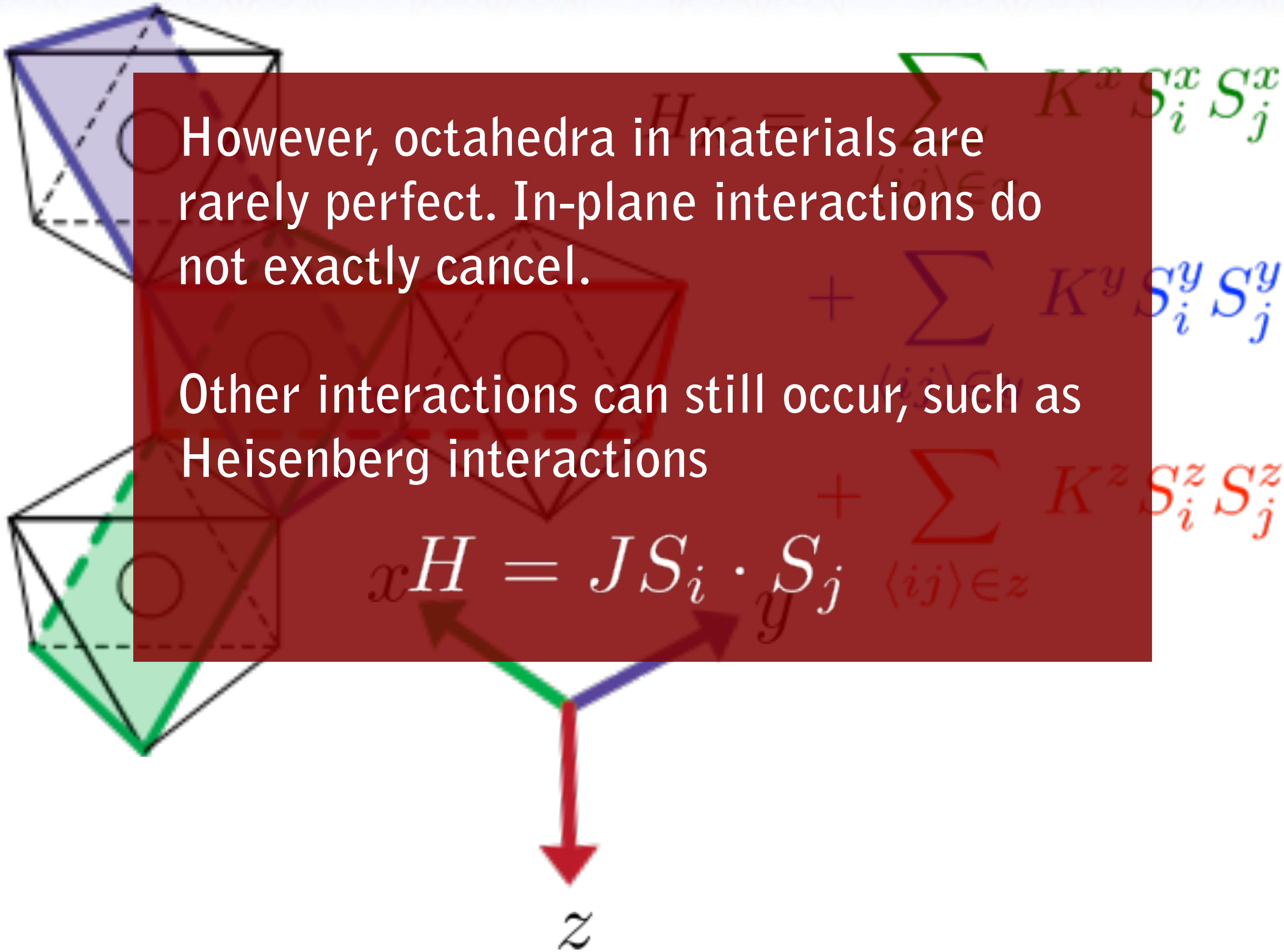


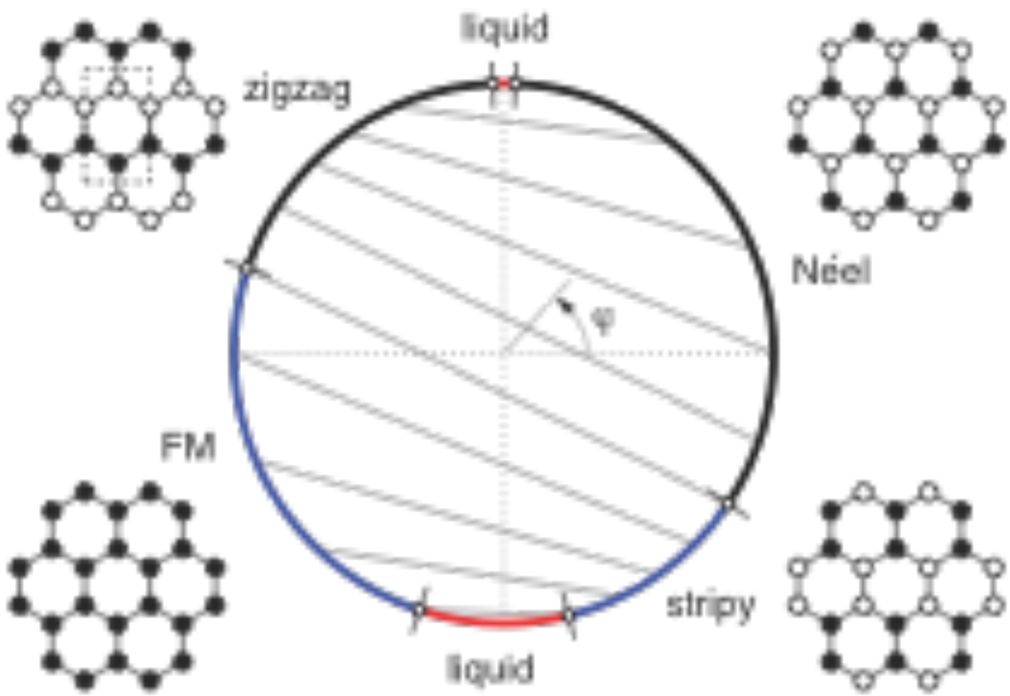
However, octahedra in materials are rarely perfect. In-plane interactions do not exactly cancel.

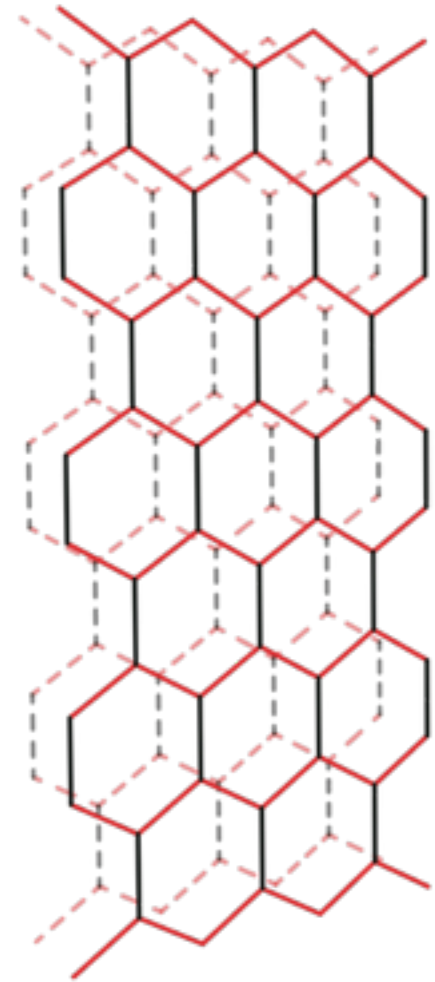
Other interactions can still occur, such as Heisenberg interactions

$$H = JS_i \cdot S_j$$

Magnetic Ordering of the Heisenberg-Kitaev Model on the Honeycomb Lattice

$$H_{ij}^{(\gamma)} = A(2\sin\phi S_i^\gamma S_j^\gamma + \cos\phi S_i \cdot S_j)$$

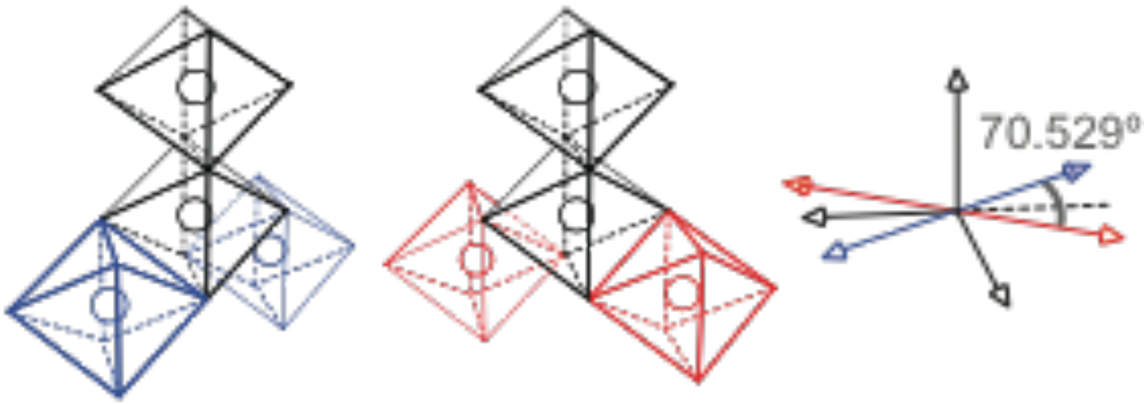




PRL 110, 097204 (2013)

Hexagonal Lattices Aren't the Only Way to Get Kitaev Candidates

Two unique bonding units



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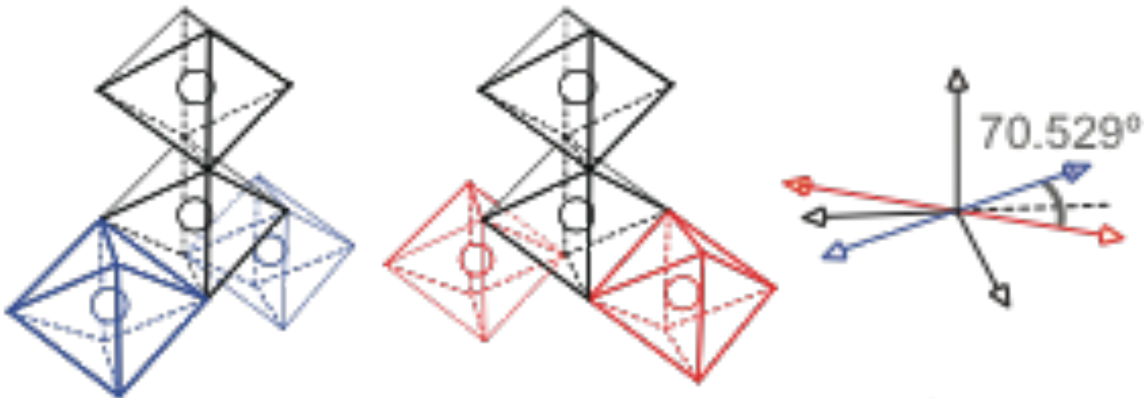
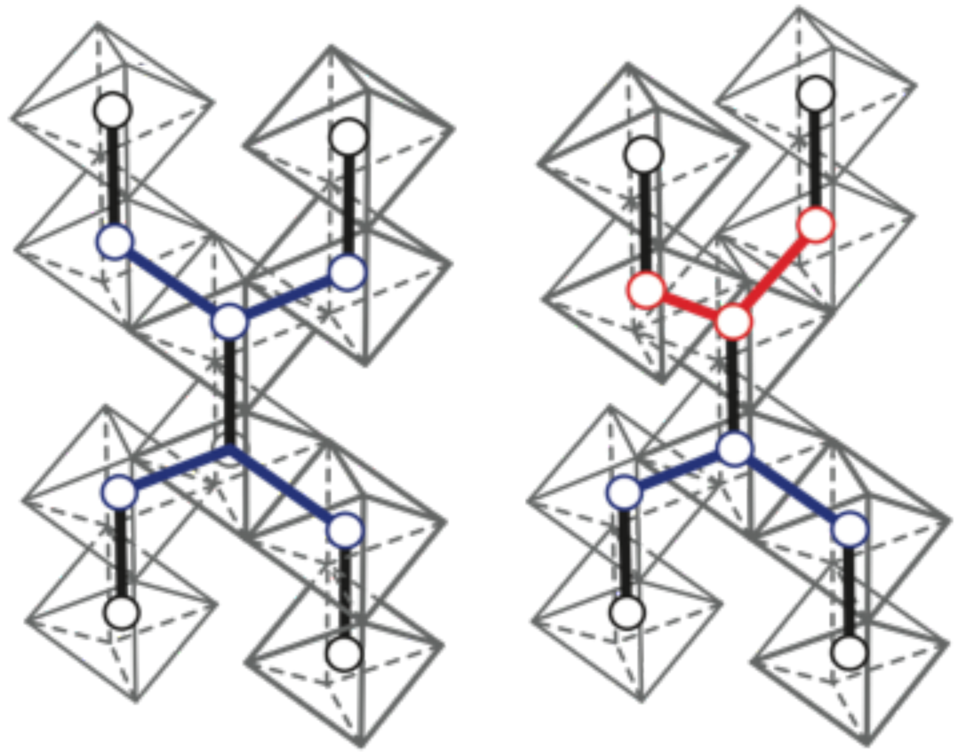


Combine to form same-plane and twisting bonds



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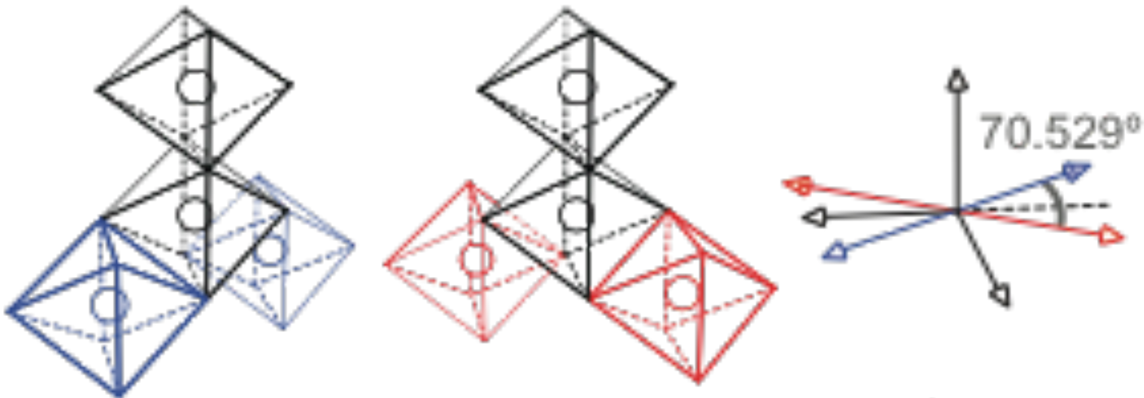

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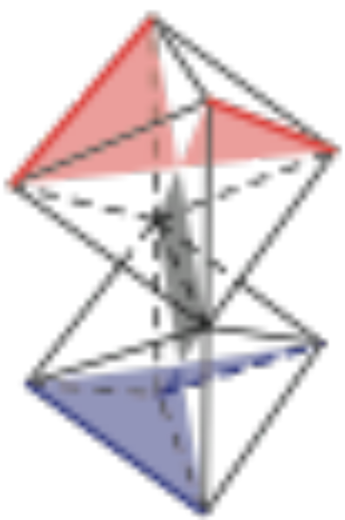
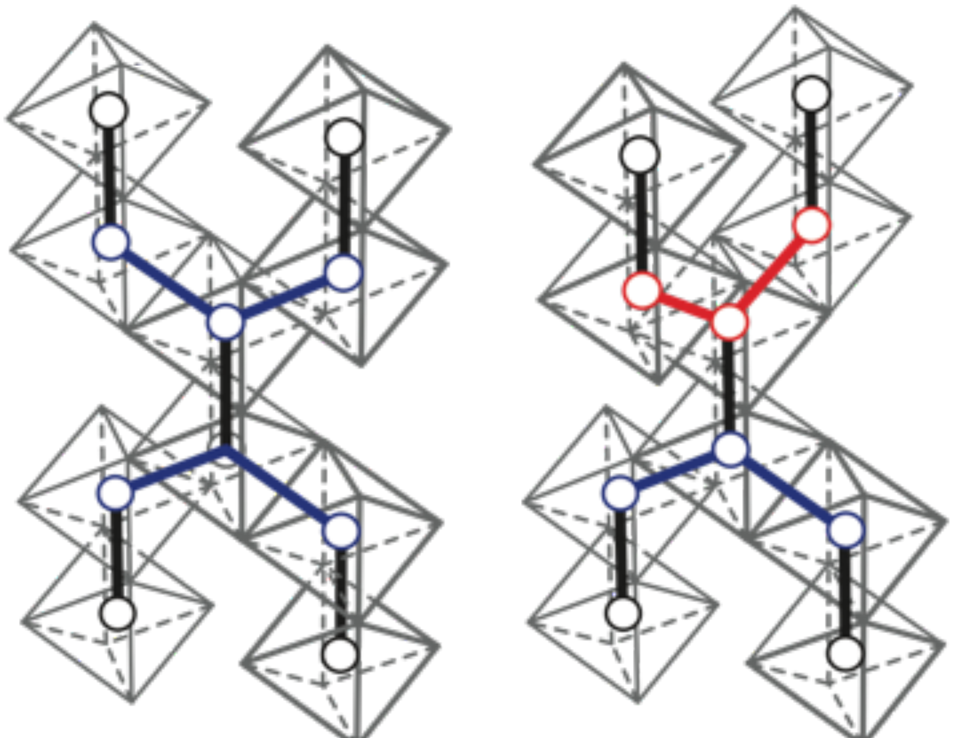
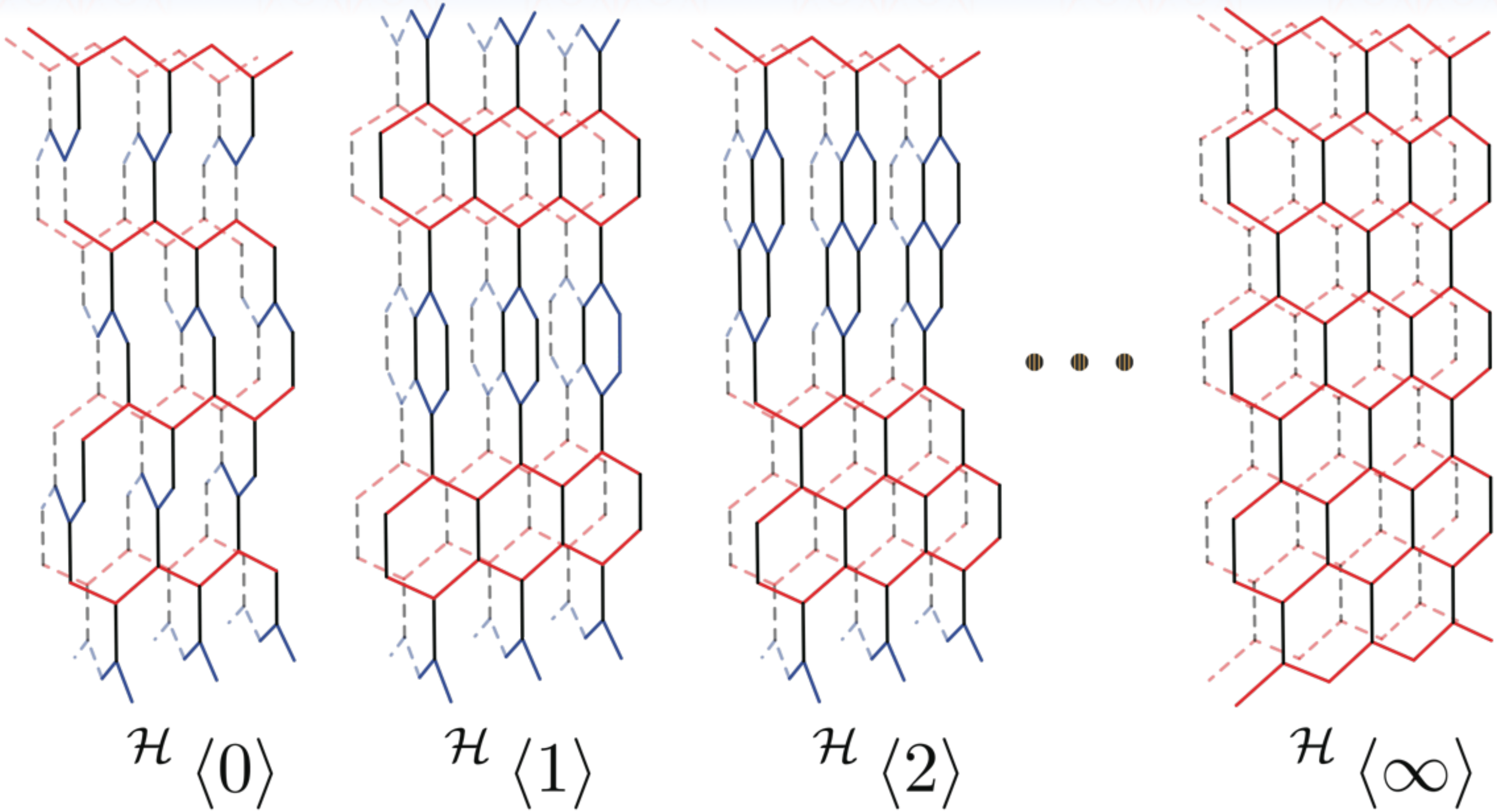


Still maintain orthogonality of bonding planes



Harmonic Honeycomb Iridates



In the Kitaev model limit, all structures are spin liquids at finite temperature.

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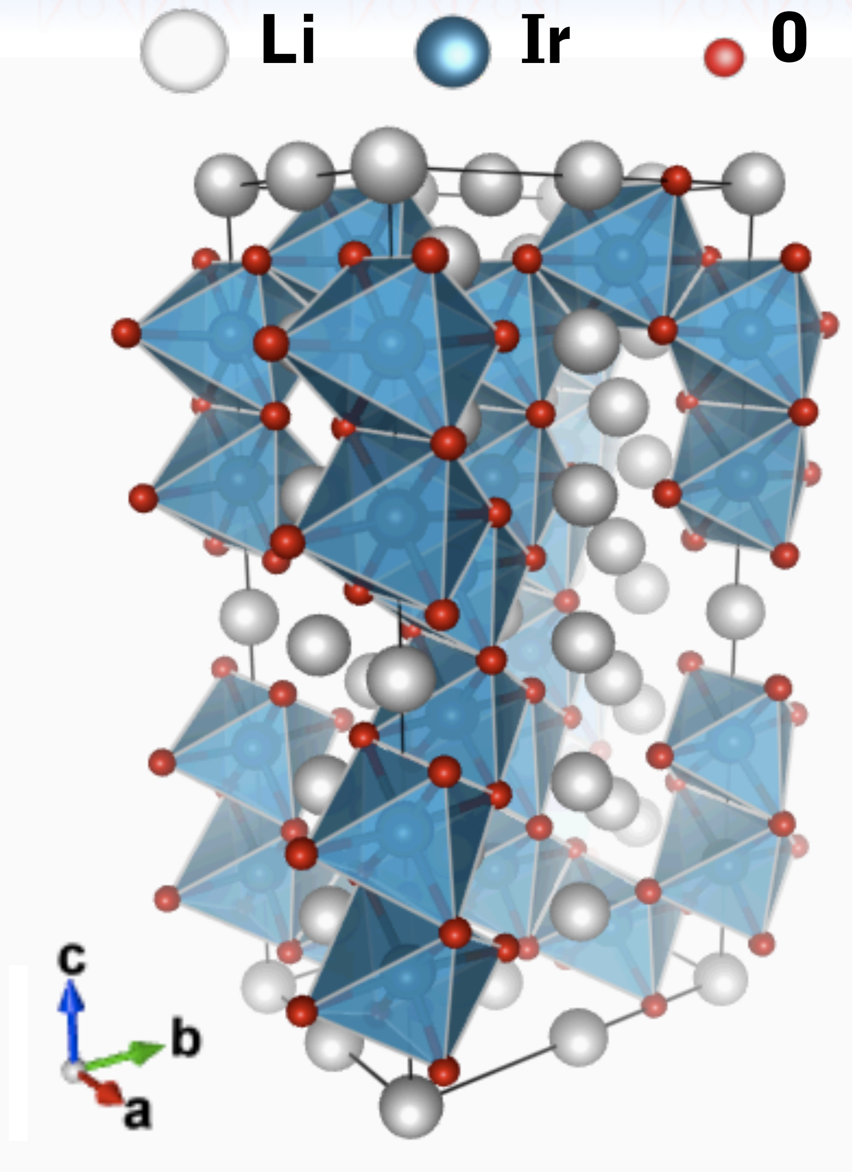
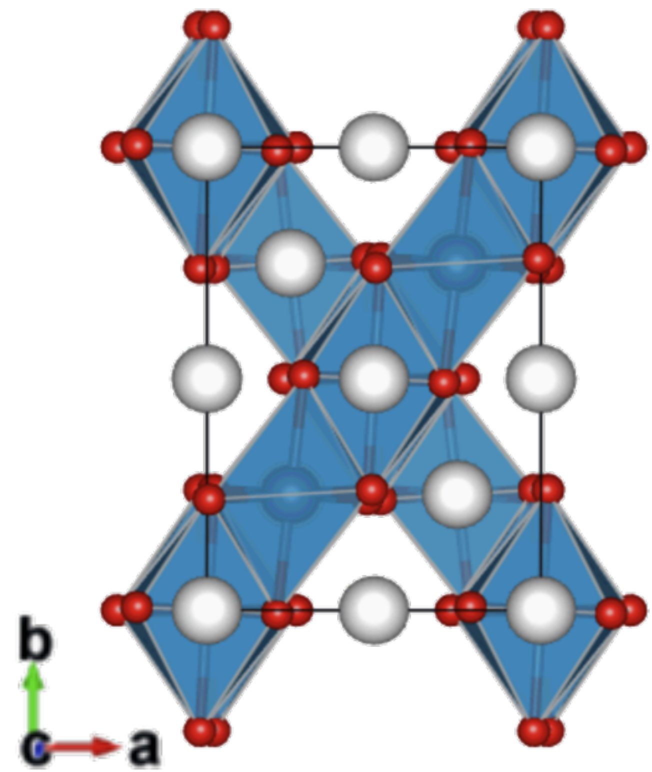
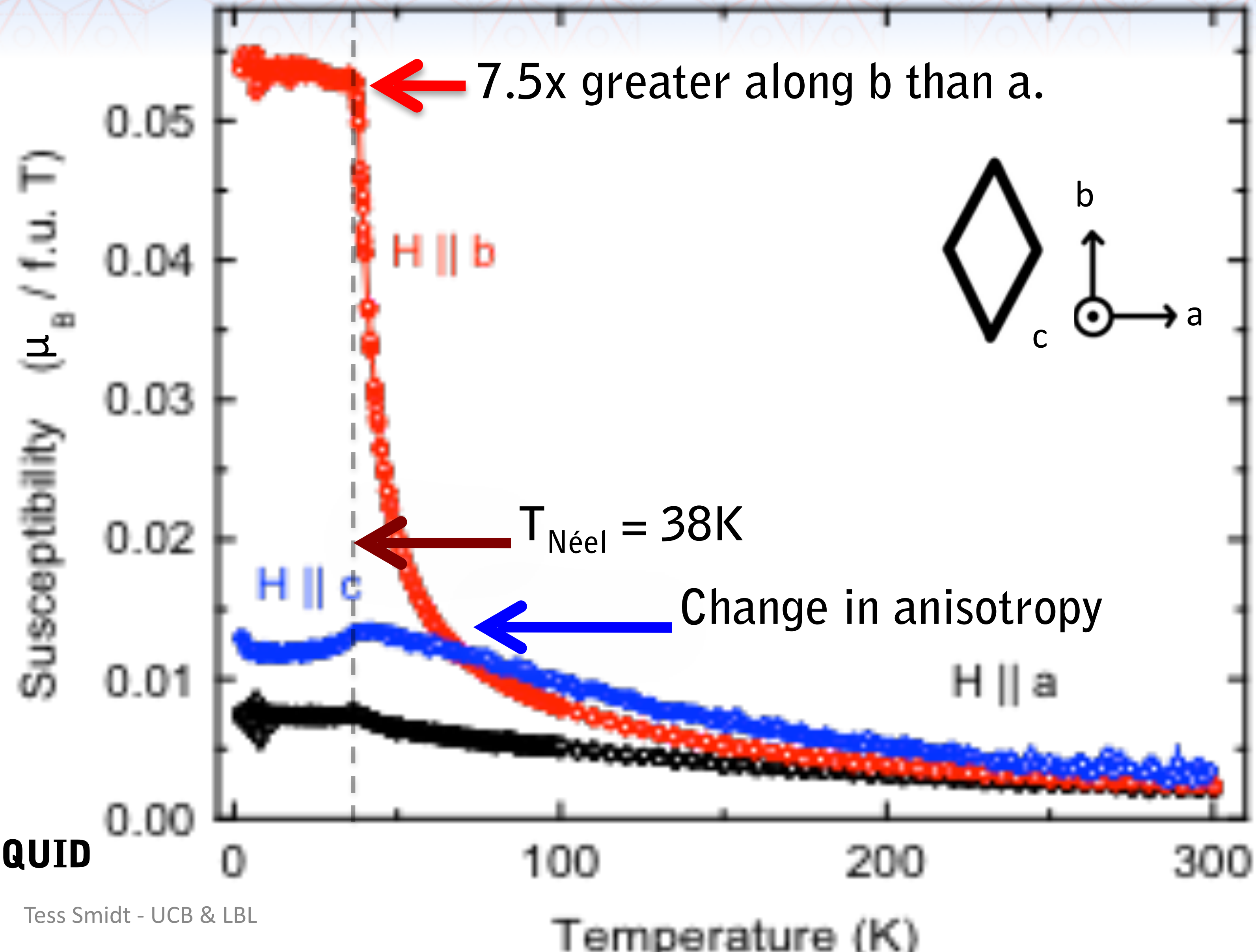
Structure: 1st Harmonic Honeycomb Lithium Iridate (Li_2IrO_3)





Magnetic Susceptibility Has Large Anisotropy



SQUID

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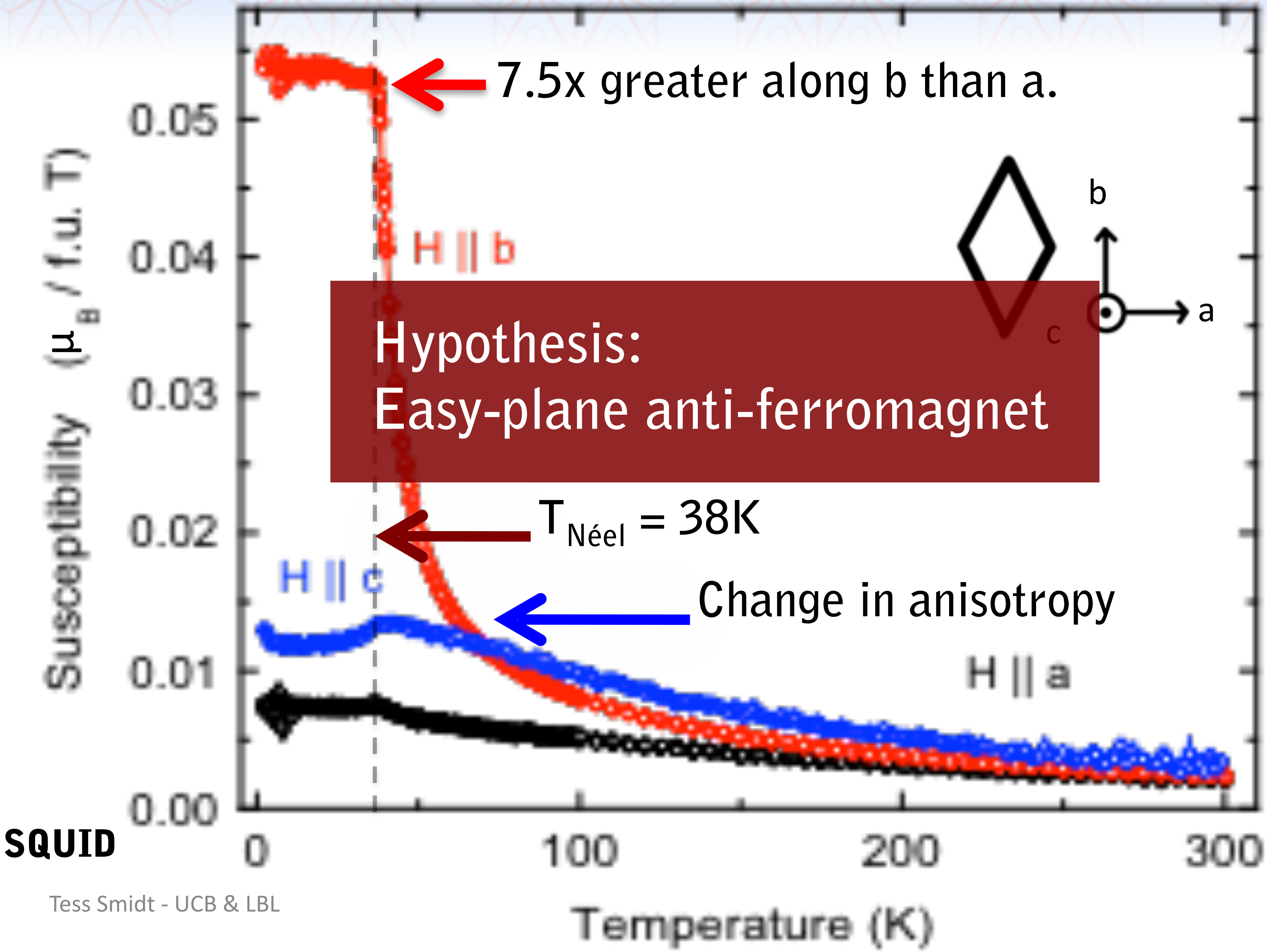
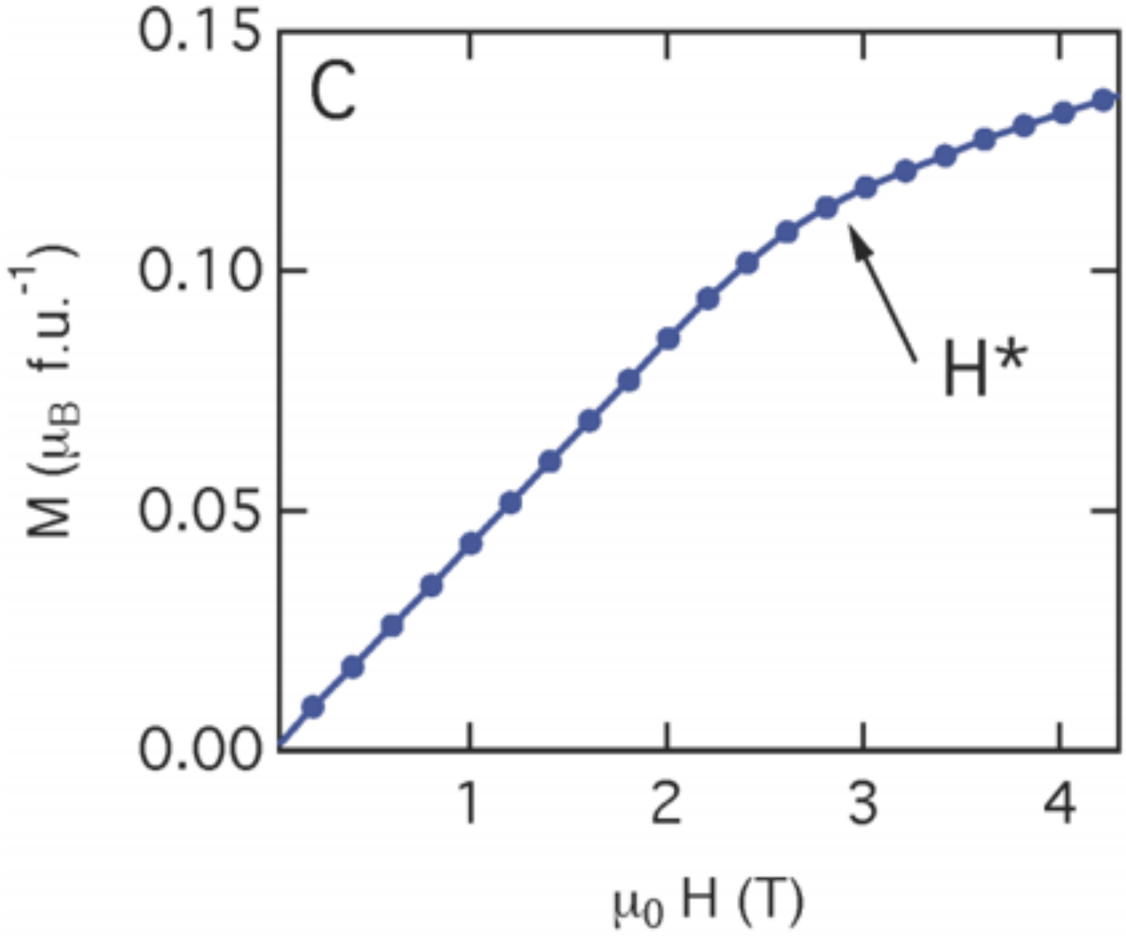


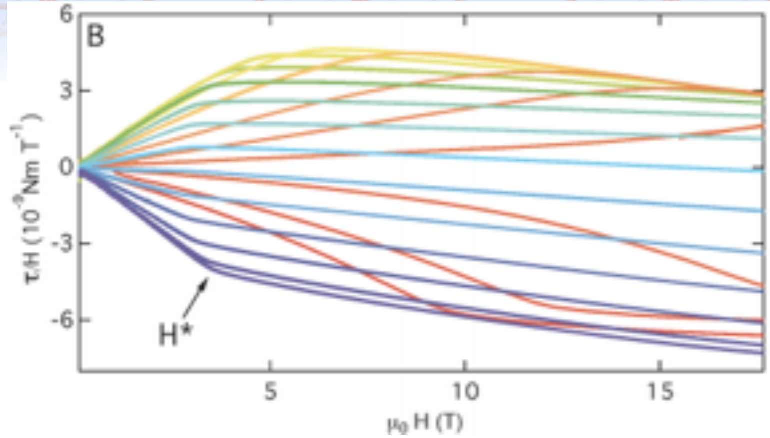
Below Transition Susceptibility Changes Slope

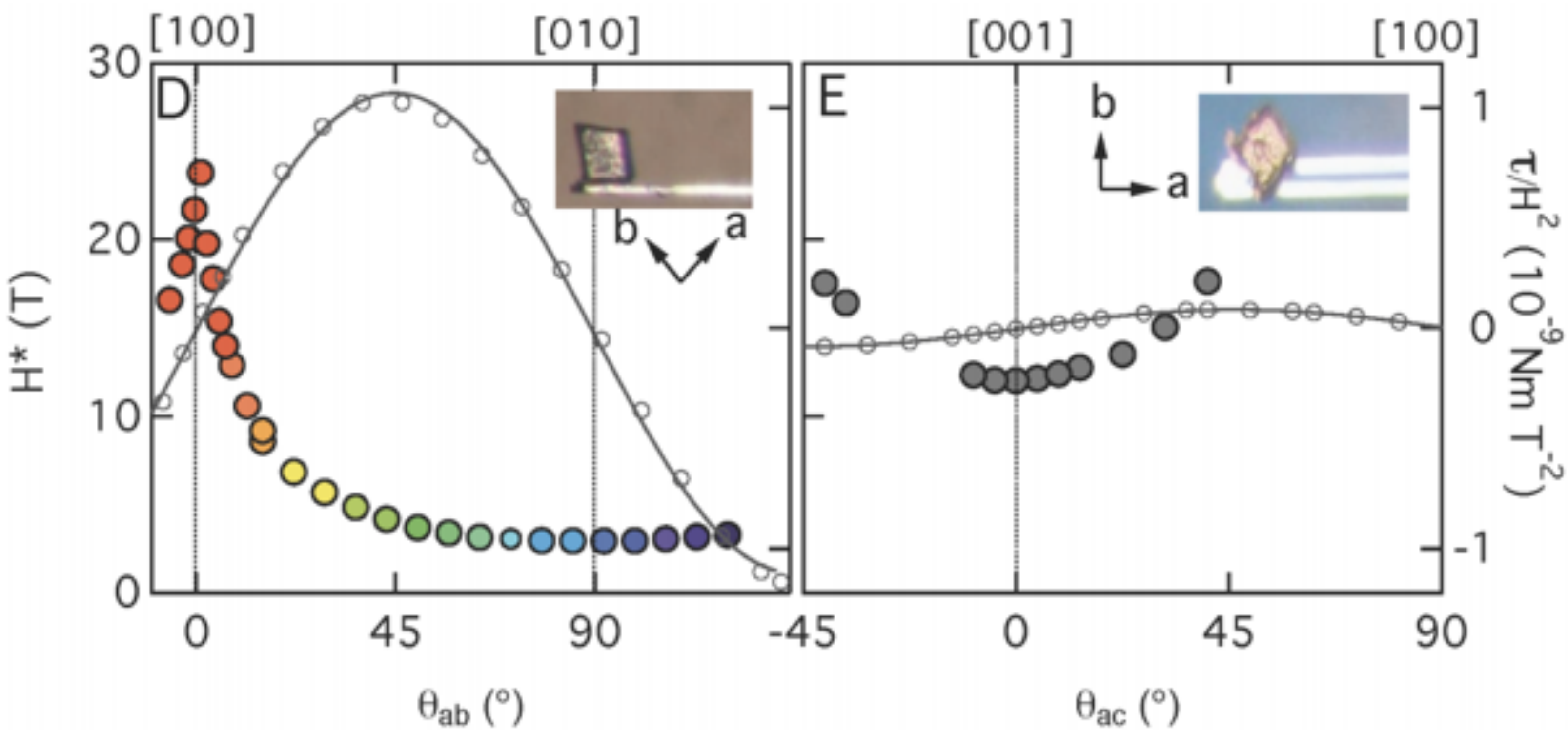
$\cancel{M = \chi H} < T_N$



Kink field is orientation dependent

2.5 T along b
12.5 T along c
25.0 T along a





Why is the B axis special?

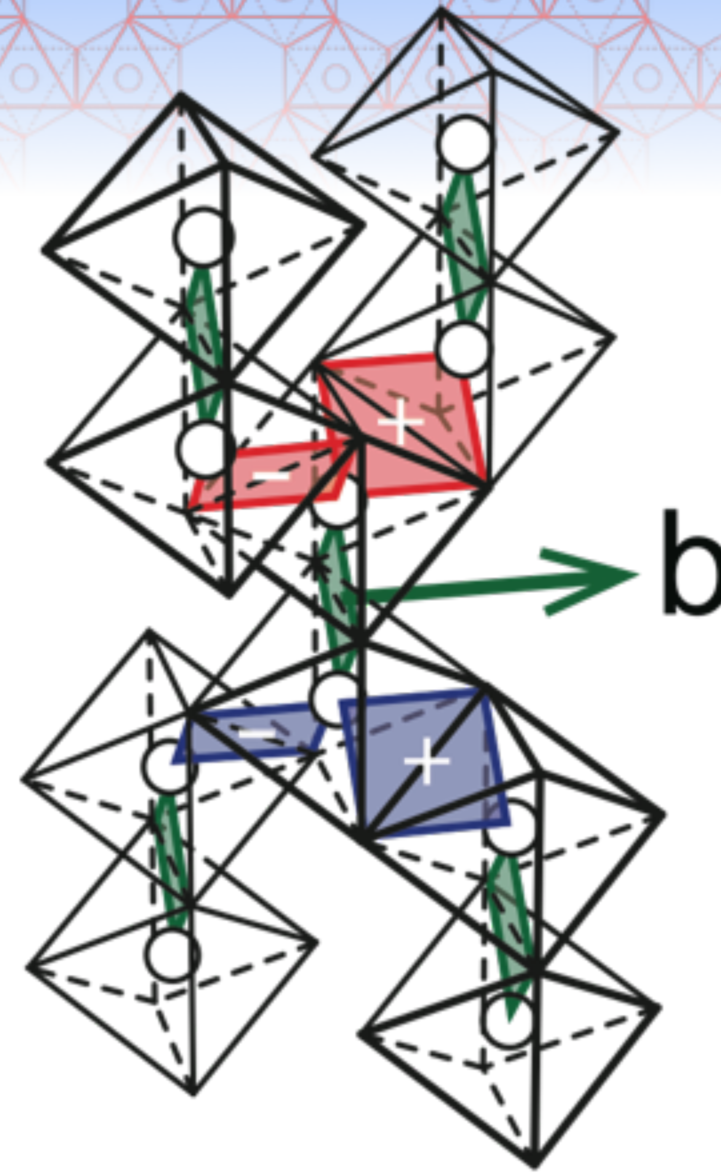
In the crystal structure,
bonds in c direction are special.

In the Kitaev Model, bonds in c direction are associated with spin interactions along b

Kitaev Model

$$H_K = -J_K^c \sum_{\langle ij \rangle \in \hat{b}_\perp} S_i^{\hat{b}} S_j^{\hat{b}}$$

$$- J_K^h \sum_{\langle ij \rangle \in (\hat{a} \pm \hat{c})_\perp} S_i^{\hat{a}\pm\hat{c}} S_j^{\hat{a}\pm\hat{c}}$$



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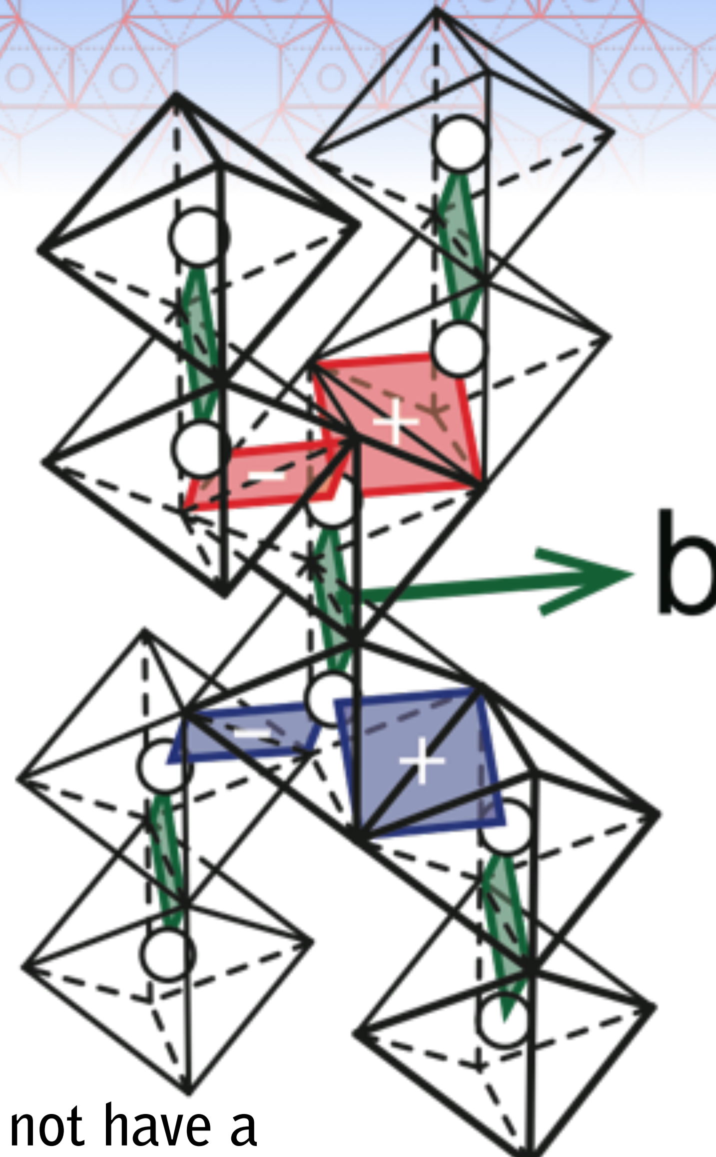

Kitaev interactions may be present, but we do not have a spin liquid (other interactions are also at play).

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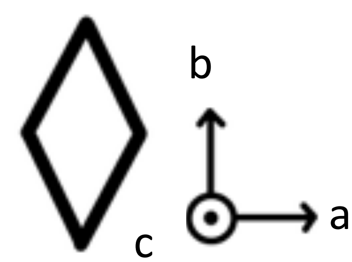
DFT Structure Agrees well with Experiment

Ir ➔ Spin-orbit coupling (SOC)   5d orbitals ➔ U to open gap

Density Functional Theory + U + SOC

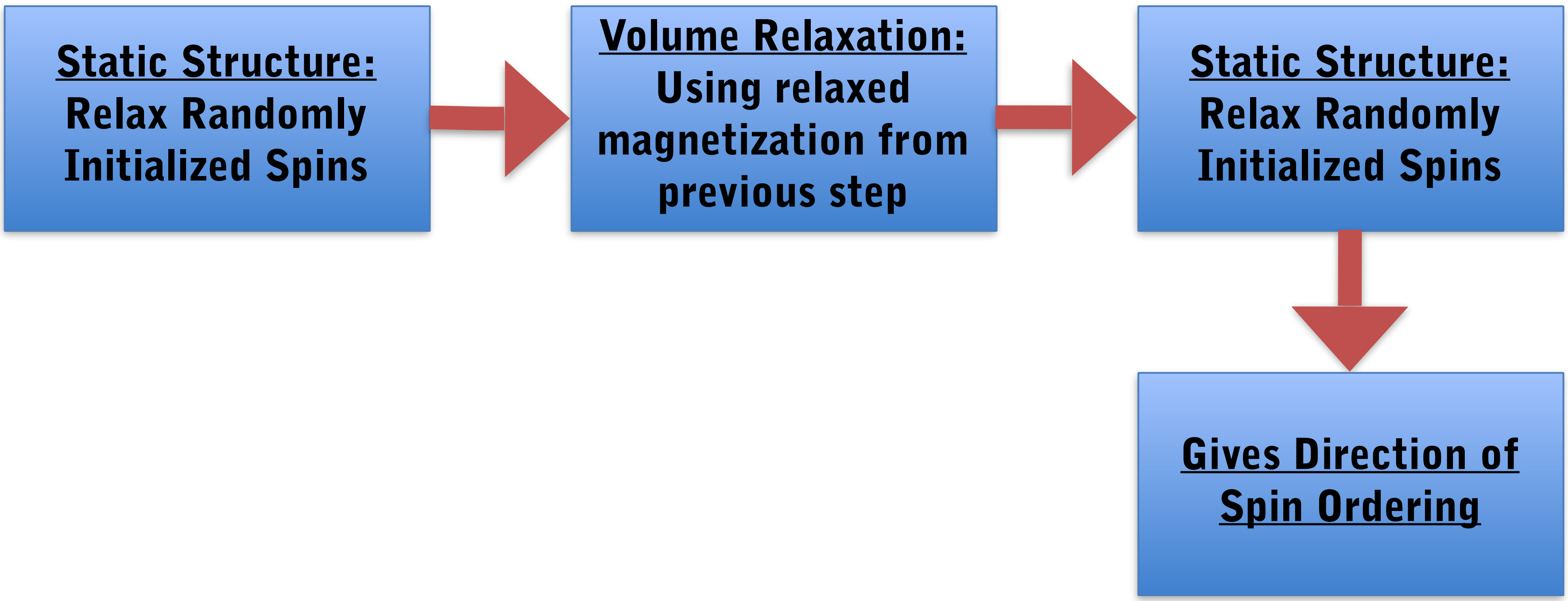
- GGA – PBE w/ PAW potentials
- Plane wave cutoff: 450 eV
- k-point Mesh: 9 x 9 x 3 (primitive cell used)
- U_{eff} = 1.5 eV
- Spin-orbit interactions treated self-consistently
- Full geometry optimization

Run	A (Å)	B (Å)	C (Å)
Experimental	*5.912*	*8.446*	*17.836*
PBE + SOC + U	*5.9(5)*	*8.4(7)*	*17.9(7)*



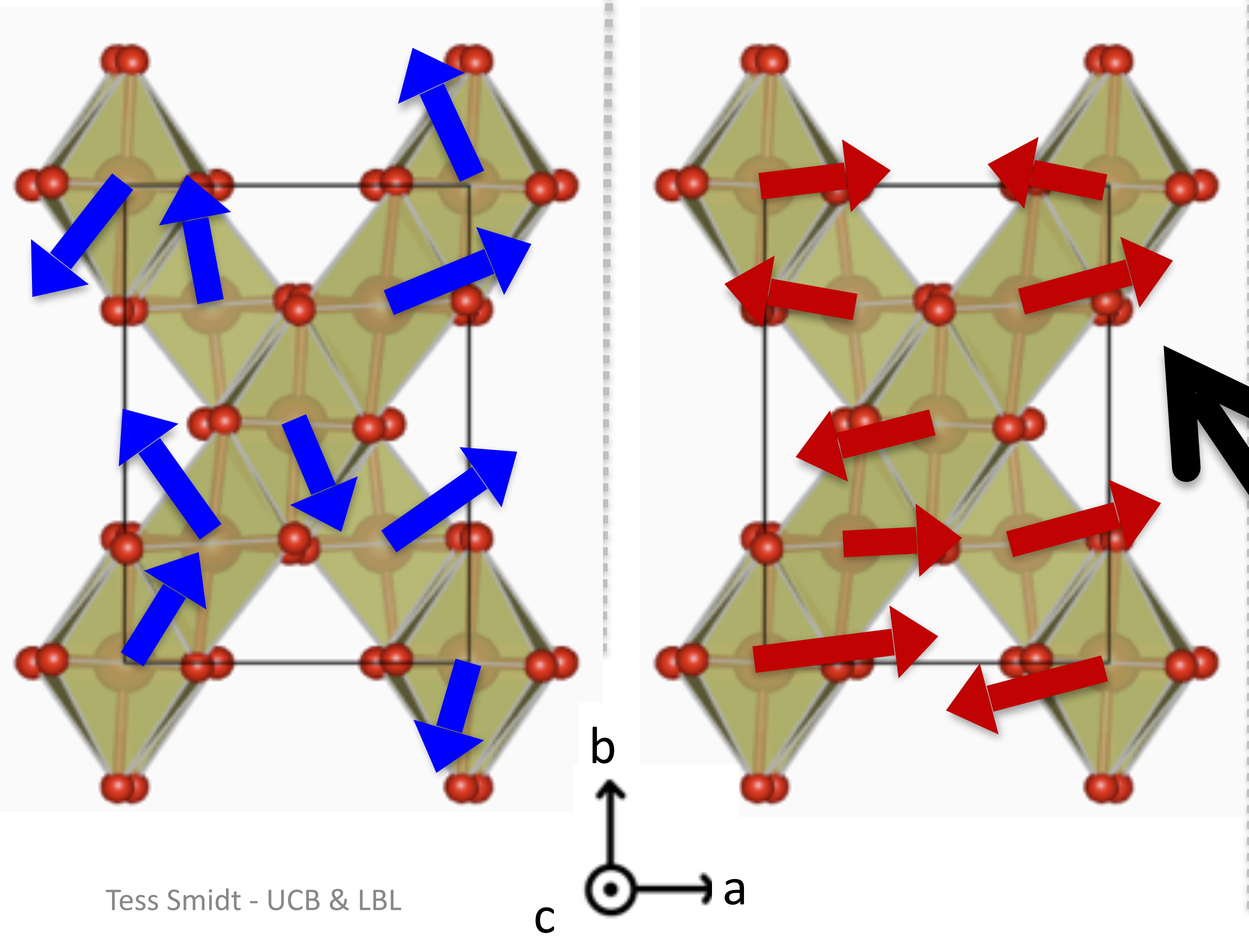
Error in lattice parameters less than 1%

Relaxing the Homologous Series



Relaxed Magnetic Structures Align in ac-plane

1. Randomly orient Ir magnetizations



Randomized magnetic structures relax prominently in ac plane – agrees with easy-plane AFM hypothesis from susceptibility.

Conclusions

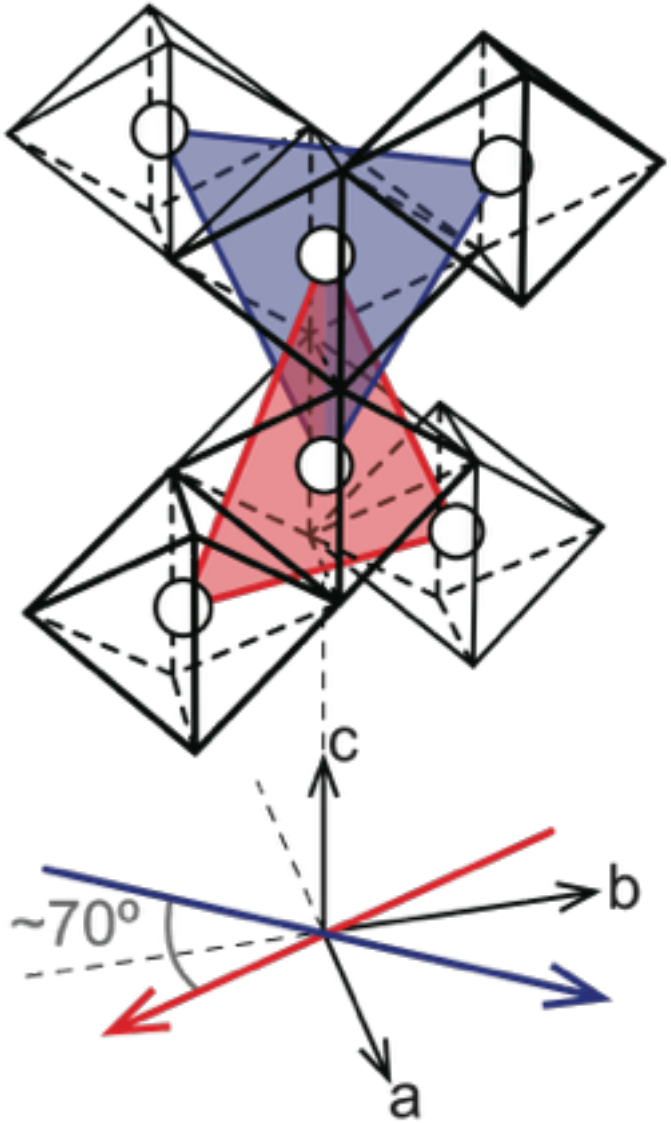
Measurements of H1-Li_2IrO_3 show evidence of strong spin-anisotropic exchange

The harmonic honeycomb family of iridates – a new series materials that may have exotic magnetism and may be candidate Kitaev materials

DFT

Backup

We understand the Anisotropy at High Temperature

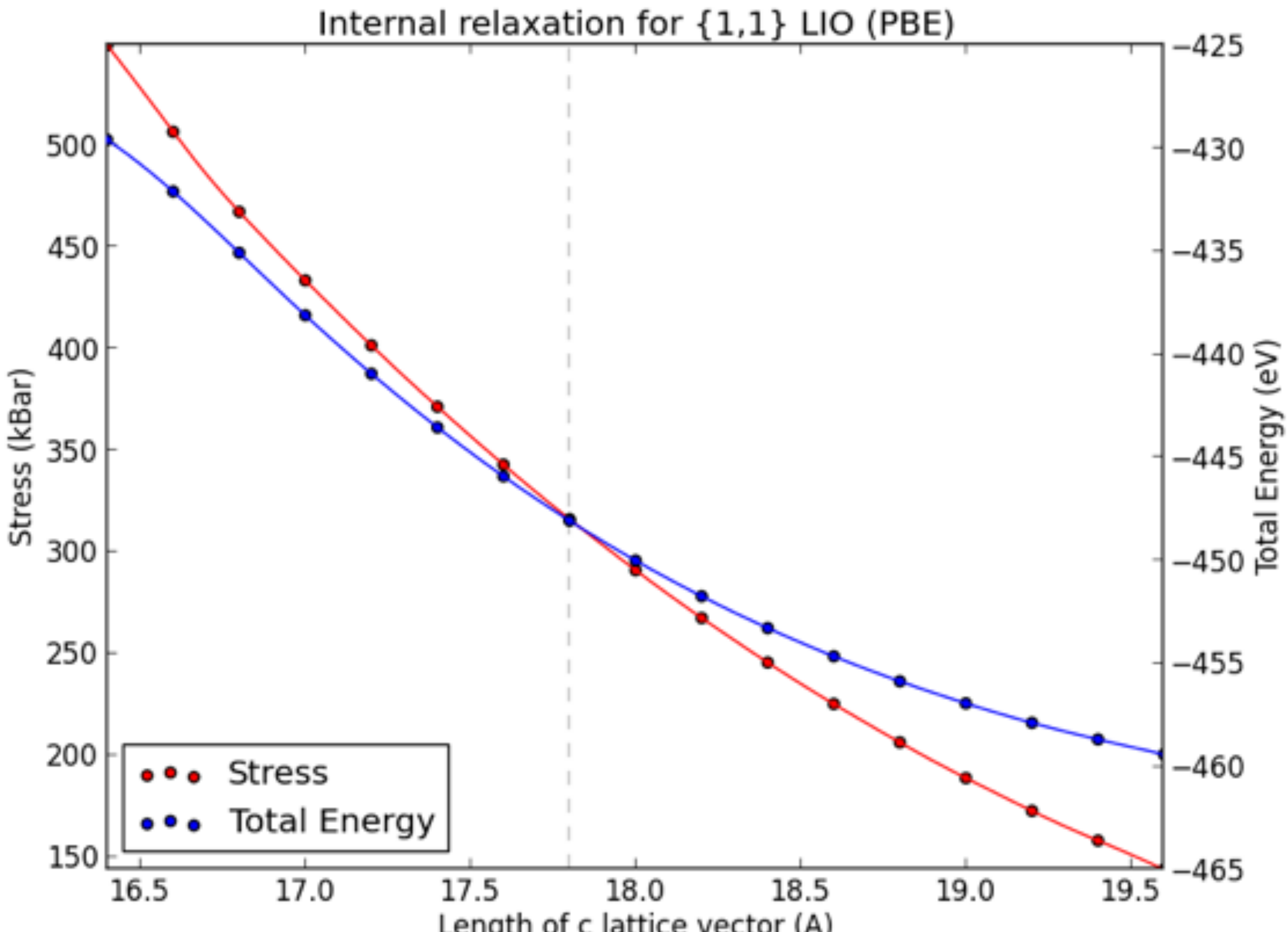


High Temperature (Infinite) Anisotropy
+ G-factor Argument

$$\chi_{\pm} = (\chi_{\parallel} \pm \chi_{\perp})/2$$

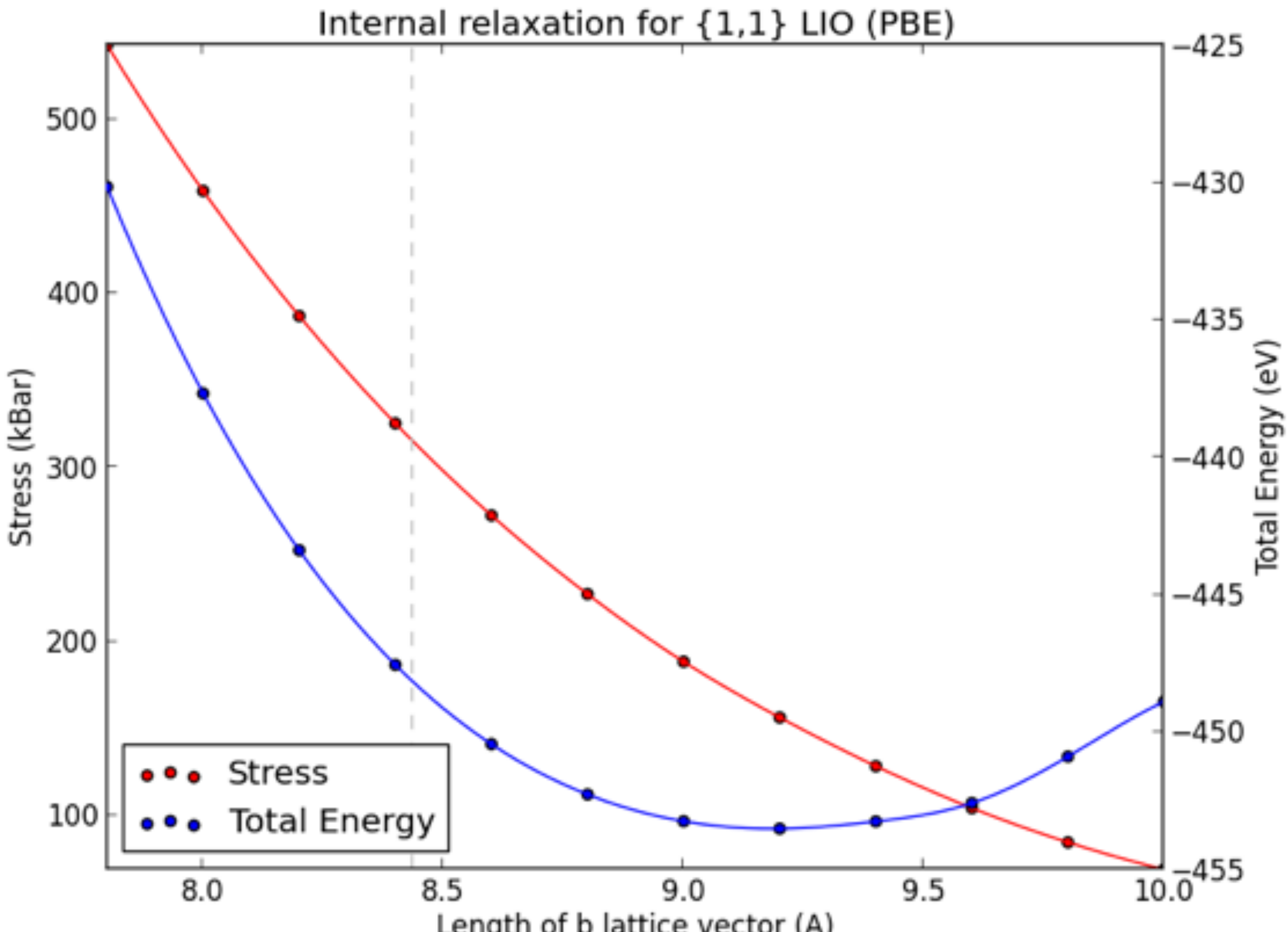
Internal relaxations with changing of one lattice parameter

PBE varying *c*



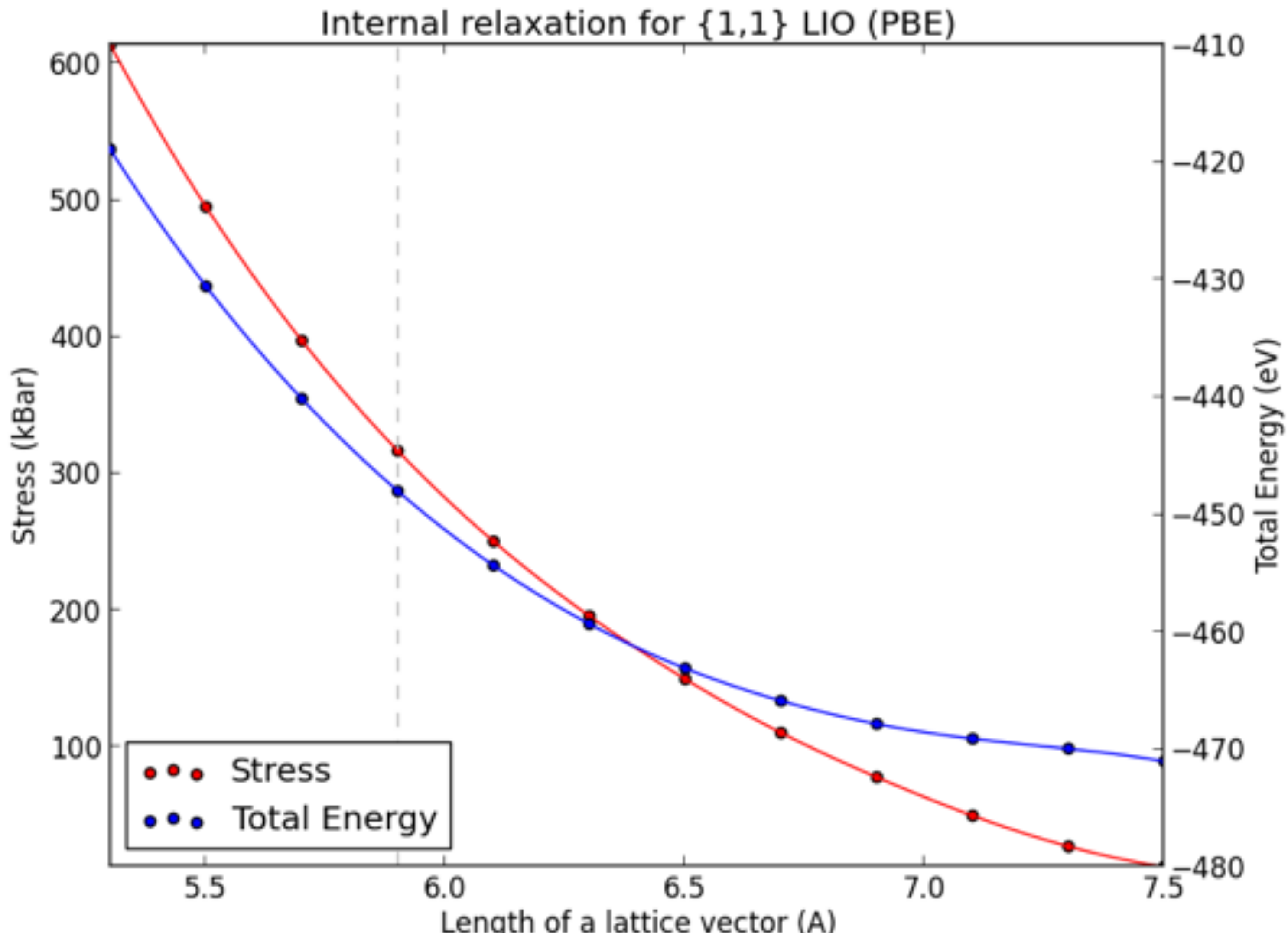
Internal relaxations with changing of one lattice parameter

PBE varying ***b***

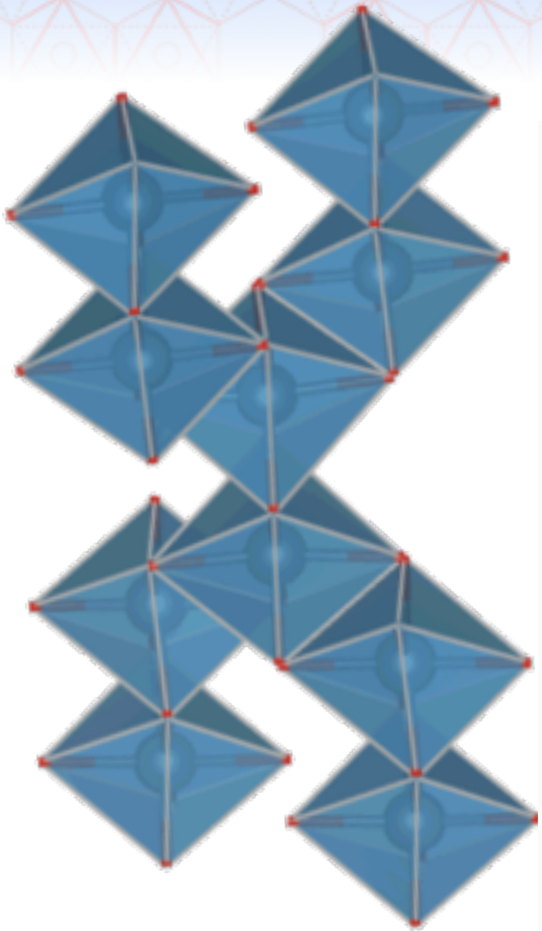


Internal relaxations with changing of one lattice parameter

PBE varying *a*

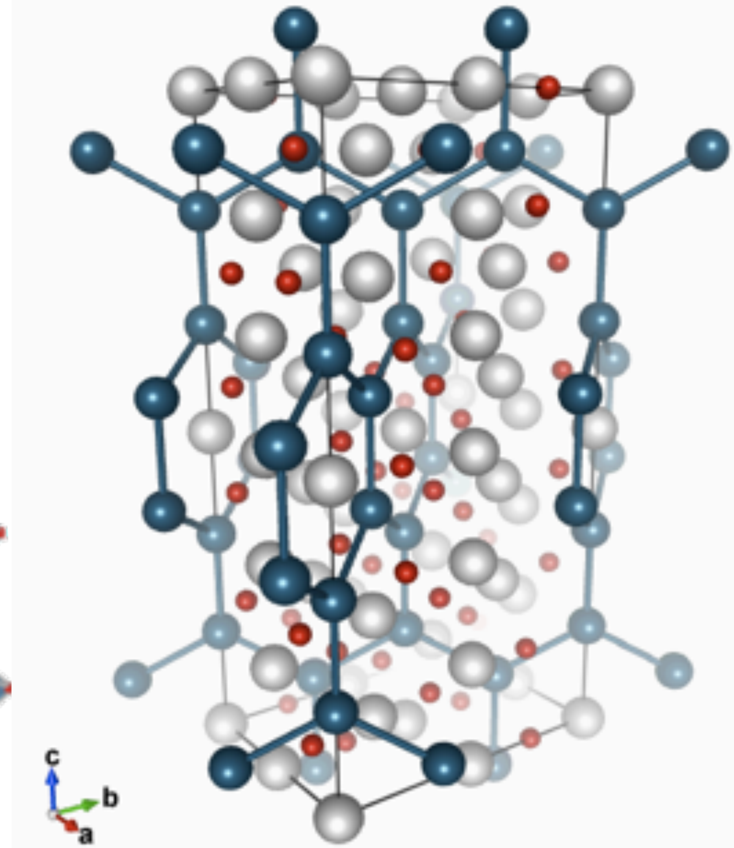


STRUCTURE: 1ST HARMONIC HONEYCOMB LITHIUM IRIDATE

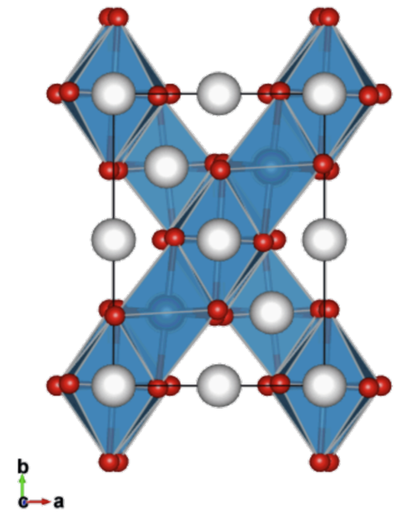


Bonds can twist out of plane

Cccm

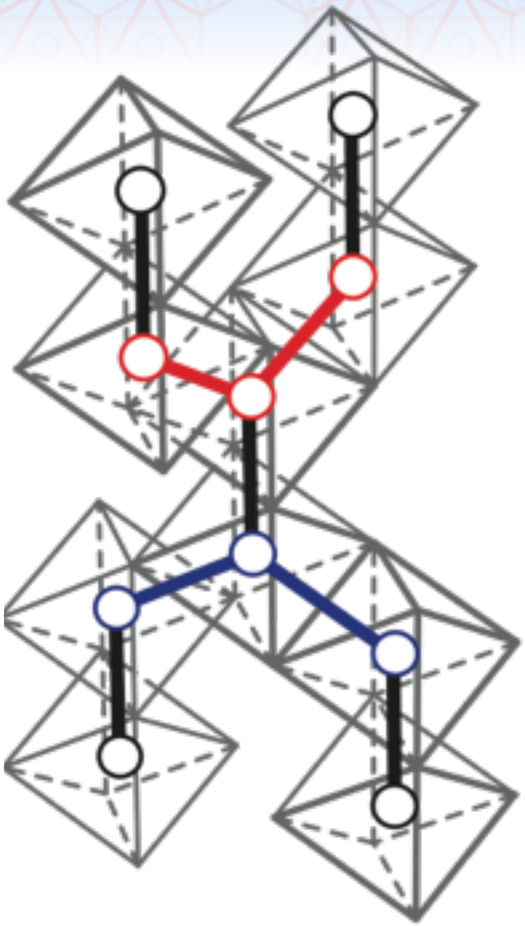


Twisting creates strips of bonded hexagons of Ir octahedra.

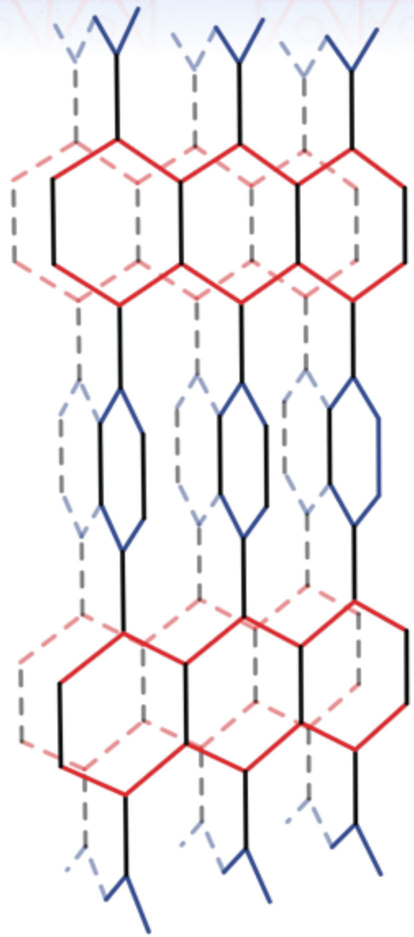


Angle created by hexagon planes visible on crystal face

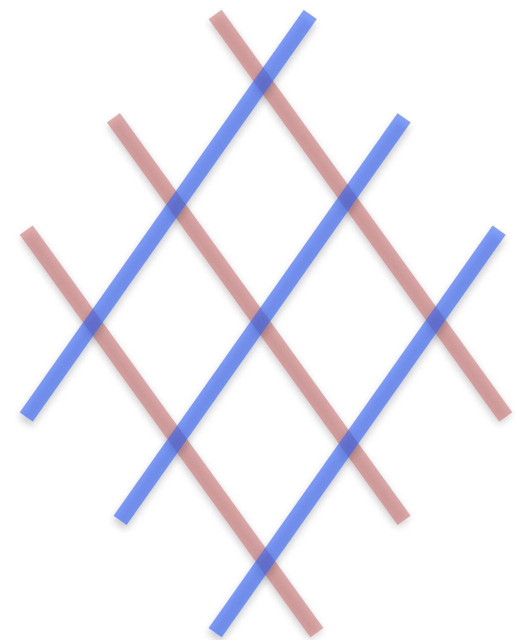
Structure: 1st Harmonic Honeycomb Lithium Iridate



Bonds can twist out of plane



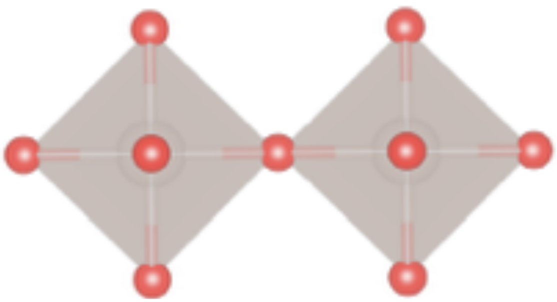
Twisting creates strips of bonded hexagons of Ir octahedra.

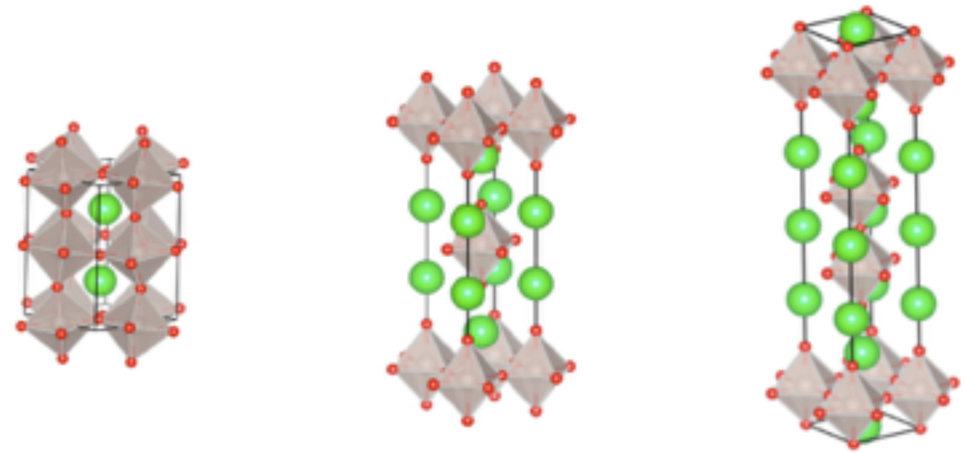


Angle created by hexagon planes visible on crystal face

Bonding of Octahedra

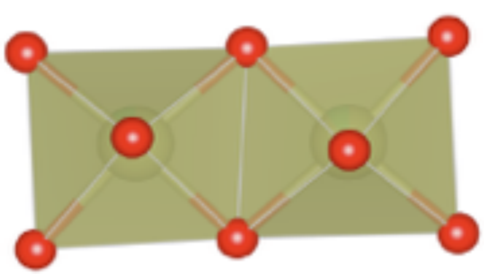
Corner-Sharing

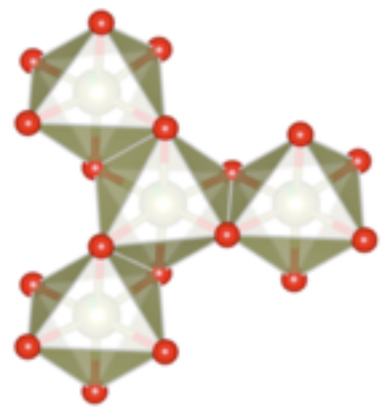




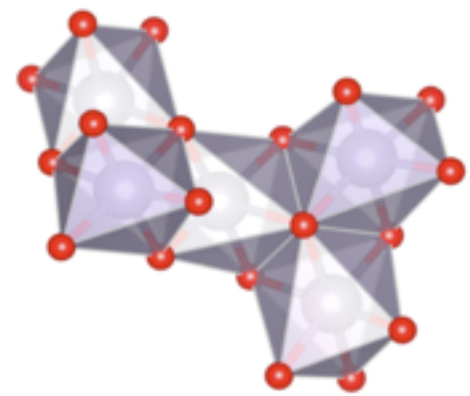
$SrIrO_3$ Sr_2IrO_4 $Sr_3Ir_2O_7$

Edge-Sharing





Honeycomb lattice



Hyper-Kagome lattice