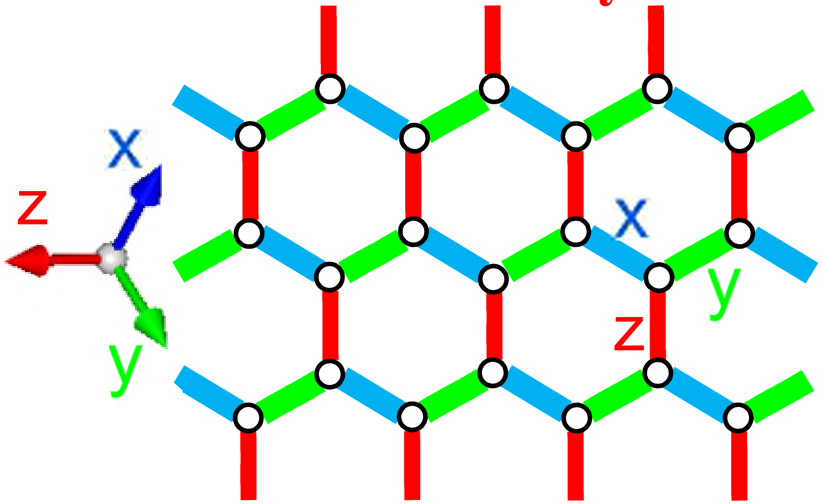
Unconventional magnetic order in 3D Kitaev materials revealed by resonant x-ray diffraction

Slides courtesy Radu Coldea, Oxford

Kitaev model on honeycomb lattice

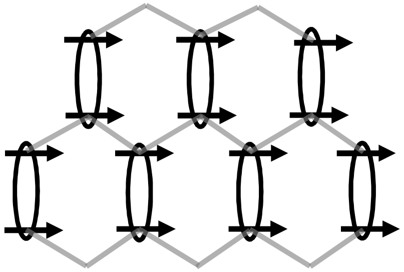


Kitaev (2006)

x-bond	$-KS_i^xS_j^x$
y-bond	$-KS_i^yS_j^y$
z-bond	$-KS_i^zS_j^z$

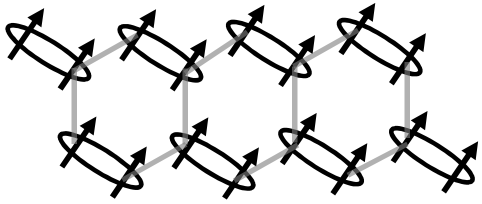
- quantum spin liquid (exactly solvable)
spinon + flux excitations

if only *z*-bonds

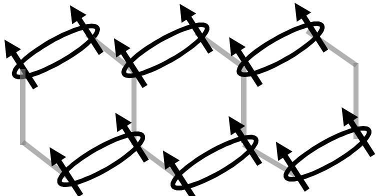


ferromagnetic dimers

if only *x*-bonds

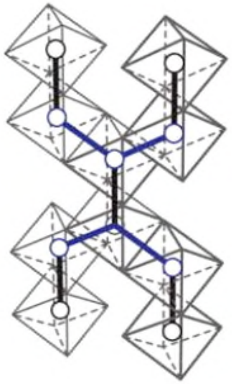


if only *y*-bonds

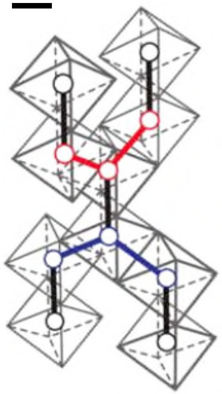


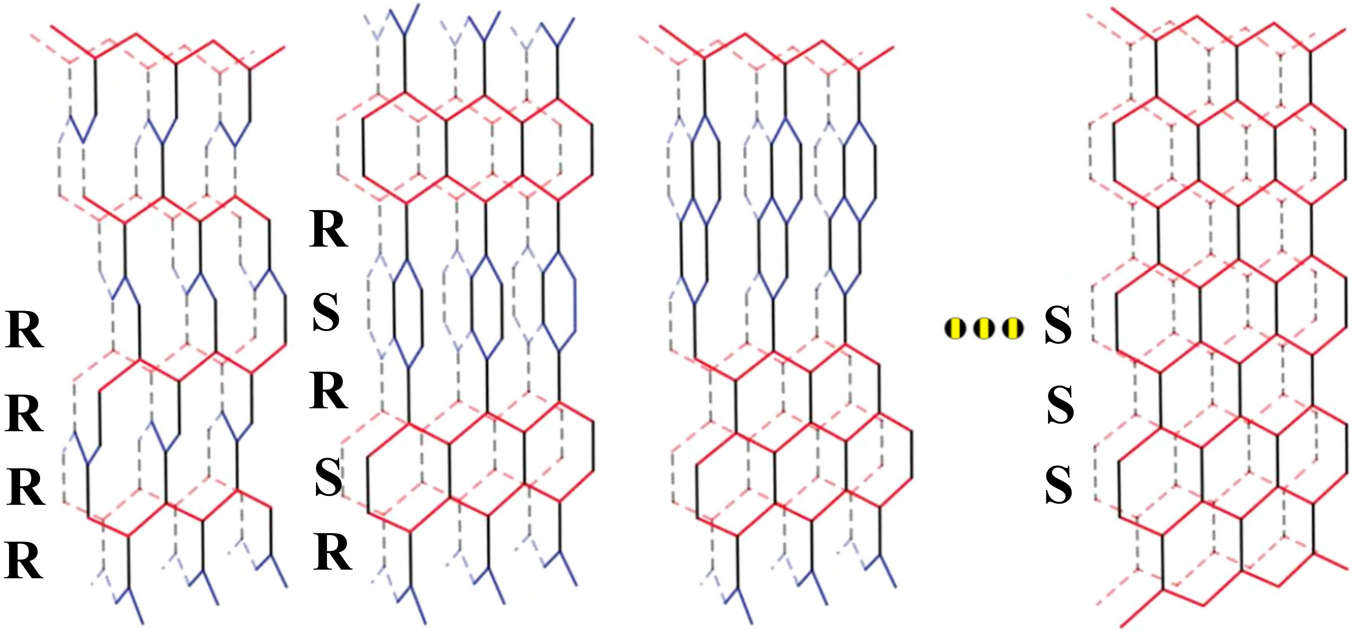
Family of polytypes of Li_2IrO_3

Same



Rotate





hyper honeycomb

Fddd

R
R
R
R

β

Takayama, …Takagi, arXiv:1403.3296

stripy honeycomb

Cccm

R
S
R
S
R

γ

K.A. Modic et al, (2014)

δ

…

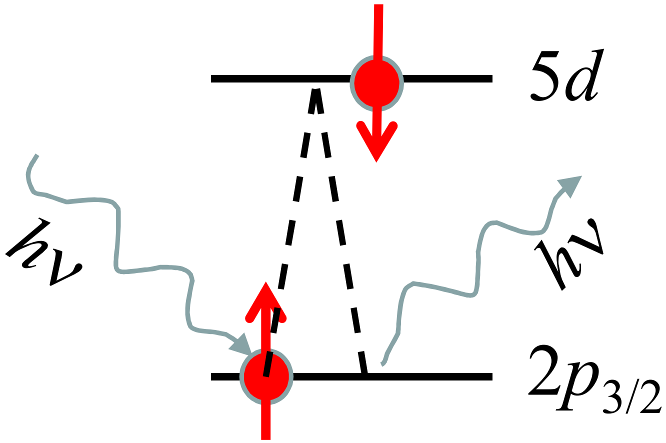
layered honeycomb

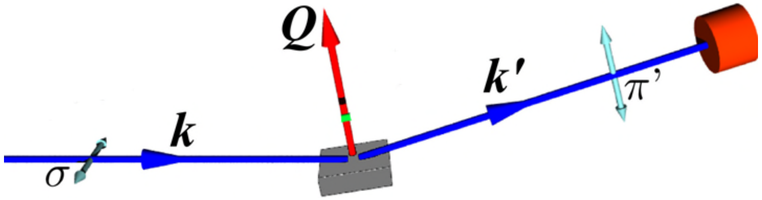
C2/m

●●● **S**
S
S

α

Magnetic Resonant x-ray diffraction at Ir L_3 edge

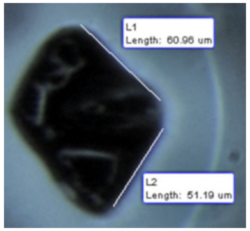


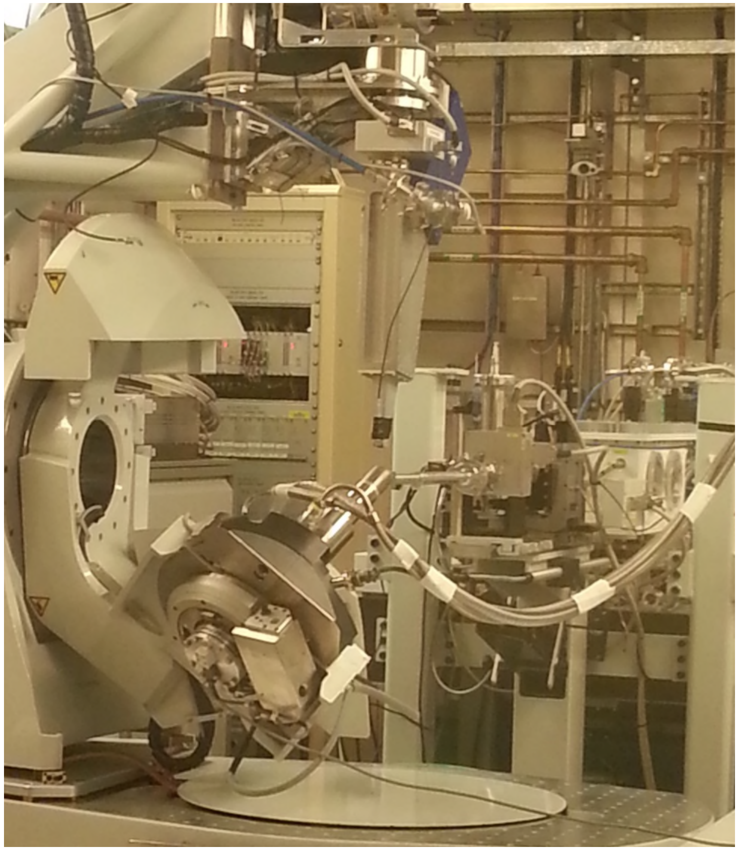


- x-ray scattering at resonance sensitive to magnetism of final state

$\phi < 60$ μm

γ-Li_2IrO_3





I16@ diamond

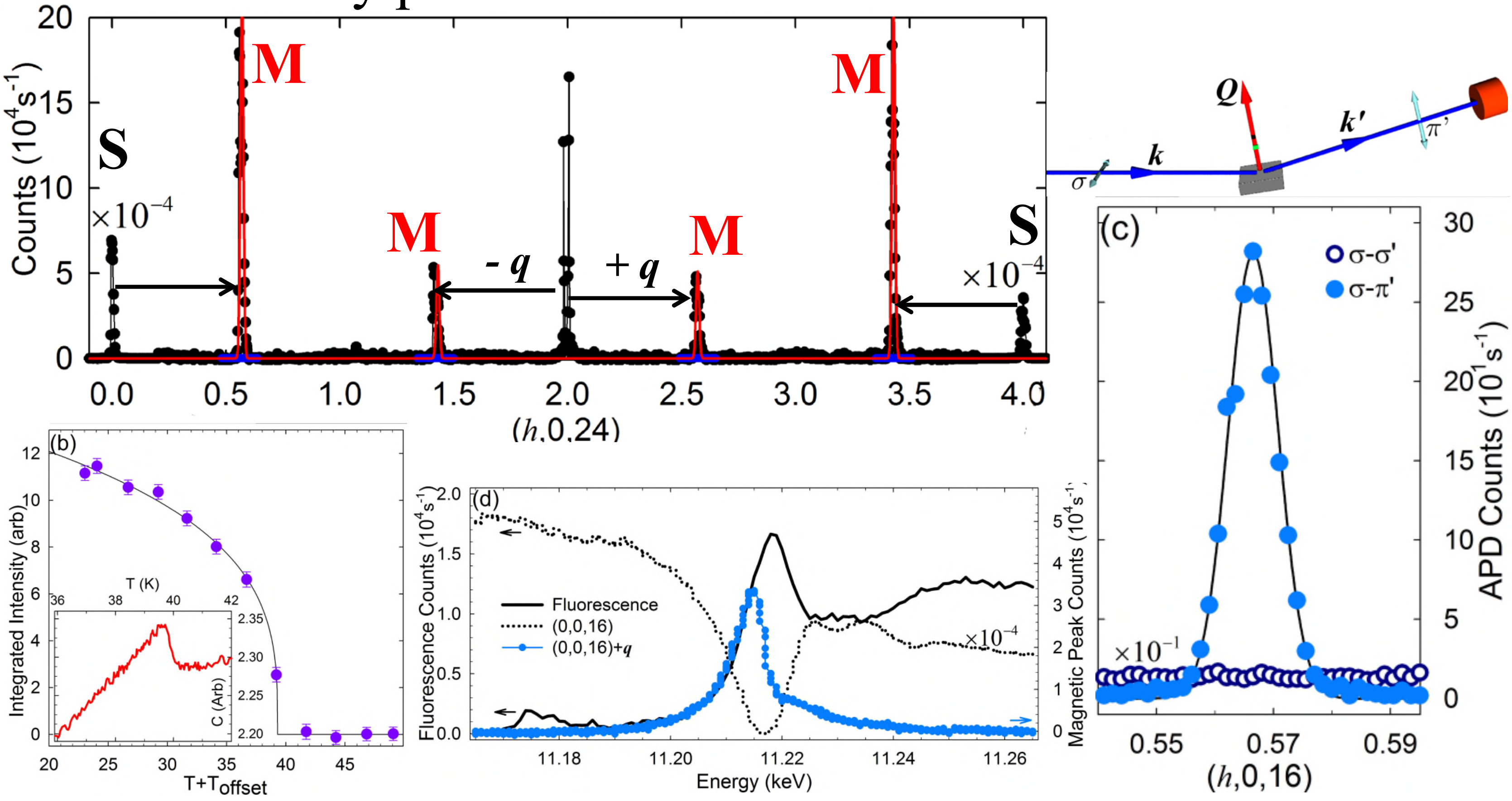
Biffen et al. Phys. Rev. B. 90, 205116 (2014); Phys. Rev. Lett. 113, 197201 (2014)

Magnetic Resonant x-ray diffraction on γ-Li_2IrO_3

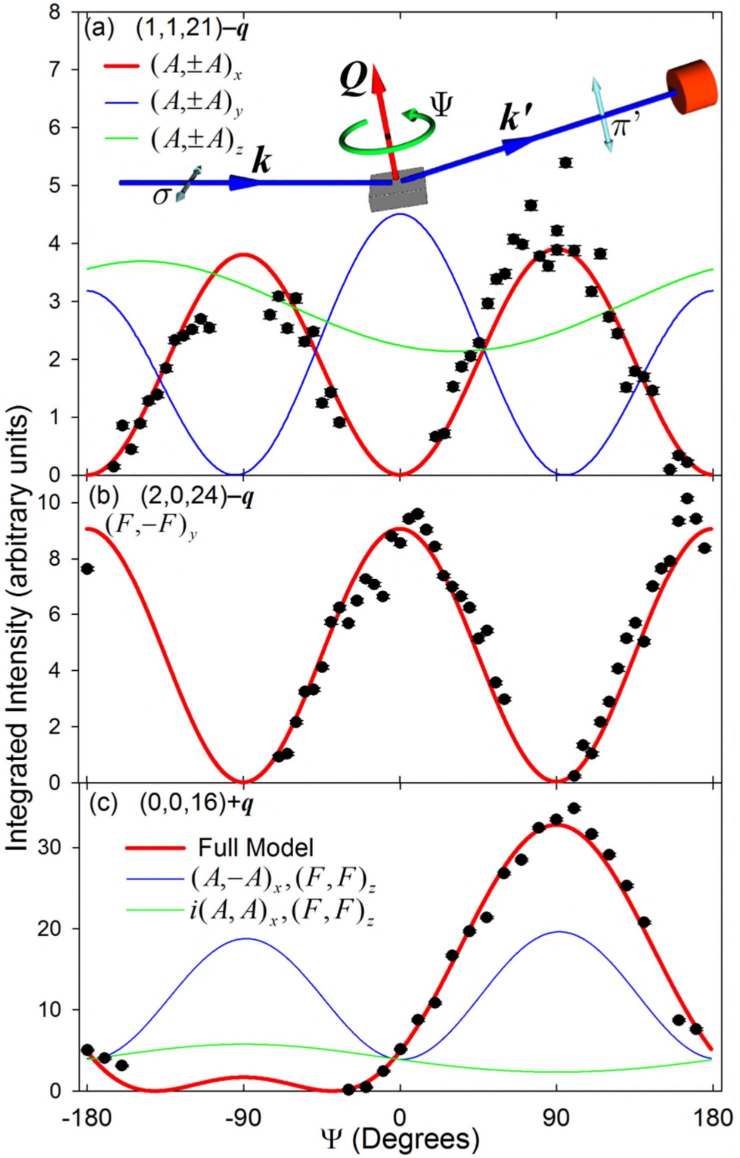
- incommensurate magnetic propagation vector

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

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



Azimuth scans on γ-Li_2IrO_3



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

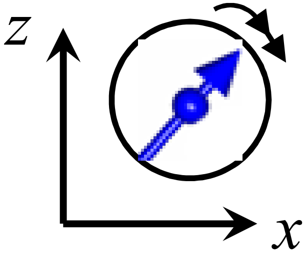
$$= |\hat{\boldsymbol{k}}' \cdot \boldsymbol{\mathcal{F}}(\boldsymbol{Q})|^2 = |\mathcal{F}_{\parallel}|^2$$

$$\downarrow$$

- projection of structure factor onto scattered beam

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

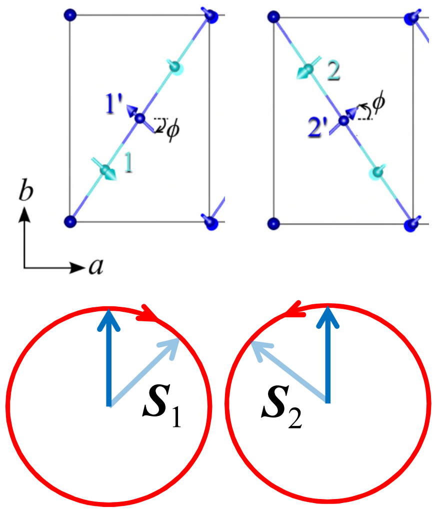
$$i(A,-A)_x, -i(F,-F)_y, (F,F)_z$$

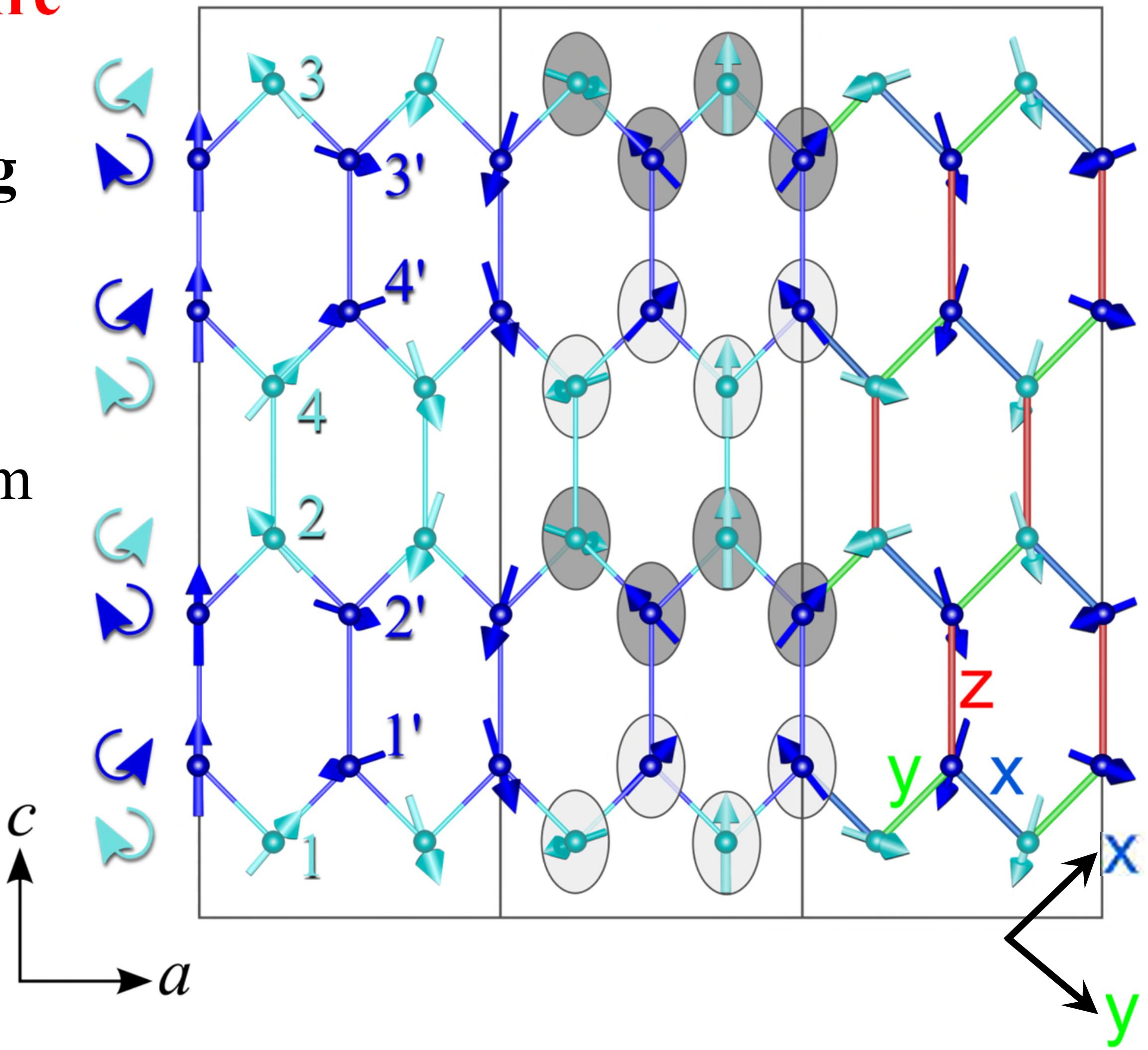


- moments rotate in a plane tilted away from the *ac* face

Magnetic structure of γ-Li_2IrO_3

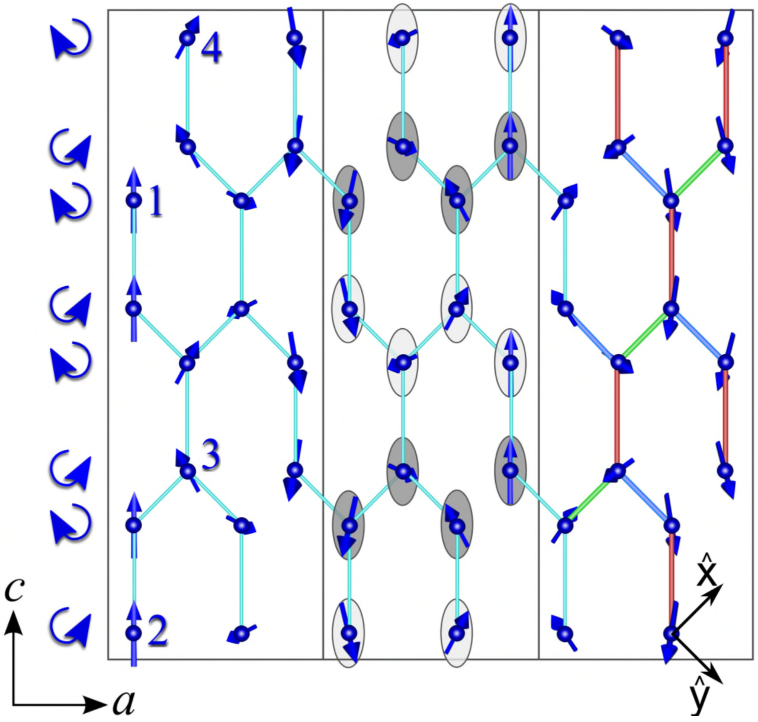
- **counter-rotating** moments between every nn sites
- **non coplanar** - alternating tilt from *ac* face



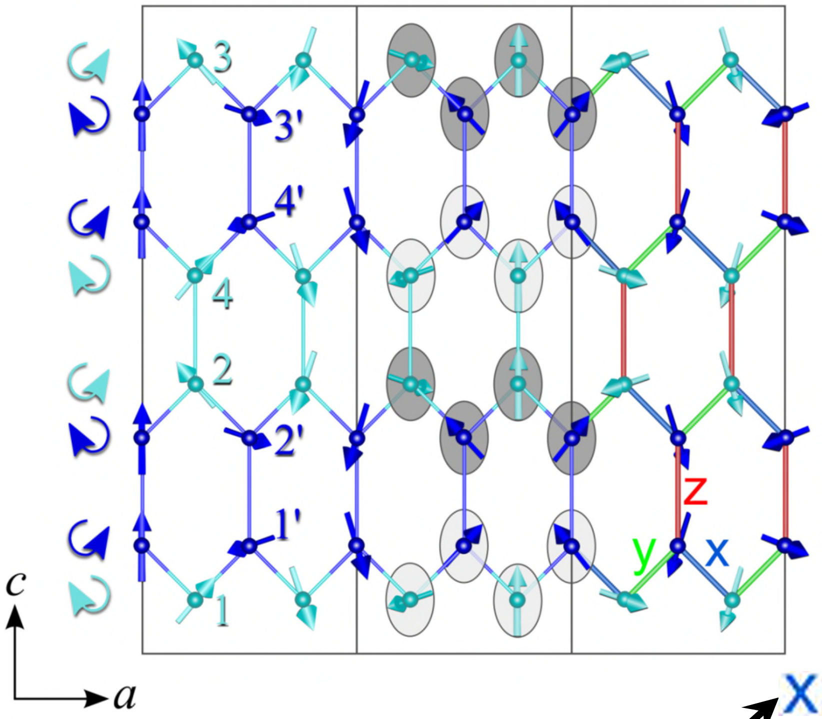


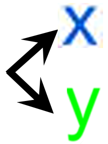
- counter-rotation -> zero energy gain for nn Heisenberg exchange $J < \boldsymbol{S}_1 \cdot \boldsymbol{S}_2 > = 0$

β-Li_2IrO_3 magnetic structure



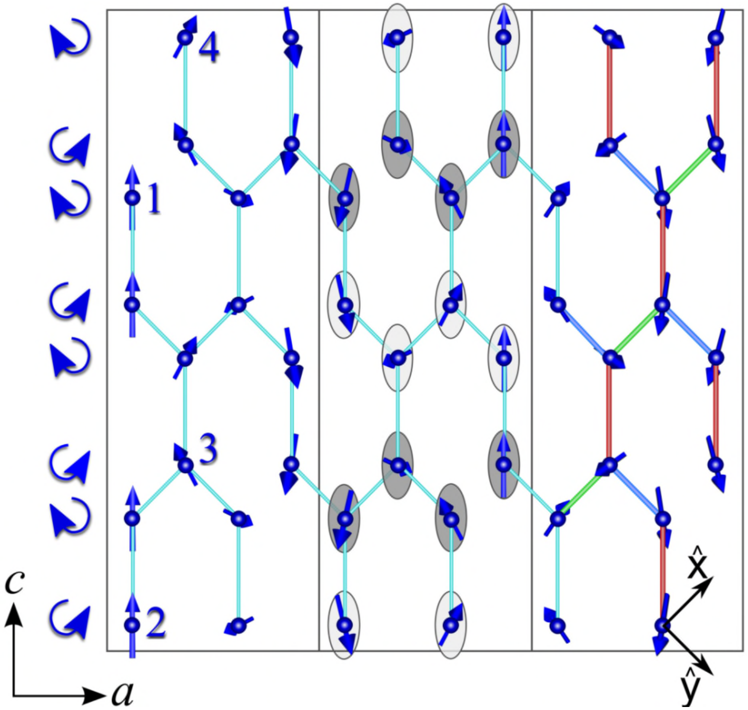
γ-Li_2IrO_3

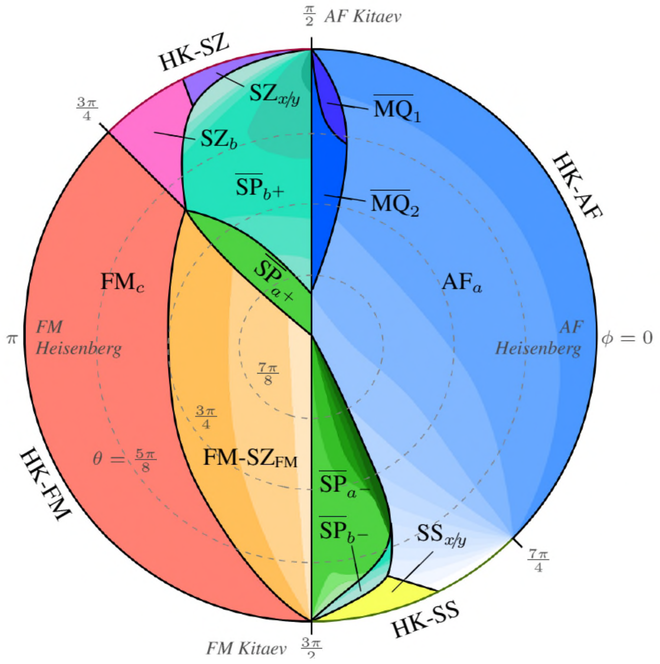




- same ***q***-vector, counter-rotating moments, alternating planes of rotation along vertical bonds
- only difference is *b*-axis position of sites
- **counter-rotation** + **non-coplanarity** difficult to explained by Heisenberg couplings

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).

Scattering Tensors and Multipoles

Templeton & Templeton; Blume; Carra and Thole; Mari and Carra; Di Matteo, Joly, Natoli; Lovesey

Structure Factor

$$\sum_j f_j(\omega)\, e^{iQ\cdot r_j}$$

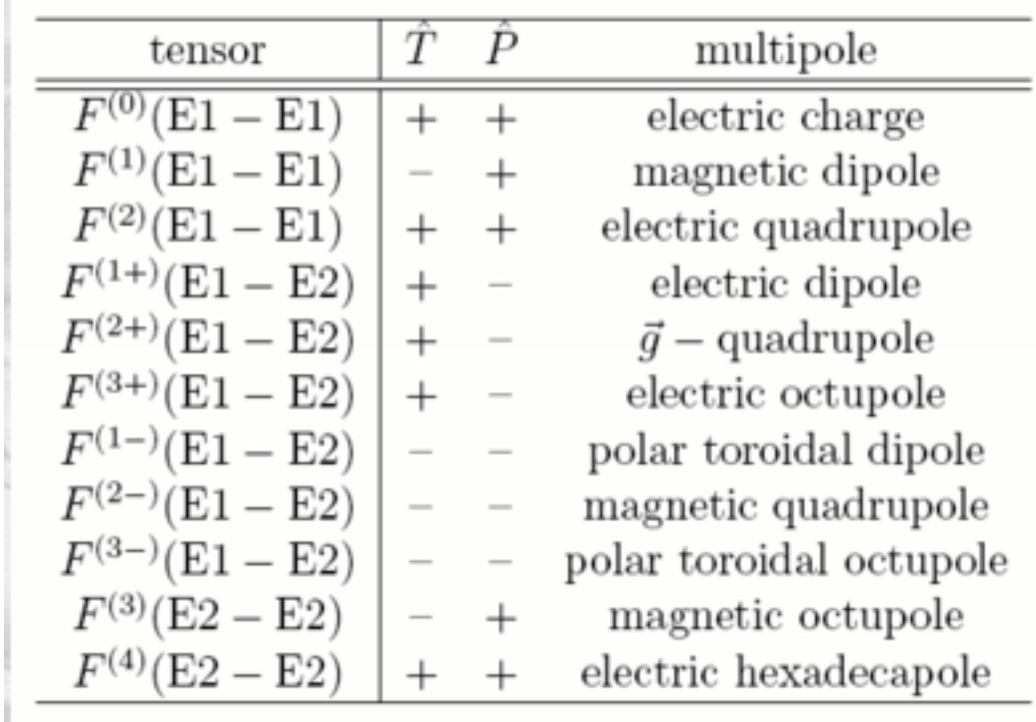
Resonant Scattering Length

$$f_j(\omega) = \frac{m}{\hbar^2}\frac{1}{\hbar\omega}\sum_n \frac{(E_n - E_g)^3 M'^{*}_{ng}(j) M_{ng}(j)}{\hbar\omega - (E_n - E_g) - i\frac{\Gamma_n}{2}}$$

Scattering Length : Product of Irreducible Tensors

$$f = \quad P^p \quad \text{x} \quad F^p$$

Photon Matter

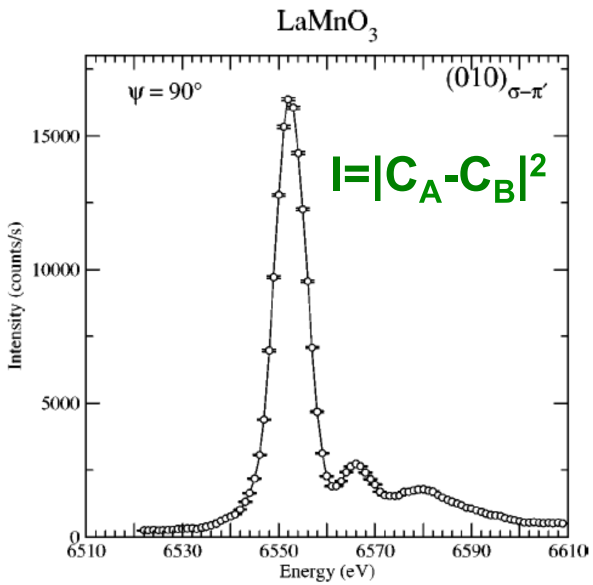


tensor	$\hat{T}$	$\hat{P}$	multipole
$F^{(0)}(\mathrm{E1}-\mathrm{E1})$	$+$	$+$	electric charge
$F^{(1)}(\mathrm{E1}-\mathrm{E1})$	$-$	$+$	magnetic dipole
$F^{(2)}(\mathrm{E1}-\mathrm{E1})$	$+$	$+$	electric quadrupole
$F^{(1+)}(\mathrm{E1}-\mathrm{E2})$	$+$	$-$	electric dipole
$F^{(2+)}(\mathrm{E1}-\mathrm{E2})$	$+$	$-$	$\vec{g}$ – quadrupole
$F^{(3+)}(\mathrm{E1}-\mathrm{E2})$	$+$	$-$	electric octupole
$F^{(1-)}(\mathrm{E1}-\mathrm{E2})$	$-$	$-$	polar toroidal dipole
$F^{(2-)}(\mathrm{E1}-\mathrm{E2})$	$-$	$-$	magnetic quadrupole
$F^{(3-)}(\mathrm{E1}-\mathrm{E2})$	$-$	$-$	polar toroidal octupole
$F^{(3)}(\mathrm{E2}-\mathrm{E2})$	$-$	$+$	magnetic octupole
$F^{(4)}(\mathrm{E2}-\mathrm{E2})$	$+$	$+$	electric hexadecapole

XRS: Probes multipolar order

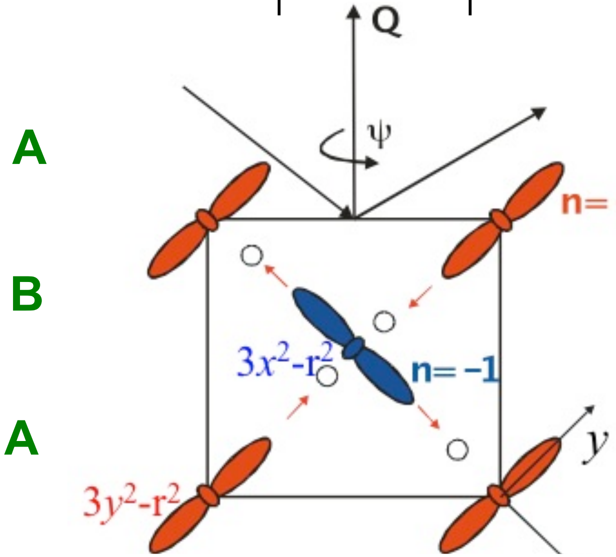
First XRS experiment to probe Orbital Ordering

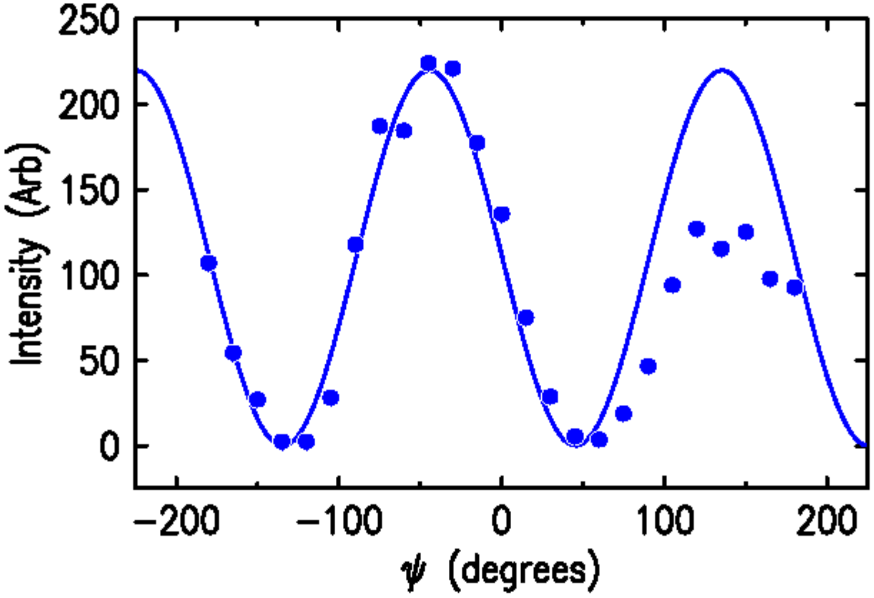
$LaMnO_3$, Murakami, *et al*., PRL (1998)



$I=|C_A-C_B|^2$

$$I = \left|\hat{\varepsilon}' \cdot C \cdot \hat{\varepsilon}\right|^2$$





- (010) forbidden reflection

- Large resonance at Mn K edge
  1s -> 4p in the σ-π' channel

- Azimuthal scan varies rotation of C with respect to photon polarization and suggests anisotropy of the 4p states

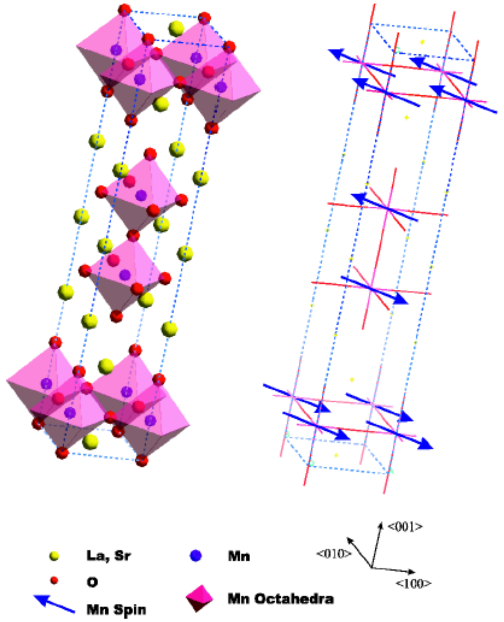
- Interpreted as arising from Jahn-Teller distortion due to orbital ordering

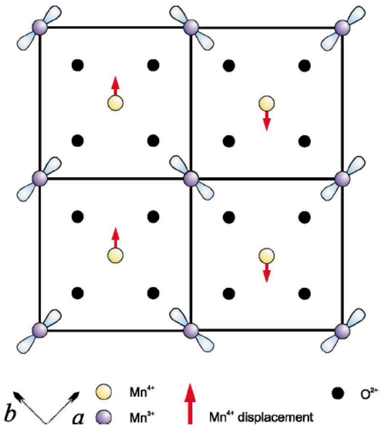
Direct observation of orbital ordering using soft XRS

Wilkins et al., PRL (2003)

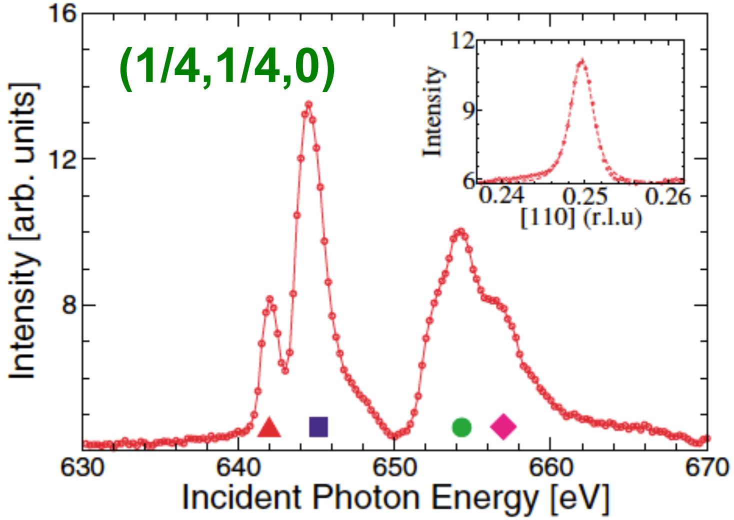
Ruddlesdon-Popper bilayer manganite

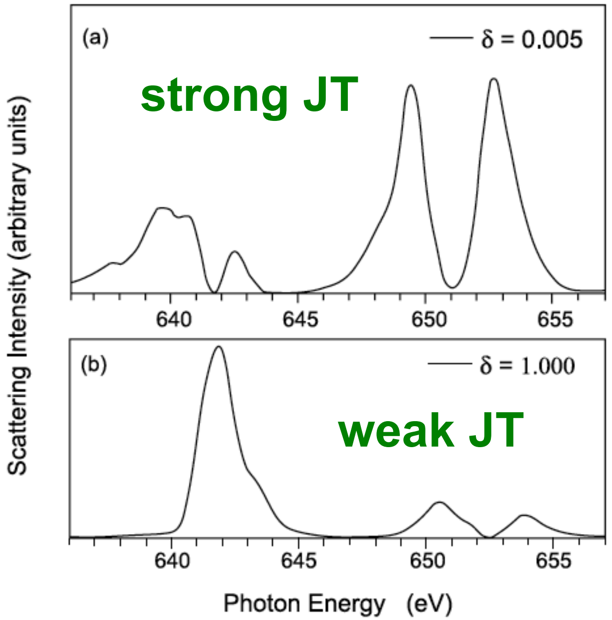
$La_{2-2x}Sr_{1+2x}Mn_2O_7$





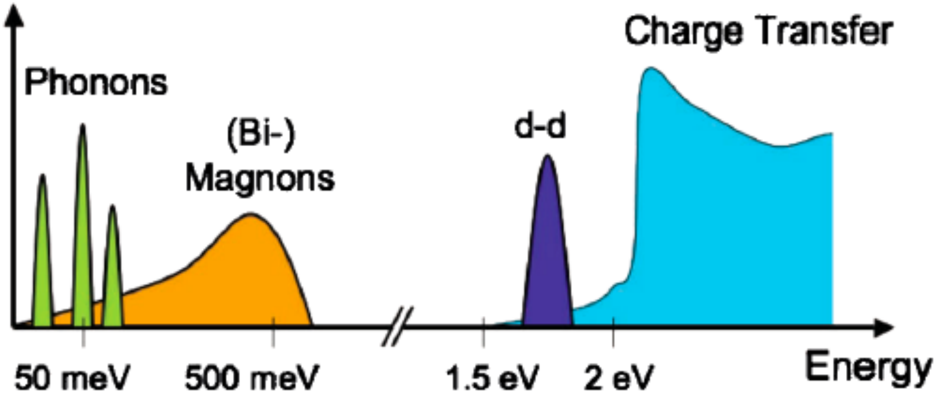
Mn L edges, 2p->3d

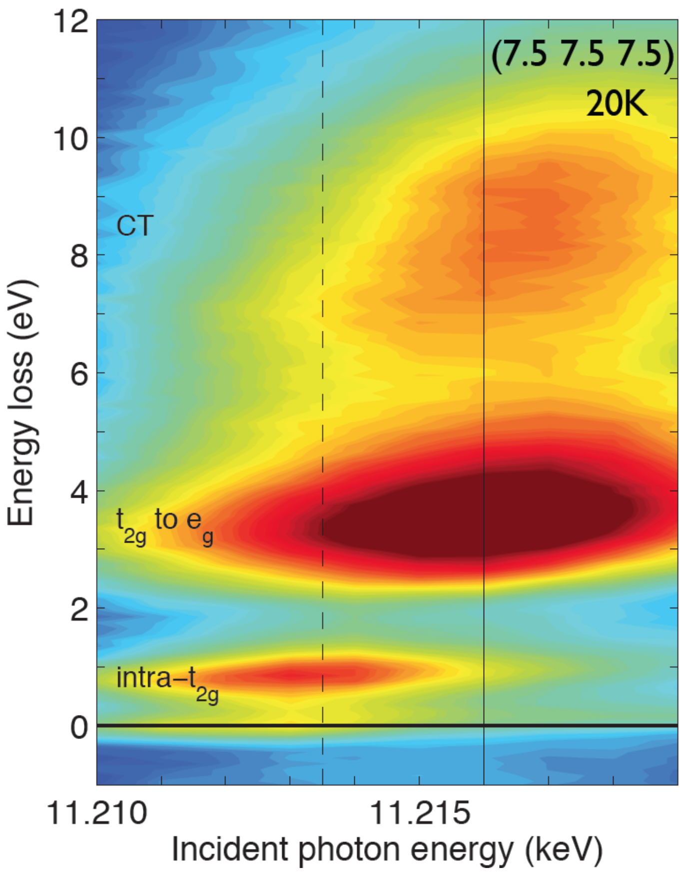


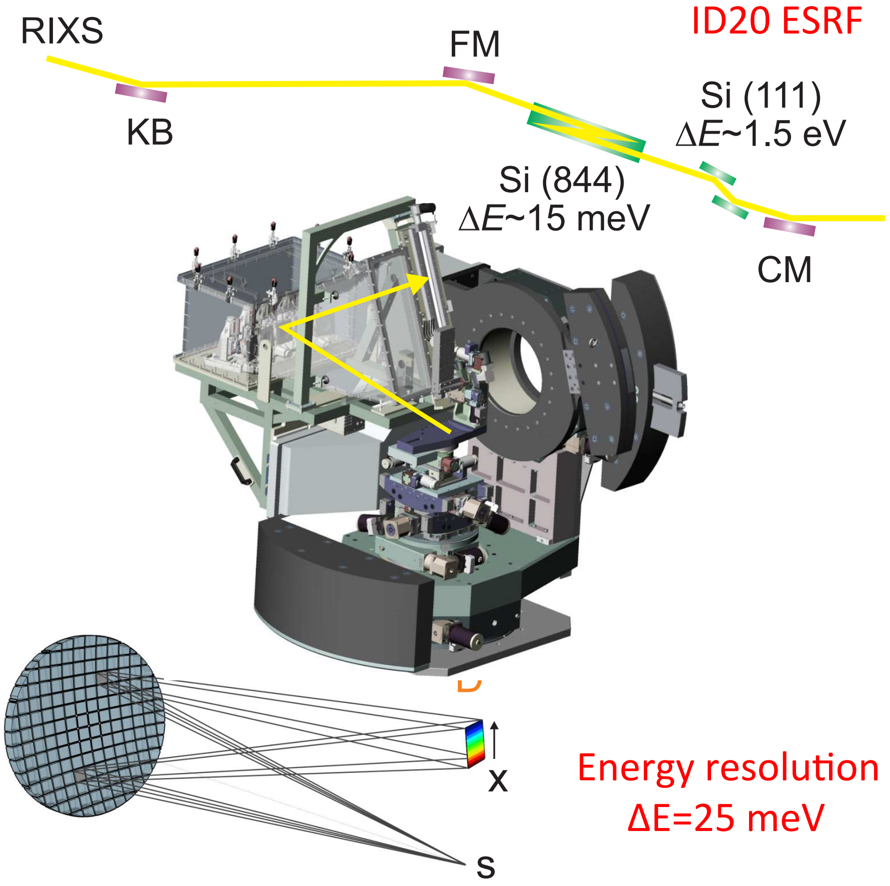


Resonant Inelastic X-ray Scattering (RIXS)

- Element and electron shell specific
- Momentum and energy resolved
- Probes excitation spectrum from meV to eV
- Large resonant enhancements possible
- Small micron sized samples can be studied
- Single magnon excitations can be measured

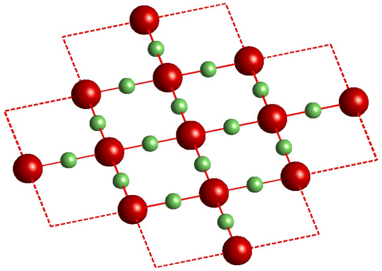






ID20 ESRF

Energy resolution
ΔE=25 meV

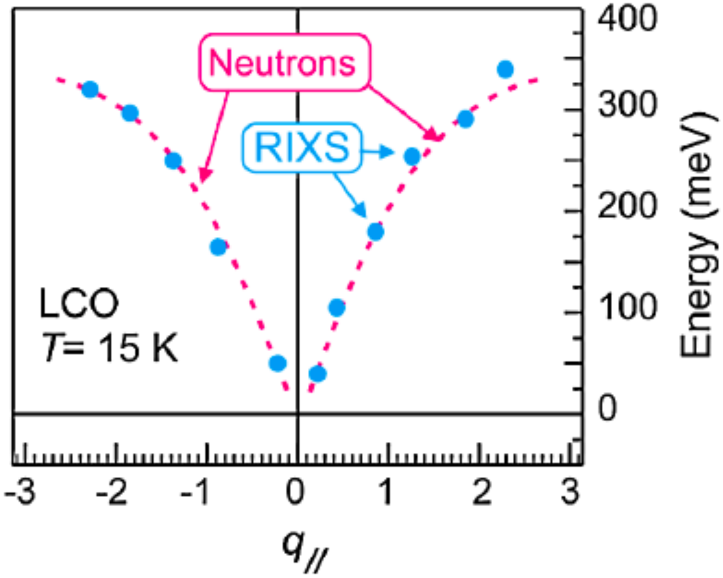


2D quantum Heisenberg antiferromagnet

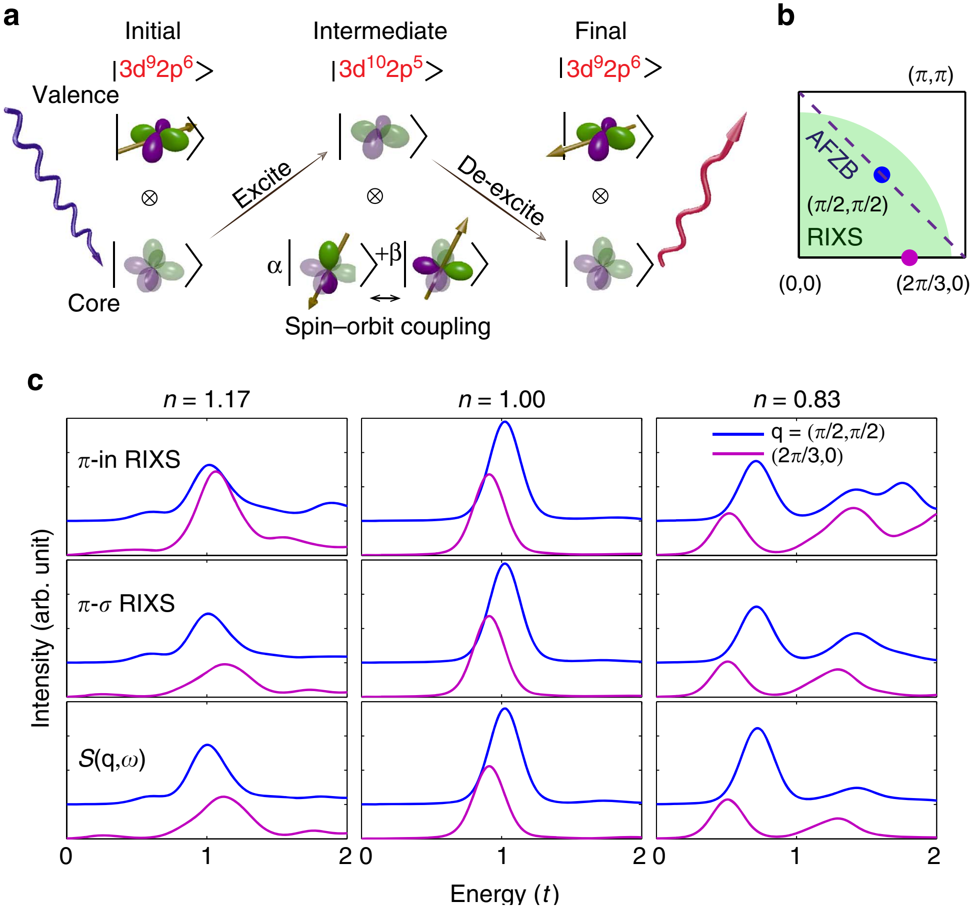
Observation of single magnons by RIXS

La_2CuO_4

RIXS Cu L_3 edge (930 eV)
Braicovich et al. PRL (2010)

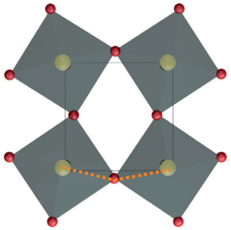


Does RIXS measure a S(Q,w) similar to magnetic neutron scattering?



Yes according to ED calculations on Hubbard model
Jia et al. Nature Comms. (2013)

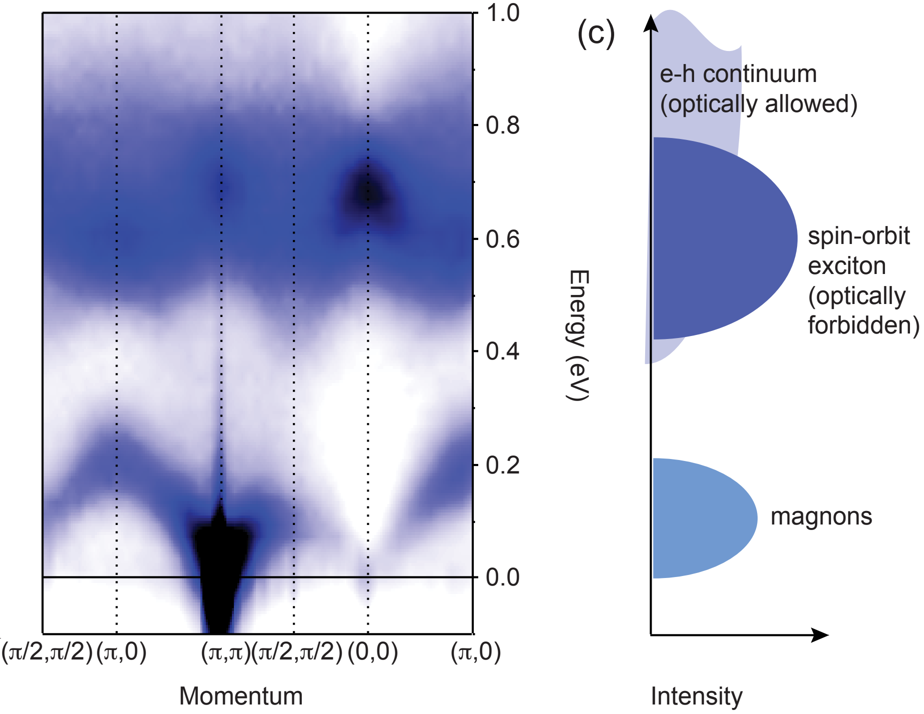
2D quantum Heisenberg antiferromagnets

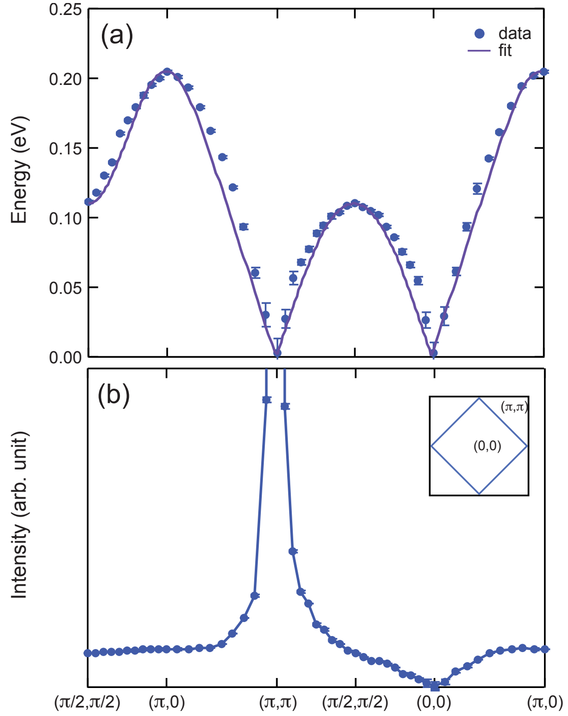


Sr_2IrO_4

- Strong spin-orbit coupling for Ir^{4+} yields $J_{eff}=1/2$ groundstate (re LCO which has S=1/2).
- RIXS excitation spectrum displays dispersing magnons up to ~250 meV and $J_{eff}=1/2\to3/2$ excitons at higher energy.
- First time X-rays have determined magnon spectrum across full BZ before neutrons (Ir strong neutron absorber)
- Fit yields J =60, J ′ =- 20, and J′′=15 meV

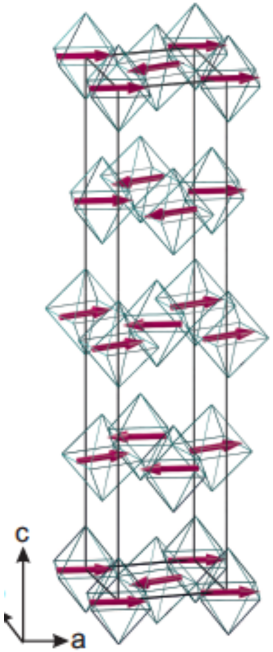
RIXS Ir L_3 edge (11.213 keV)
Kim et al. PRL (2012)



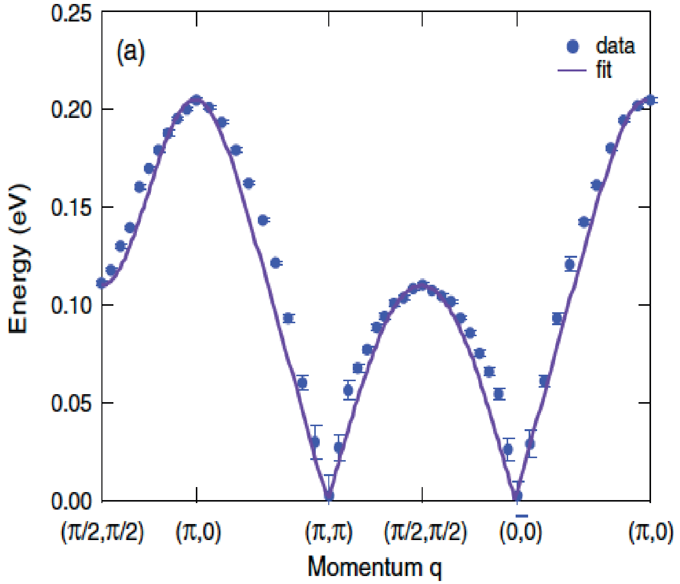


See Vale et al. PRB (2015) for importance of XY anisotropy

Magnetic ground states and excitations of the Mott insulating state in $Sr_{n+1}Ir_nO_{3n+1}$

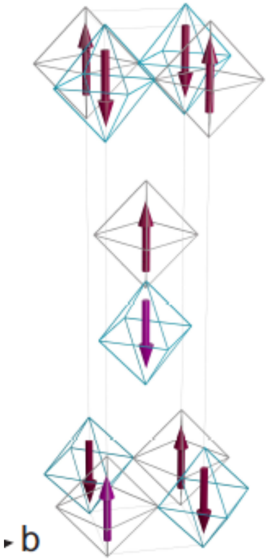


Sr_2IrO_4, J. Kim et al. PRL 108 (2012).

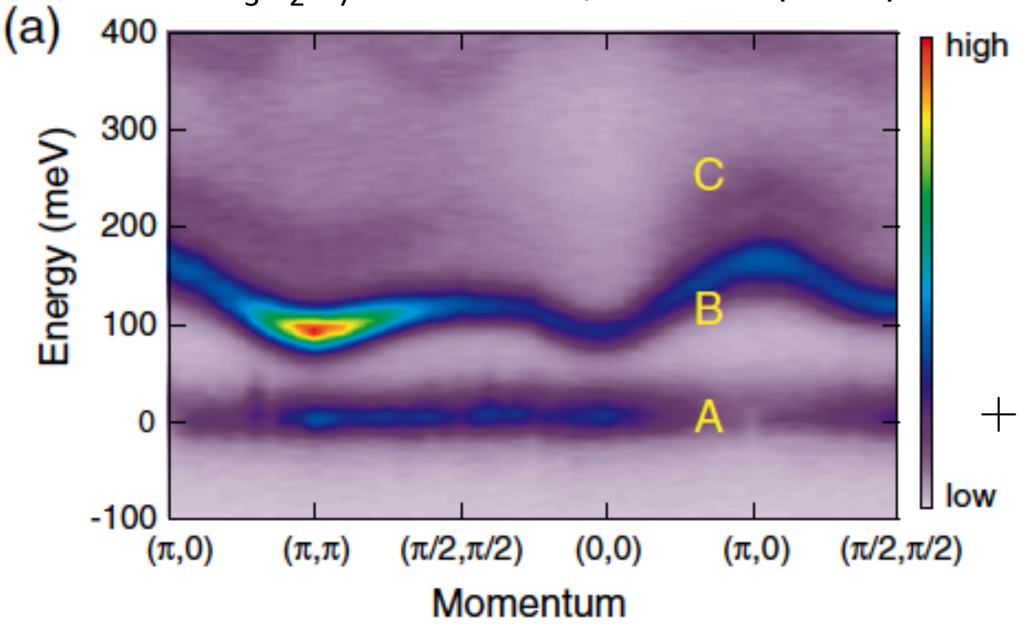


Isotropic
Heisenberg
Exchange

$$J_1 \mathbf{S}_i \cdot \mathbf{S}_j$$



$Sr_3Ir_2O_7$ J. Kim et al., PRL 109 (2012)

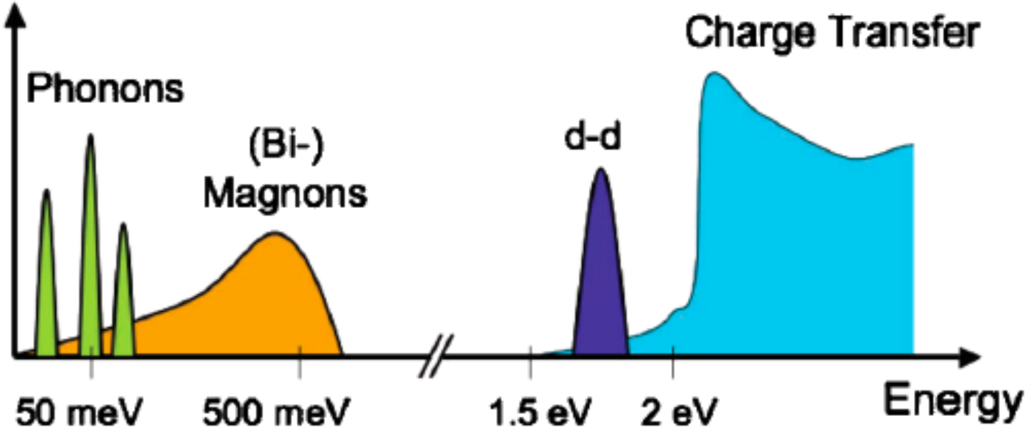


Anisotropic
Pseudo-dipolar
Exchange

$$J_1 \mathbf{S}_i \cdot \mathbf{S}_j + J_2(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})$$

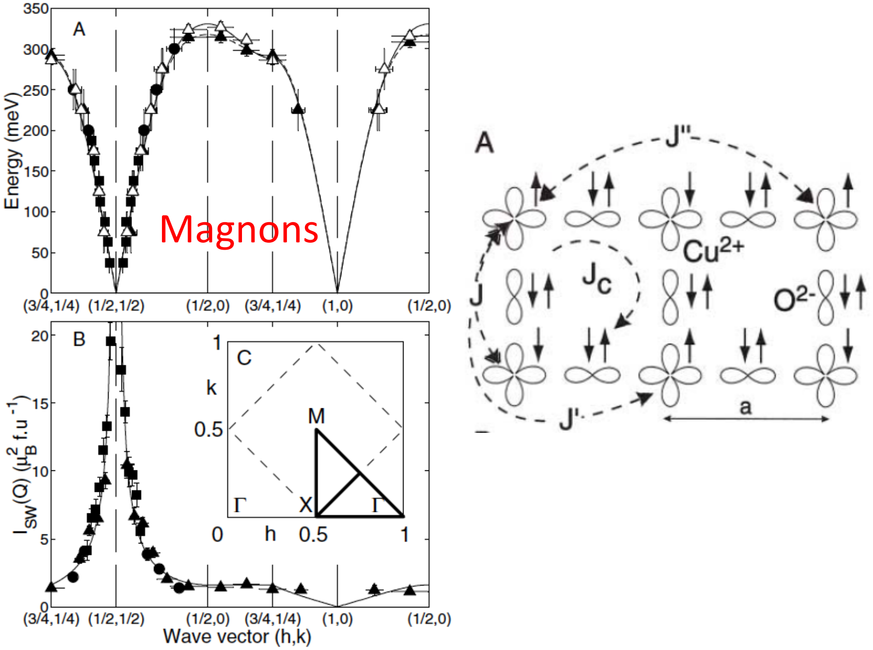
Emergent Excitations and the Quasi-particle Zoo

Neutron and X-ray Spectroscopy

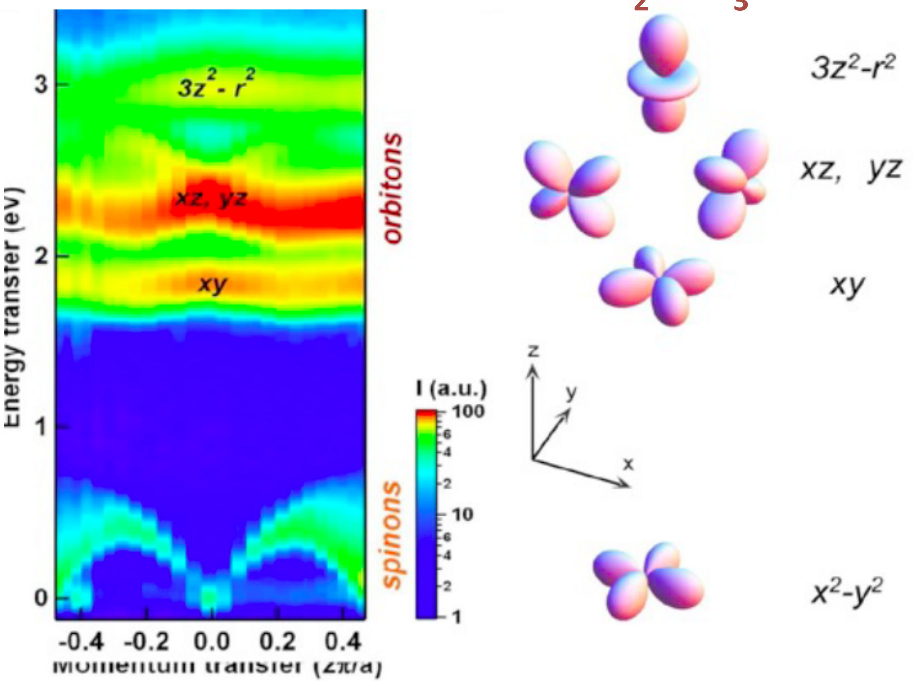


Inelastic Neutron Scattering
2D Mott Insulator La_2CuO_4

Resonant Inelastic X-ray Scattering
1D Mott Insulator Sr_2CuO_3



Coldea et al. Phys. Rev. Lett. (2001)



Schlappa et al. Nature (2012)

Summary: Iridates

- Study of magnetic structures and excitations provide unique insights into the role of spin-orbit coupling in iridates including symmetry of wavefunctions and effective low-energy Hamiltonian

- $(Sr,Ba)_2IrO_4$ are spin-orbit Mott insulators with Jeff=1/2 groundstate

  - Evidence from XRMS, RIXS, ARPES, XAS etc

- Magnetically $(Sr,Ba)_2IrO_4$ are remarkably similar to La_2CuO_4

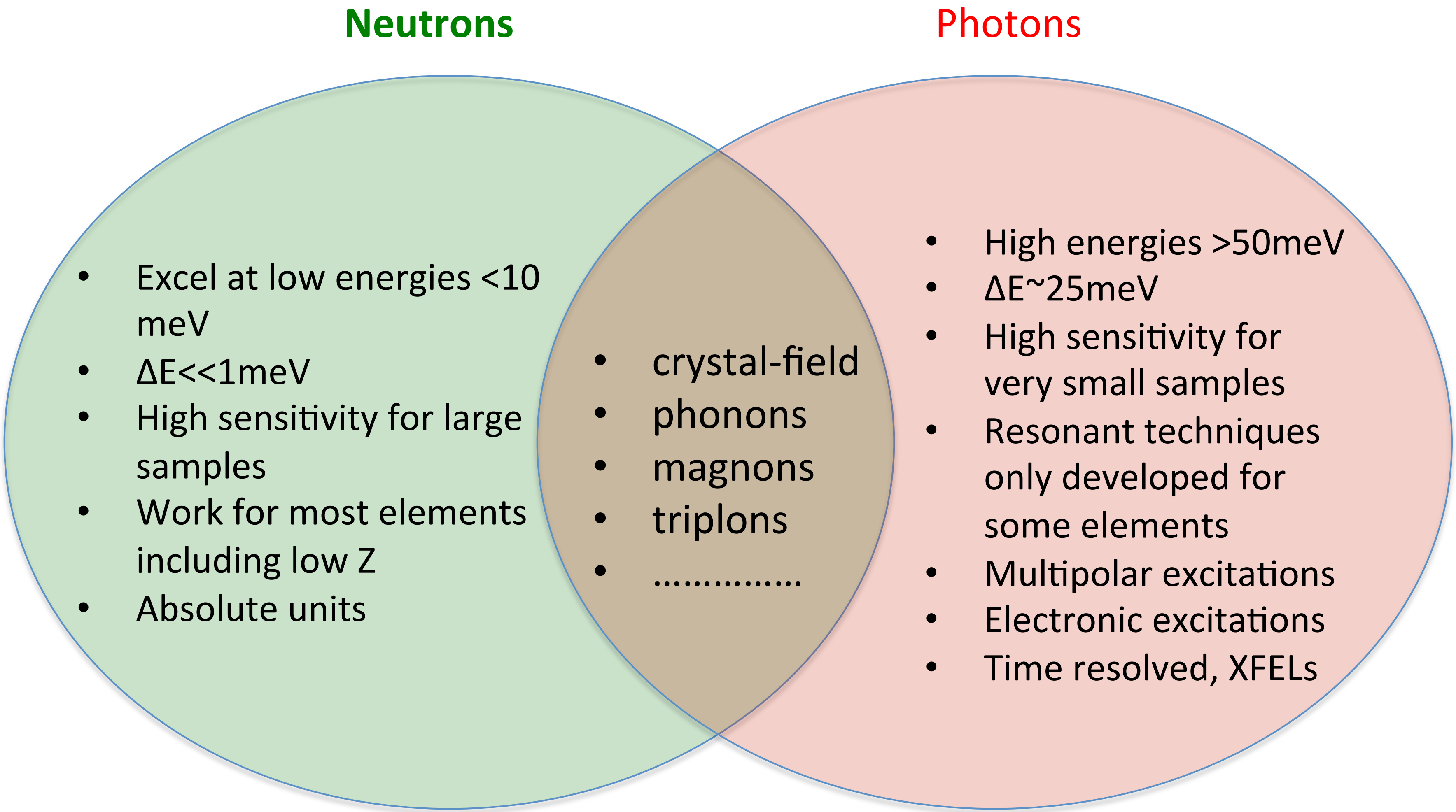
  - High-Tc Superconductivity? If not, why not?

- Spin reorientation in $Sr_3Ir_2O_7$ driven by competition between isotropic and bond-directional, anisotropic interactions unique to Jeff=1/2 state

- Novel magnetic structures displayed by honeycomb iridates provide compelling evidence for the realisation of Kitaev physics

  - How to tune interactions to create a quantum spin liquid?

Excitations with neutrons and X-rays



Neutrons

- Excel at low energies <10 meV
- ΔE<<1meV
- High sensitivity for large samples
- Work for most elements including low Z
- Absolute units

- crystal-field
- phonons
- magnons
- triplons
- ……………

Photons

- High energies >50meV
- ΔE~25meV
- High sensitivity for very small samples
- Resonant techniques only developed for some elements
- Multipolar excitations
- Electronic excitations
- Time resolved, XFELs