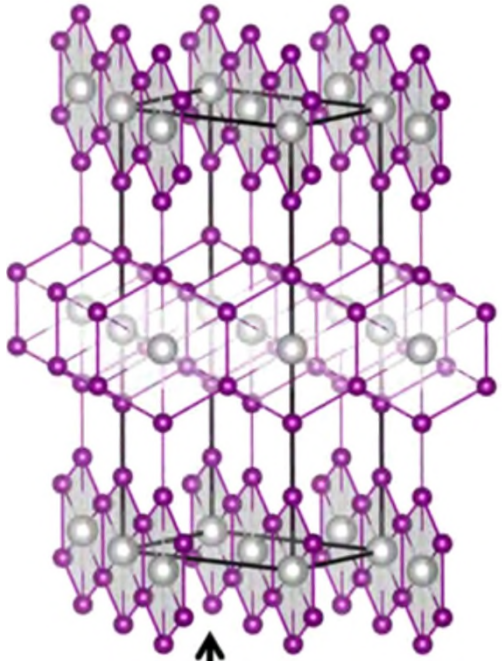
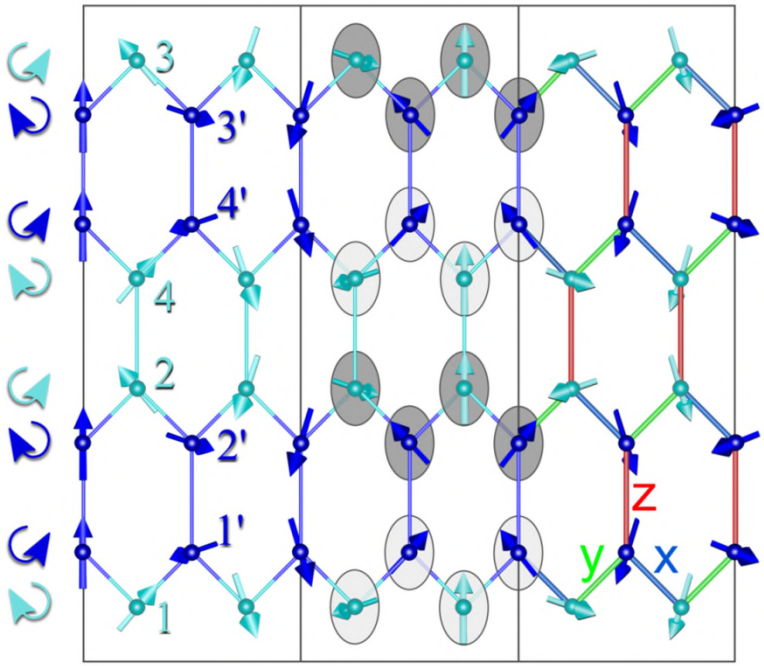
Unconventional magnetic order in 3D Kitaev materials revealed by resonant x-ray diffraction

Radu Coldea

Oxford





Collaborators

Alun Biffin (Oxford->PSI)

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S. Choi

P. Manuel

A. Bombardi

Sample synthesis

F. Freund, S. Manni (β-Li_2IrO_3) P. Gegenwart (Ausburg)

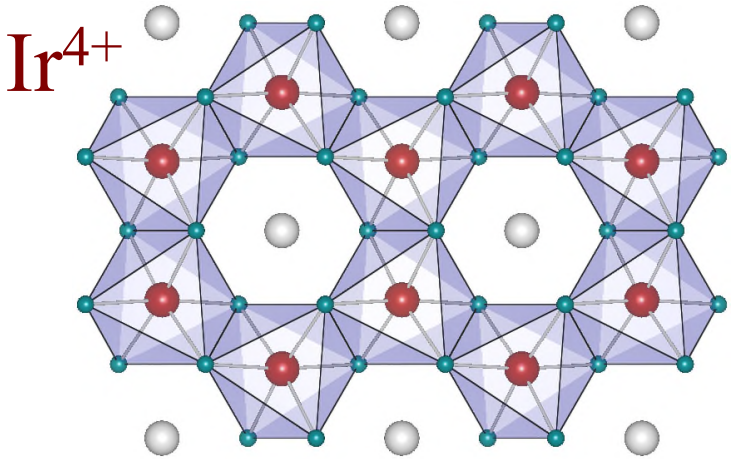
J. Analytis (γ - Li_2IrO_3) (Berkeley)

Theory

Itamar Kimchi + Ashvin Vishwanath (Berkeley)

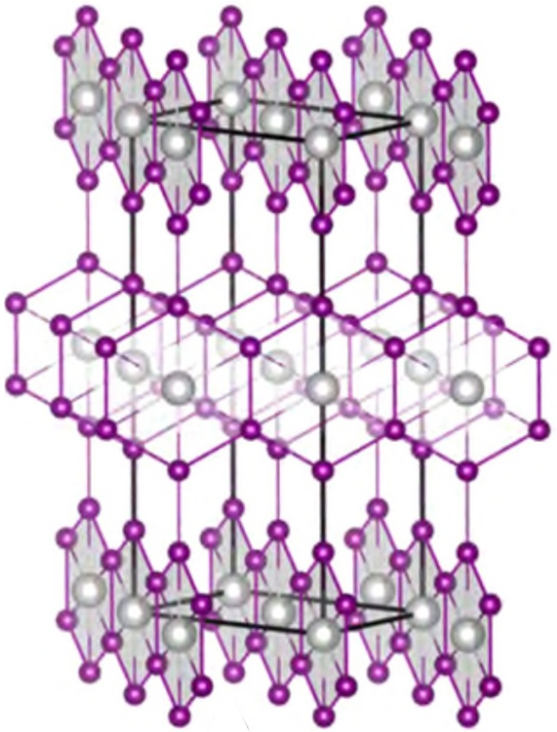
Outline

- Kitaev model on honeycomb lattice

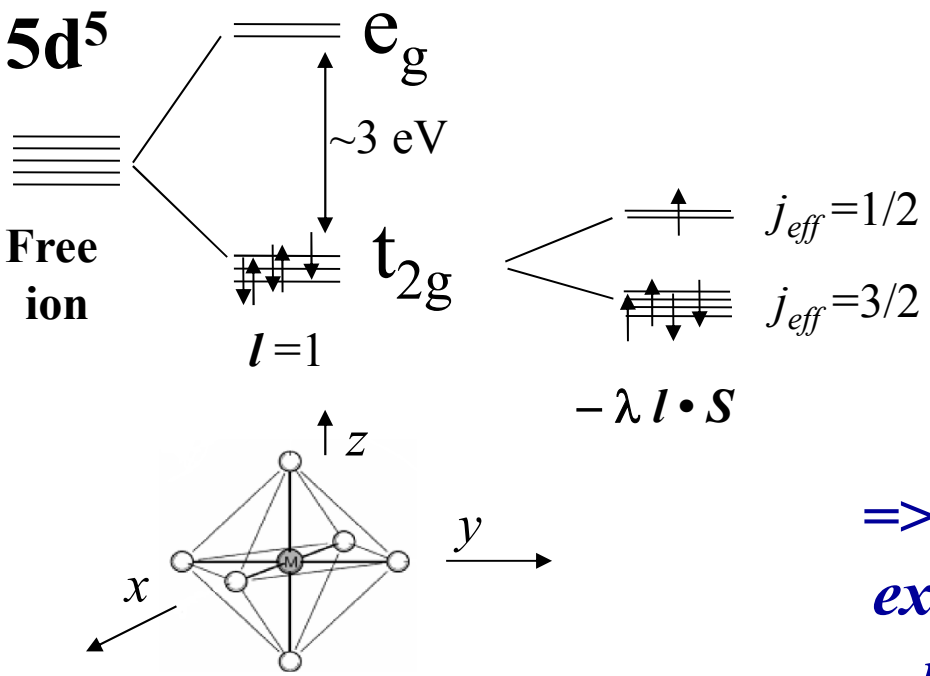


- 3D structural polytypes of Li_2IrO_3

- resonant x-ray experiments to solve the magnetic order in 3D γ- and β-Li_2IrO_3



Spin-orbit coupling in Ir^{4+} ($\lambda \sim 0.4$ eV)

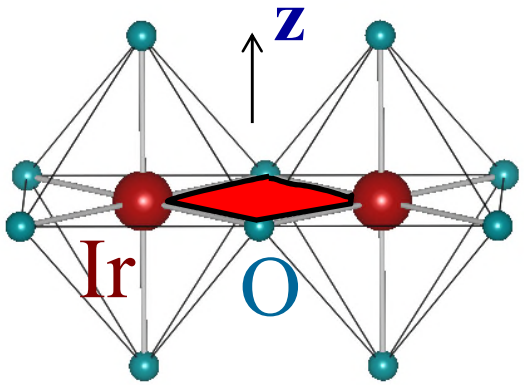


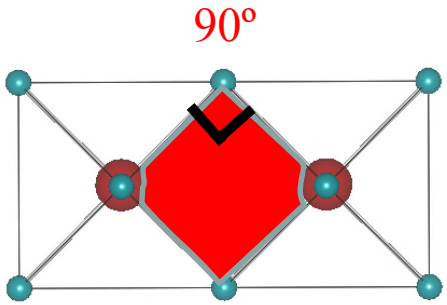
- composite spin-orbital moment

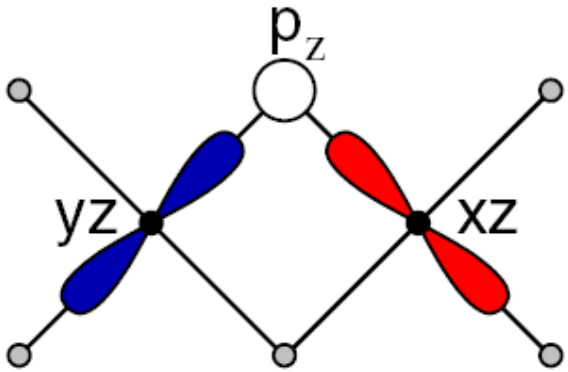
=> potentially non-Heisenberg exchanges & novel cooperative magnetism stabilized by SO coupling

Bond-directional exchange in edge-sharing IrO_6 octahedra

Jackeli, Khaliulin (2009)





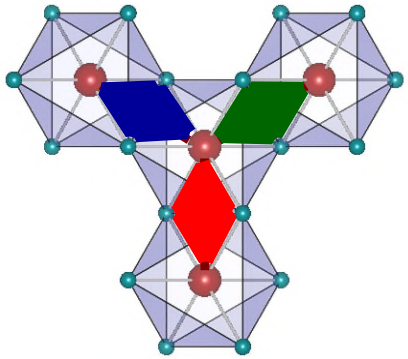


$$|j^z_{eff}=+\tfrac{1}{2}\rangle = \frac{1}{\sqrt{3}}\left(d_{xy}\uparrow + (i\,d_{xz}+d_{yz})\downarrow\right)$$

$$|j^z_{eff}=-\tfrac{1}{2}\rangle = \frac{1}{\sqrt{3}}\left(d_{xy}\downarrow + (-i\,d_{xz}+d_{yz})\downarrow\right)$$

- 90° Ir-O_2-Ir superexchange => Ising form - $K\,S_1^z S_2^z$

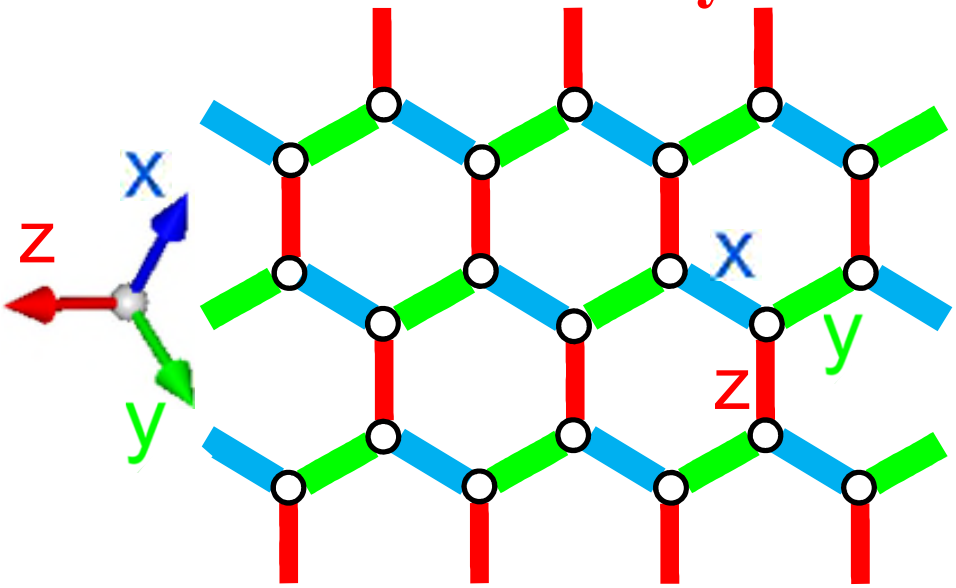
$j_{\text{eff}}=1/2$



- 3-fold coordination => orthogonal Ising axes for the 3 bonds

- frustration from bond-dependent anisotropic interactions

Kitaev model on honeycomb lattice



Kitaev (2006)

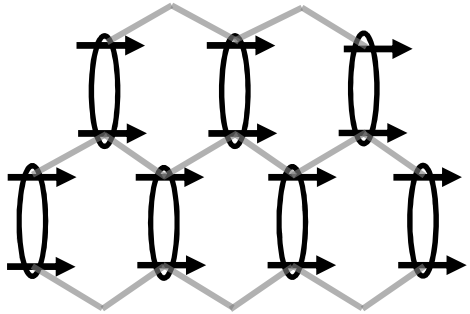
$$x\text{-bond} \quad -KS_i^x S_j^x$$

$$y\text{-bond} \quad -KS_i^y S_j^y$$

$$z\text{-bond} \quad -KS_i^z S_j^z$$

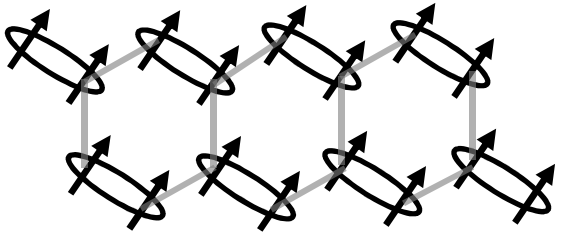
- quantum spin liquid (exactly solvable)
spinon + flux excitations

if only *z*-bonds

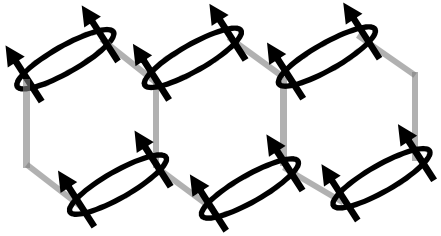


ferromagnetic dimers

if only *x*-bonds

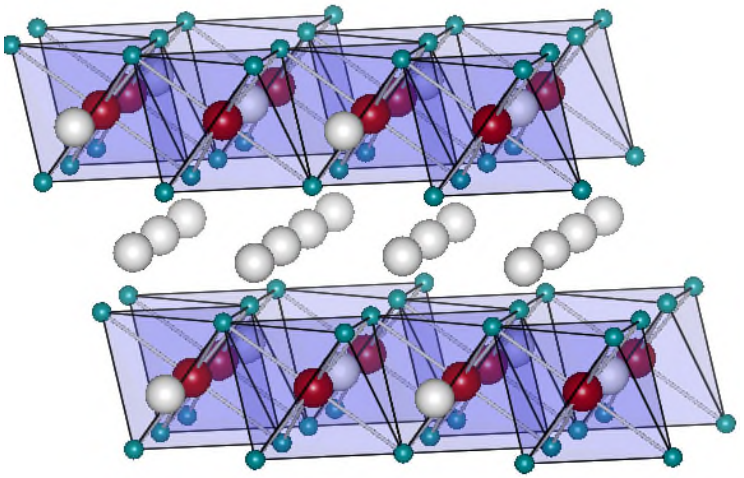


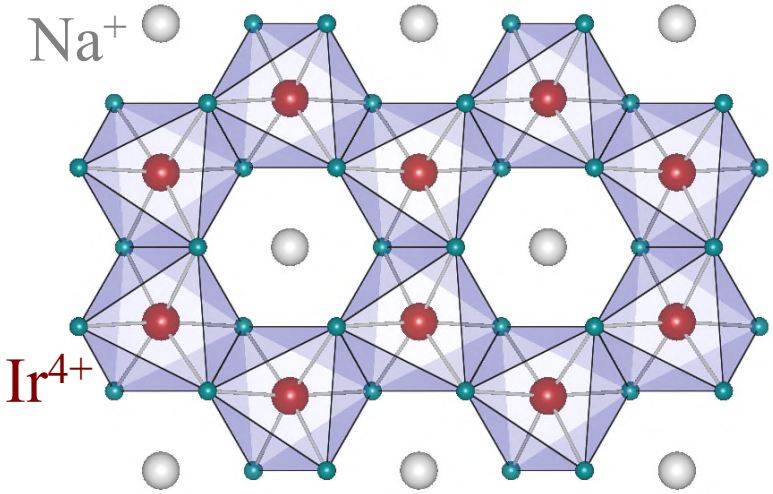
if only *y*-bonds



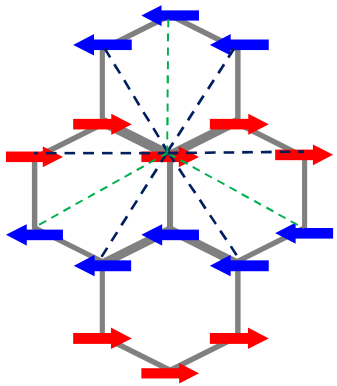
Honeycomb magnet α-Na_2IrO_3

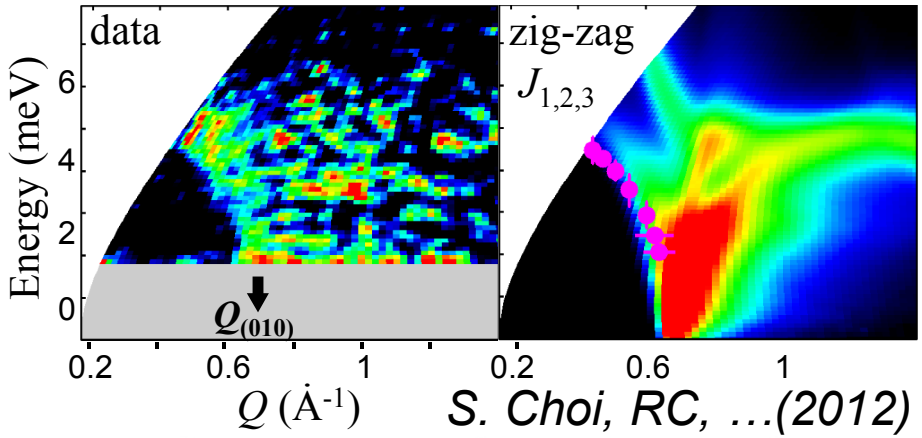
- edge-shared MO_6 octahedra
- alternating layers of hexagonal Na and honeycomb Na:Ir=1:2 layers



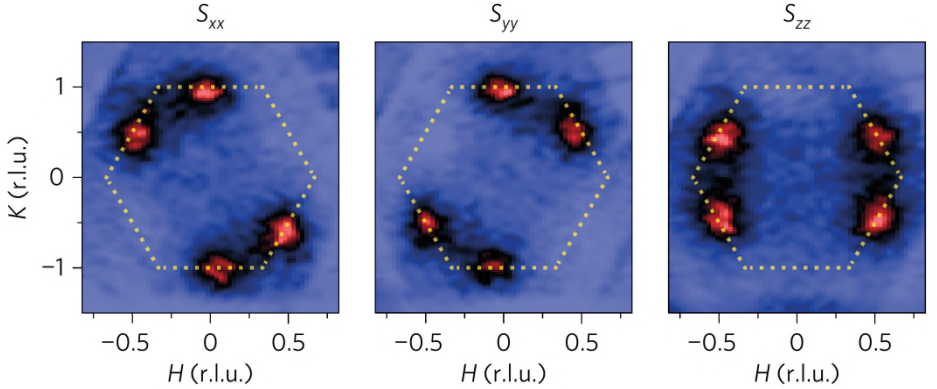


- zig-zag magnetic order



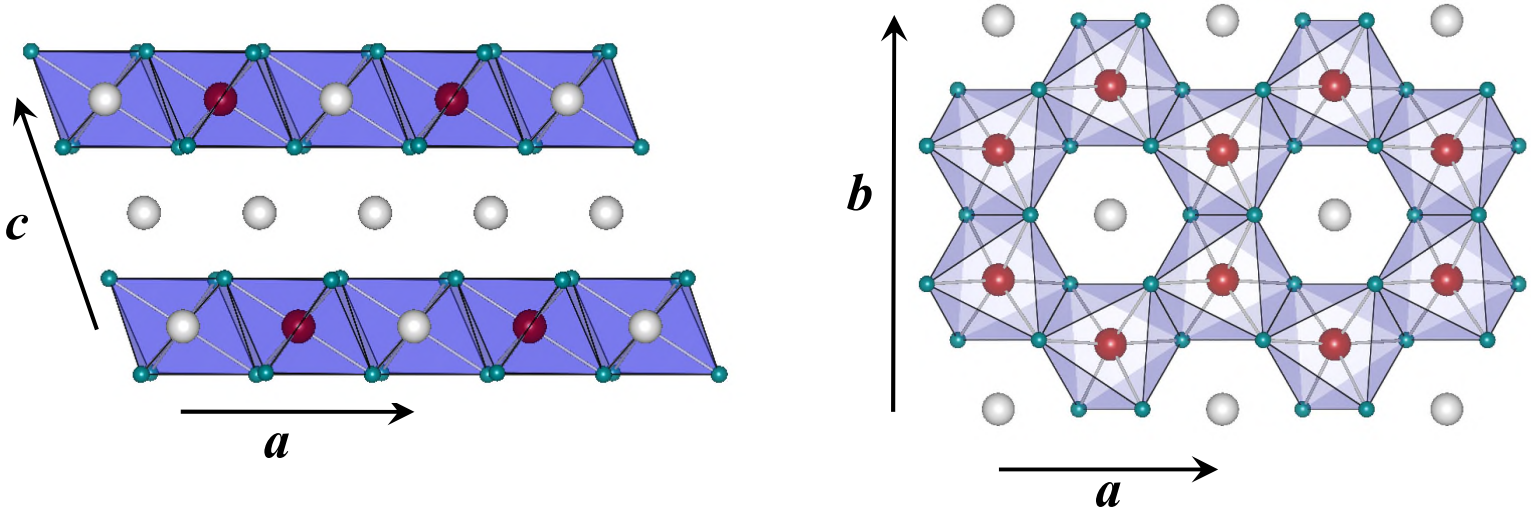


S. Choi, RC, …(2012)



BJ Kim (2015)

α-Na_2IrO_3 and α-Li_2IrO_3



r(Li^+)= 0.76 Å

r(Na^+)= 1.02 Å

r(Ir^{4+})= 0.625 Å

layered honeycomb structure, IrO_6 in planes

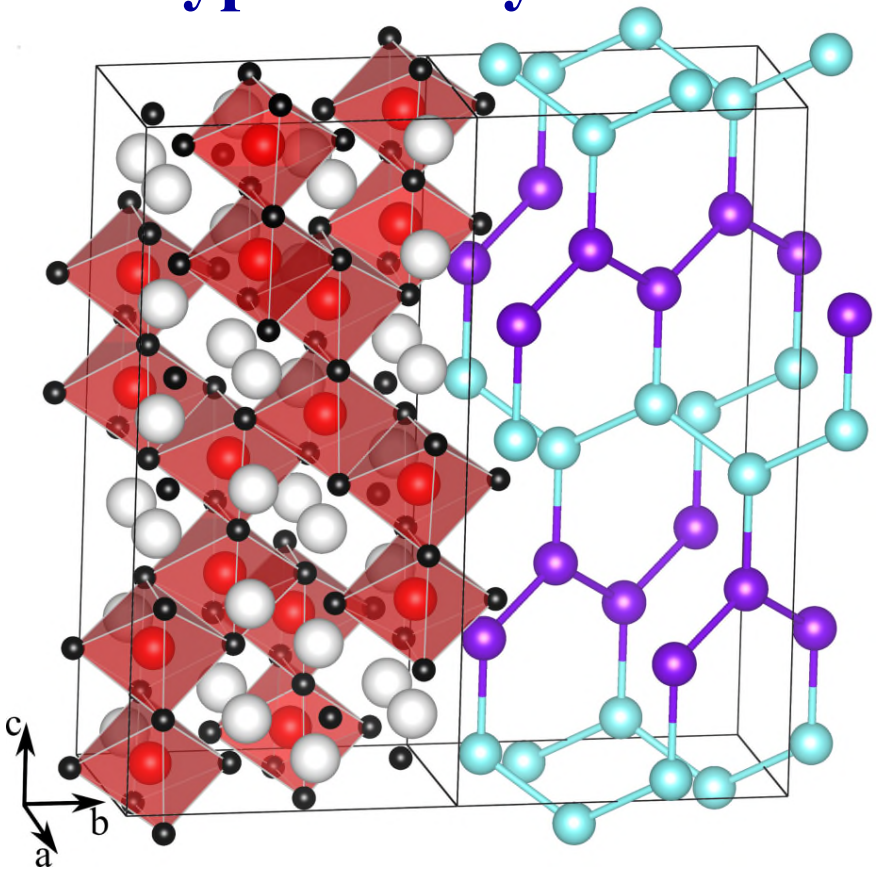
honeycomb Na_2IrO_3 a=5.427(1) Å, b=9.395(1) Å, c= 5.614(1) Å

honeycomb Li_2IrO_3 a=5.1633(2) Å, b= 8.9294(3) Å, c=5.1219(2) Å

Li^+ small, close to Ir^{4+}, IrO_6 and LiO_6 can more easily interchange

3D polytypes of β- and γ-Li_2IrO_3

hyper-honeycomb

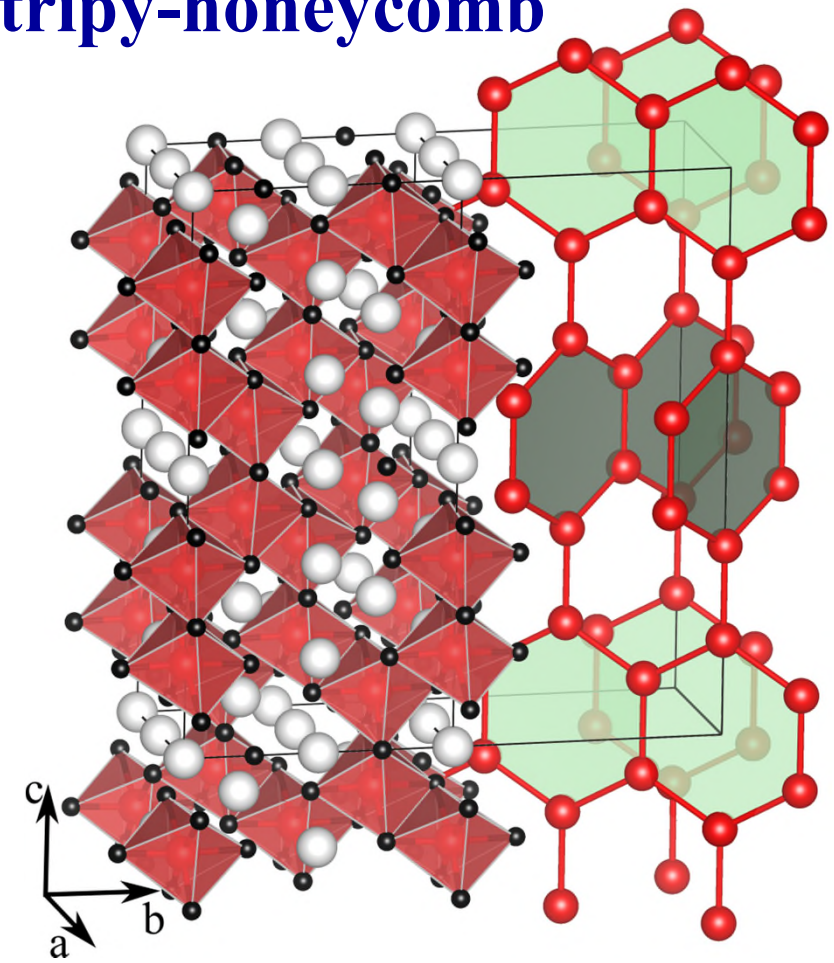


Takayama, …Takagi, arXiv:1403.3296

(Na_2PtO_3 structure type)

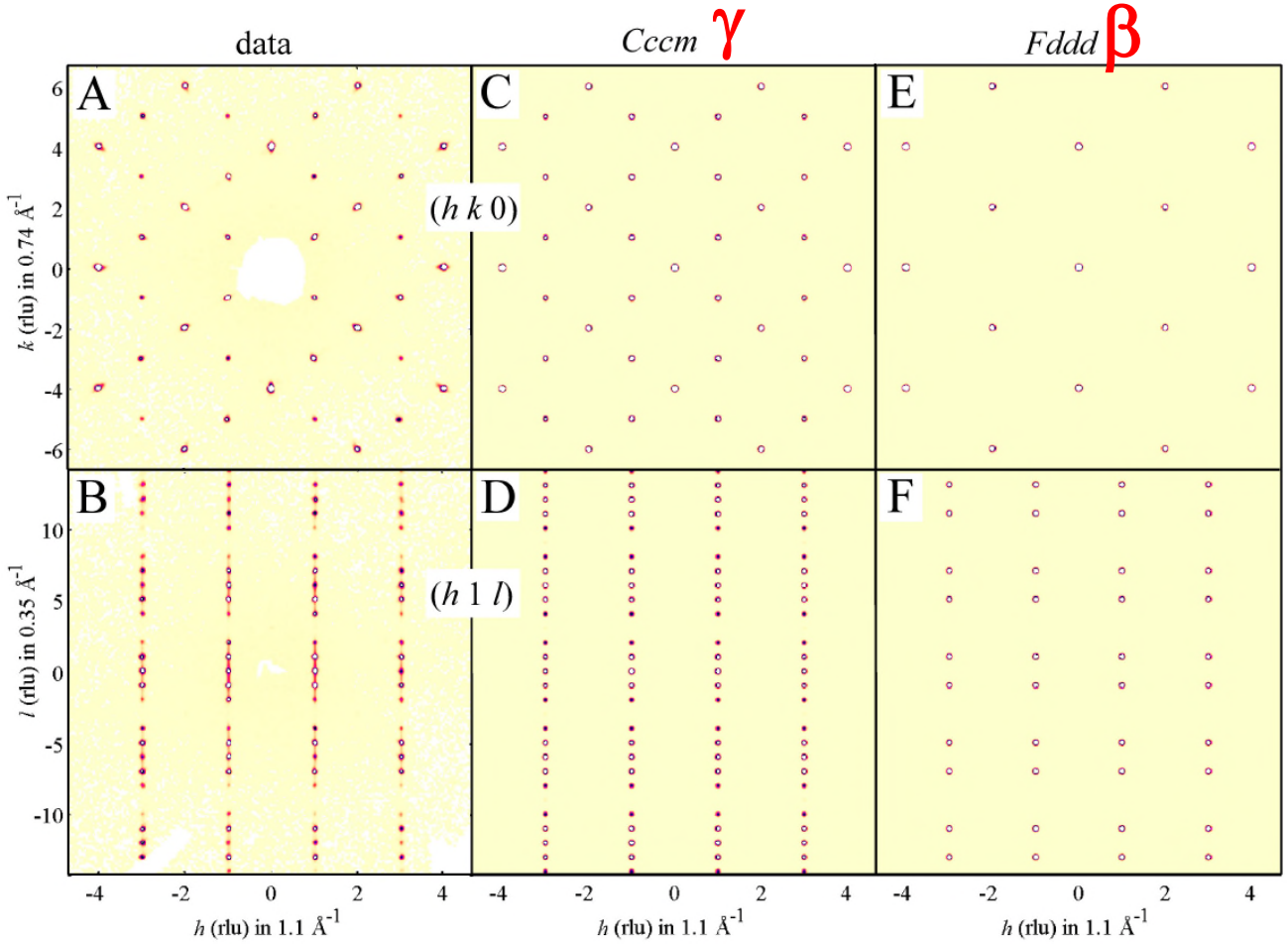
- edge-shared IrO_6 octahedra
- 3-fold coordination

stripy-honeycomb



Modic, …, RC… ,Analytis, Nature Comm. (2014)

X-ray diffraction from single crystals of γ-Li_2IrO_3



K.A. Modic et al, Nature Comm. (2014)

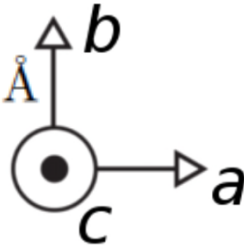
~60μm

orthorhombic

$a = 5.9119(3)$ Å,

$b = 8.4461(5)$ Å

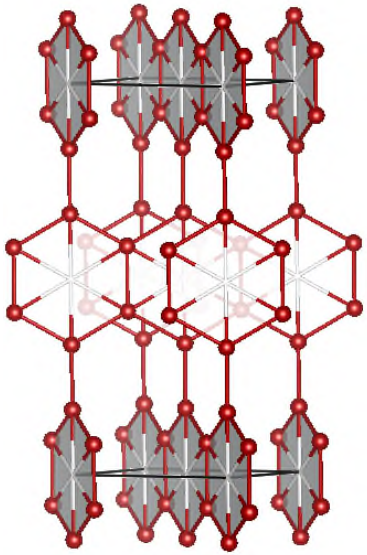
$c = 17.8363(10)$ Å



- unit cell volume = 4 x u.c. volume (*C2/m*)

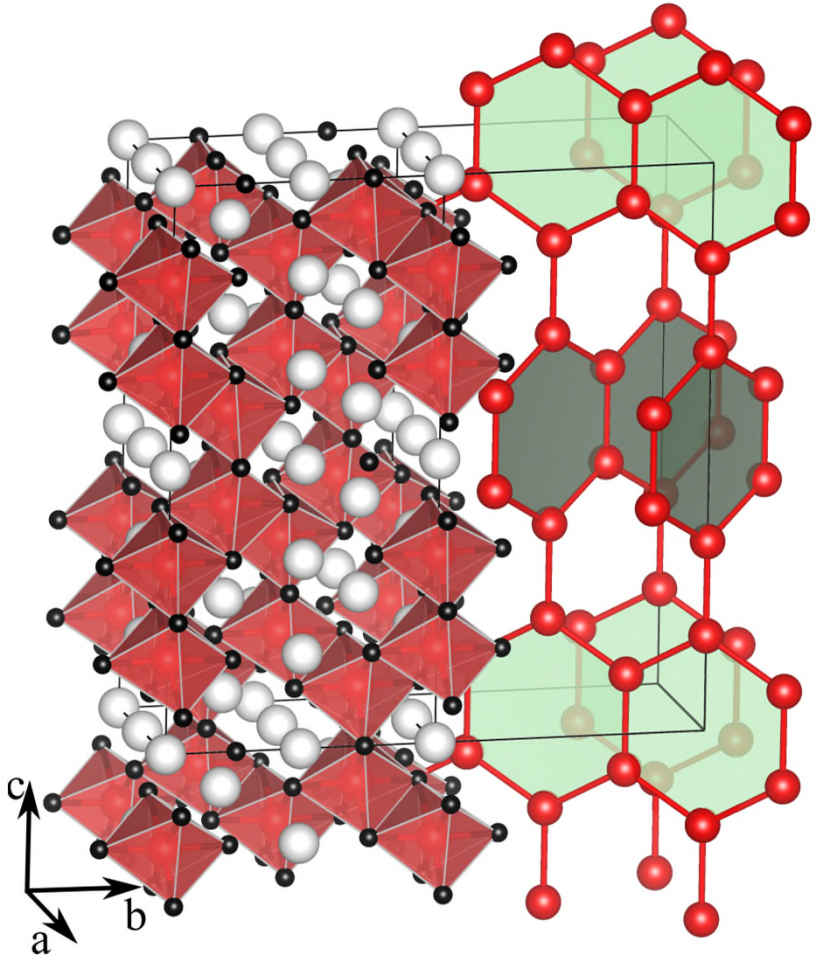
$c = 2\ b_m$

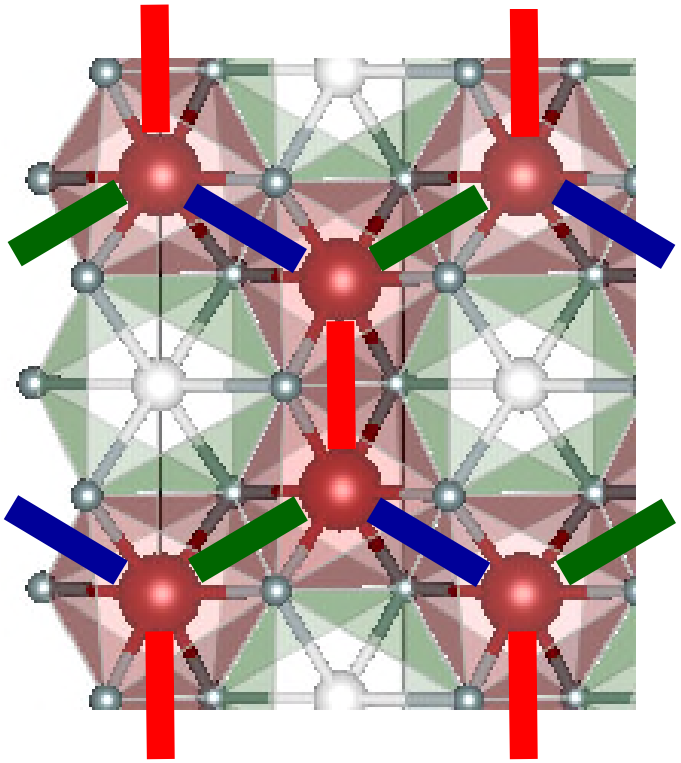
- highest-symmetry orth. space group that explains all diffraction peaks is *Cccm (#66)*



Stripyhoneycomb Kitaev lattice in γ-Li_2IrO_3

- edge-sharing IrO_6 octahedra
- 3-fold coordination



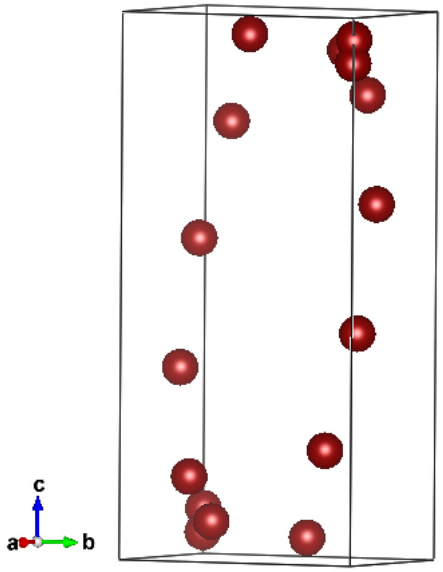


Further tests : simulated annealing fits in $P\bar{1}$

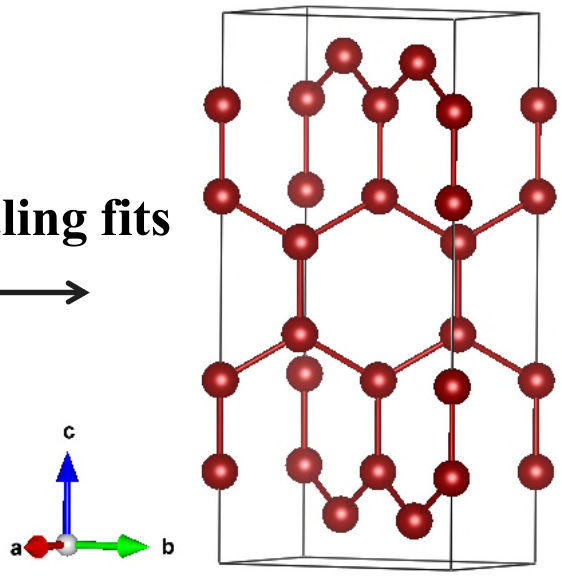
$a = 5.9119(3)$ Å, $b = 8.4461(5)$ Å, $c = 17.8363(10)$ Å

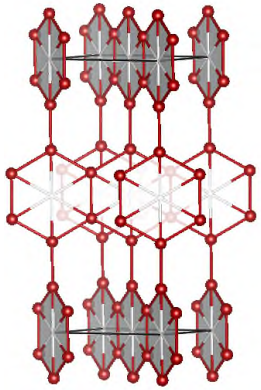
- use orthorhombic a x b x c unit cell and assume only inversion symmetry, so $P\bar{1}$
- allow 8 Ir (+ inversion images) to move anywhere in unit cell (simulated annealing fits)

- fit all diffraction peaks (without assuming any symmetry apart from Friedel pair equivalence)



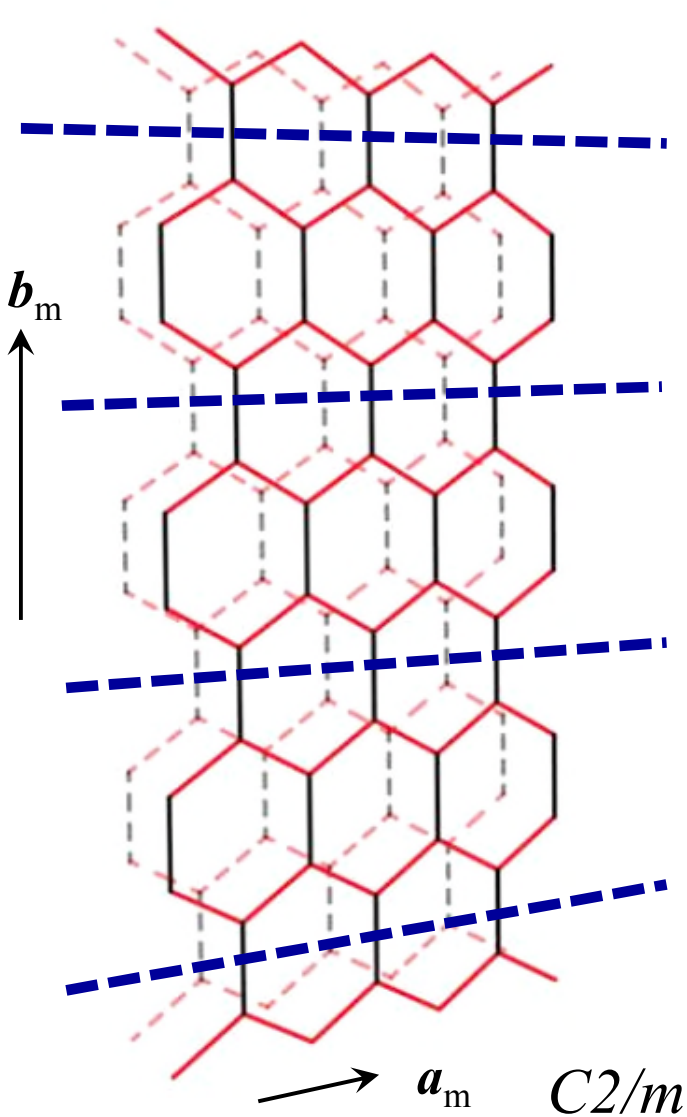
-simulated annealing fits





Ir backbone network of Cccm

from α to γ-Li_2IrO_3

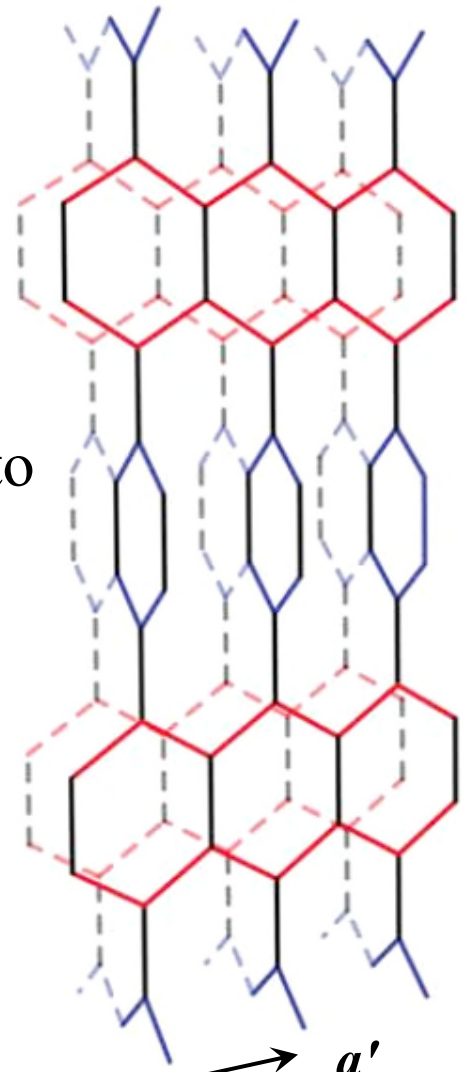


b_m

a_m

rotate every other stripe to run along *c*, not *a*

C2/m → *P2/m* primitive

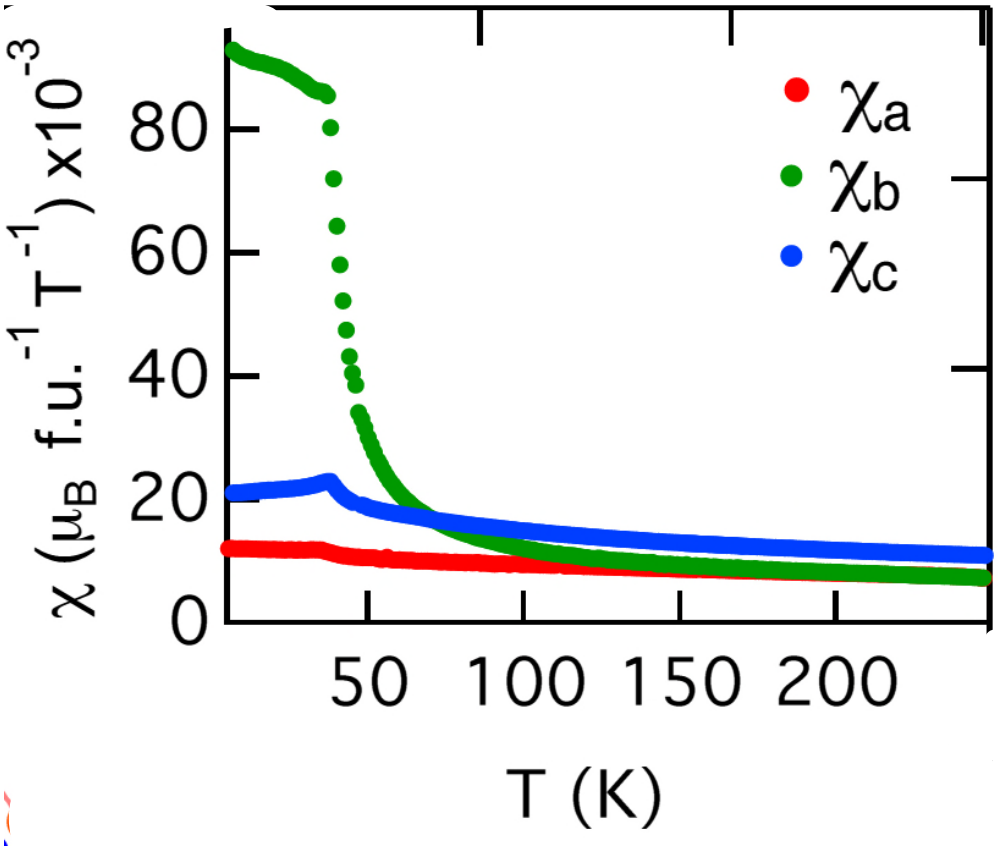


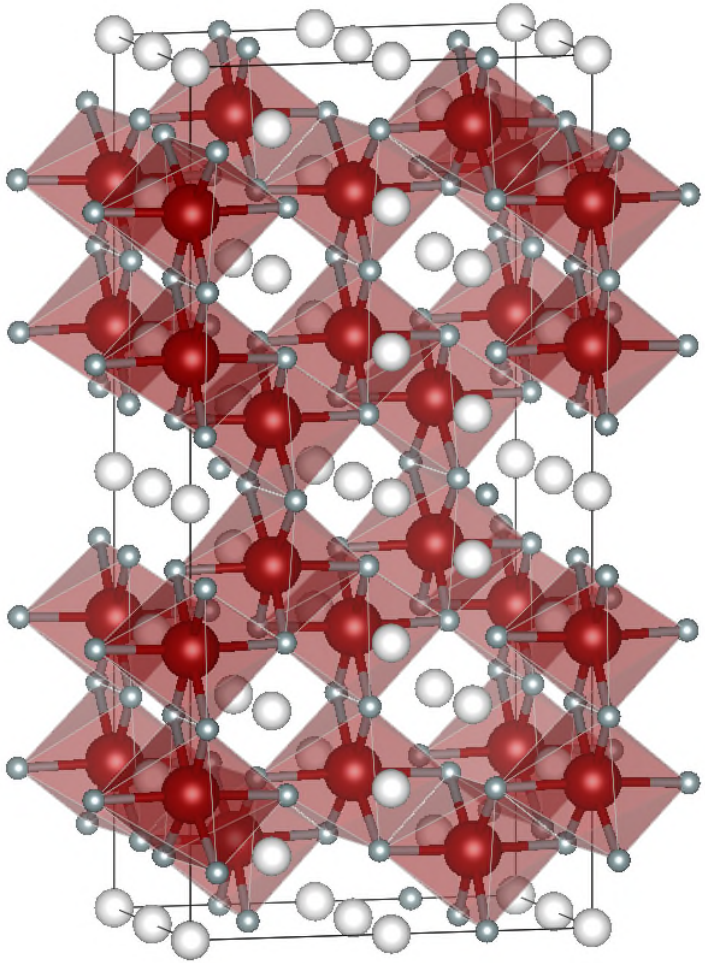
$b'=2b_m$

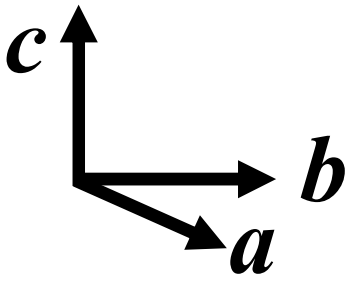
a'

a_m'=c_m' by symmetry

γ-Li_2IrO_3 - anisotropic susceptibility



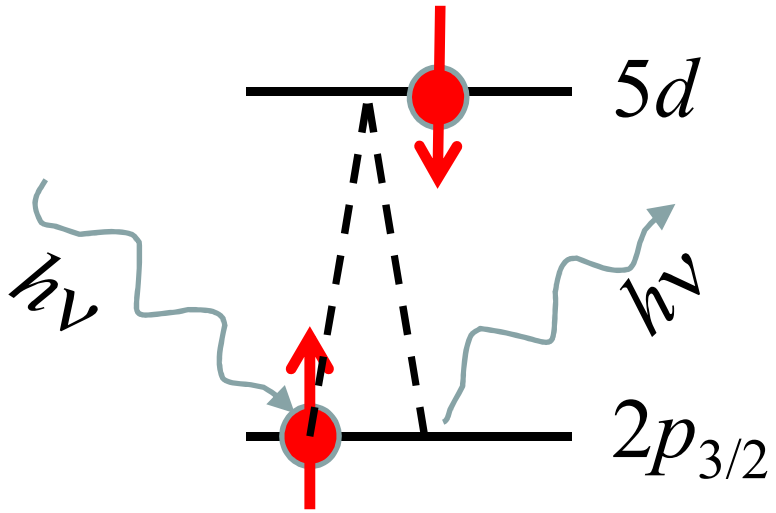


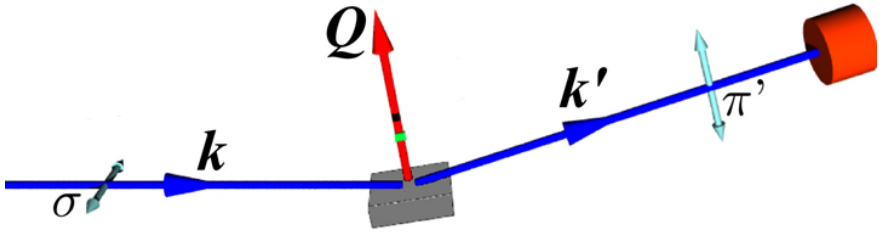


- strongly anisotropic along *a,b,c* axes, anisotropy is T-dependent, attributed to anisotropic exchanges

K.A. Modic et al, Nature Comm. (2014)

Magnetic Resonant x-ray diffraction at Ir L_3 edge

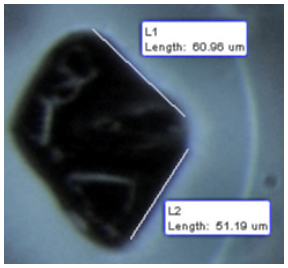


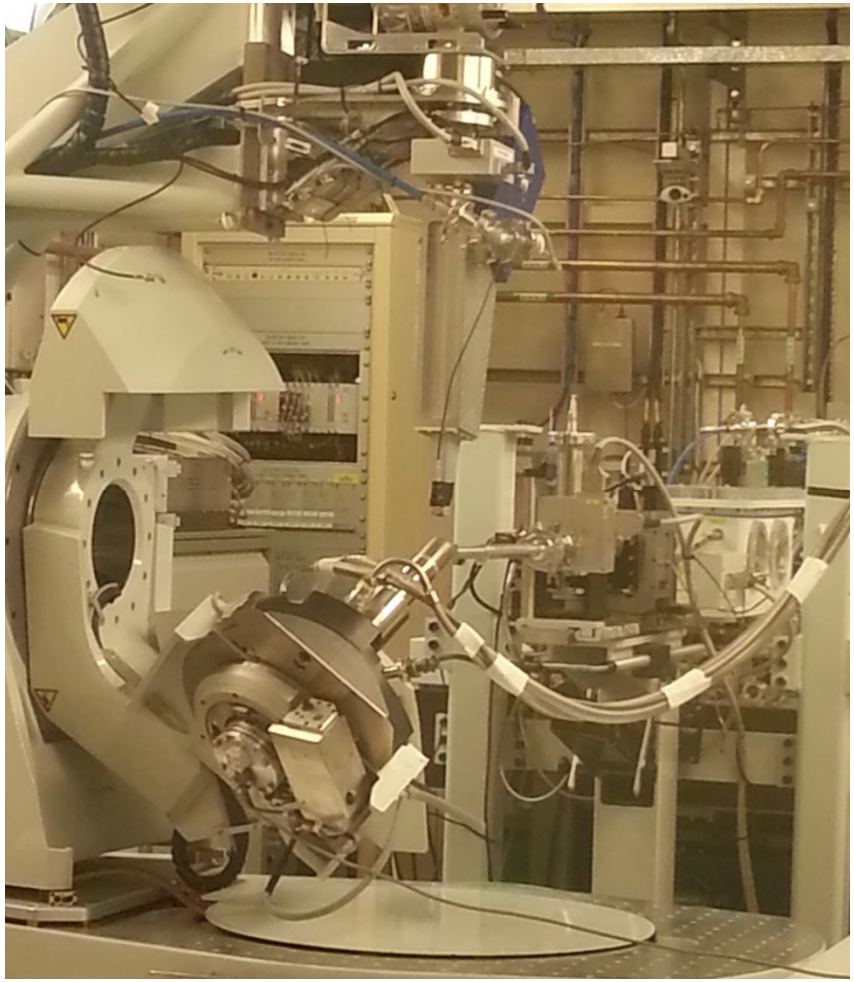


- x-ray scattering at resonance sensitive to magnetism of final state

$\phi < 60\ \mu m$

γ-Li_2IrO_3





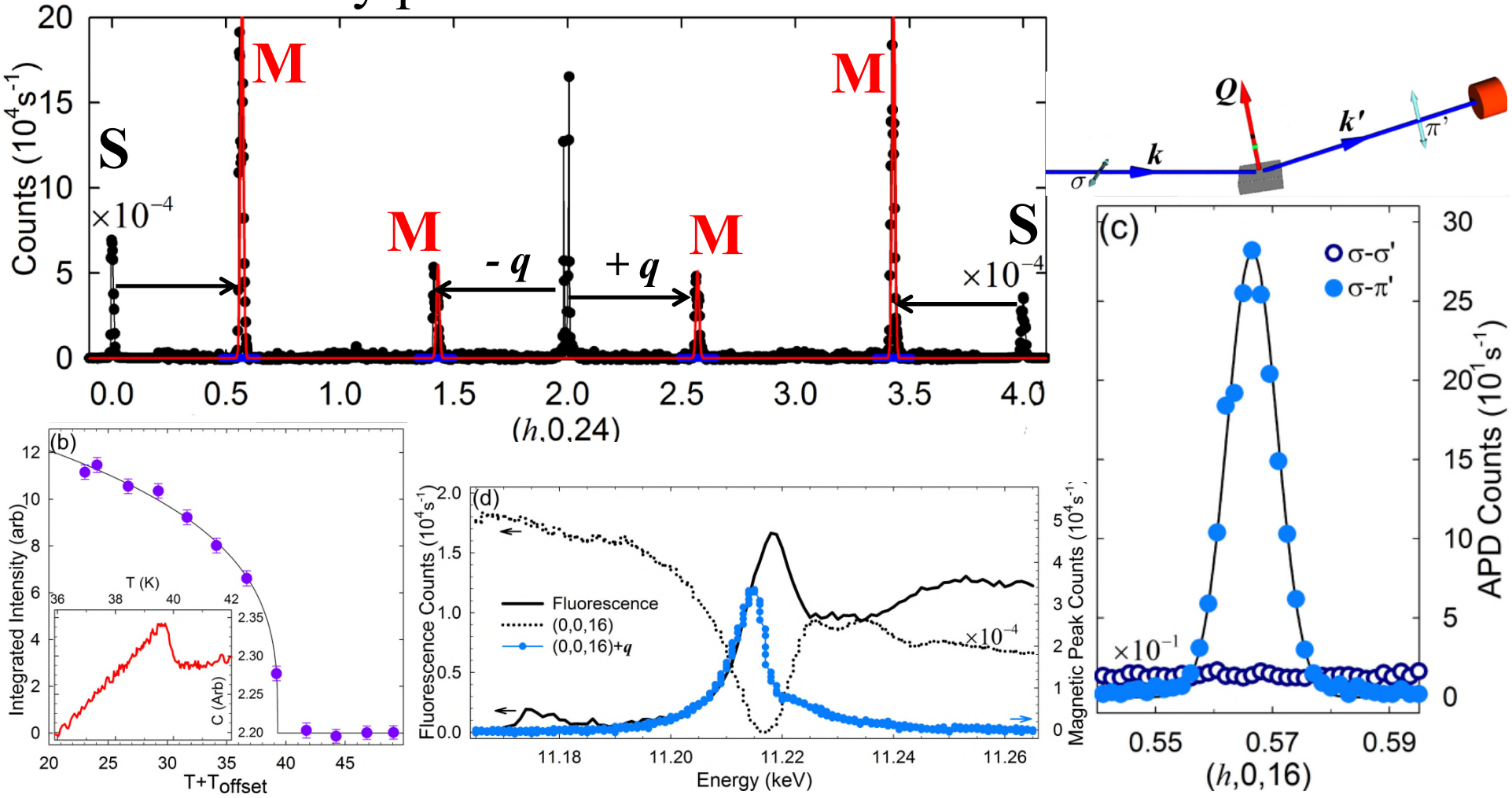
I16@ diamond

Magnetic Resonant x-ray diffraction on γ-Li_2IrO_3

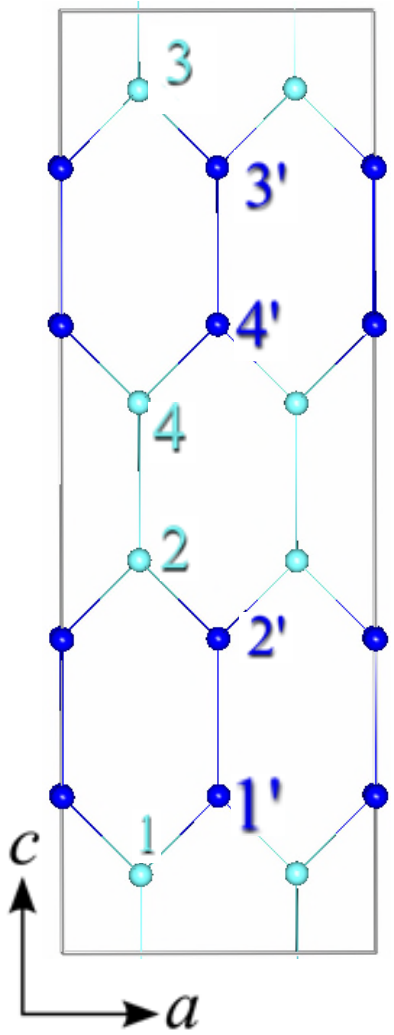
- incommensurate magnetic propagation vector

  $\boldsymbol{q}$ = (0.57(1),0,0)

- peaks go away upon heating, appear only at resonance, rotate x-ray polarization



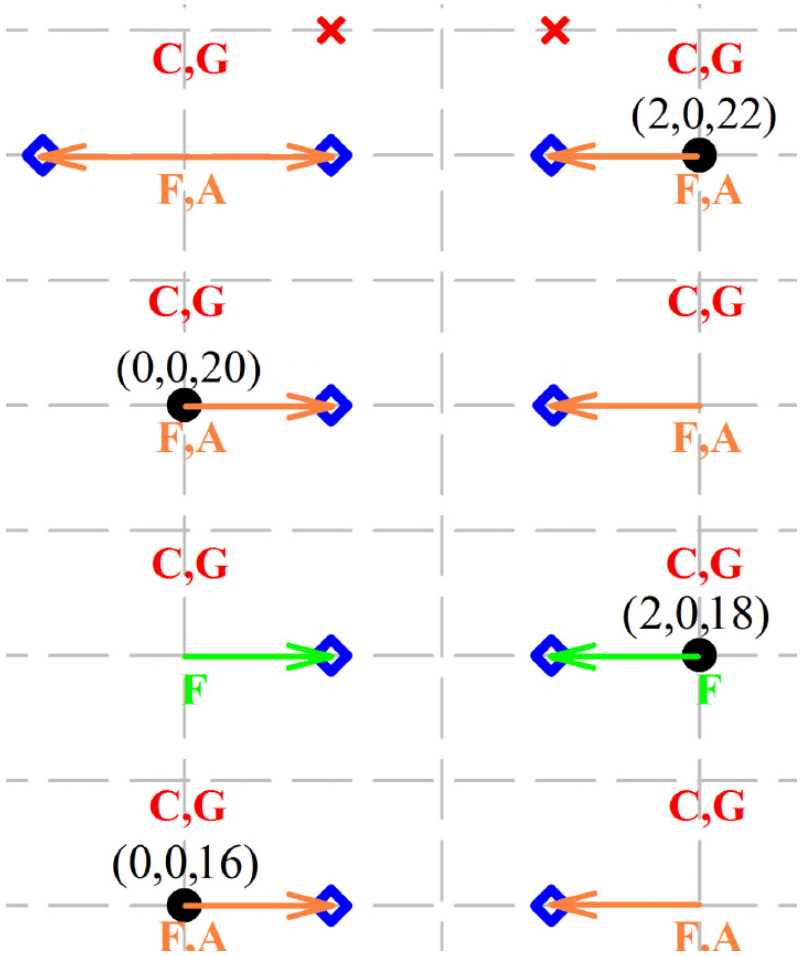
Solving the magnetic structure of γ-Li_2IrO_3



16 Ir sites/unit cell, 2 (independent) Ir sublattices
each 4 sites/primitive cell **1- 4** , **1'- 4'**

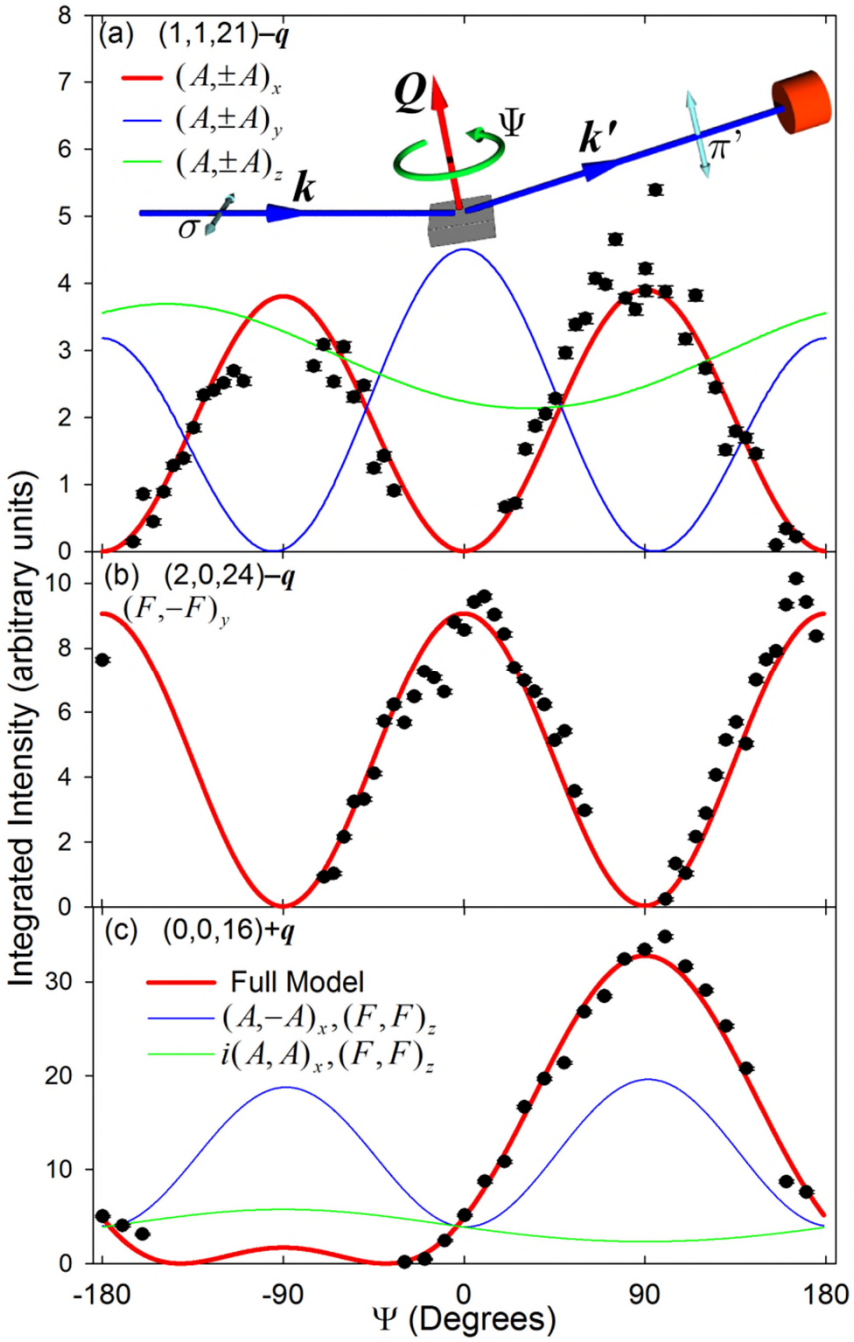
4 types of magnetic basis vectors

F ++++
C ++−−
A +−−+
G +−+−



- selection rules identify
F and **A** present

Azimuth scans on γ-Li_2IrO_3

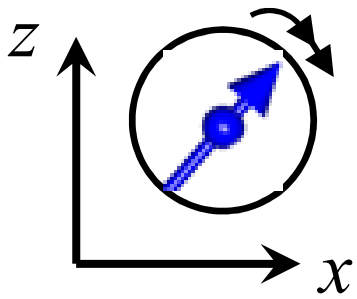


$$I \sim \left|(\hat{\epsilon}' \times \hat{\epsilon}) \cdot \boldsymbol{\mathcal{F}}(\boldsymbol{Q})\right|^2$$
$$= |\hat{\boldsymbol{k}}' \cdot \boldsymbol{\mathcal{F}}(\boldsymbol{Q})|^2 = |\mathcal{F}_{\|}|^2$$

- projection of structure factor onto scattered beam

$$M_x : M_y : M_z = 0.65(4) : 0.58(1) : 1$$

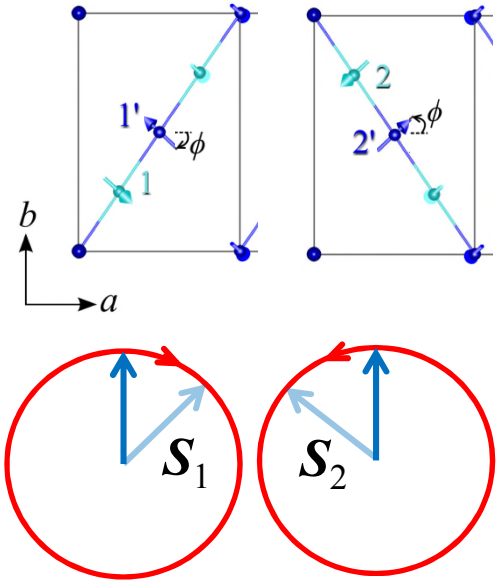
$$i(A,-A)_x, -i(F,-F)_y, (F,F)_z$$

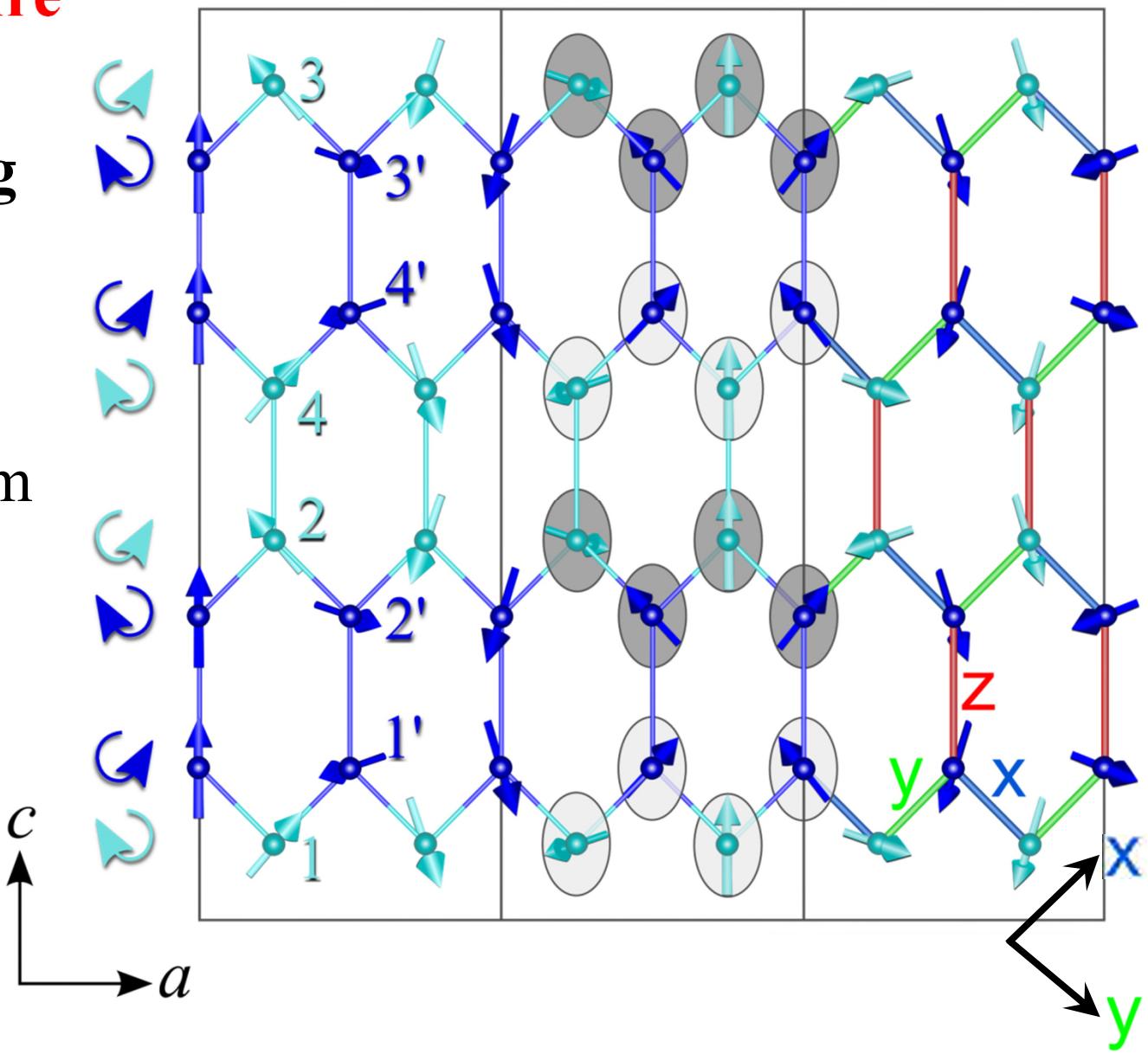


- moments rotate in a plane tilted away from the *ac* face

Magnetic structure of γ-Li_2IrO_3

- **counter-rotating** moments between every nn sites
- **non coplanar** - alternating tilt from *ac* face

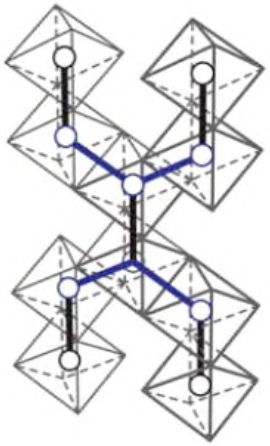




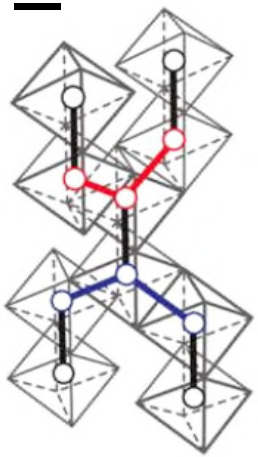
- counter-rotation -> zero energy gain for nn Heisenberg exchange $J < \boldsymbol{S}_1 \cdot \boldsymbol{S}_2 > = 0$

Family of polytypes of Li_2IrO_3

Same

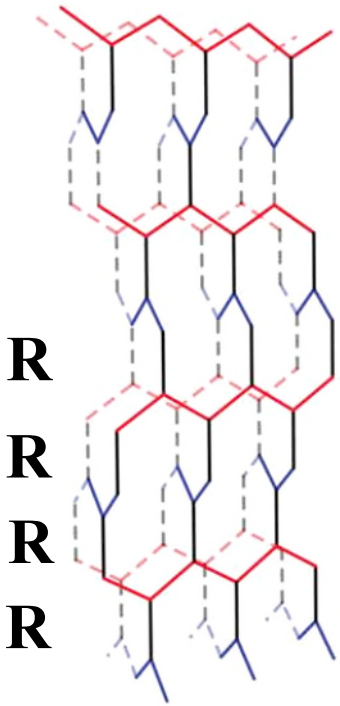


Rotate



hyper honeycomb

Fddd

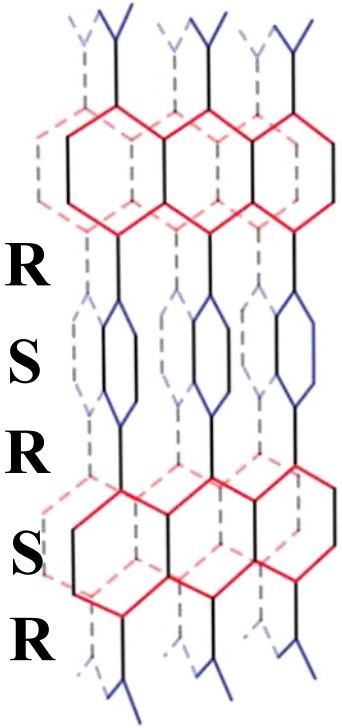


β

Takayama,…Takagi, arXiv:1403.3296

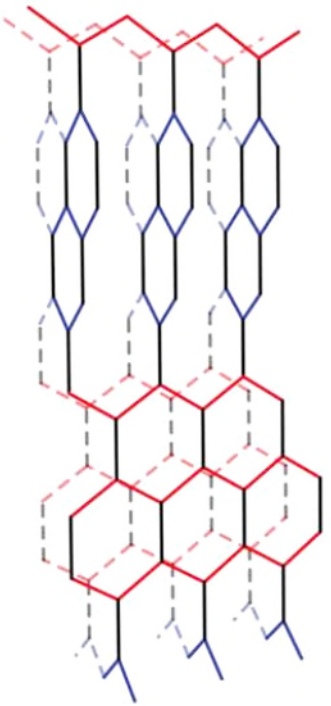
stripy honeycomb

Cccm



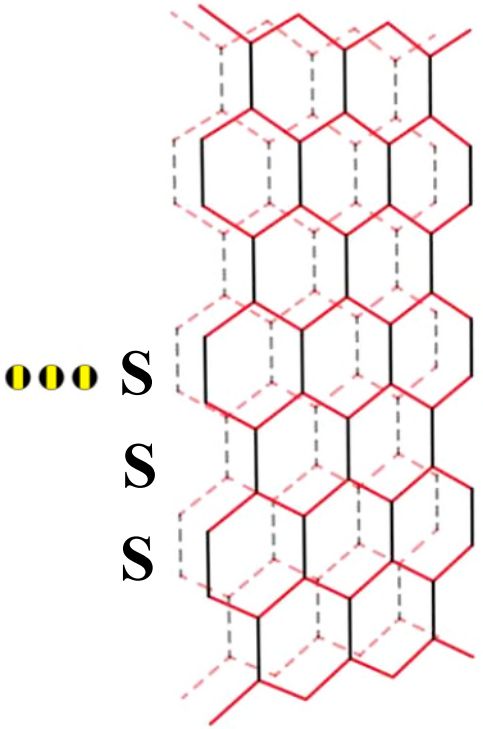
γ

K.A. Modic et al, (2014)



δ

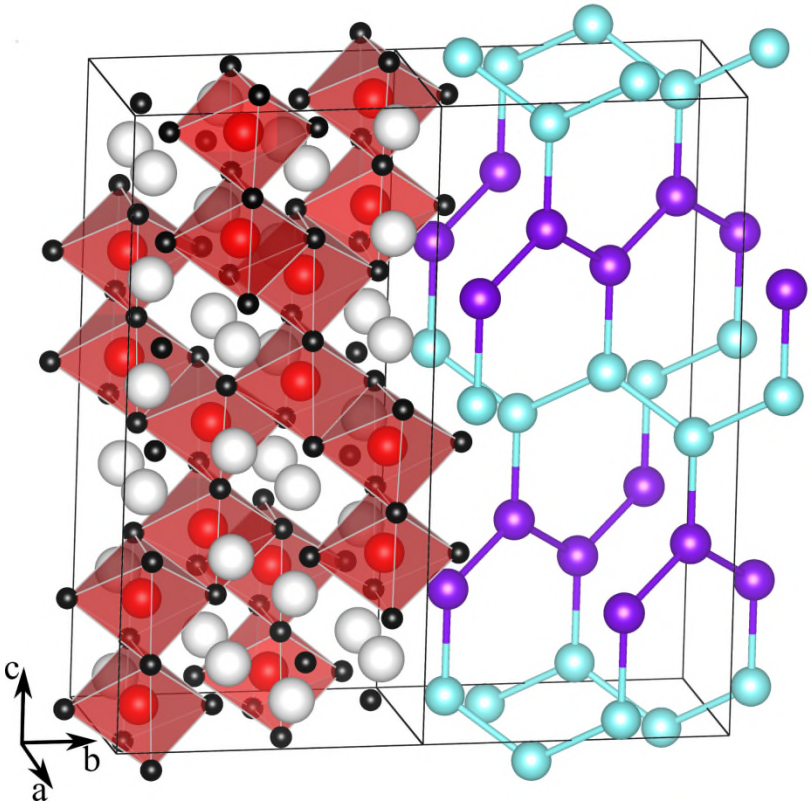
…



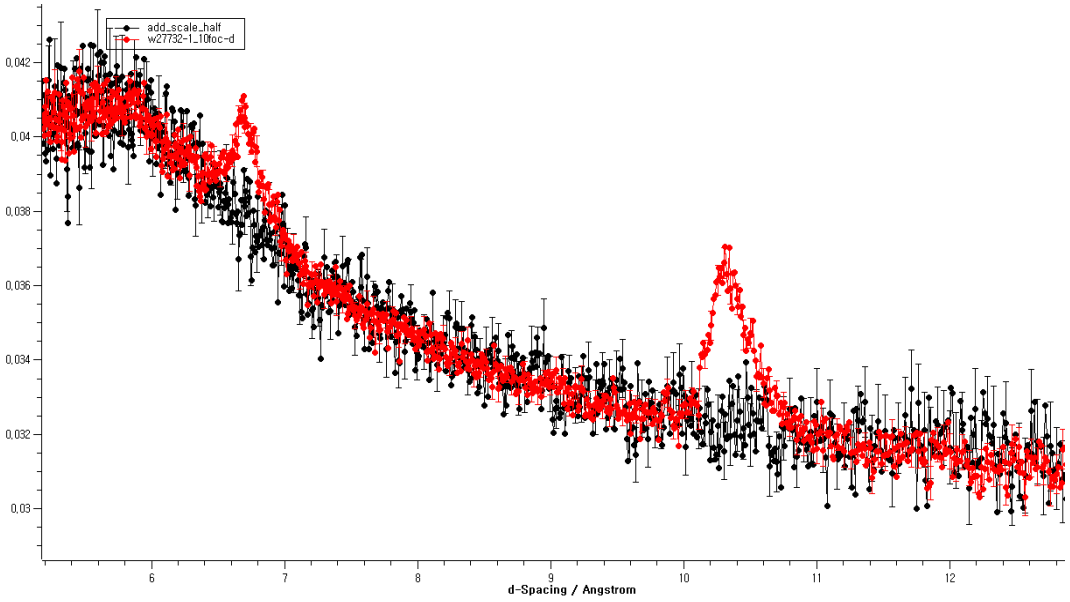
α

Magnetic order in hyper-honeycomb β-Li_2IrO_3

Takayama, ...Takagi,
arXiv:1403.3296



- see magnetic Bragg peaks in powder neutron diffraction

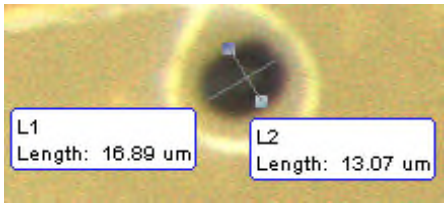


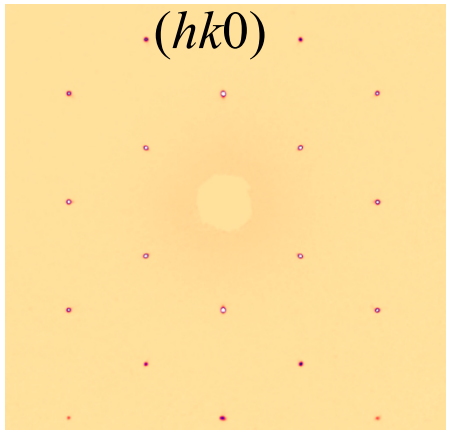
WISH@ISIS

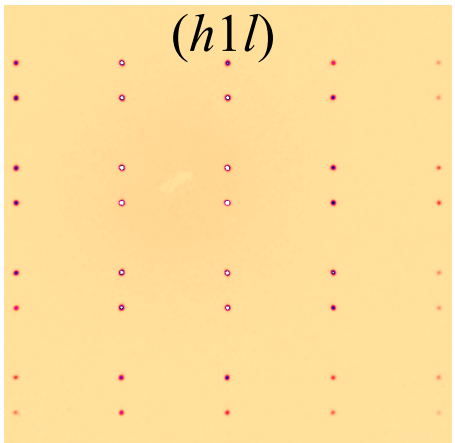
- orthorhombic space group *Fddd*
- susceptibility indicates magnetic order below ~38 K

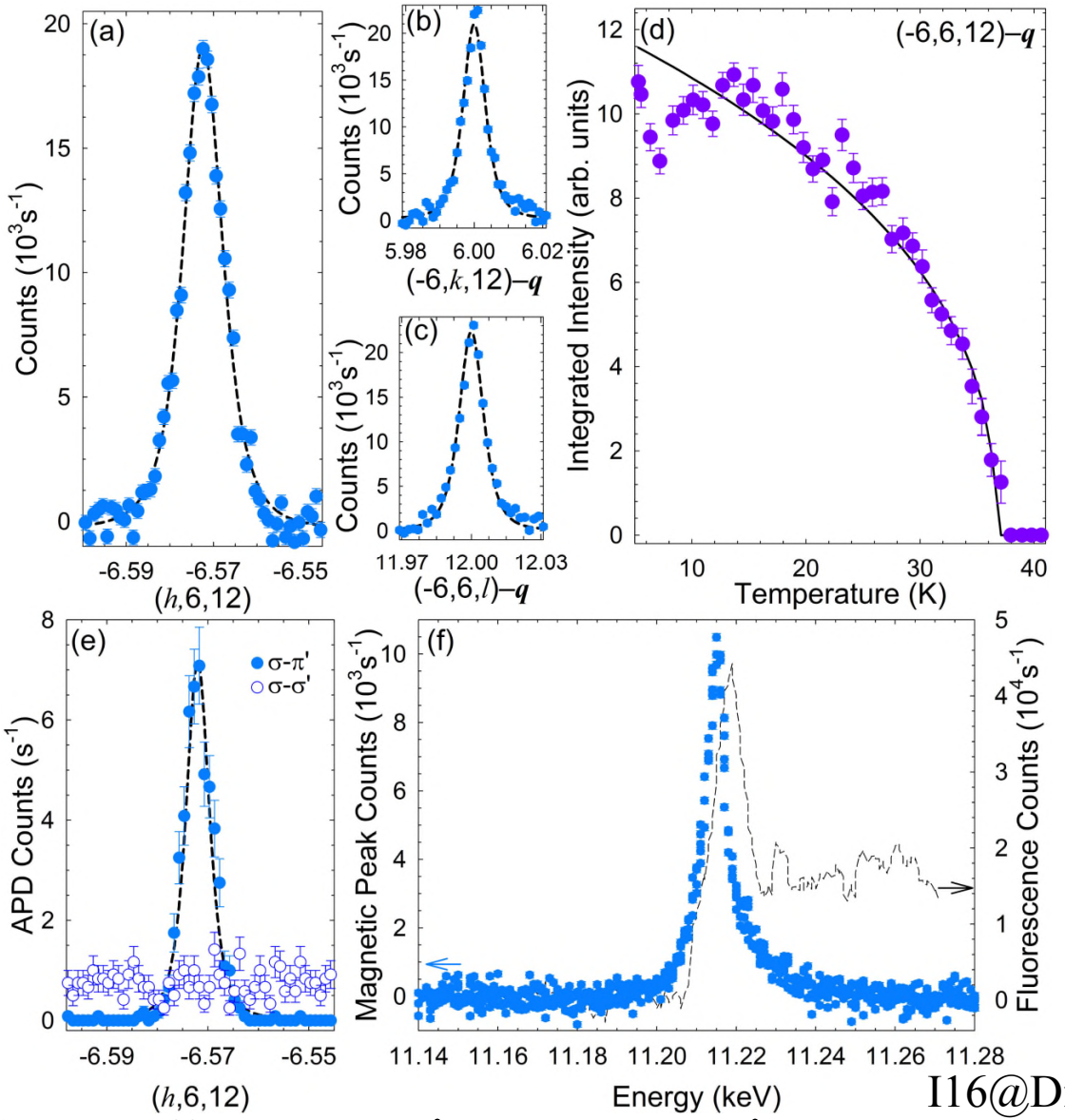
Resonant magnetic x-ray diffraction on a single-crystal of β-Li_2IrO_3

diameter < 17 μm









I16@Diamond

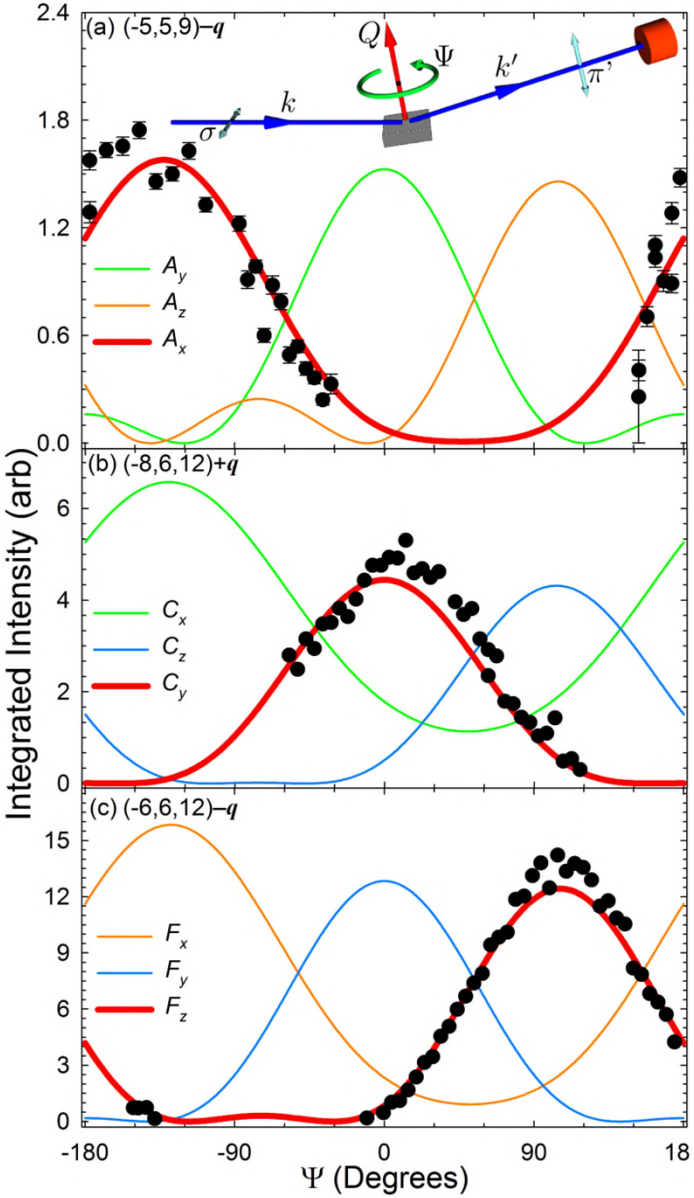
- "same" magnetic propagation vector as in γ-Li_2IrO_3 (within experimental accuracy)

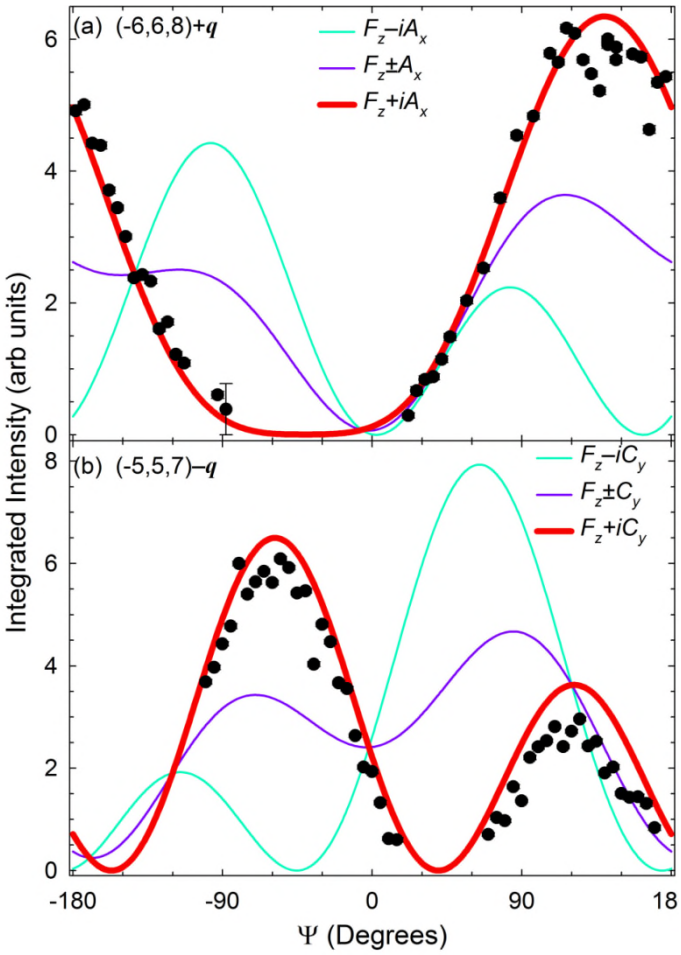
β-Li_2IrO_3 azimuth scans: complete magnetic structure

one Ir sublattice, 4 sites/primitive

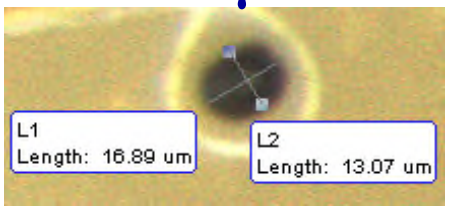
(iA_x, iC_y, F_z) single irrep

$M_x : M_y : M_z = 0.45(1):0.65(1):1$

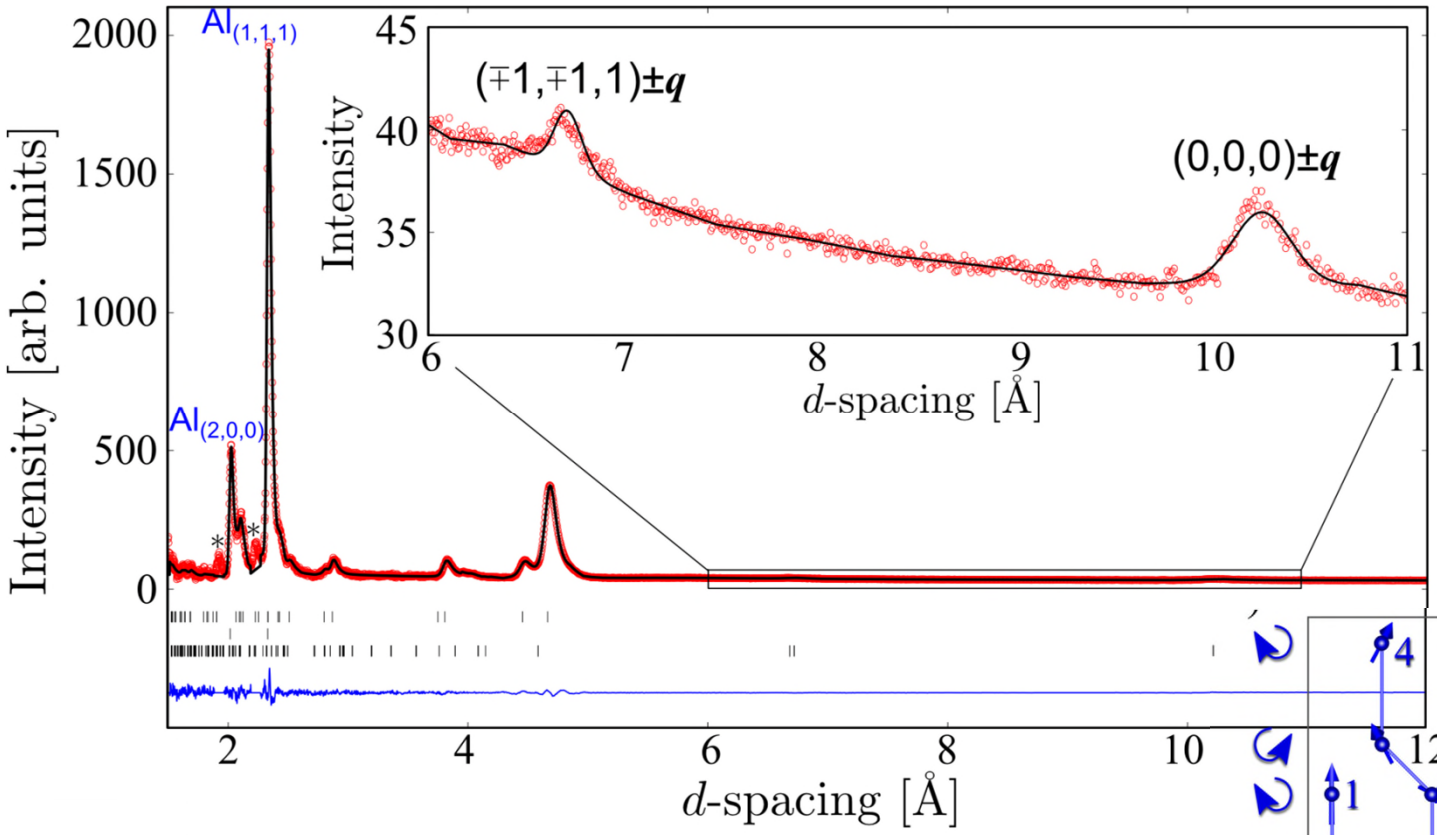


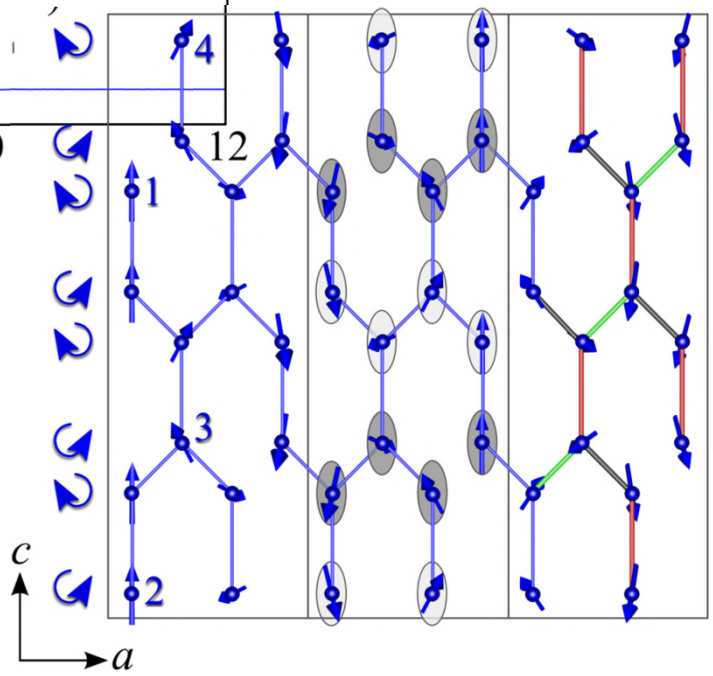


< 17 μm



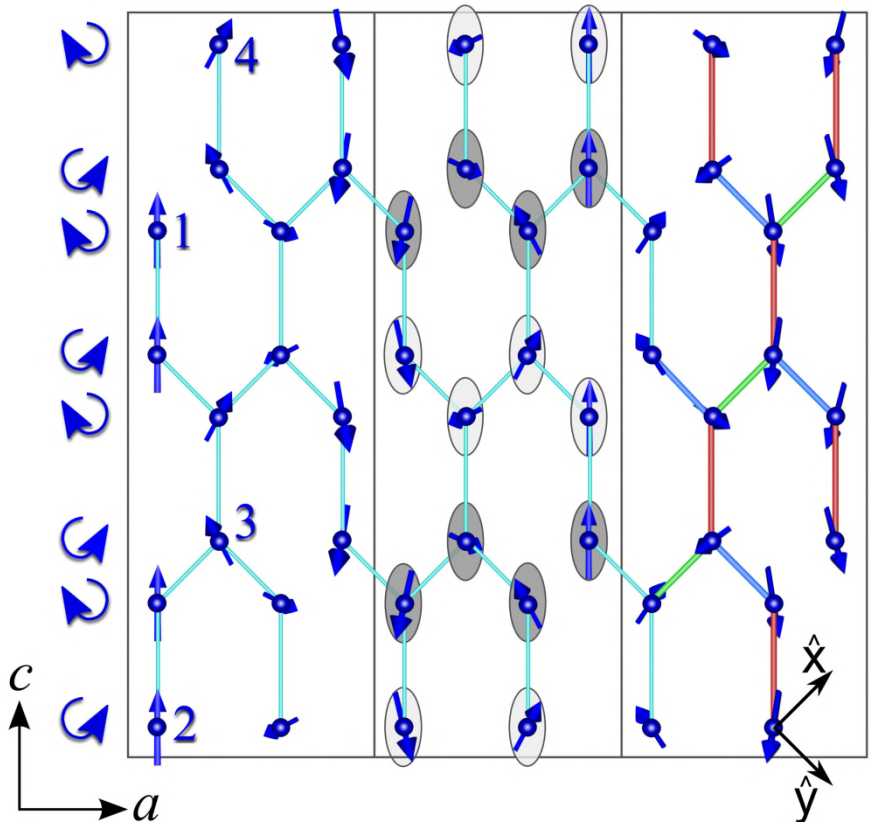
Powder neutron diffraction in β-Li_2IrO_3



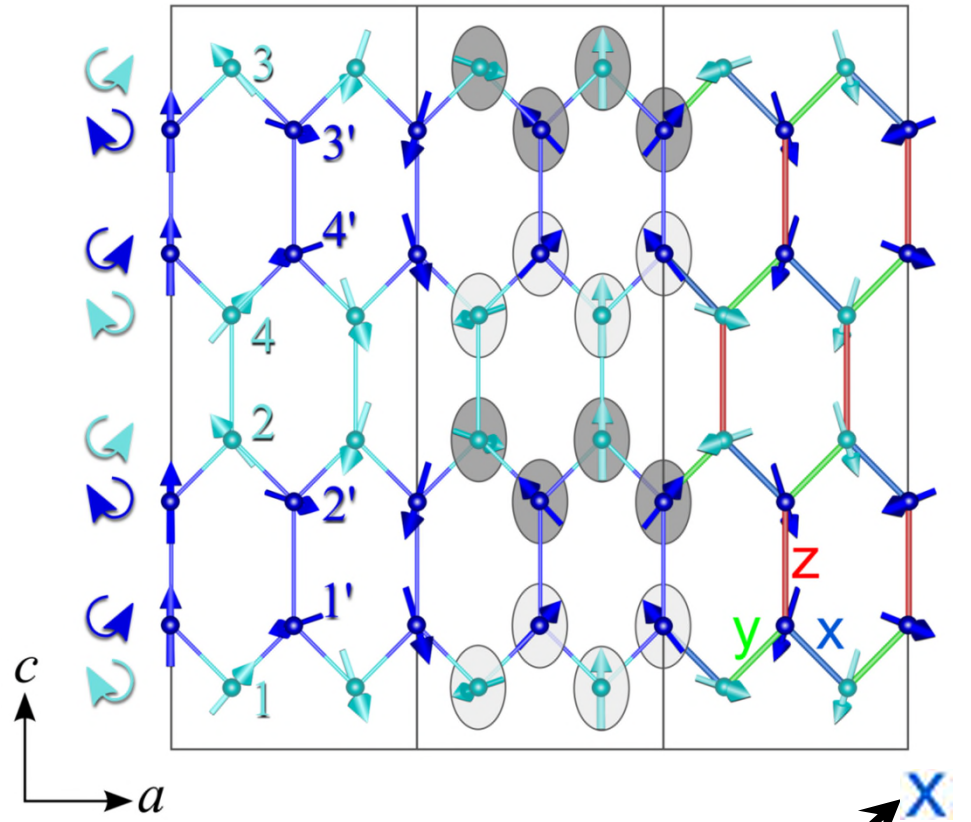


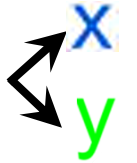
- fit full magnetic structure model found from RXD to get ordered moment magnitude ~0.46(2) μ_B

β-Li_2IrO_3 magnetic structure



γ-Li_2IrO_3





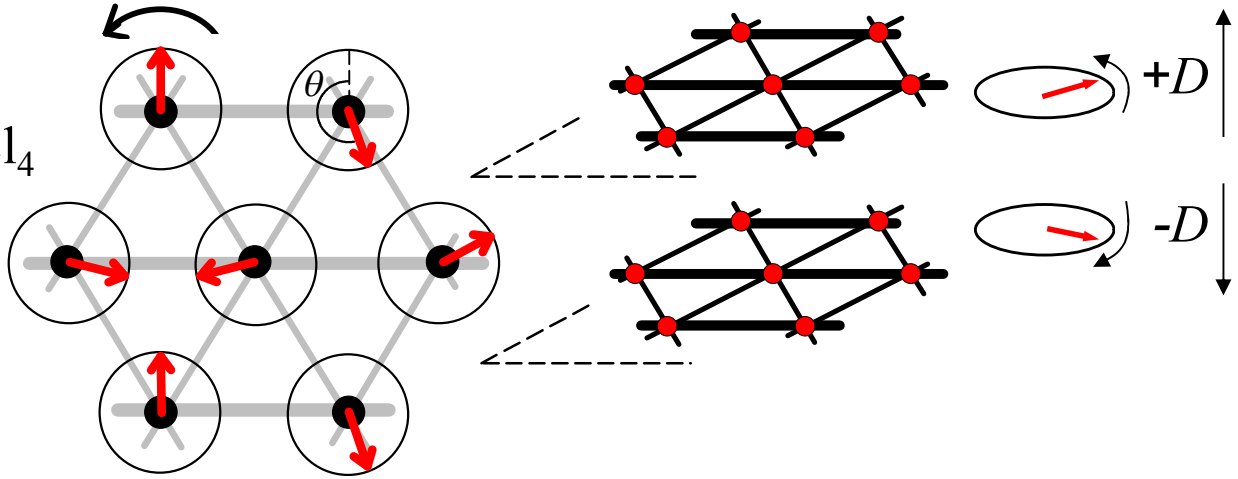
- same ***q***-vector, counter-rotating moments, alternating planes of rotation along vertical bonds
- only difference is *b*-axis position of sites
- **counter-rotation** + **non-coplanarity** difficult to explained by Heisenberg couplings

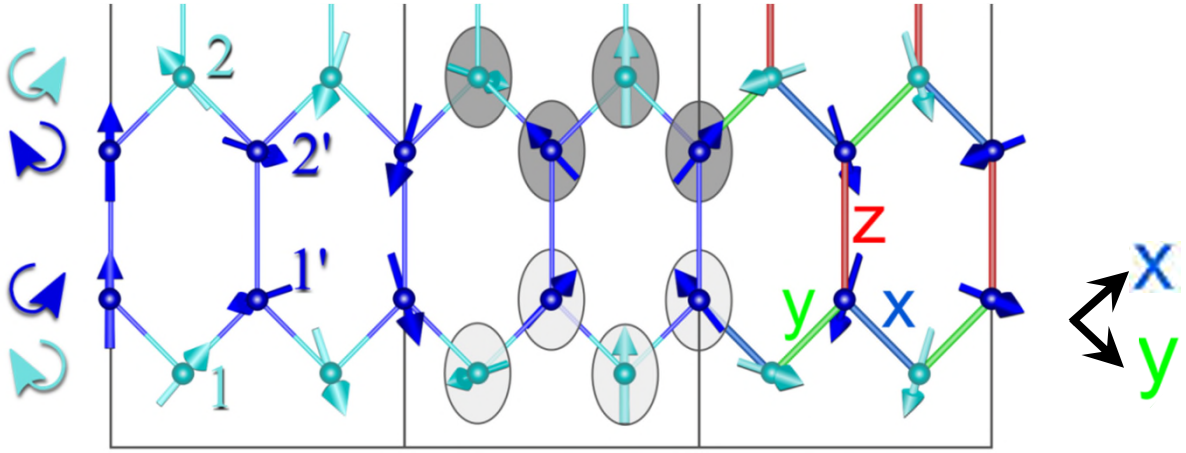
Counter-rotation of moments

- for dominant Heisenberg exchanges multi-sublattice spiral orders can counter-rotate, but on the weakest bonds, and co-rotate on the strongest bonds

quasi-2D Heisenberg Cs_2CuCl_4

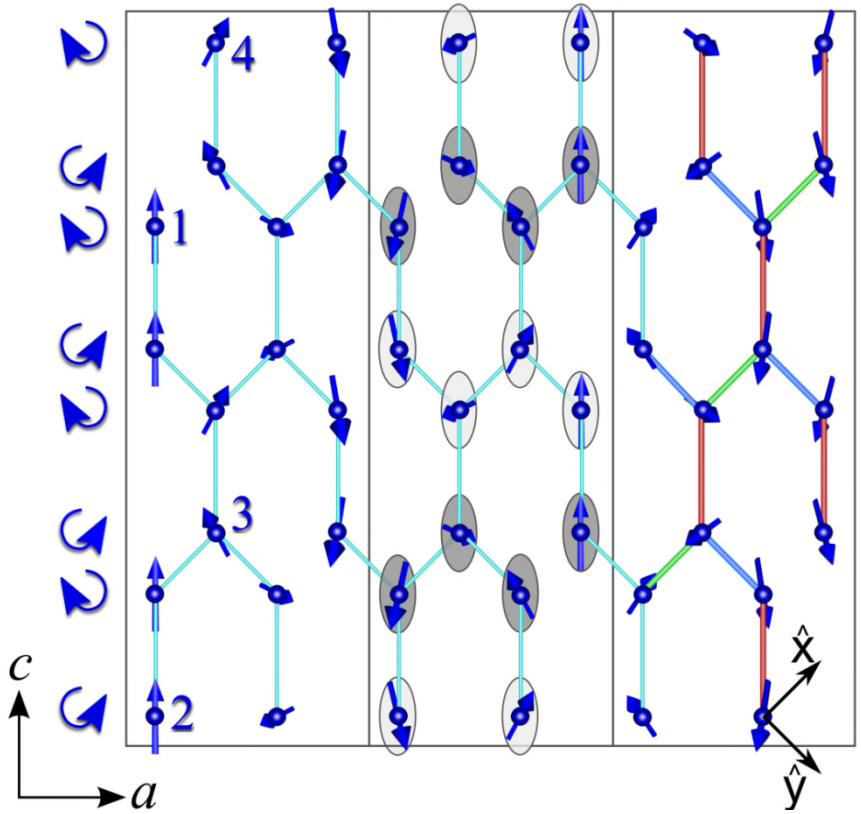
$J_{interlayer}$, $D \sim 0.05\ J$
R.C. et al (1997,2001)

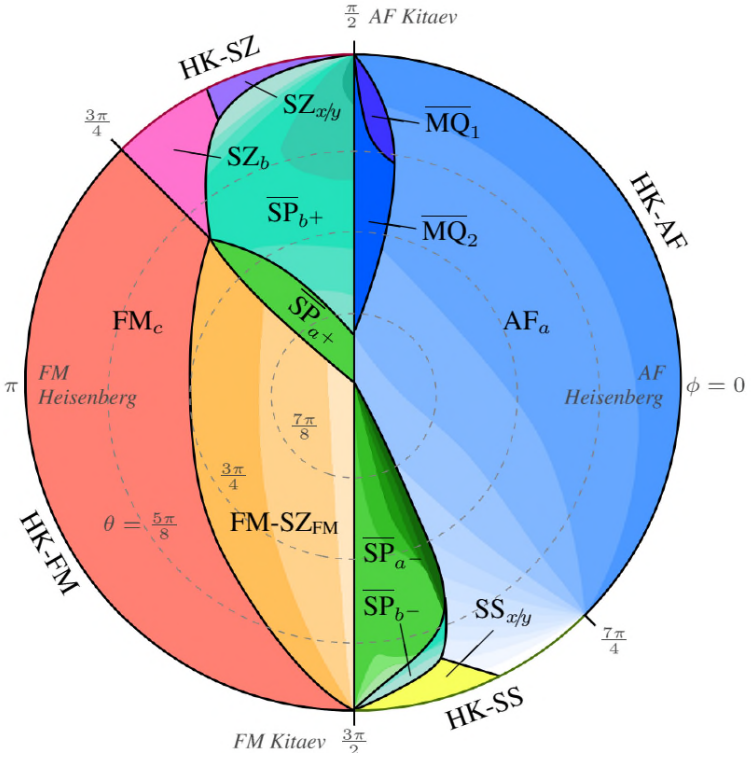




- counter-rotation on every nn bond
- along x-bonds when spins along x then ~FM, when along y then ~AFM
  => favoured by a FM Kitaev and AFM HB J

Perturbations around FM Kitaev limit: JKΓ model





J K Γ model : FM Kitaev K

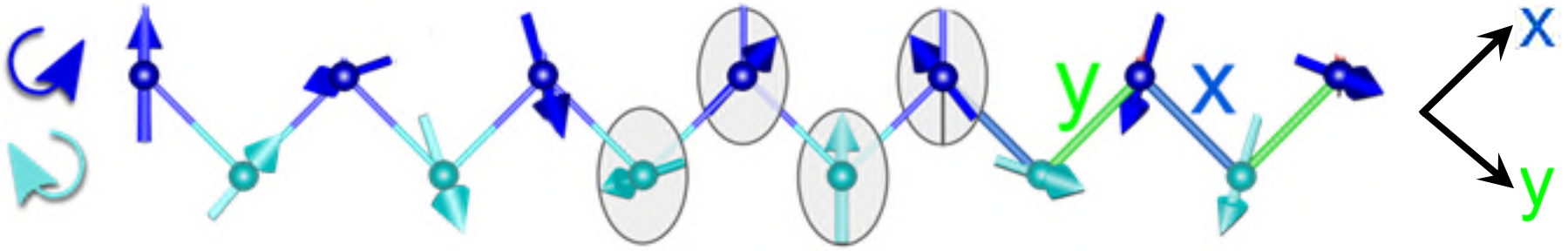
small AFM Heisenberg J $\boldsymbol{S}_i \cdot \boldsymbol{S}_j$

small Γ $(S^xS^y+S^yS^x)$ for *all* bonds

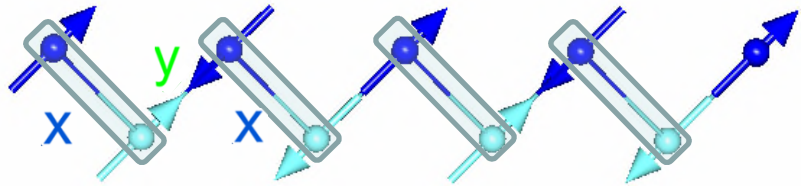
β-phase (yes) and γ (almost, not coplanarity pattern)

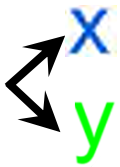
E.K-H. Lee … Y.B. Kim PRB (2015), arXiv (2015).

Minimal model: Kitaev zig-zag chain

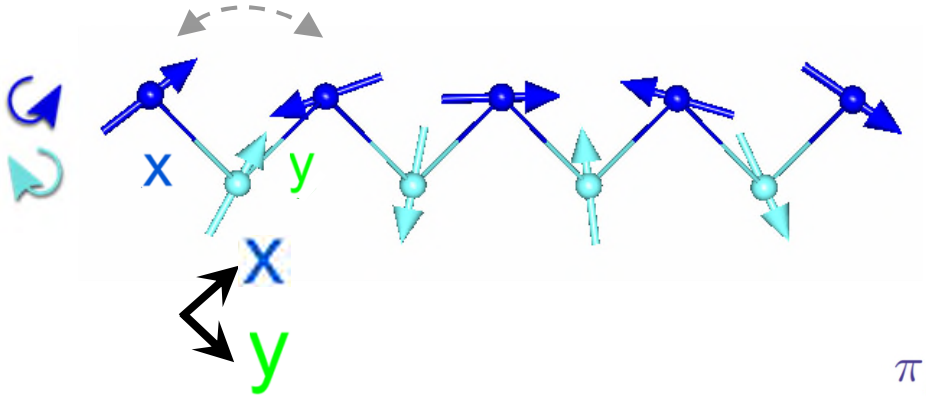


rotating version of "stripy" order



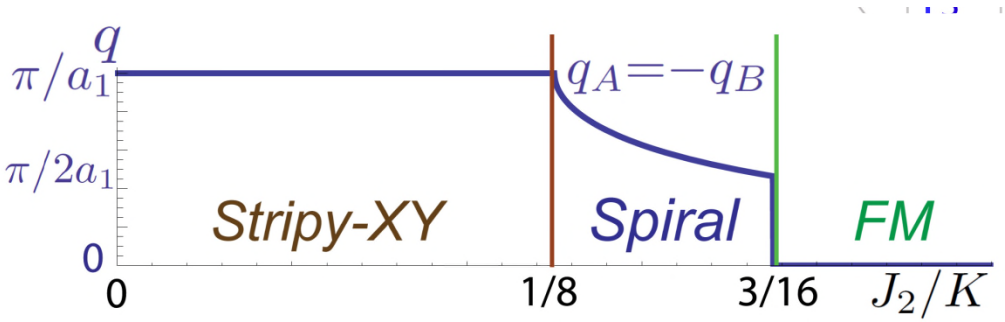


FM Kitaev K
+ small AF Heisenberg J

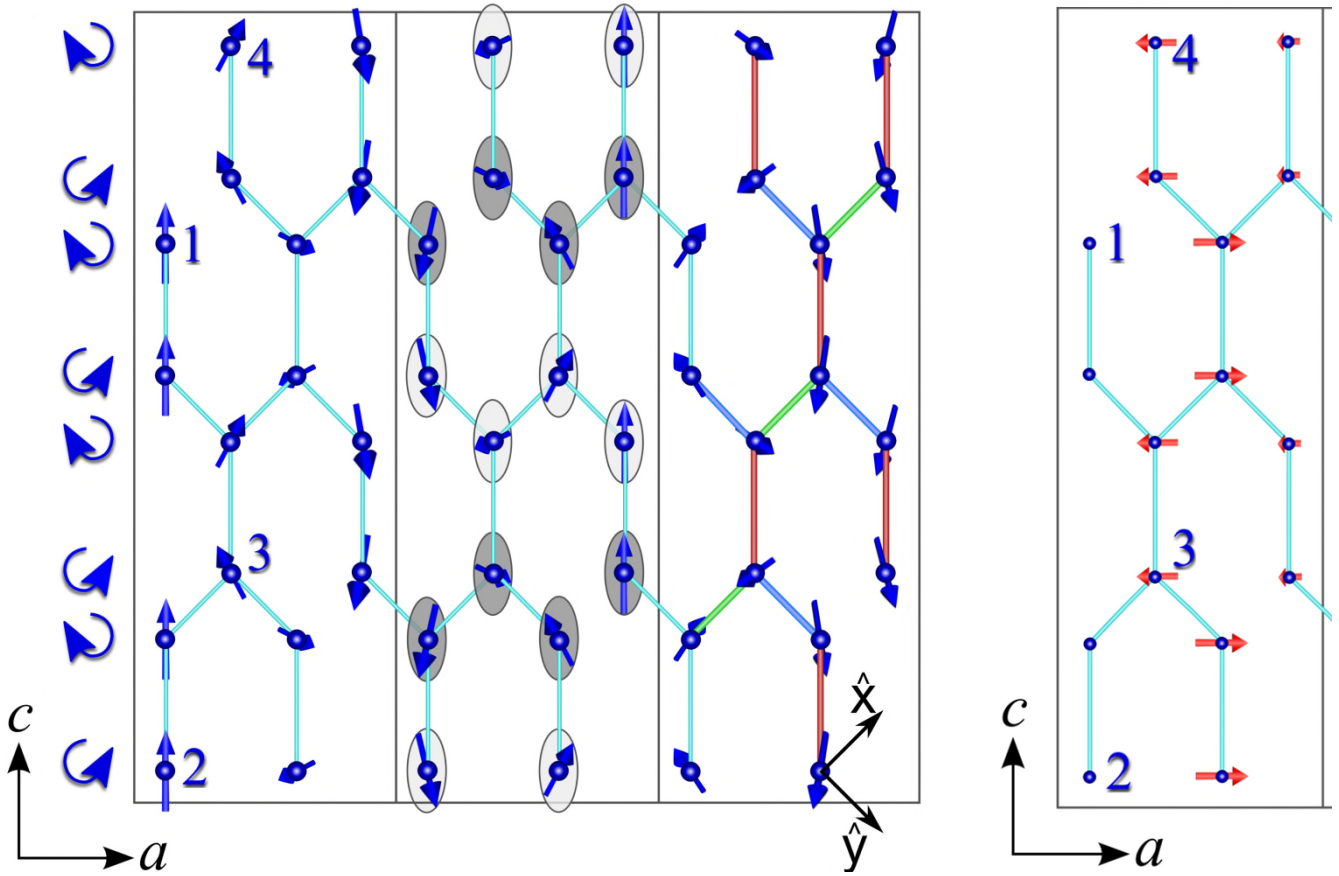


frustrate with small FM J_2

Itamar Kimchi, R.C, A.Vishwanath, arXiv (2014) PRB(2015)



Non-coplanarity due to Kitaev couplings along c-bonds

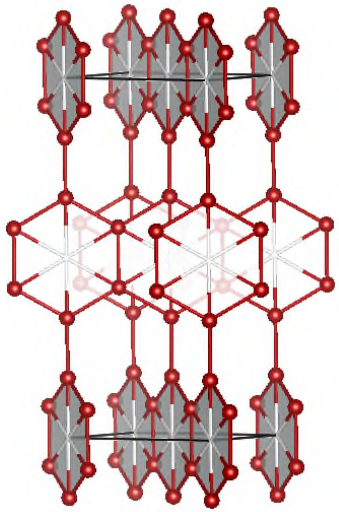


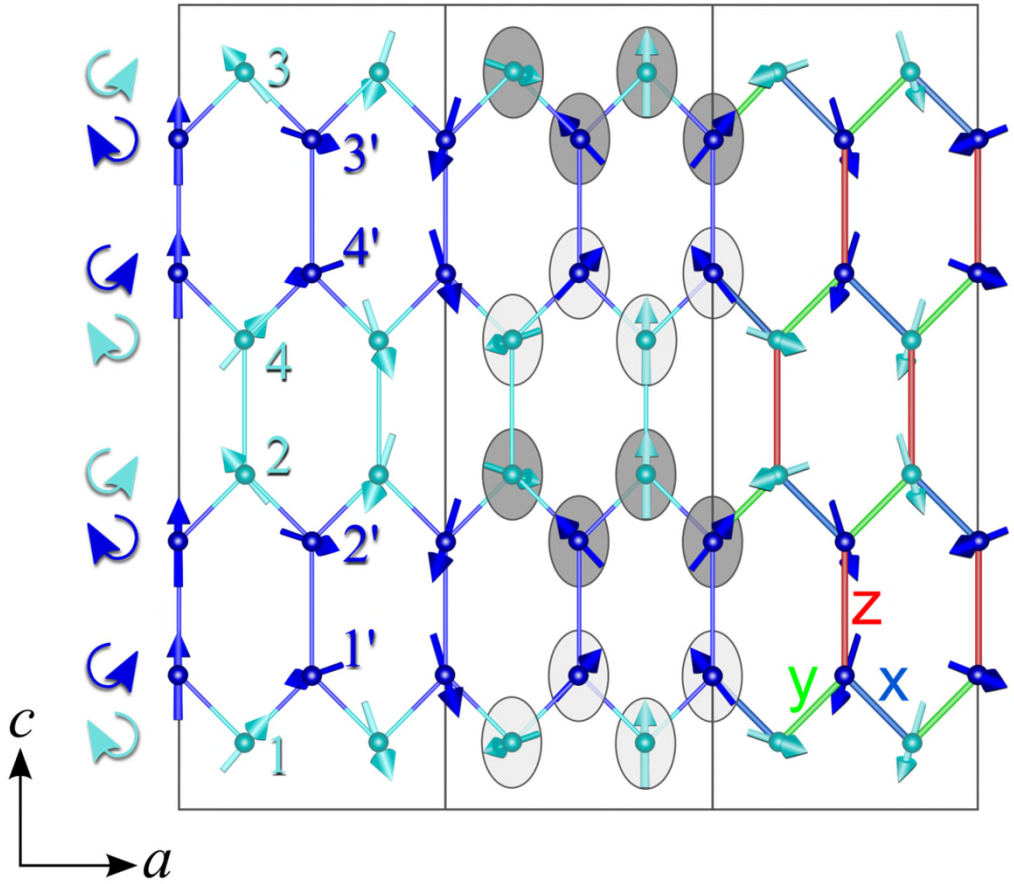
- non-coplanar along each vertical bond, FM aligned $S^b = S^z$ for all c-bonds
- full structure captured (soft spin approach) by FM Kitaev K + small AFM J +small Ising I_c in *both* β and γ polytypes

Itamar Kimchi, R.C, A.Vishwanath, arXiv (2014) PRB(2015)

Summary

- solved crystal structure of new polytype γ-Li_2IrO_3
- β- and γ-Li_2IrO_3 have non-coplanar counter-rotating spirals





- structure stabilized by dominant Kitaev terms + small interactions

A. Biffin, R.D. Johnson, ...R.C. PRL, PRB (2014)