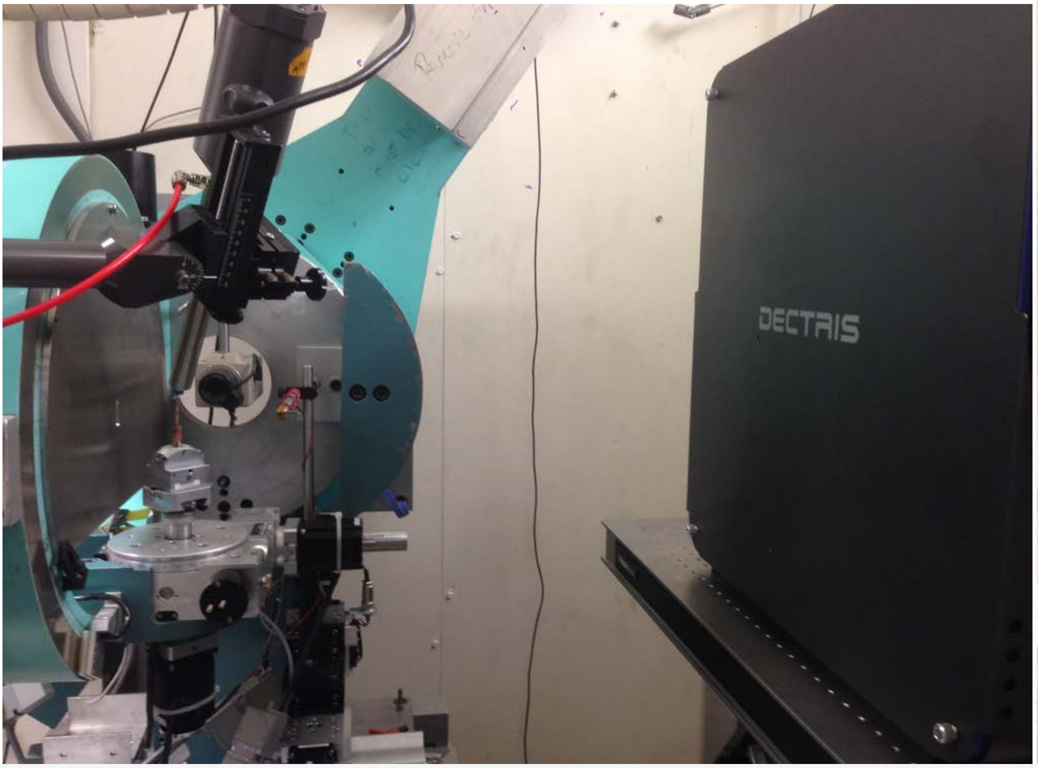
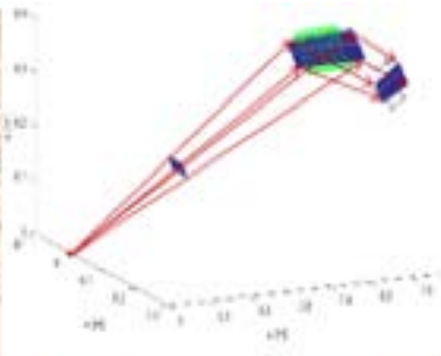
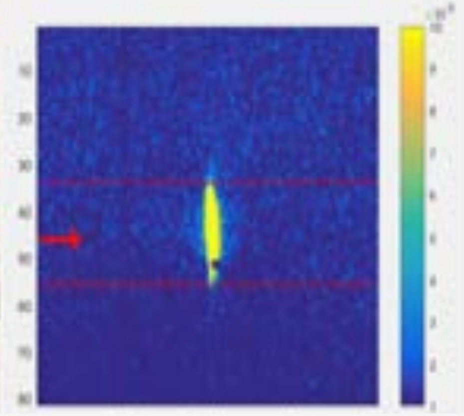
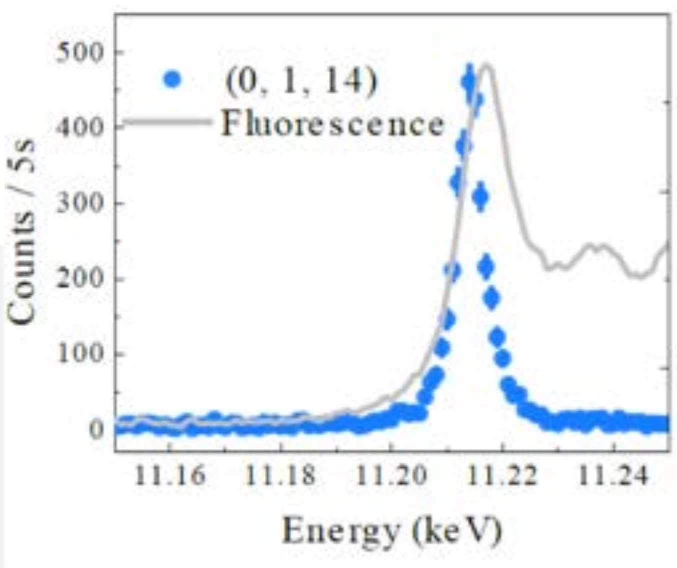
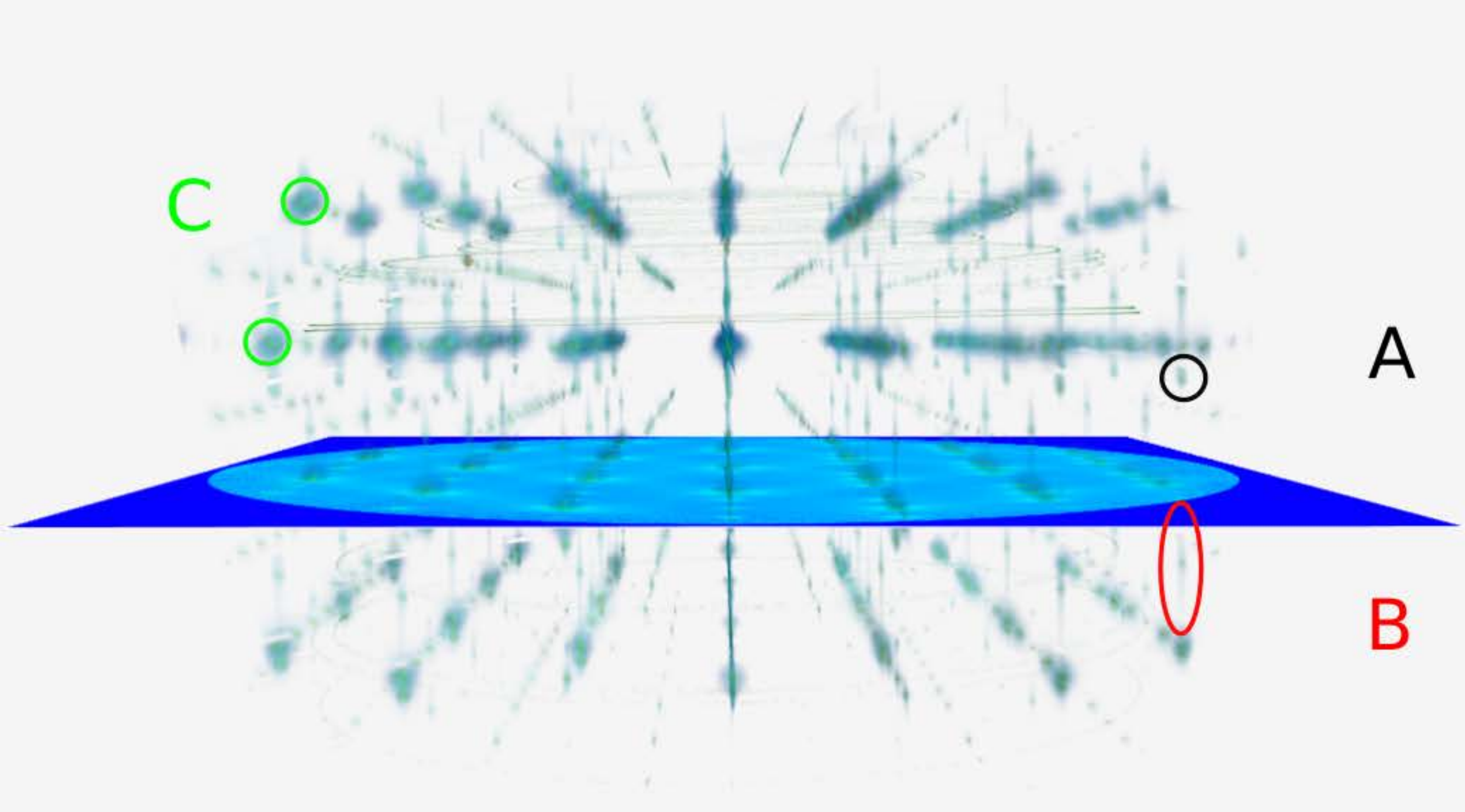
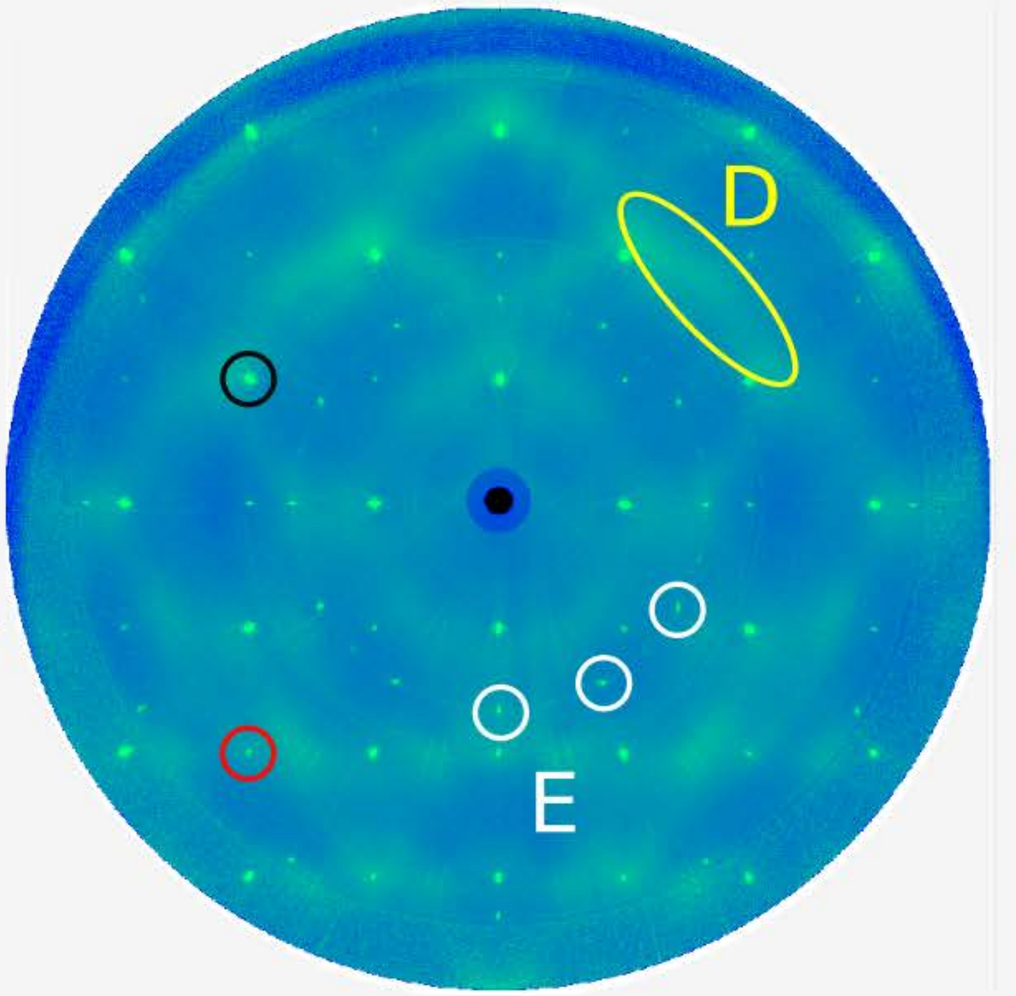

DECTRIS






(0, 1, 14)
Fluorescence
Counts / 5s
500
400
300
200
100
0
11.16
11.18
11.20
11.22
11.24
Energy (keV)

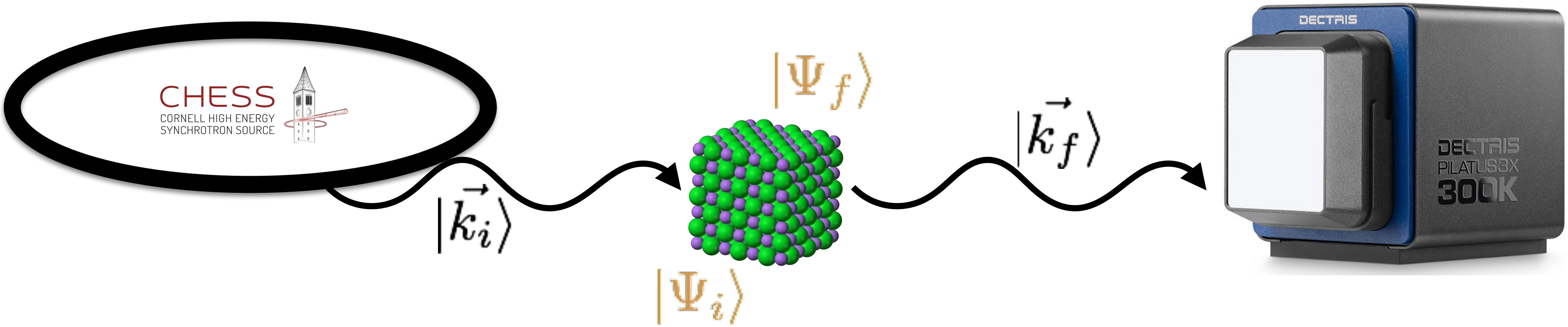

C
A
B


D
E

1. Preamble - Properties of X-rays

What I'm going to talk about:

Using bright, accelerator-based x-ray facilities to perform photon-in, photon-out studies of quantum materials.



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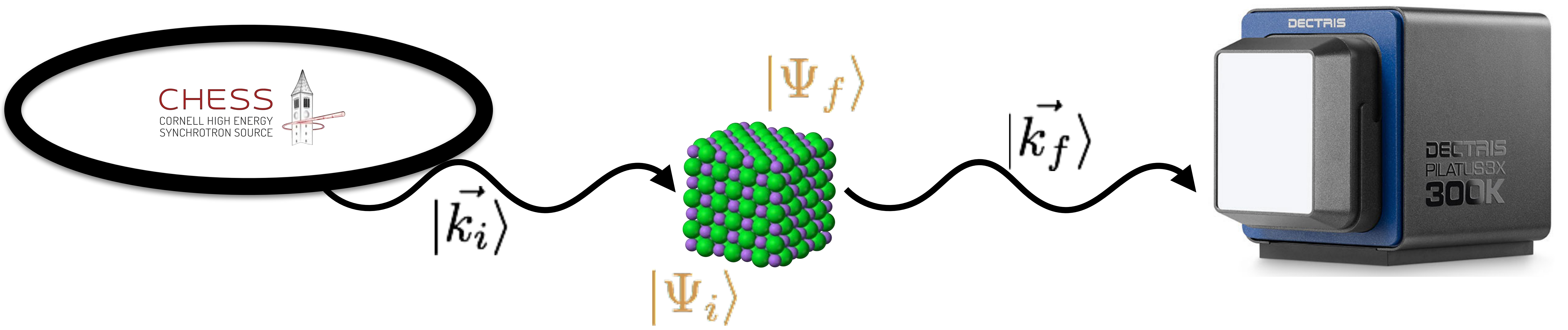
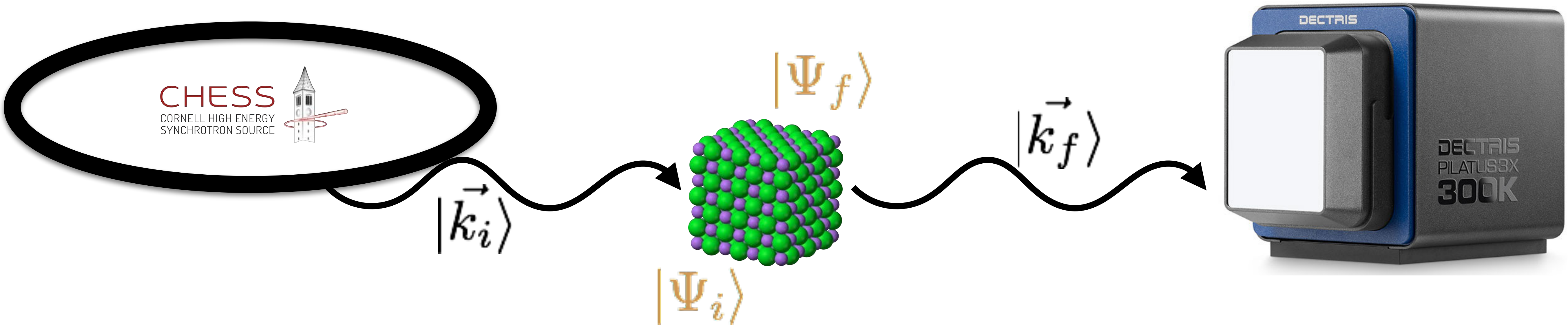


What I'm NOT going to talk about:

Photo-emission, x-ray "home labs", UV / IR / THz, details of sources / optics

What I'm going to talk about:

Using bright, accelerator-based x-ray facilities to perform photon-in, photon-out studies of quantum materials.

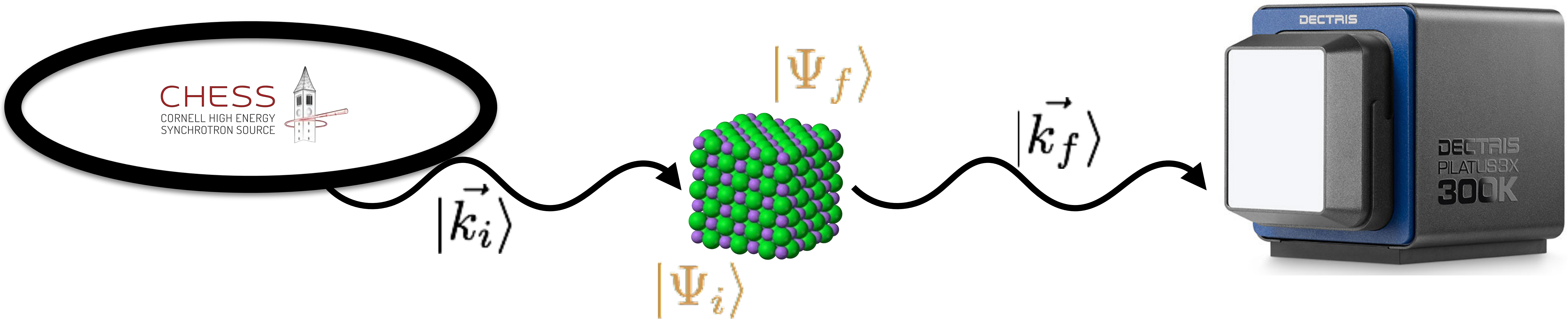


Goals for these lectures:

(i) Help you become discriminating consumers of x-ray data

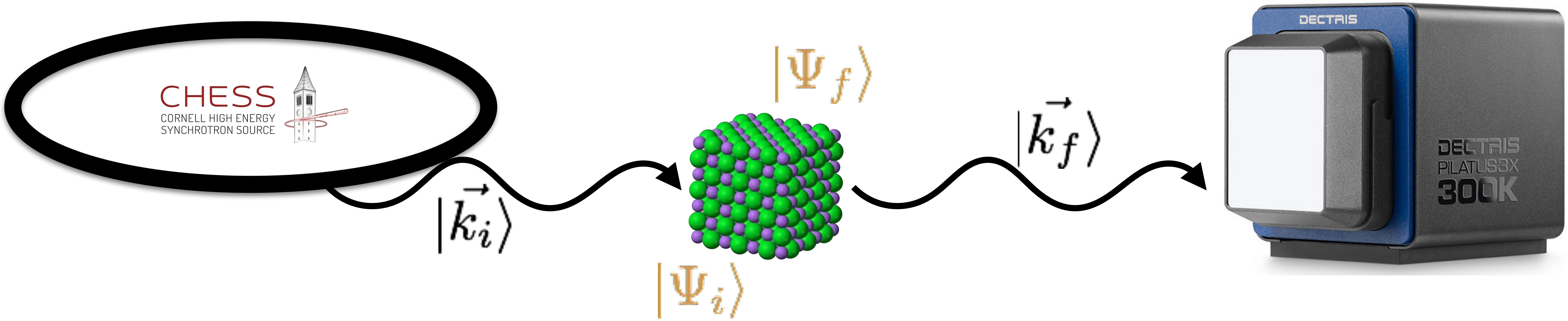
(ii) Introduce techniques that are potentially useful for your research

(iii) Recruit quantum materials users for the lightsources; maximize our "slice of the pie"



Single X-ray photon properties of interest

Energy	$E = \left(\frac{hc}{\lambda}\right)$
Wavelength	λ
Polarization	$\hat{\epsilon}$
Vector Momentum	$\vec{k}$



Single X-ray photon properties of interest

Energy $E = \left(\frac{hc}{\lambda}\right)$

Wavelength λ

Polarization $\hat{\epsilon}$

Vector Momentum $\vec{k}$

X-ray beam properties of interest

Bandwidth $\frac{\Delta E}{E}$

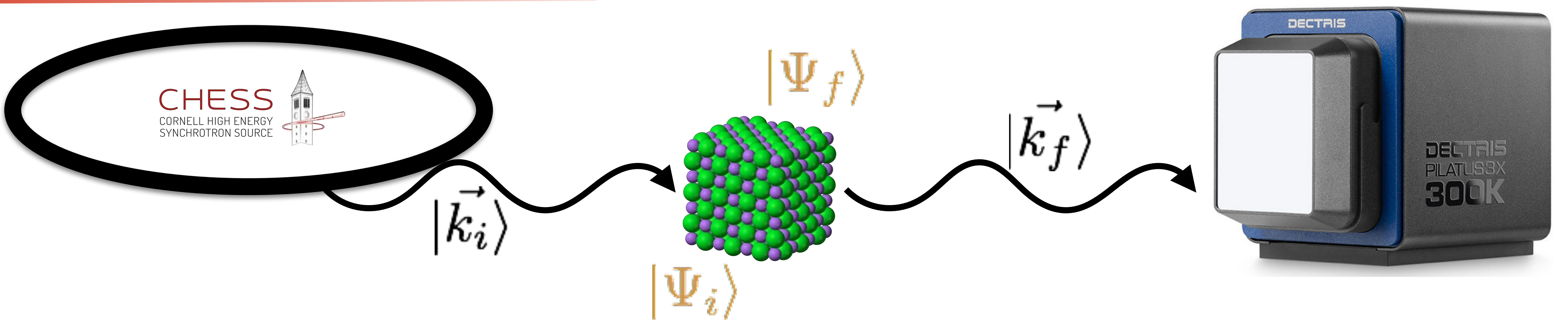
Size, Divergence s, ν

Avg. Polarization P

Coherence Length ξ_t

Flux (Photons/s)

Time Structure, Pulse Width, Rep Rate



Single X-ray photon properties of interest

Energy	$E = \left(\frac{hc}{\lambda}\right)$
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X-ray beam properties of interest

Bandwidth	$\frac{\Delta E}{E}$
Size, Divergence	s, ν
Avg. Polarization	P
Coherence Length	ξ_t
Flux	(Photons/s)
Time Structure, Pulse Width, Rep Rate	

For an ideal x-ray expt, all of these properties would be tunable for $|\vec{k}_i\rangle$ and resolvable for $|\vec{k}_f\rangle$. Typically, the more desirable beams have more similar (~identical) incident photons.

What is achievable? Typical beam properties at a modern synchrotron x-ray light source:

$E = \left(\frac{hc}{\lambda}\right)$	0.2 keV - 200 keV	*Electron binding energies*
λ	60$\mathring{A}$ - 0.06$\mathring{A}$	*Atomic scale*
$\frac{\Delta E}{E}$	10^{-2} - 10^{-7}	*Resolution / Resolving Power*
s	50 nm - 5 mm	*Mesoscale, domains, phase sep.*
ν	3μrad - 300μrad	*Intrinsic rocking curves*
P	Tunable linear / circular	*Dichroism, magnetism*
ξ_t	microns	*Mesoscale, domains, phase sep.*
Flux	10^9 - 10^{14} ph/s	*Trade flux for precision*
Pulse Length	picoseconds	
Rep Rate	MHz	

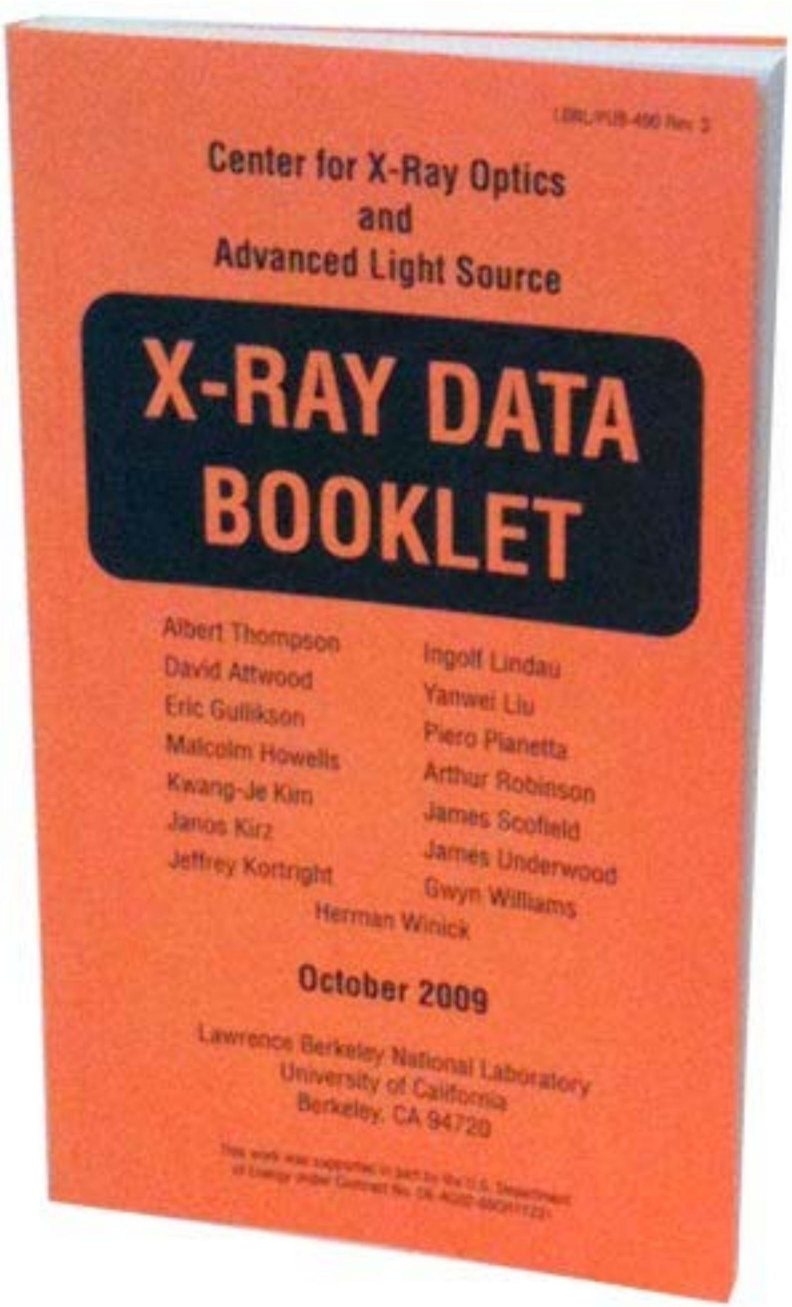


Table 1-1: Electron binding energies

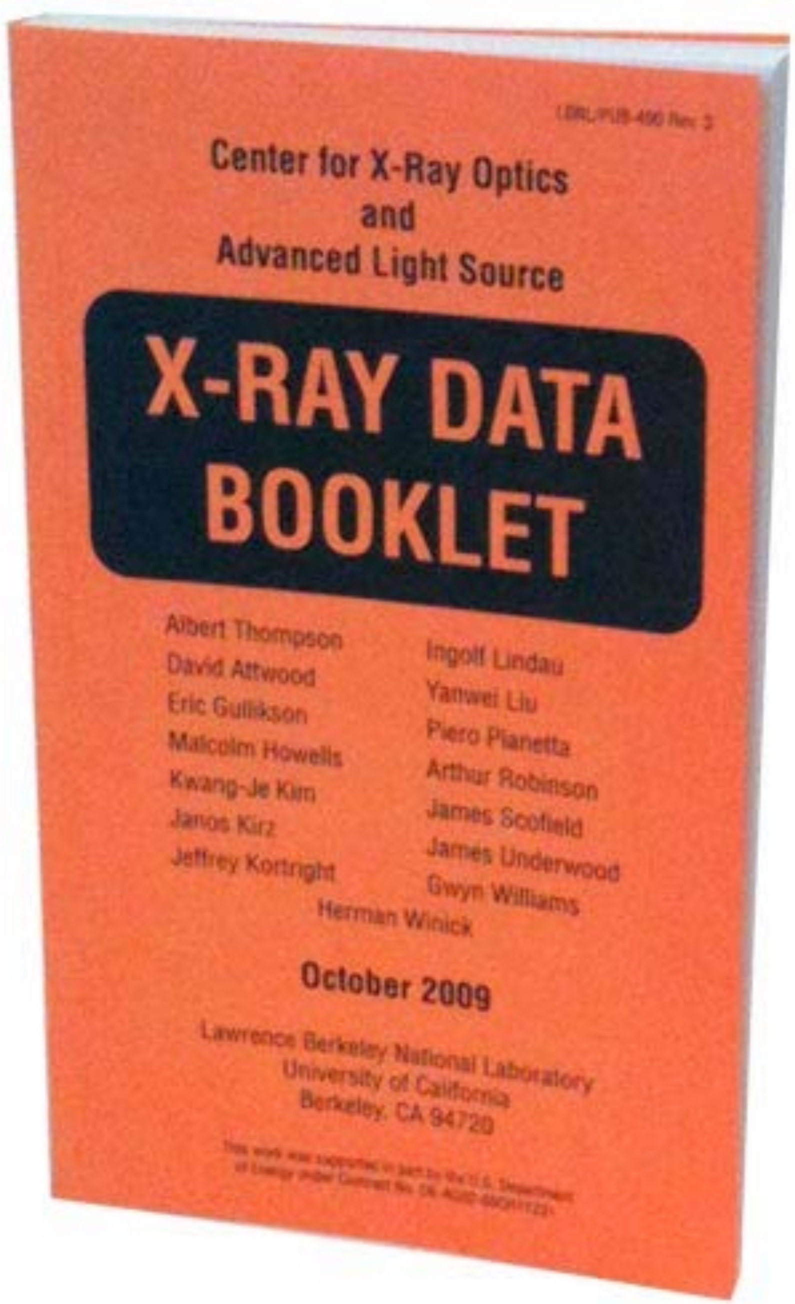
Table 1-2: Energies of x-ray emission lines

Section 2: Details of synchrotron radiation generation

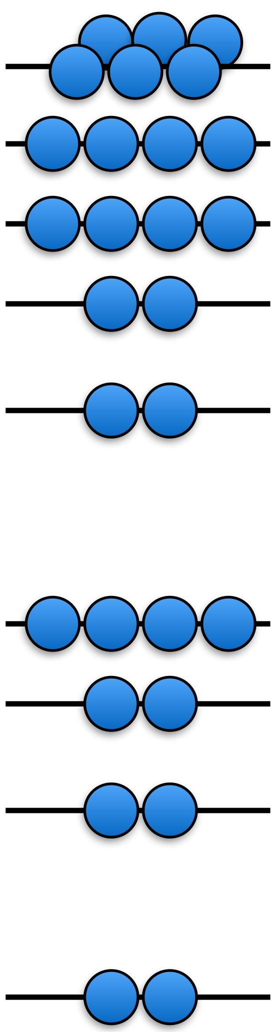
Section 4: X-ray optics and detectors

http://cxro.lbl.gov/x-ray-data-booklet

Notes on "X-ray Notation"



$n\,\ell_{m+s}$	X-ray	$(n,\ell,m+s)$
$3d_{5/2}$	M_5	(3,2,5/2)
$3d_{3/2}$	M_4	(3,2,3/2)
$3p_{3/2}$	M_3	(3,1,3/2)
$3p_{1/2}$	M_2	(3,1,1/2)
3s	M_1	(3,0,1/2)
$2p_{3/2}$	L_3	(2,1,3/2)
$2p_{1/2}$	L_2	(2,1,1/2)
2s	L_1	(2,0,1/2)
1s	K	(1,0,1/2)



s: $\ell=0$
p: $\ell=1$
d: $\ell=2$
f: $\ell=3$

Summary: Properties of X-rays

- X-rays penetrate into the bulk of a material, and probe average structure / chemistry
- X-rays interact strongly with electron charges, and more weakly with spins and nuclei
- Flux, polarization, bandwidth, and coherence can be prepared to order, within limits, using accelerator-based sources and crystal optics
- X-ray energies are comparable to electronic energy levels in atoms
- X-ray wavelengths are comparable to size of atoms and unit cells

2. X-ray Light Sources

World-wide suite of light sources: More than 50 user facilities, various specialties

Accelerate electrons to relativistic speed, wiggle them to produce x-rays

lightsources.org

X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

Argonne NATIONAL LABORATORY

CHESS CORNELL HIGH ENERGY SYNCHROTRON SOURCE

USA, Low/Mid Energy Storage Rings

ALS ADVANCED LIGHT SOURCE

BROOKHAVEN NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

USA, Free Electron Laser

SLAC NATIONAL ACCELERATOR LABORATORY

Canada & Brazil, Mid-Energy Storage Rings

Canadian Light Source | Centre canadien de rayonnement synchrotron

LNLS

X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

Argonne NATIONAL LABORATORY

CHESS CORNELL HIGH ENERGY SYNCHROTRON SOURCE

~ 6 GeV Rings
Best choice for E > 10 keV

USA, Low/Mid Energy Storage Rings

ALS ADVANCED LIGHT SOURCE

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ALS ADVANCED LIGHT SOURCE

BROOKHAVEN NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

1 - 3 GeV Rings
Best choice for E < 10 keV
Most coherence @ NSLS-II

USA, Free Electron Laser

SLAC NATIONAL ACCELERATOR LABORATORY

Canada & Brazil, Mid-Energy Storage Rings

Canadian Light Source
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LNLS

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ALS ADVANCED LIGHT SOURCE
BROOKHAVEN NATIONAL LABORATORY
SLAC NATIONAL ACCELERATOR LABORATORY

USA, Free Electron Laser

SLAC NATIONAL ACCELERATOR LABORATORY

↔

2.5 - 17 GeV LINAC
Coherent, brilliant, femtosecond pulses, 100Hz rep rate, E < 10 keV.

Canada & Brazil, Mid-Energy Storage Rings

Canadian Light Source
Centre canadien de rayonnement synchrotron
LNLS

X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

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ALS ADVANCED LIGHT SOURCE

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SLAC NATIONAL ACCELERATOR LABORATORY

USA, Free Electron Laser

SLAC NATIONAL ACCELERATOR LABORATORY

Canada & Brazil, Mid-Energy Storage Rings

Canadian Light Source | Centre canadien de rayonnement synchrotron

LNLS

1 - 3 GeV Rings
Best for E < 10 keV
Some specialized beamlines

QUESTION 1:

You have synthesized a novel cuprate compound. You want to perform x-ray absorption spectroscopy studies of the Cu L-edges, to understand doping of the d-bands. The next round of user experiments will occur in February. Choose a suitable light source where you would apply for beam time.

A — CHESS, Cornell High Energy Synchrotron Source

B — Argonne National Laboratory

C — ALS, Advanced Light Source

D — Canadian Light Source / Centre canadien de rayonnement synchrotron

E — LNLS

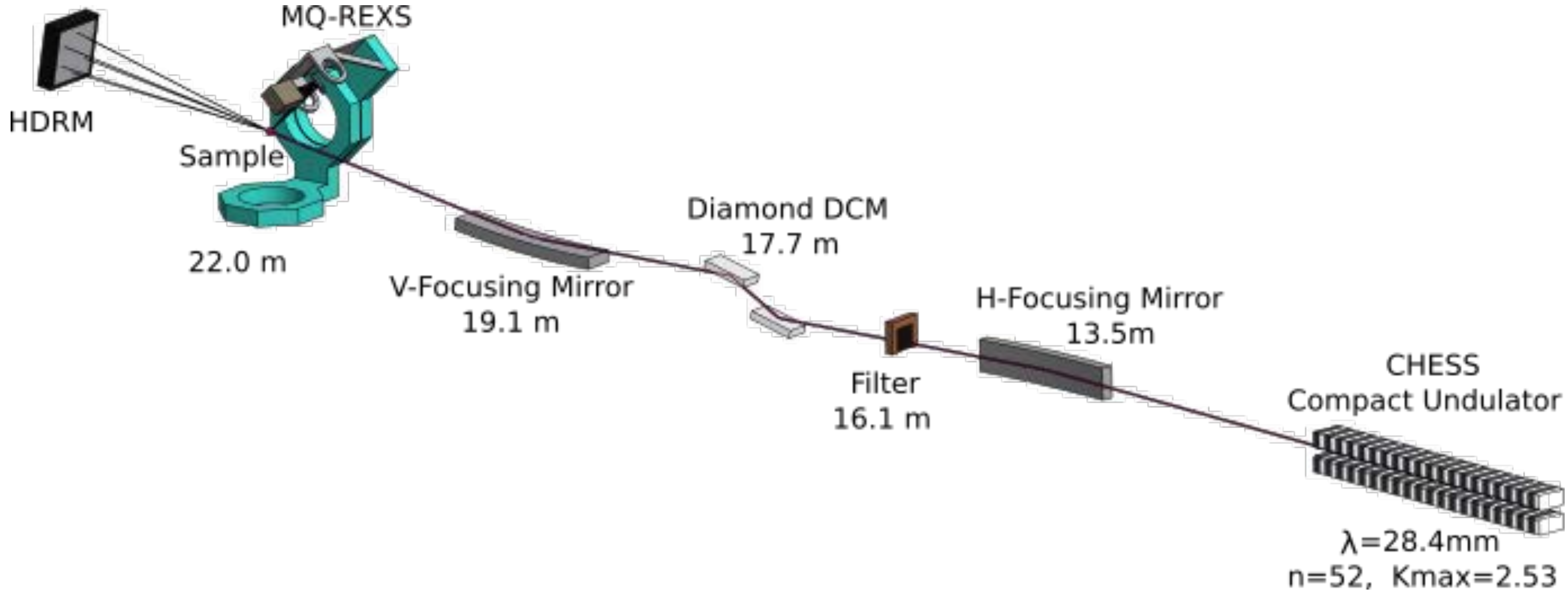
What is a “beamline”?

(i) Insertion device to make x-rays

(ii) Optics to condition the beam

(iii) Hutch to perform experiments without irradiating ourselves

(iv) Experimental equipment (Diffractometers, spectrometers, magnets, lasers, fridges, etc.)



Lightsources represent a massive investment in science!

Total US expenditures by state and federal agencies on the construction and operation of lightsources is of order **$1B / year.** There are ~200 beamlines in operation in the Amercias.

These facilities are almost exclusively run as free, open resources for academic users, with beam time and new instrument construction based on merit of scientific proposals from domain scientists like you.

Lightsources are interdisciplinary facilities, where quantum science competes for resources against life science, chemistry, engineering, medicine, etc.

Getting involved with lightsources can enrich your research, while also making sure that a larger share of these resources are allocated towards the problems you find most interesting.

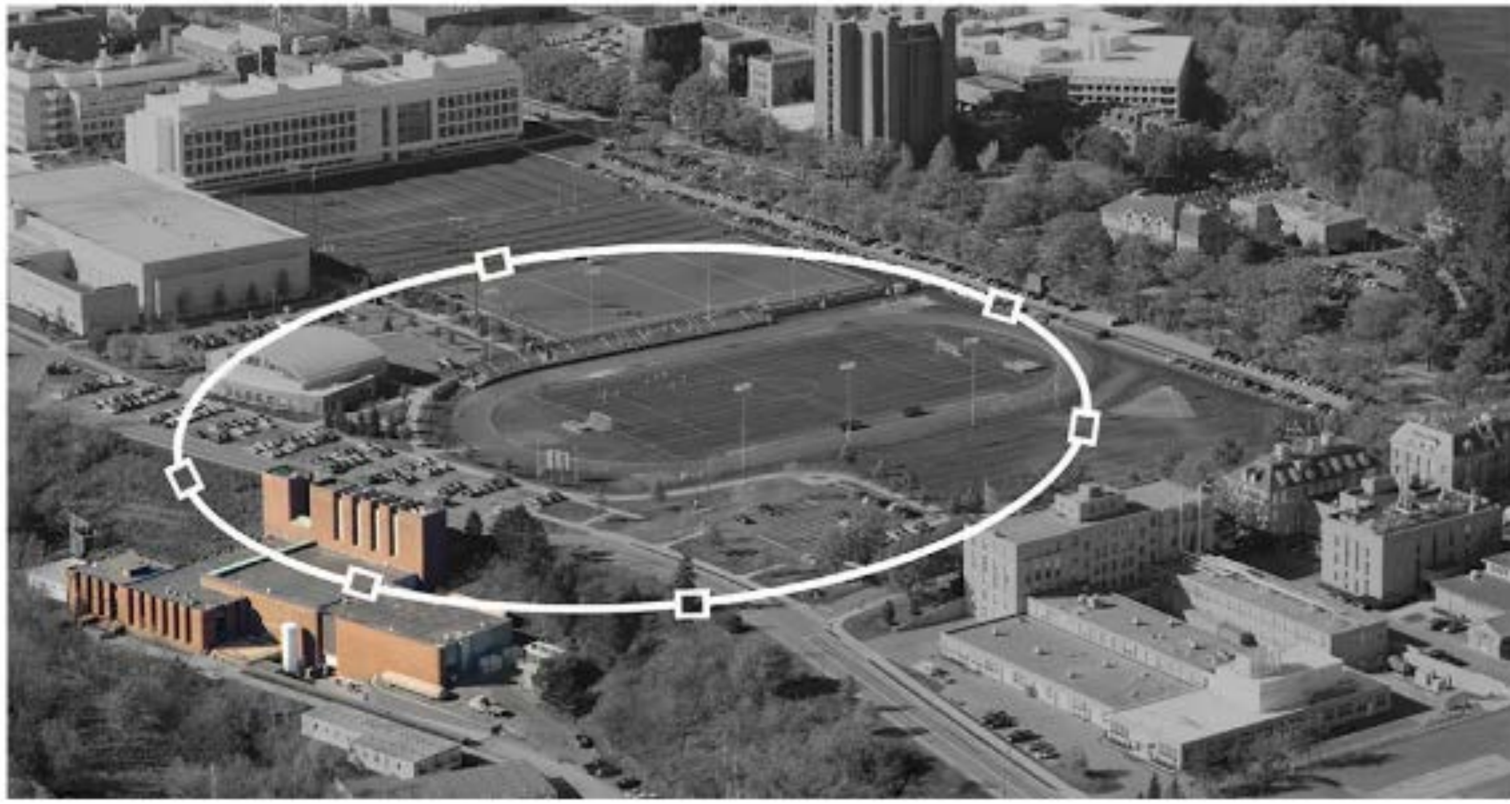
Commercial break:

Storage Ring (CESR):

- 768 m circumference
- 5 stories under ground
- 5.3 GeV (1 of 5 in world)
- 120 mA of both e^- and e^+

CHESS:

- 1,300 user visits/year
- 11 Experimental stations
- 3,800 hours/year of user operations

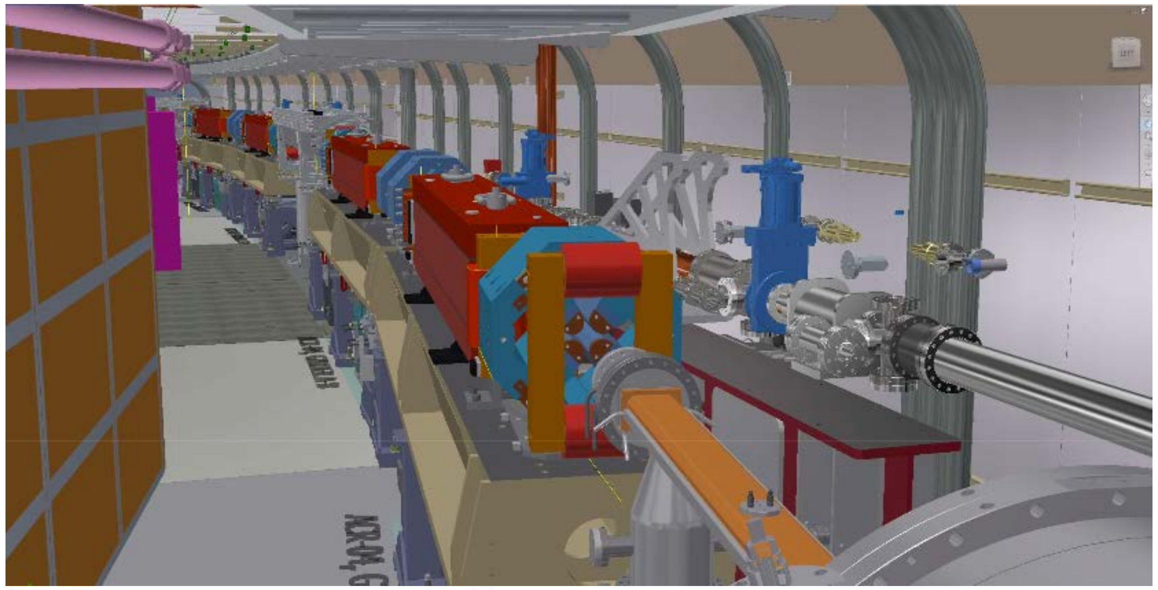


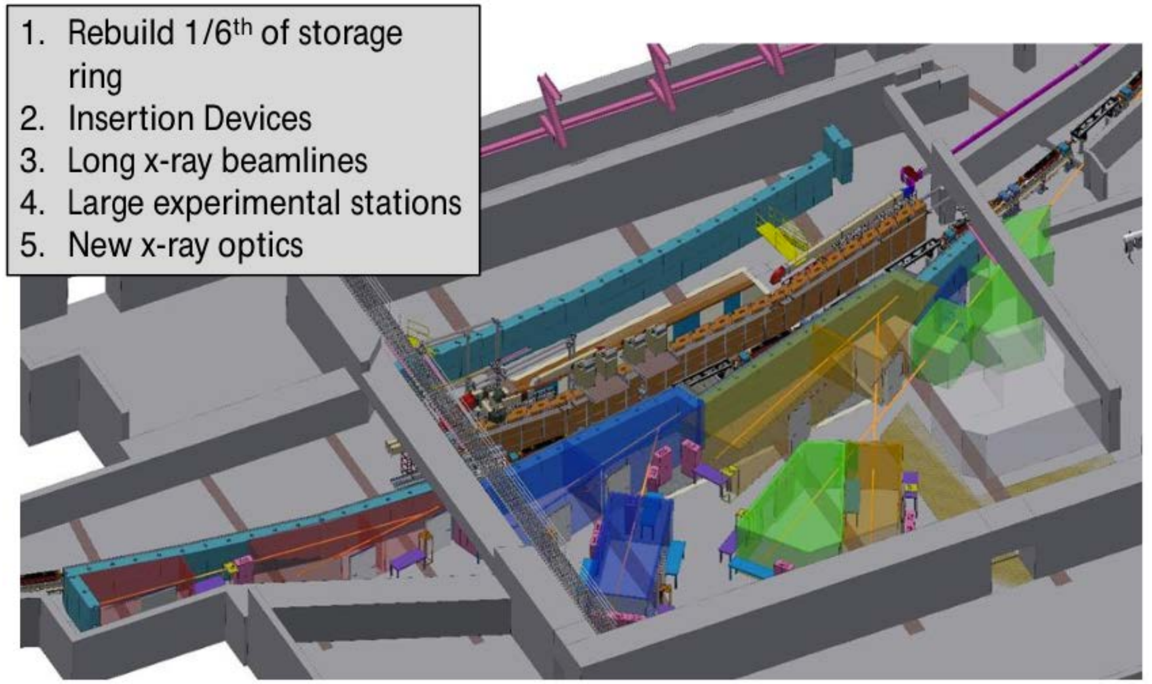
CHESS is one of 5 high-energy synchrotrons in the world, specializing in hard x-rays (5-100 keV). It is also the only synchrotron located on a university campus in the US. CHESS has a strong focus on teaching early career scientists and developing novel x-ray techniques.

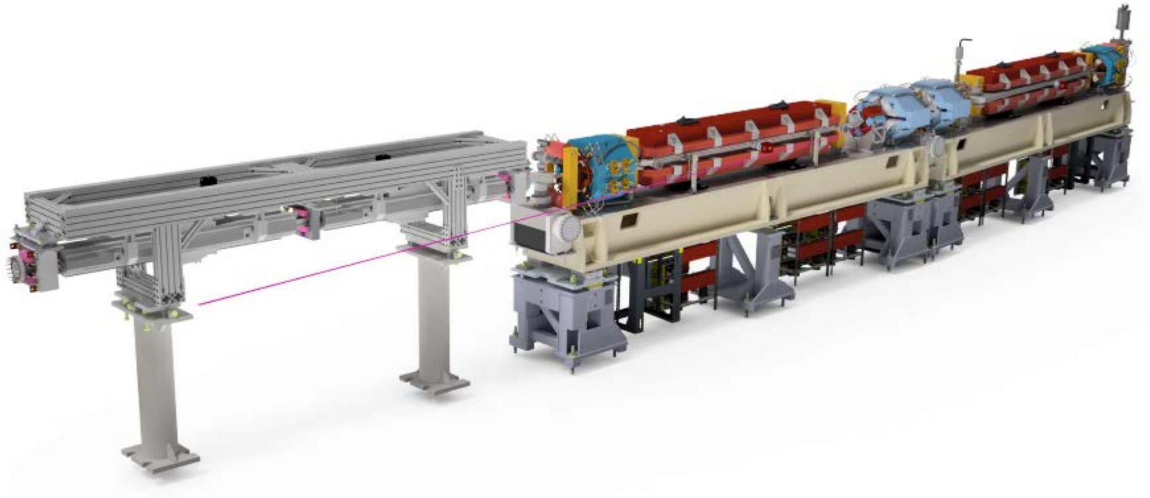
Commercial break:

CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE

Currently, the lab is undergoing a $15M upgrade (*CHESS-U*), which began on June 4. (Sorry, no tour!) After the upgrade, CHESS will deliver among the best high energy x-ray beams available anywhere worldwide. In addition to upgrades of the storage ring, CHESS-U will build out 6 new undulator beamlines for x-ray science.

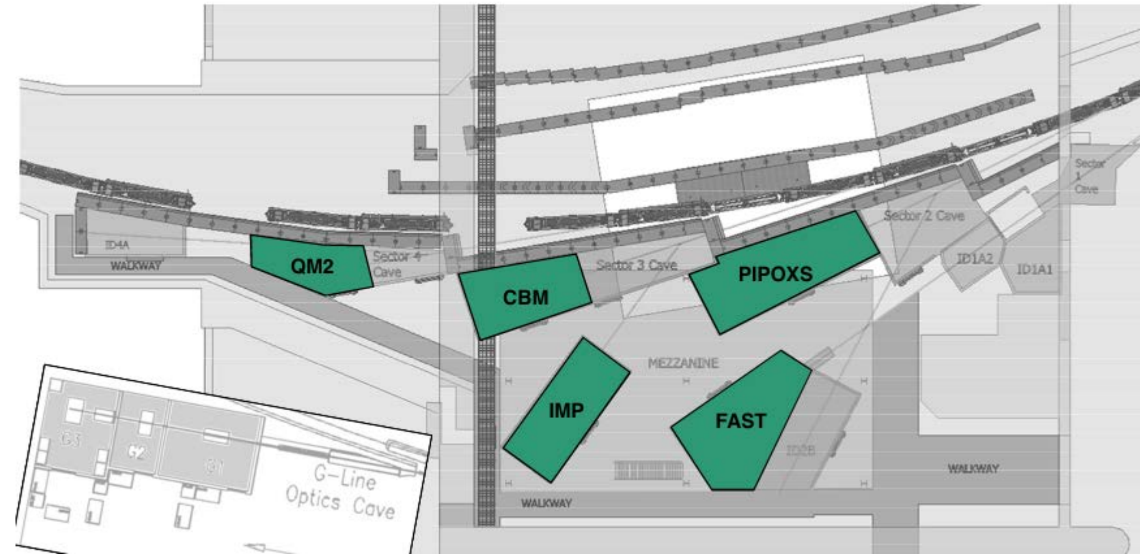






Commercial break: CHESS CORNELL HIGH ENERGY SYNCHROTRON SOURCE

BEAMLINES and Science Drivers



Two of the new beamlines will address forefront research problems in quantum materials.

<QM>^{2}: Q-Mapping for Quantum Materials. Optimized for speed and ease of use, we will map extensive regions of Q-space, using resonant and non-resonant elastic scattering. Uncover intertwined quantum correlations of spins, charges, and orbitals, from high to low temperatures and spanning entire phase diagrams.

PIPOXS: Photon-In, Photon-Out X-ray Spectroscopy. Spectroscopic studies of valence electronic states in functional materials, operable by domain scientists who are not synchrotron X-ray experts. The facility will enable in situ spectroscopic measurements of manmade catalysts and enzymes, research on fuel-cells, batteries, and electronic excitations in quantum materials.

Commercial break:

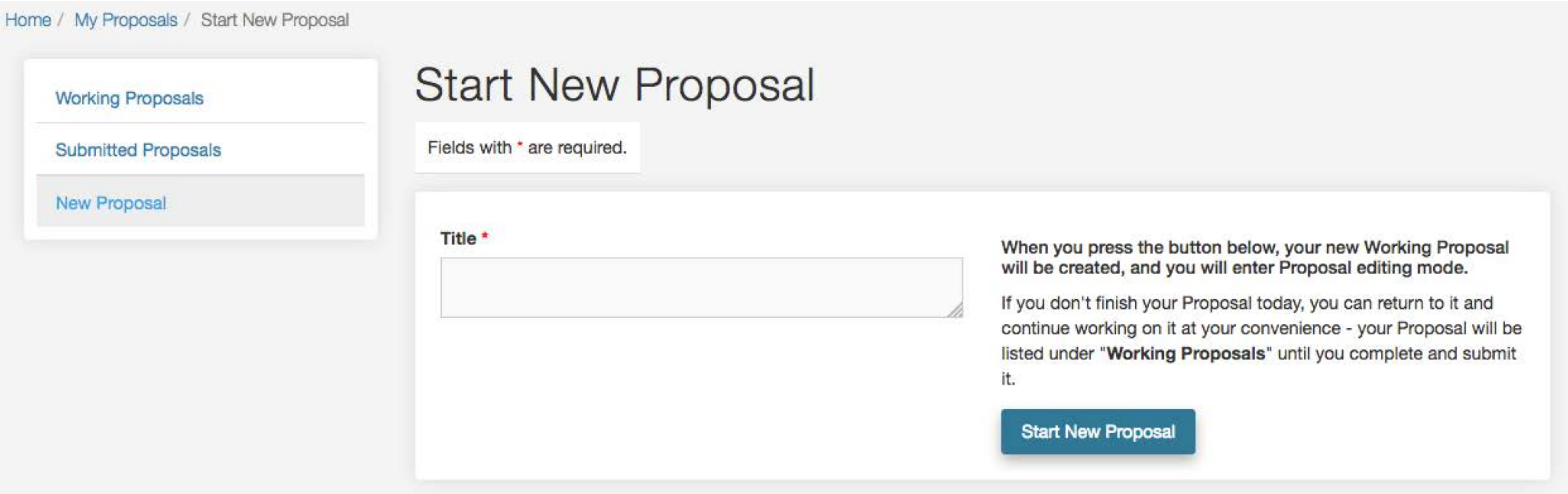
CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE

Beamline information is available at www.chess.cornell.edu

Proposals for user experiments can be submitted at userdb.chess.cornell.edu

Commissioning experiments will begin in early 2019.

If you want to take advantage of your x-ray facilities, but aren't sure how, feel free to contact me directly with inquiries: jruff@cornell.edu

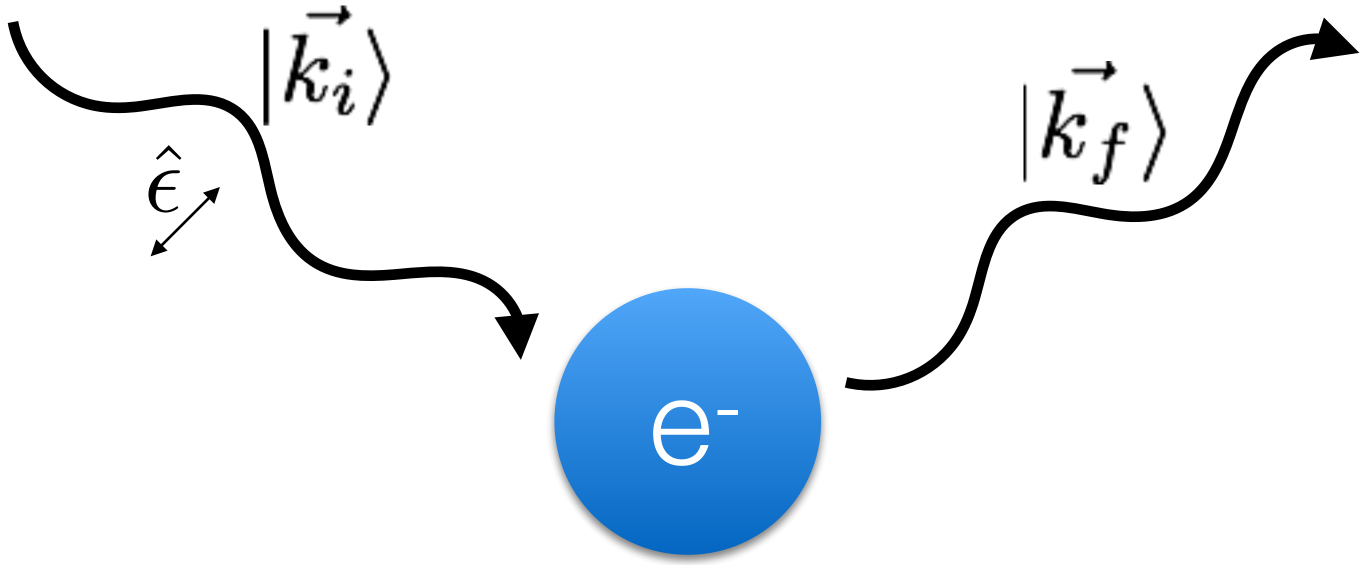


Summary: Light Sources

- X-ray light sources are a key component of international scientific infrastructure
- They are a worldwide multi-billion dollar investment in interdisciplinary science
- Engaging with the light sources as a quantum scientist is good for the light sources, and good for quantum science.
- Light sources are also a great place to build your network as an early career researcher (Meet more collaborators, give more seminars, etc.)

3. X-ray Interactions with Matter

X-rays interact strongly with all of the electrons in the bulk.
What are the possible outcomes when an x-ray is incident on a material?



Elastic (Unmodified / Thomson) Scattering

Electron is accelerated by EM wave, and re-radiates at the same frequency. Spherical wave. Elastic and coherent.

Scattering plane perpendicular to $\hat{\epsilon}$:

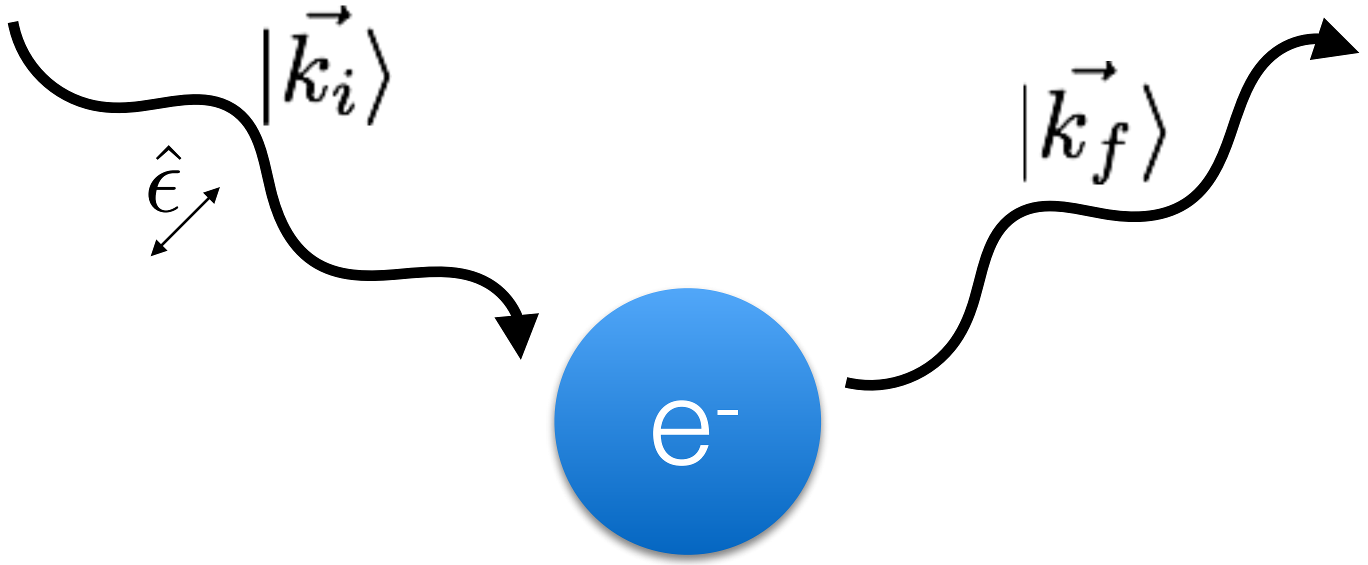
$$I = I_0 \frac{e^4}{m^2 c^4 R^2}$$

Scattering plane contains $\hat{\epsilon}$:

$$I = I_0 \frac{e^4}{m^2 c^4 R^2} cos^2(\phi)$$

Where ϕ is the angle between $\vec{k}_i$ and $\vec{k}_f$ in the plane of $\hat{\epsilon}$

X-rays interact strongly with all of the electrons in the bulk.
What are the possible outcomes when an x-ray is incident on a material?



Inelastic (Modified / Compton) Scattering

Electron and Photon exchange energy and momentum. Inelastic and incoherent.

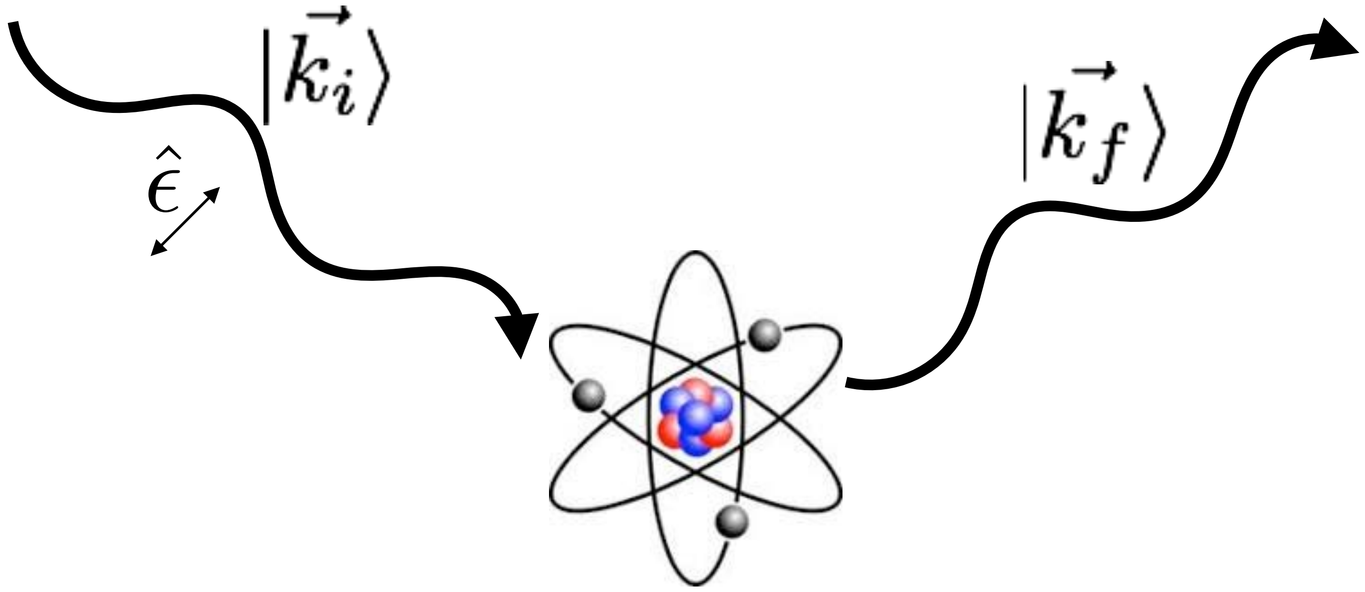
Klein-Nishina Formula

$$I = I_0 \left[\frac{\hbar\alpha}{mcR}\right]^2 Q^2(E_i,\theta)\left[\frac{1}{Q(E_i,\theta)} + Q(E_i,\theta) - 2 + 4cos^2(\theta)\right]$$

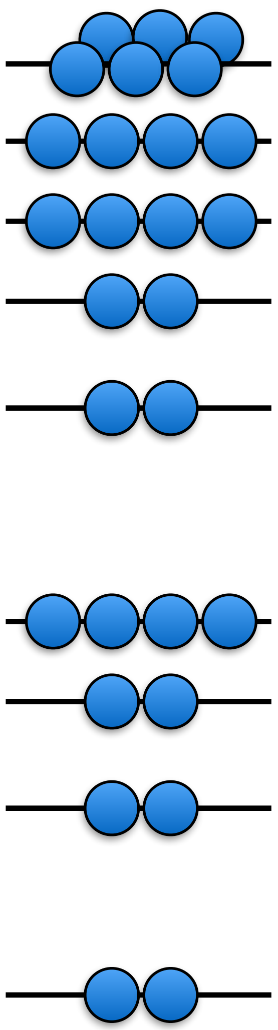
Where

$$Q(E_i,\theta) = \frac{E_f}{E_i} = \frac{1}{1+(E_i/mc^2)(1-cos\theta)}$$

X-rays interact strongly with all of the electrons in the bulk.
What are the possible outcomes when an x-ray is incident on a material?



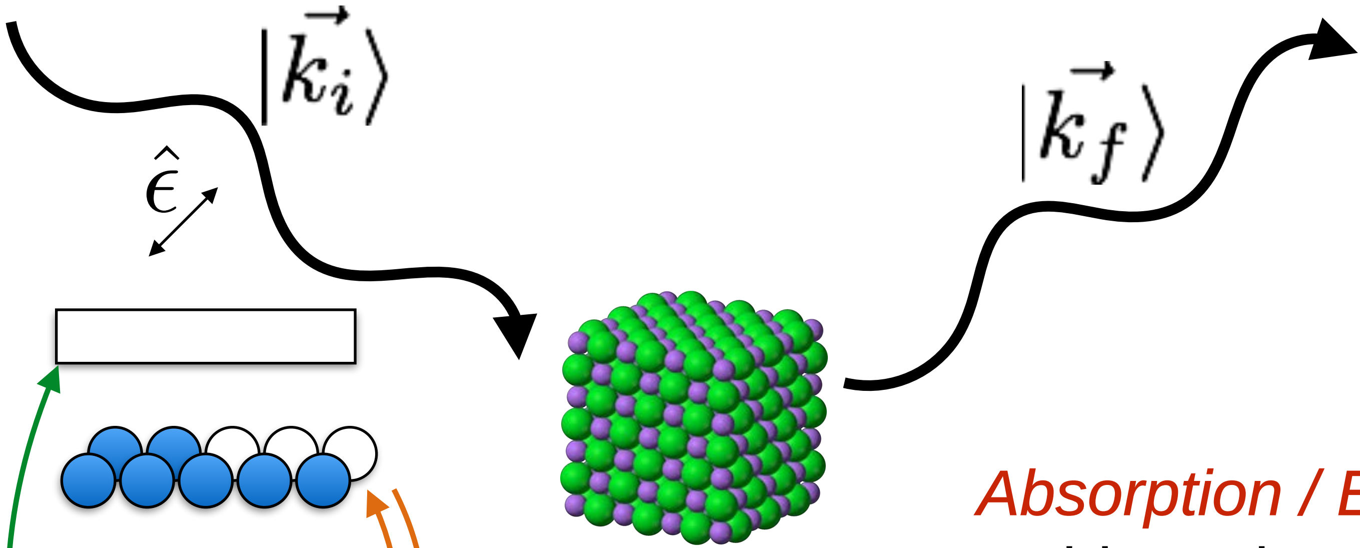
$3d_{5/2}$	M_5	(3,2,5/2)	
$3d_{3/2}$	M_4	(3,2,3/2)	
$3p_{3/2}$	M_3	(3,1,3/2)	
$3p_{1/2}$	M_2	(3,1,1/2)	
3s	M_1	(3,0,1/2)	
$2p_{3/2}$	L_3	(2,1,3/2)	
$2p_{1/2}$	L_2	(2,1,1/2)	
2s	L_1	(2,0,1/2)	
1s	K	(1,0,1/2)	



Of course, most electrons in a solid are not free

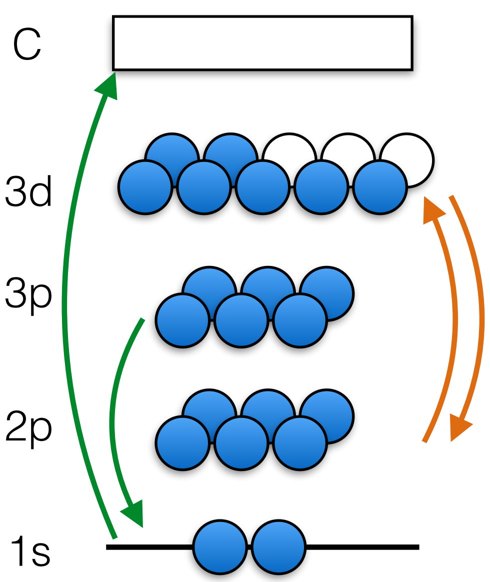
Binding energy keeps electrons in particular orbitals, unless they are photo-excited via x-ray absorption. They can still contribute to coherent unmodified (Thomson) scattering, but we expect some frequency response (forced damped oscillations). Scattering near absorption edges is more complicated - more on that later.

X-rays interact strongly with all of the electrons in the bulk.
What are the possible outcomes when an x-ray is incident on a material?



Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]



Absorption / Emission

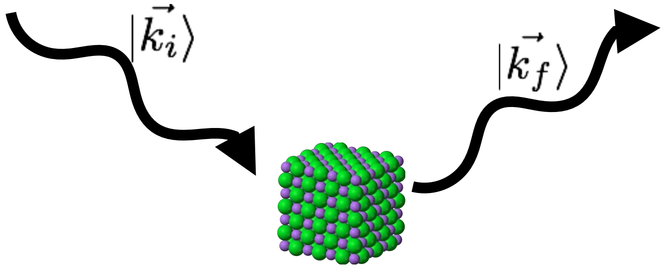
Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe *chemistry*, *bands, local moments.* [XANES, EXAFS, XES, XMCD]

Resonant Scattering

Incident photon excites a core electron into an empty state. The *"same electron"* returns to (or fills) the core hole, and emits a photon with close to the initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probes the valence band, i.e. magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Non-Resonant Inelastic Scattering

Incident photon transfers some finite amount of energy and momentum to the sample, creating an elementary excitation. [Compton, HERIX, X-ray Raman]



Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

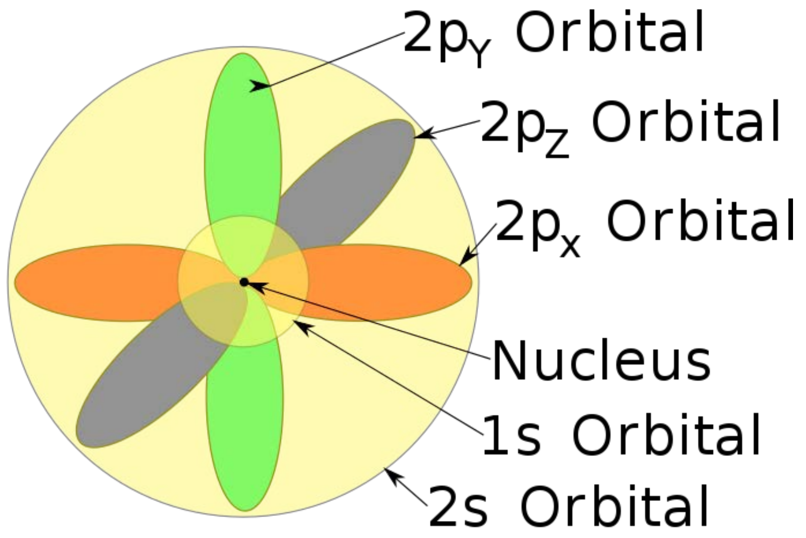
Elastic scattering from an atom

Sum up plane-wave scattering from each volume element of each electron cloud. This is the *Atomic Form Factor.*

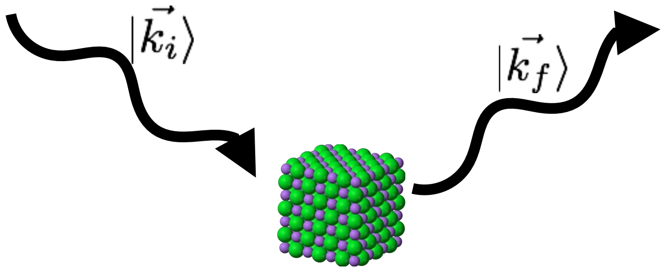
$$f_0 = \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \; ; \quad \text{where} \quad \vec{q} = \vec{k}_i - \vec{k}_f$$

$$f_0(|\vec{q}| \to 0) = Z \qquad \text{(No. of electrons)}$$

f_0 falls off for large values of $|\vec{q}|$, but remains finite



Tabulated using relativistic calculations, available in the International Tables of Crystallography.



Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

Elastic scattering from a solid, made of atoms

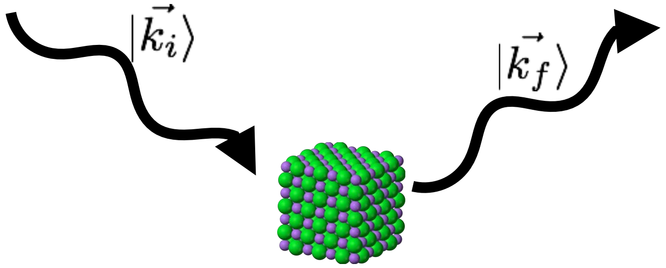
Sum up scattering from each atom.
This is the *Structure Factor.* Measured Intensity follows the square of the structure factor.

$$F(\vec{q}) = \sum_{m}^{atoms} f_{0m} e^{i\vec{q}\cdot\vec{R}_m} \; ; \quad \text{where} \quad \vec{q} = \vec{k}_i - \vec{k}_f$$

and atoms are at positions $\vec{R}_j$

$$I(\vec{q}) \propto F^* F = \sum_{m,n}^{atoms} f_{0n}^* f_{0m} e^{i\vec{q}\cdot(\vec{R}_m - \vec{R}_n)}$$

X-Ray diffraction measures the Fourier transform of the 2-body correlation function between pairs of atoms in a material.



Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

Elastic scattering from a crystalline solid, made of repeating unit cells of atoms

Measured Intensity follows the square of the structure factor. Correlation of pairs of atoms. **For idealized crystals**, intensity is only non-zero when $\vec{q}$ is a vector in the reciprocal lattice.

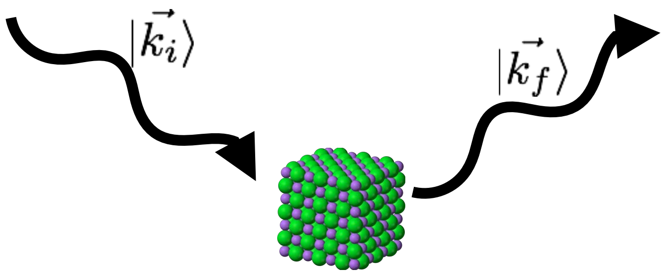
$$I(\vec{q}) \propto F^* F = \sum_{m,n}^{atoms} f_{0n}^* f_{0m} e^{i\vec{q}\cdot(\vec{R_m} - \vec{R_n})}$$

$$\vec{R} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3}$$

$$I(\vec{q}) \neq 0 \quad \text{only if} \quad \vec{q} \in G(\vec{h,k,l}) = (h\vec{b_1} + k\vec{b_2} + l\vec{b_3})$$

i.e. $$e^{i\vec{G}\cdot\vec{R}} = 1$$

This is the basis of x-ray crystallography, and average unit-cell structure determination.



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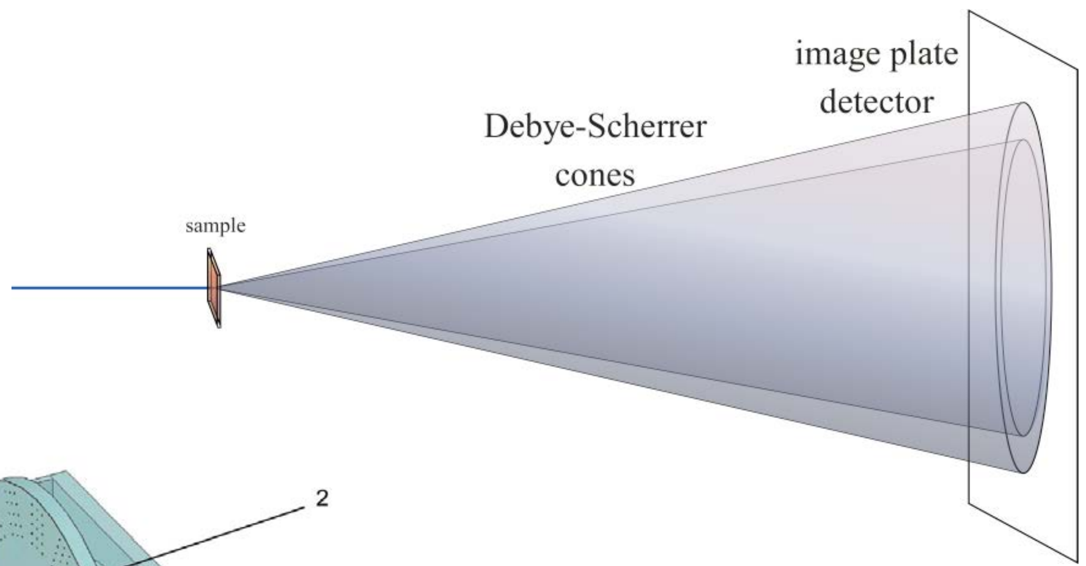
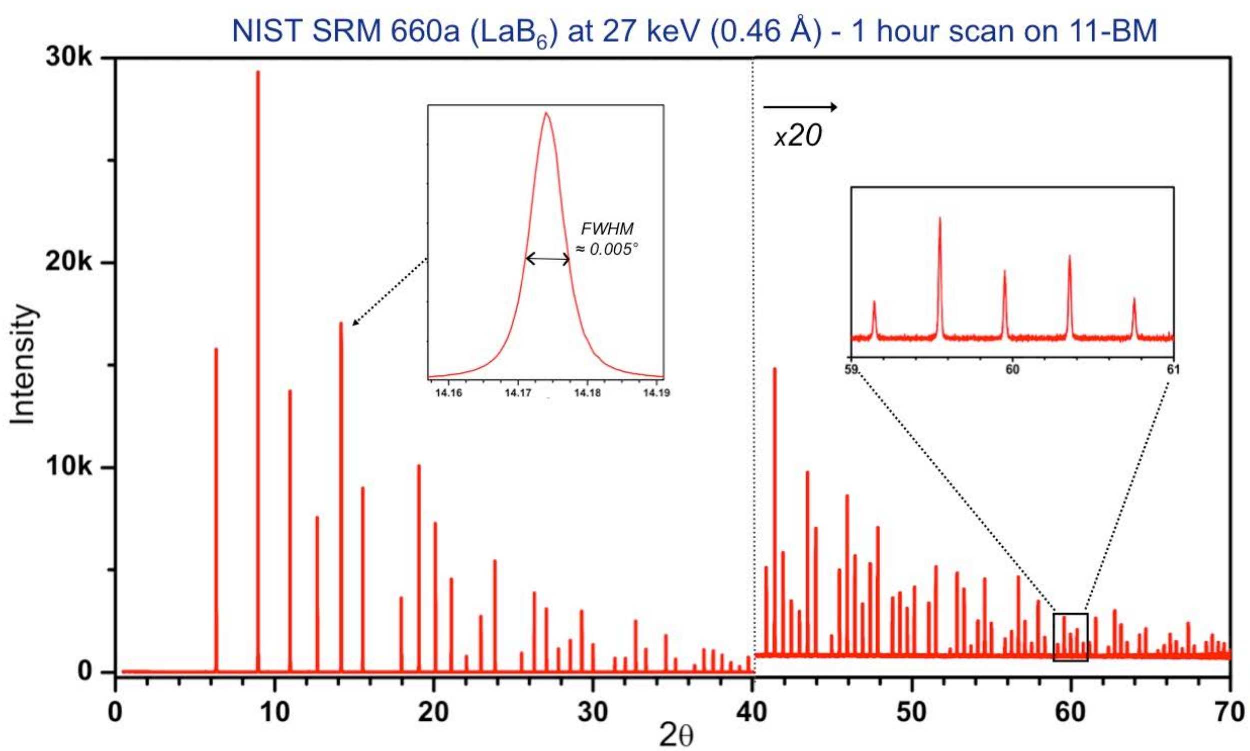
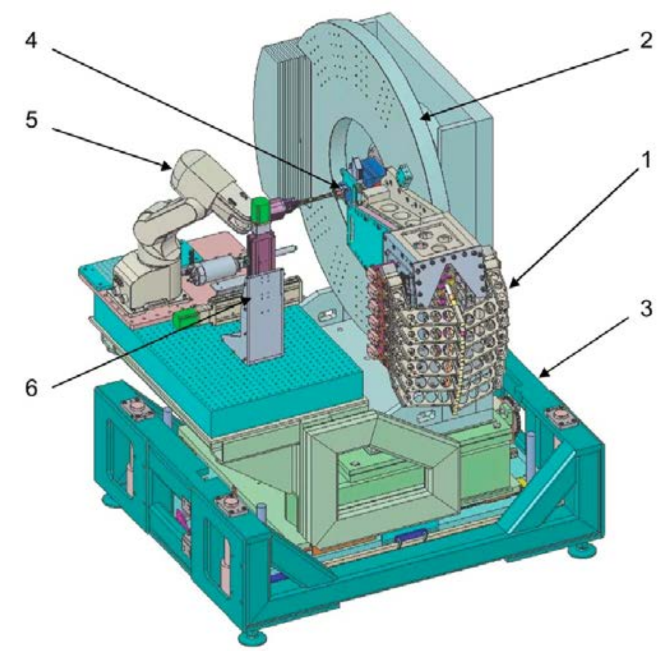
Methods for x-ray structure solution at light sources

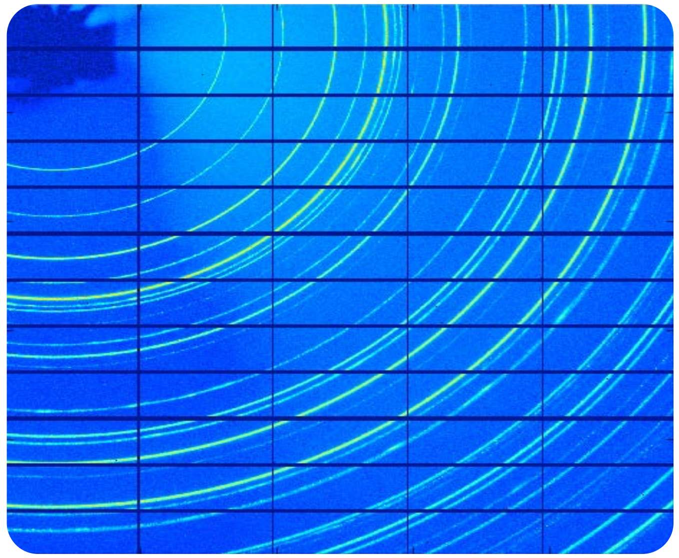
(a) Powder diffraction
Measure a statistical distribution of crystal orientations.
Refine structures using Rietveld method.
(GSAS, Fullprof)



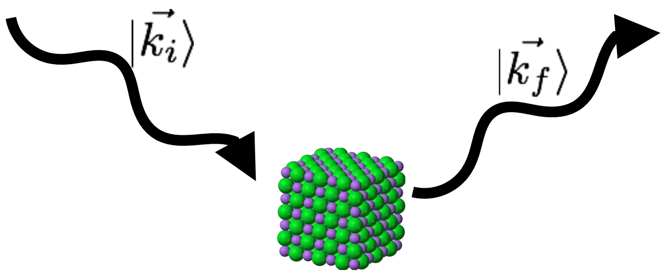




11-BM Diffractometer Schematic: (1) 12-analyzer detector system, (2) two-circle goniometer, (3) supporting table, (4) sample stages, (5) sample mounting robot, (6) stages for cryostream etc.



http://11bm.xray.aps.anl.gov/



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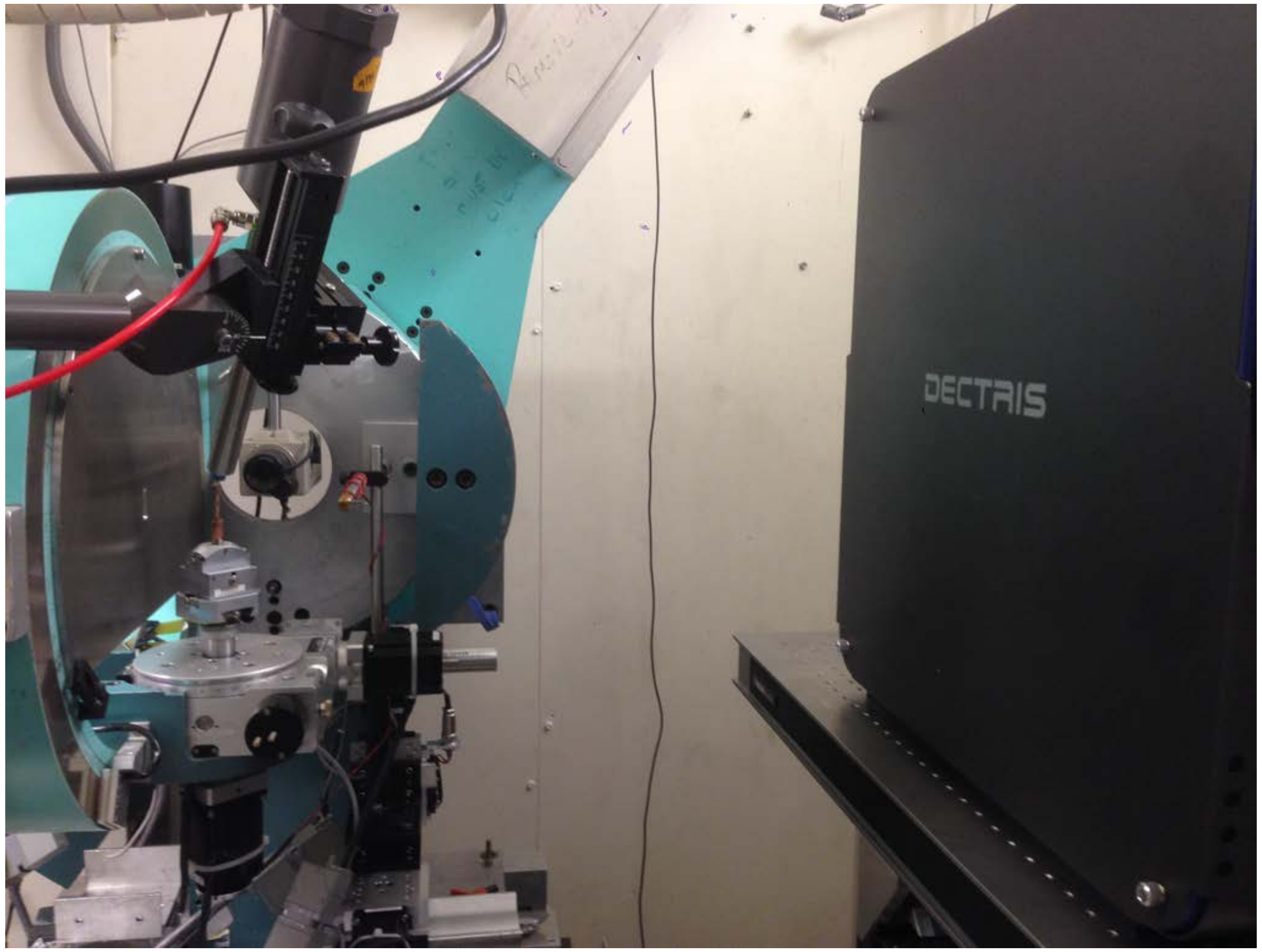
Methods for x-ray structure solution at light sources

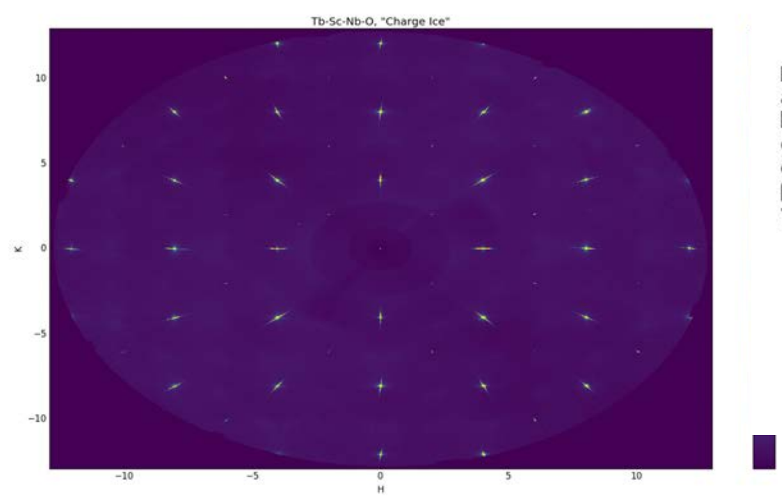
(b) Single Crystal Diffraction

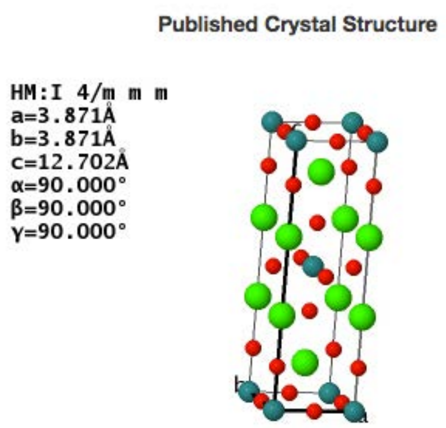
Collect thousands of Bragg intensities from a single, highly perfect crystal. 360º rotations. Refine structures using open source software (shelx)

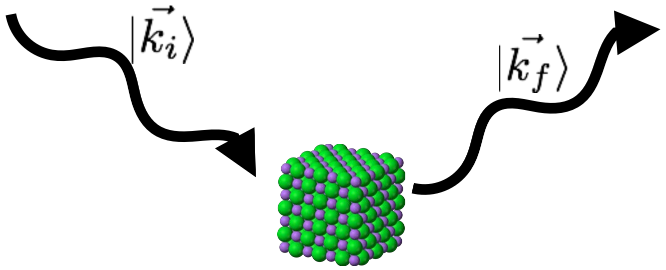


Goal is to generate a list of H,K,L and Intensity values, and “solve” the structure.

A solution is typically (i) a space group; (ii) a list of atoms along with fractional coordinates in the unit cell; (iii) Thermal parameters.







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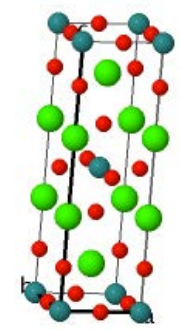
Example structural solution, from ICSD, for Sr_2RuO_4.

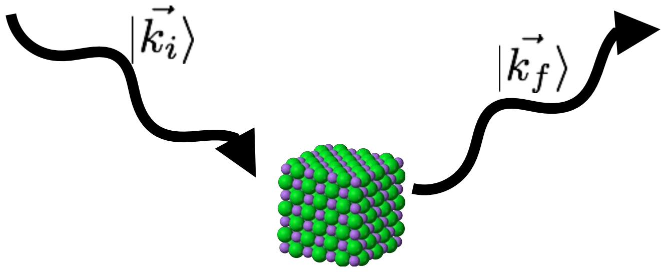
Published Crystal Structure



▾ Standardized Crystal Structure Data

Cell Parameters	3.8710 3.8710 12.7020 90.000 90.000 90.000				
Volume	190.33	Formula Units per Cell	2	Calc. Dens.	5.94
Space Group	I 4/m m m(139)	Pearson Symbol	tI14		
Crystal System	tetragonal	Crystal Class	4/mmm	Laue Class	4/mmm
Wyckoff Sequence	e2 c a				
Axis Ratios	a/b 1.0000	b/c 0.3048	c/a 3.2813		
Transformation Method	Tidy				
Transformation Info					
Remark					

EL	Lbl	OxState	Wyck Symb	X	Y	Z	B	SOF
Sr	1	+2.00	4 e	0.0000	0.0000	0.3538	0.3300	
Ru	1	+4.00	2 a	0.0000	0.0000	0.0000	0.3500	
O	1	-2.00	4 c	0.0000	0.5000	0.0000	0.5300	
O	2	-2.00	4 e	0.0000	0.0000	0.1630	0.4800	



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Beyond Crystallography:

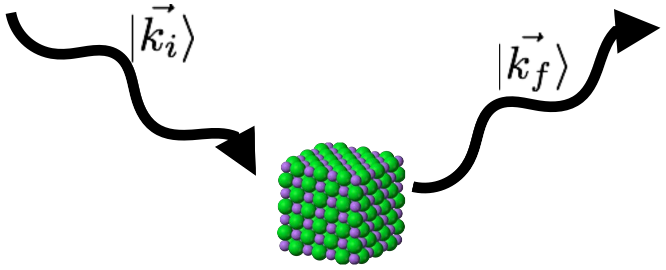
Elastic scattering can tell us much more than just the average unit cell.

Key Ideas: Resolution, Coverage, Dynamic Range

Synchrotron X-ray diffraction has high resolution, can see subtle lattice distortions

High energy X-ray scattering can cover wide ranges of Q space - comprehensive data

Extremely high flux of synchrotron sources lets us observe intense and weak features simultaneously



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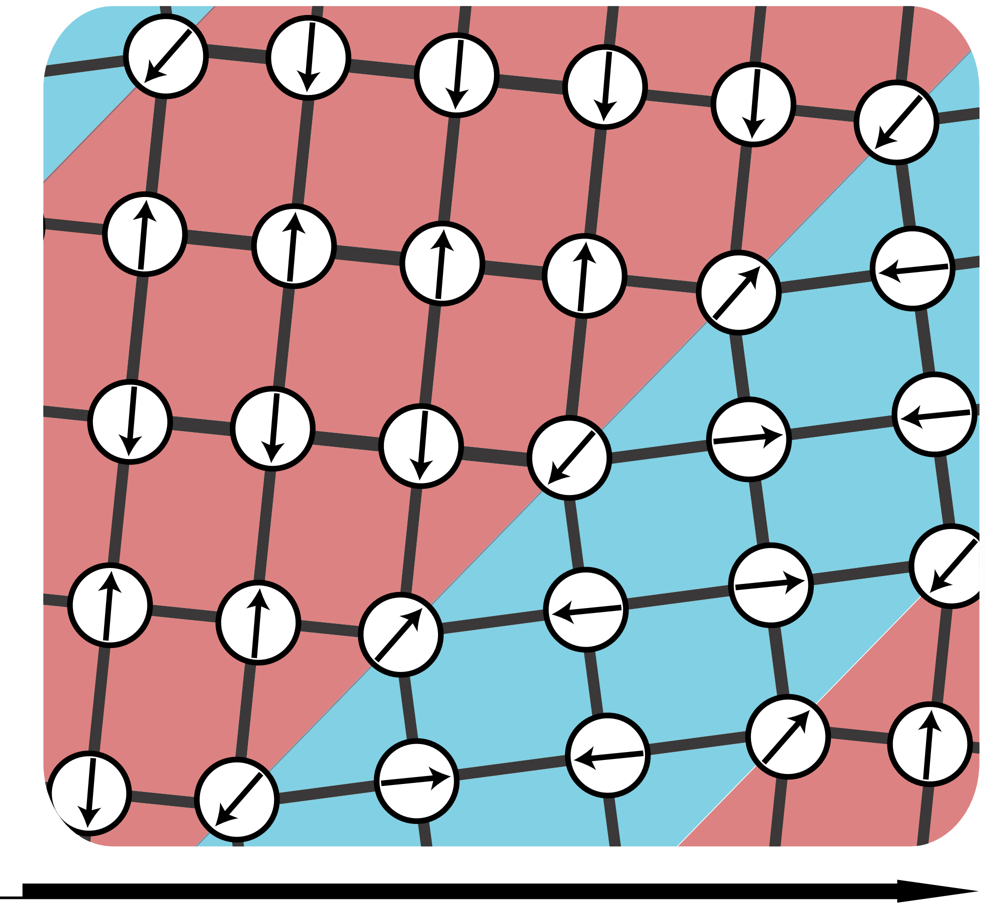
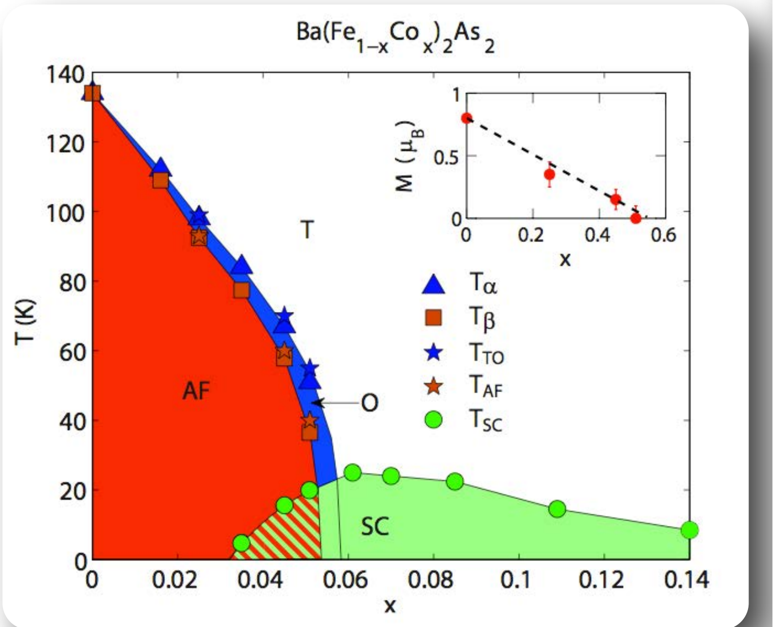
Beyond Crystallography: Phase transitions

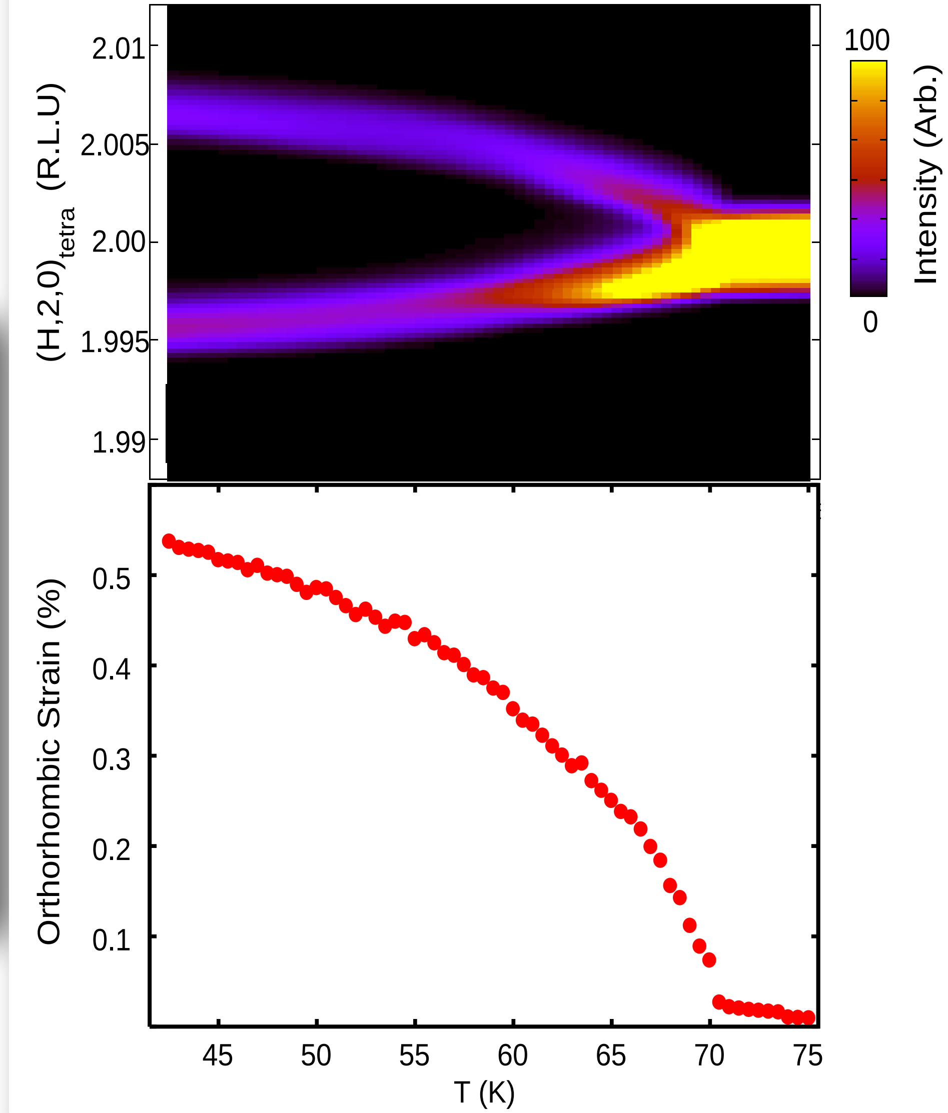
Parameterize a single Bragg peak as a function of temperature. Observe splitting at tetra-ortho transition.

Twinning: Diffraction resolves mesoscale structures and microscopic order parameter simultaneously.

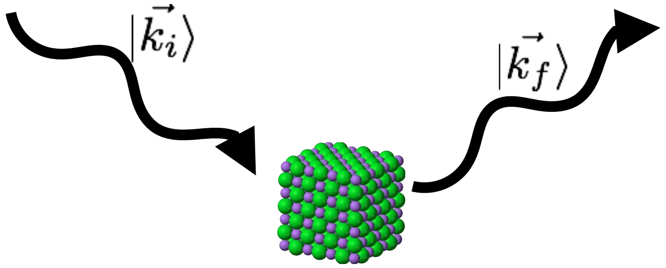


Direction of x-ray momentum transfer





CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE



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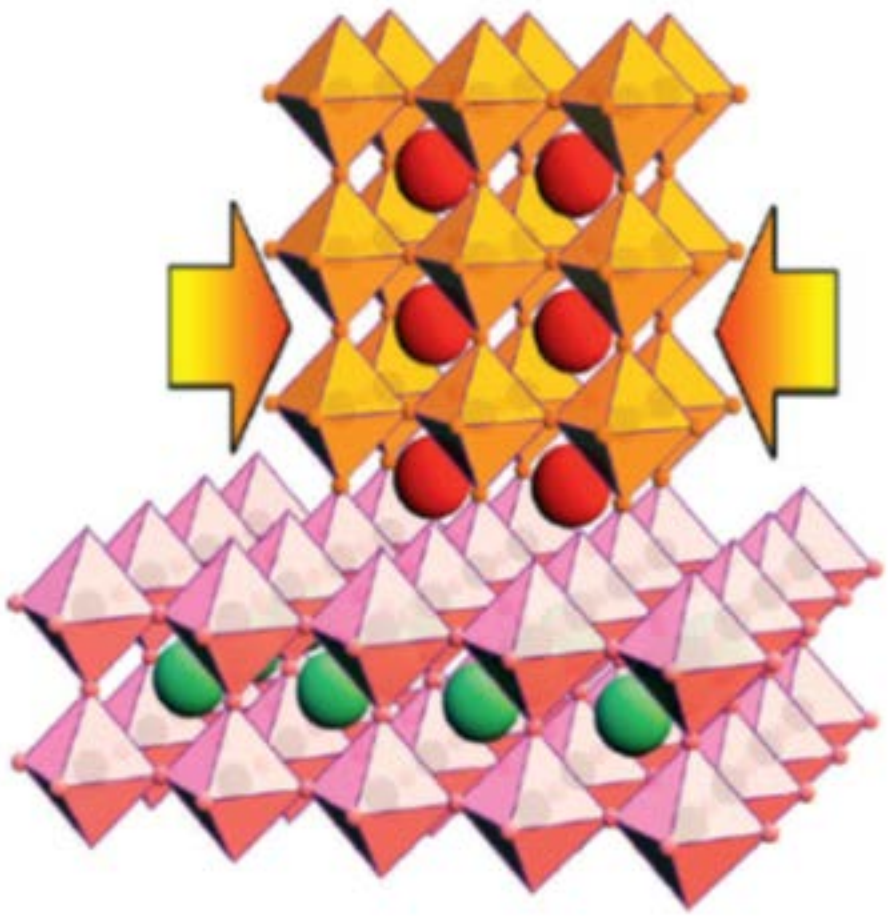
Beyond Crystallography: Thin Films and heterostructures

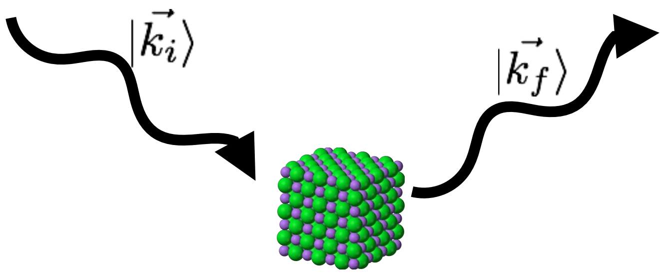
Simultaneously resolve scattering from substrate, film, and interface.



Hard x-rays fully penetrate an epitaxial layer, so scattering is recorded from both film and substrate in reflection geometry.

Very high energy x-rays transmit through the substrate as well, allowing transmission geometry measurements.

2D interface structure also generates a unique scattering signature. Fourier transform of 2D object is 1D in reciprocal space.



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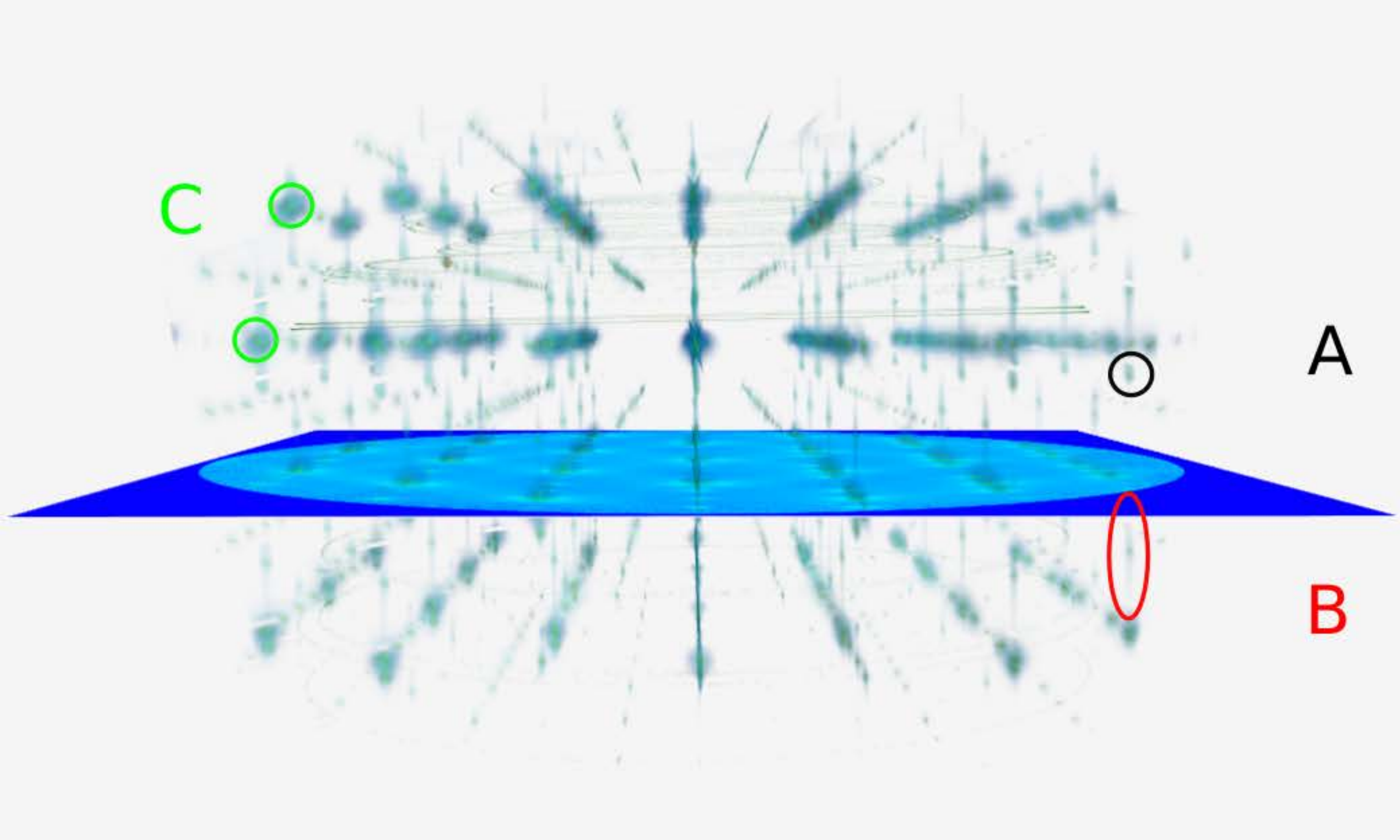
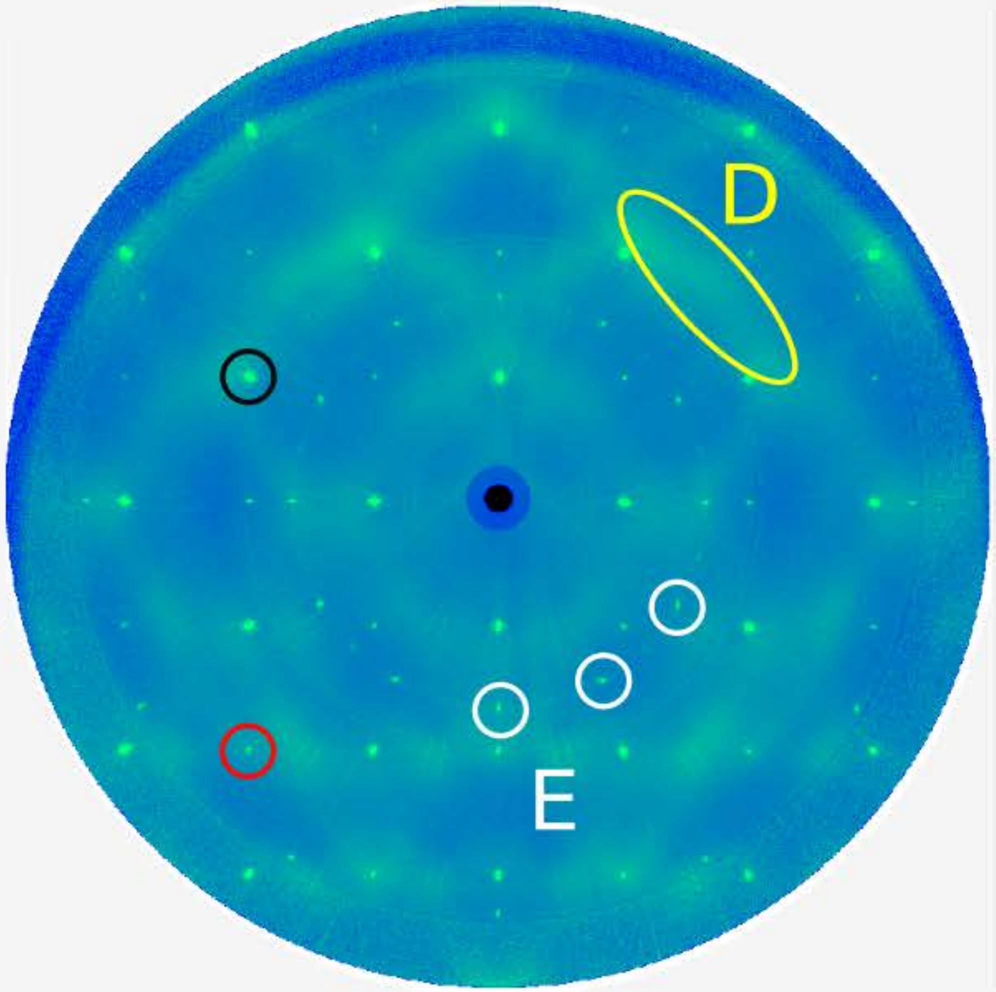
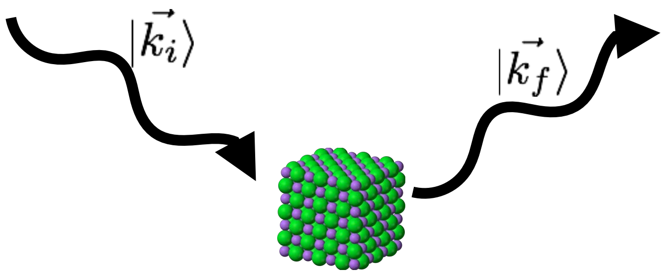




Can collect volumetric 3D datasets with $>2^{10}$ distinct measurements of I(q) (Sr_2RuO_4 thin film on oxide substrate). Only 20 mins data collection.



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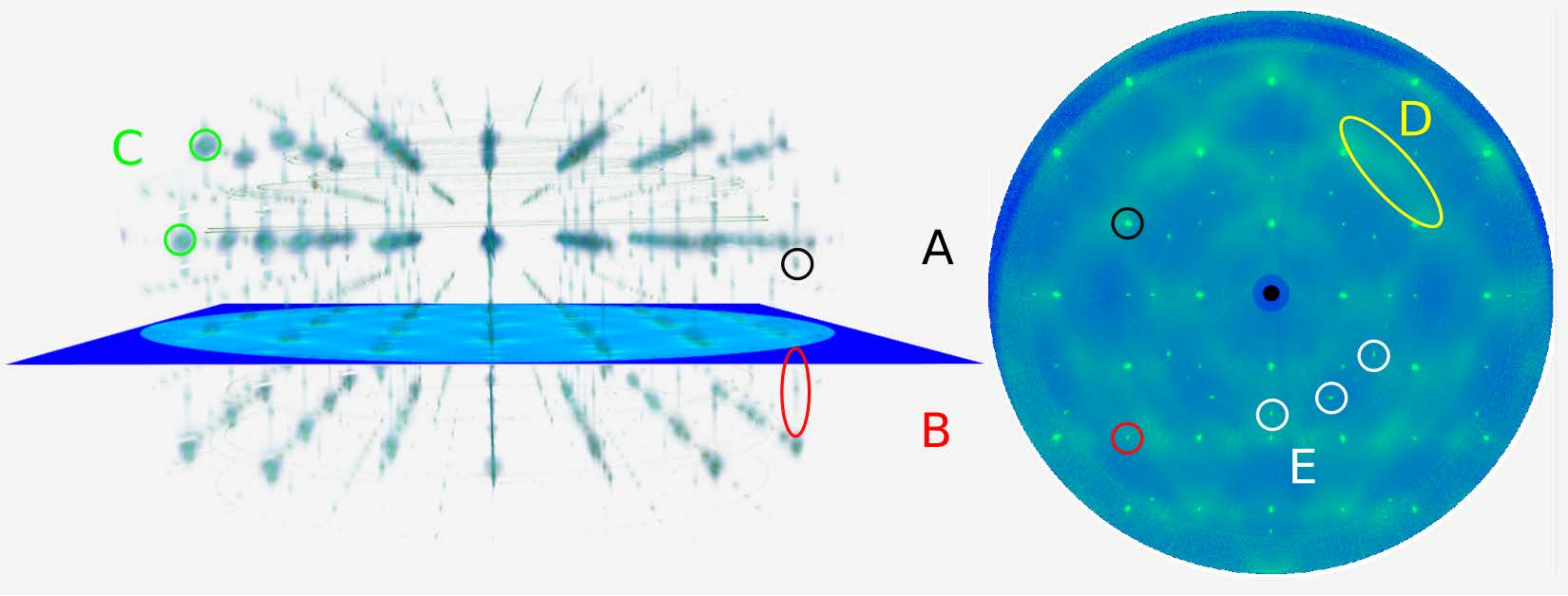
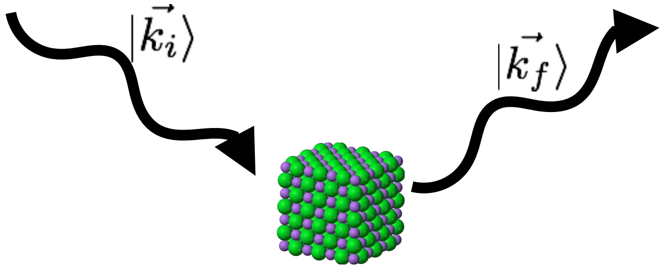


(A) Film peak; (B) Truncation rod; (C) Substrate peak; (D) Diffuse Scattering, most likely Substrate phonon modes; (E) Textured epitaxial defect phase



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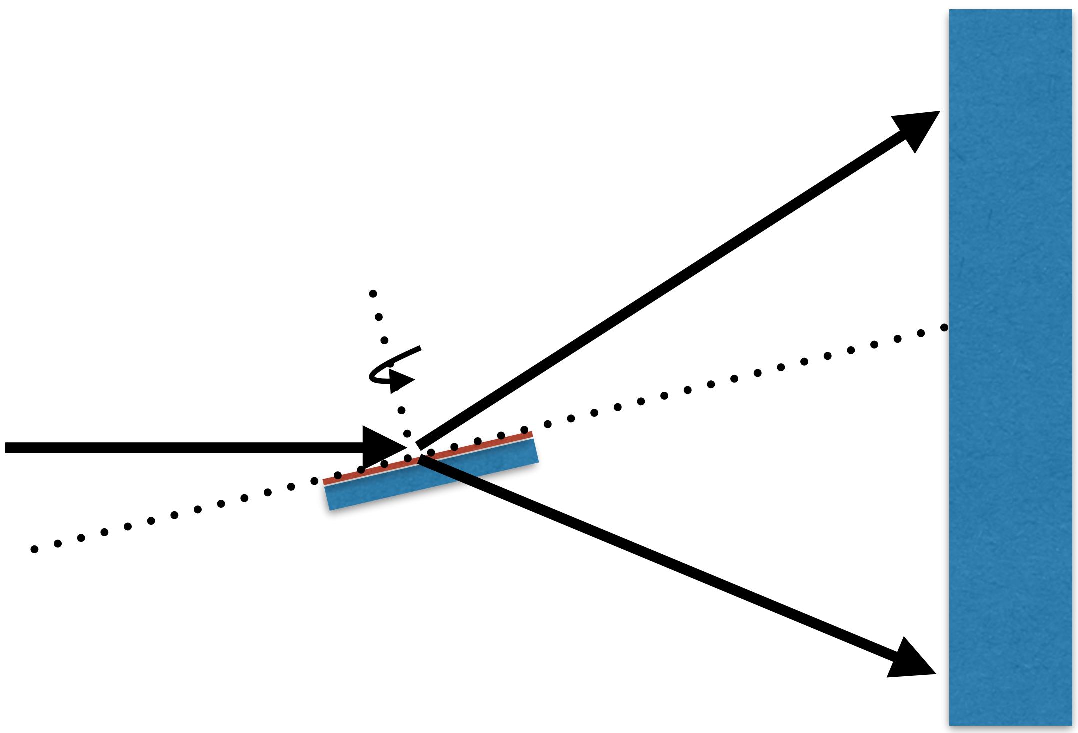

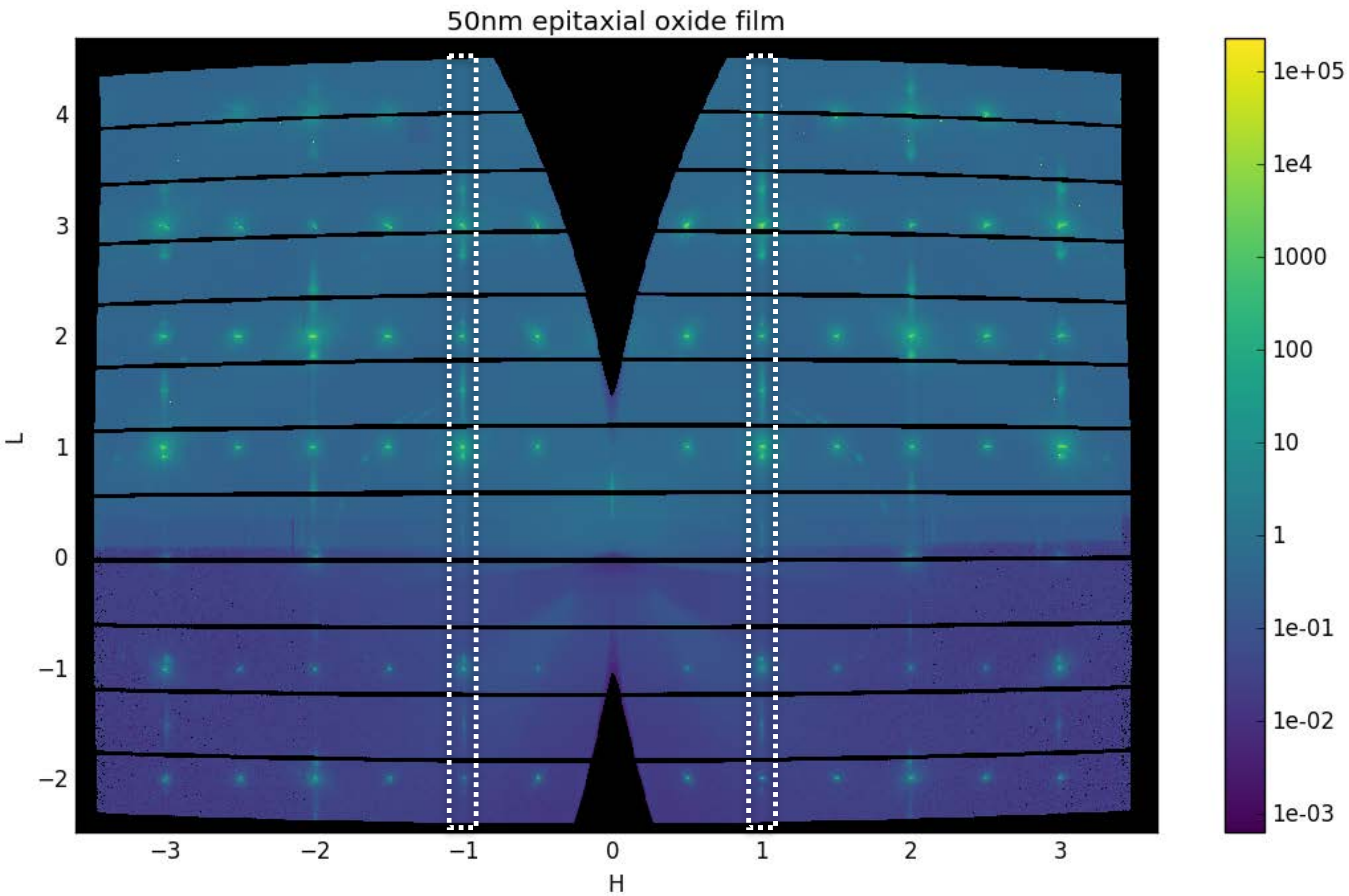

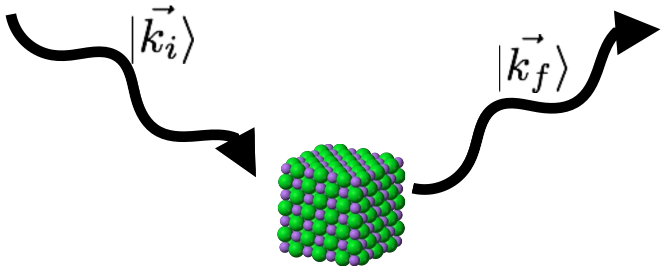

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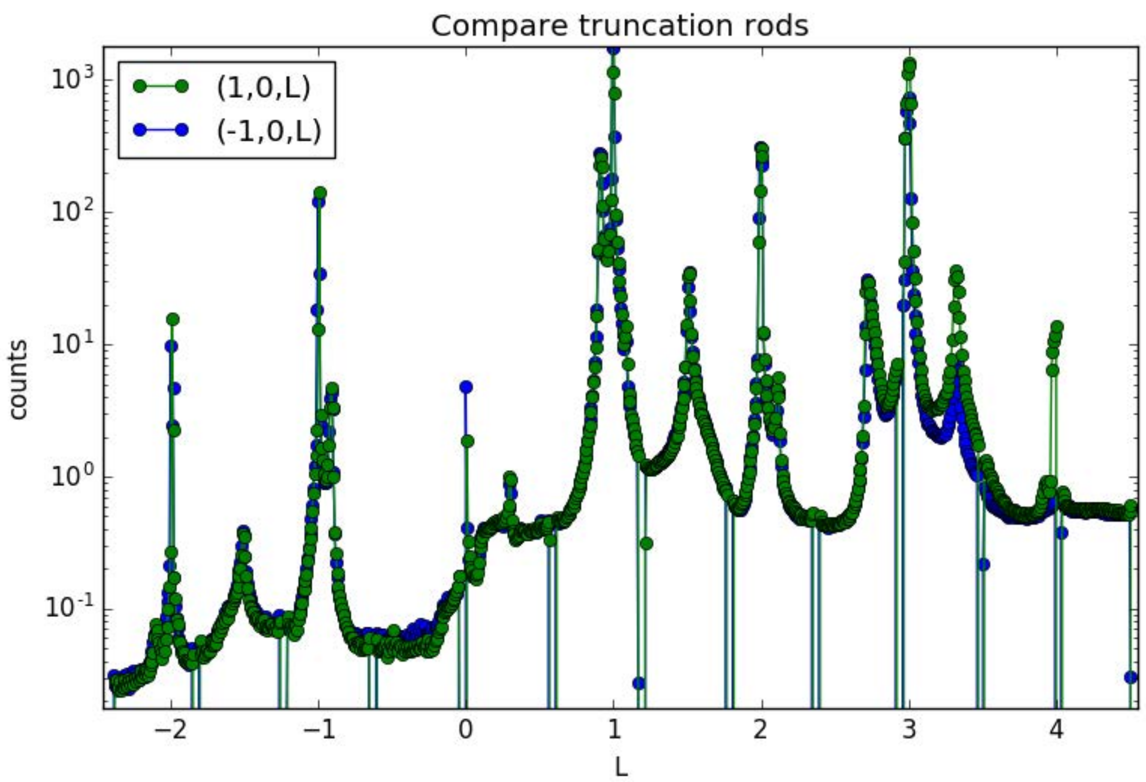
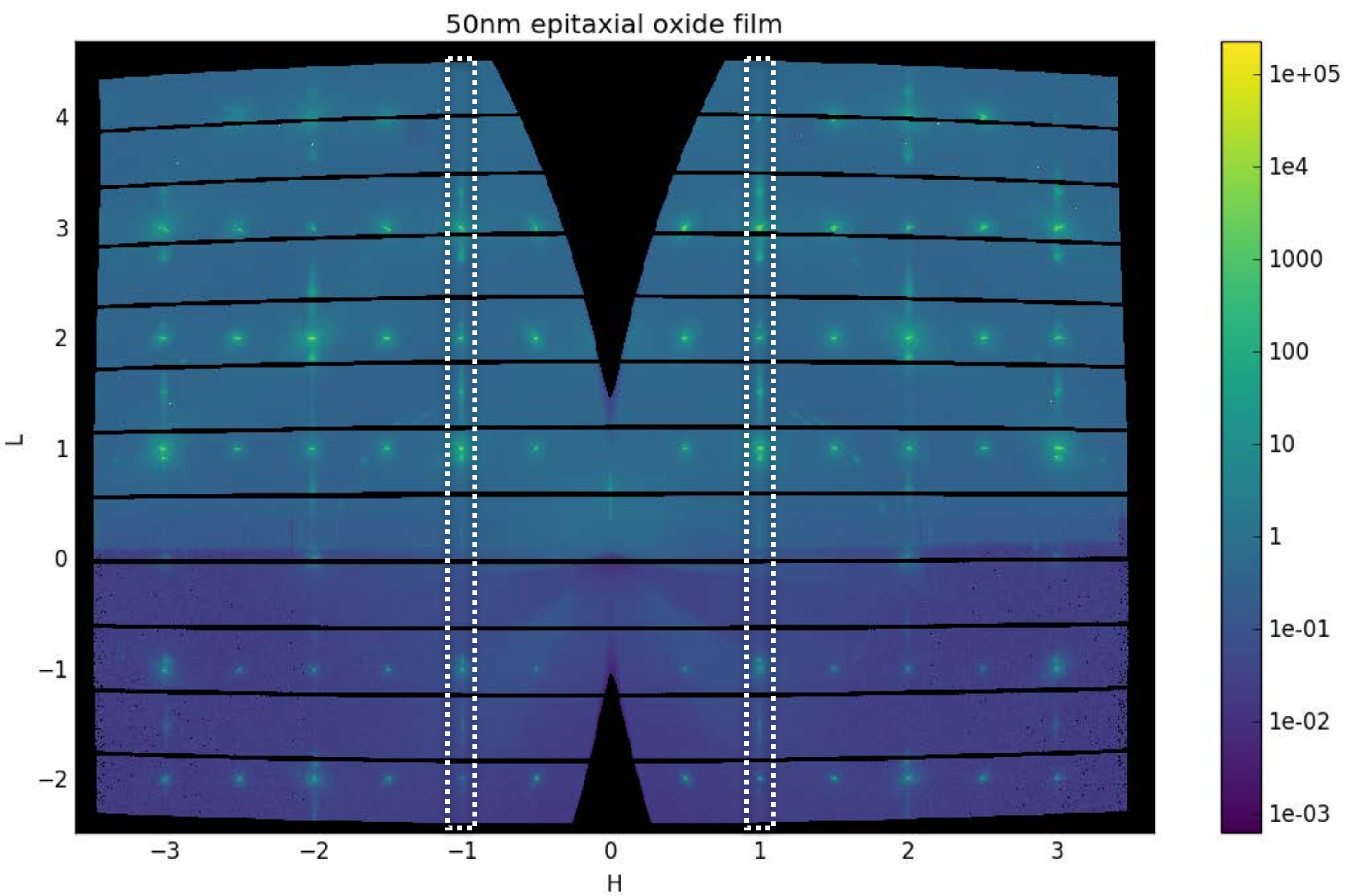
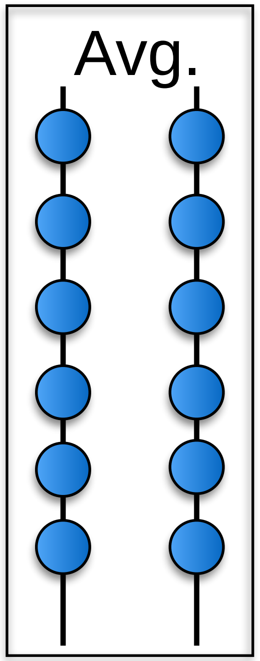




COBRA: Coherent Bragg Rod Analysis. Transform and fit 1D rods of scattering to resolve surface / interface structure. [Gustafson, Science 343 6172 (2014)]

QUESTION 2:

Your suspect that your sample harbors spin-Peierls physics at low temperature. Theory suggests that above T_{SP}, there are 1D chains of atoms with spin-1/2 moments running along the $\hat{c}$ direction, which dimerize to form spin-singlets. This doubles the unit cell along the chain direction, but there are no correlations between the chains. Then, below T_{SP}, the dimerization of the different chains locks in phase, and there is a long range 3D distortion of the lattice. If the theory is correct, what new features would you see in the elastic scattering, besides the Bragg peaks from the average structure?



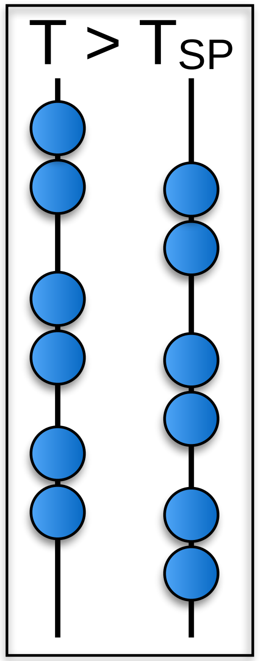
(A) Rods of scattering along L at integer (H,K) positions above T_{SP}
New Bragg peaks at (1/2,1/2,1/2) below T_{SP}

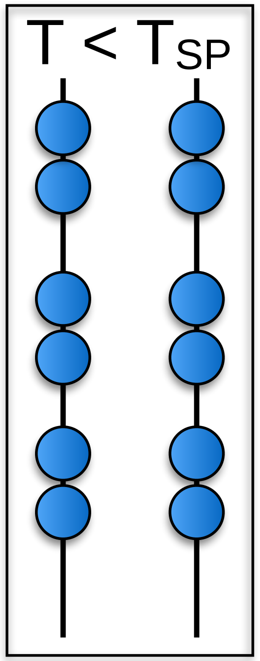
(B) Sheets of scattering in the (H,K) planes at half-integer L positions above T_{SP}
New Bragg peaks at (0,0,1/2) below T_{SP}.

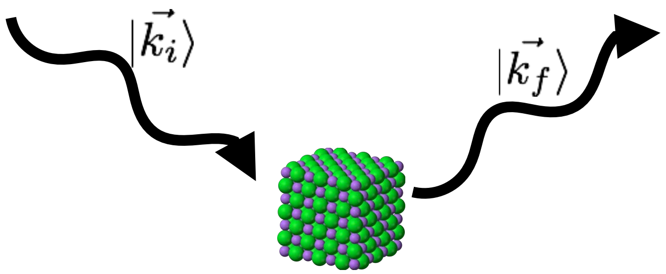
(C) Rods of scattering along L at half-integer (H,K) positions above T_{SP}
New Bragg peaks at (0,0,1/2) below T_{SP}.

(D) No new scattering above T_{SP}
New Bragg peaks at (1/2,0,0) below T_{SP}.

(E) None of the above.







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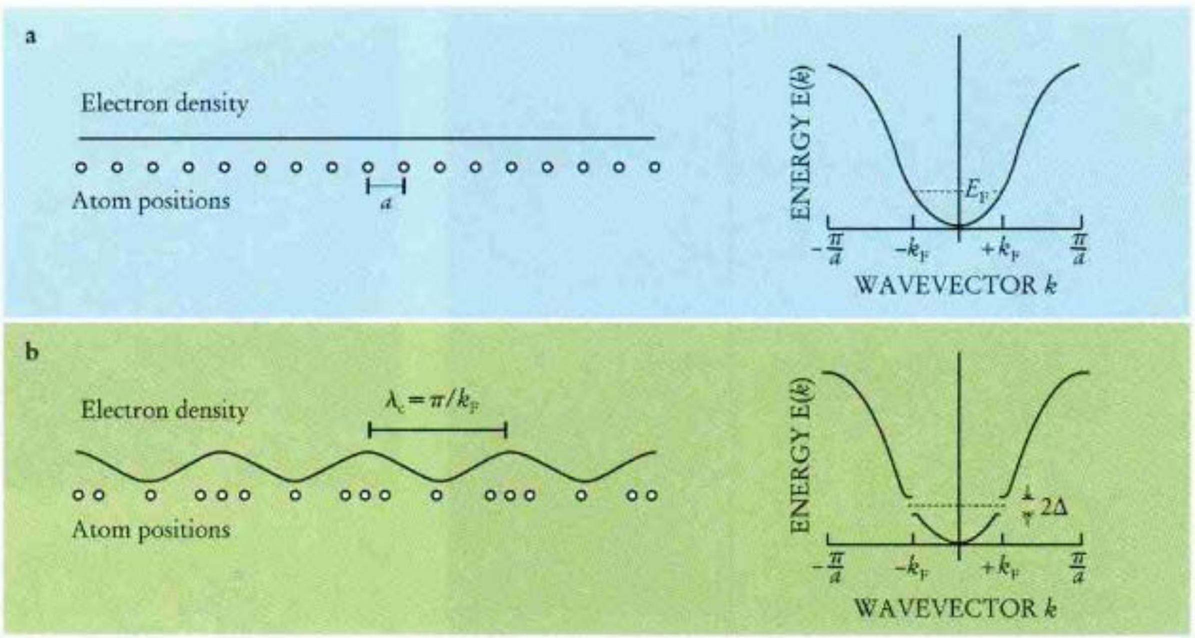
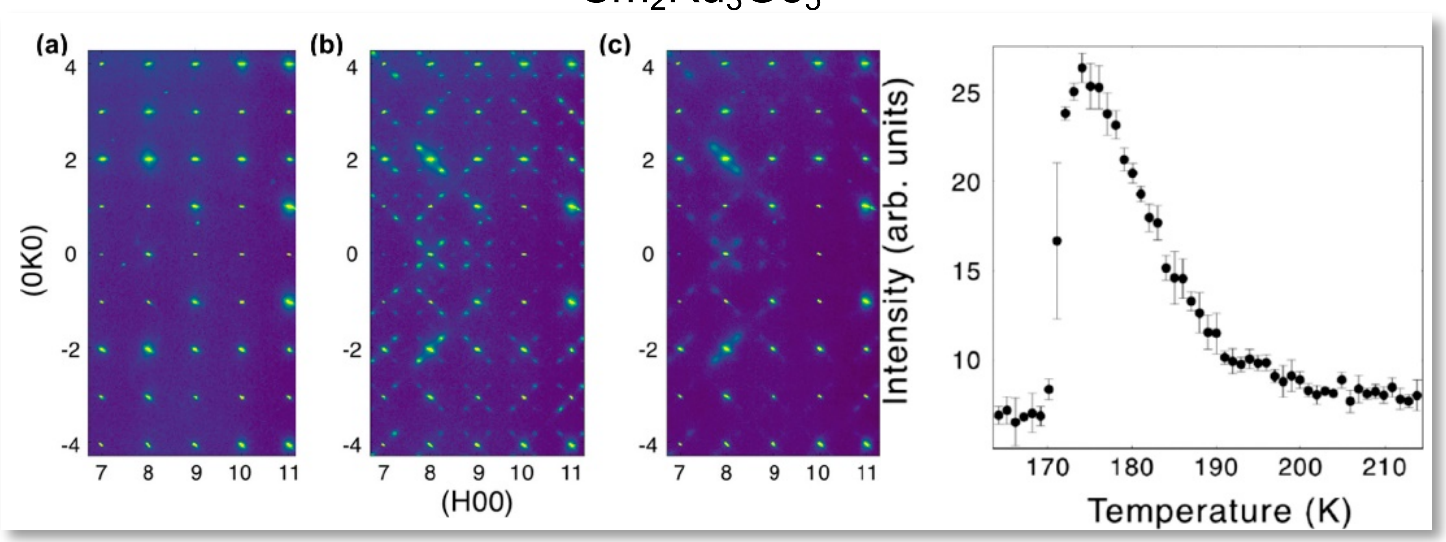
Beyond Crystallography: Charge Density Waves

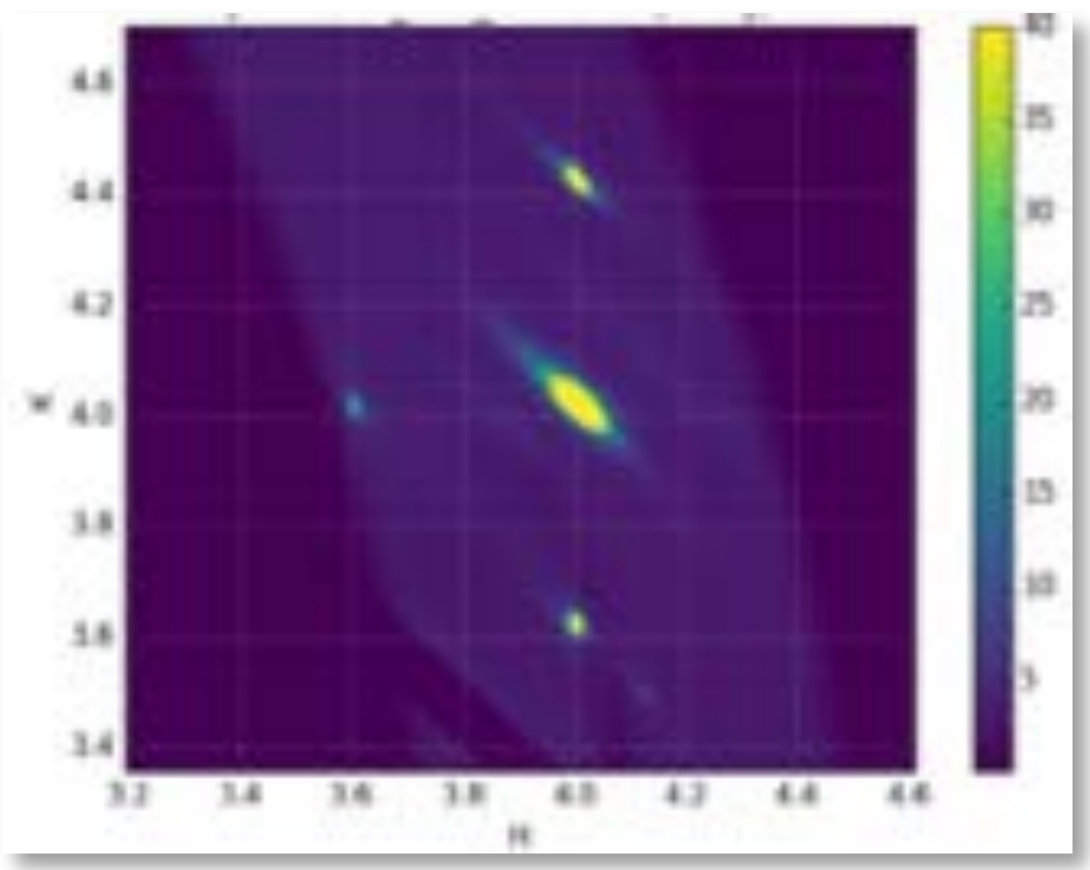
Lattice is sympathetic to electronic symmetry breaking - electron-phonon, excitonic, etc



$Sm_2Ru_3Ge_5$

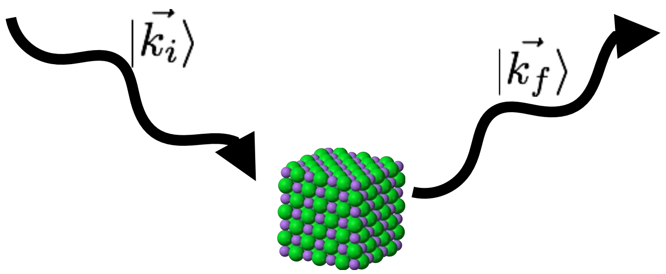


UPt_2Si_2



Ubiquitous CDW distortions

Small distortion gives weak peak!



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J. Phys. Soc. Jpn., Vol. 77, No. 2

Table I. Refinement of the single crystal neutron diffraction data, carried out at 50 K, on as-grown UPt_2Si_2, with the $CaBe_2Ge_2$ lattice (space group *P4/nmm*).

	x	y	z	U_{11} ($Å^2/8\pi^2$)	U_{22} ($Å^2/8\pi^2$)	U_{33} ($Å^2/8\pi^2$)
U	1/4	1/4	0.7484(2)	0.45(4)	0.45(4)	0.08(4)
Pt(1)	1/4	1/4	0.3785(2)	0.10(3)	0.10(3)	0.28(4)
Pt(2)	3/4	1/4	0	1.86(5)	1.86(5)	0.14(4)
Si(1)	3/4	1/4	1/2	0.10(6)	0.10(6)	0.18(7)
Si(2)	1/4	1/4	0.1330(3)	0.94(8)	0.94(8)	0.29(8)

Lattice parameters: $a = 4.186$ Å, $c = 9.630$ Å.
$R_{\rm Bragg} = 6.6\%$; $R_w = 5.0\%$

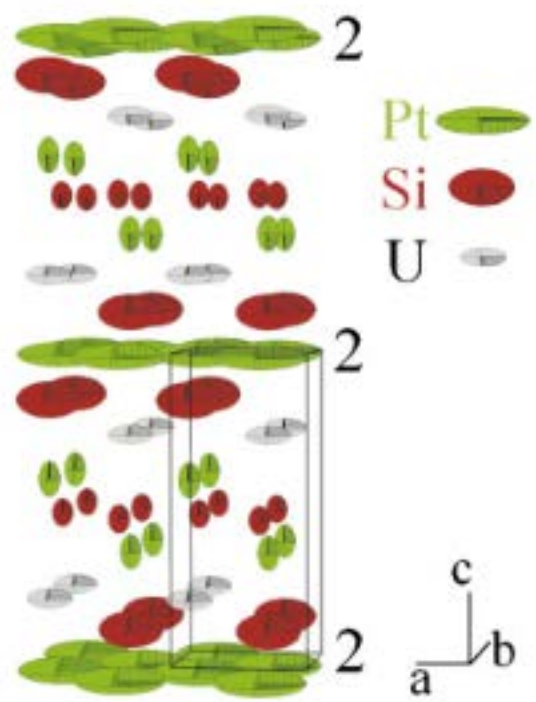
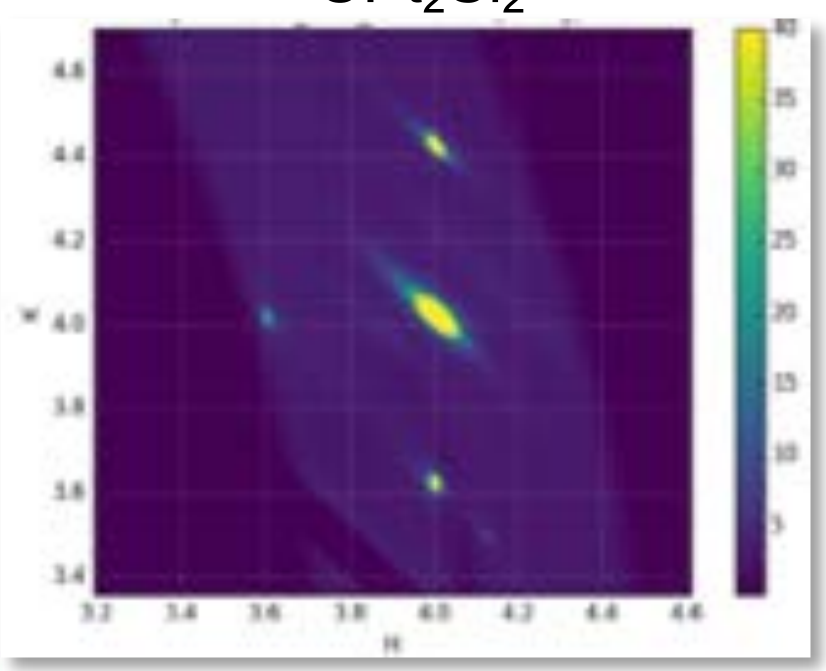
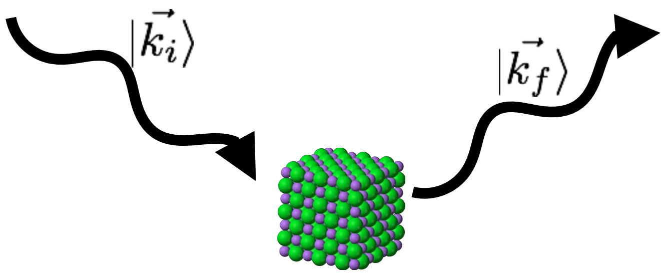


Fig. 2. (Color online) The crystal structure (space group *P4/nmm*) in ellipsoidal representation of UPt_2Si_2, with the unit cell indicated.

UPt_2Si_2



Crystallography "fails" for weakly modulated structures, but these failures are not always obvious! "Disorder" can be a convenient excuse, leading us to overlook interesting physics.



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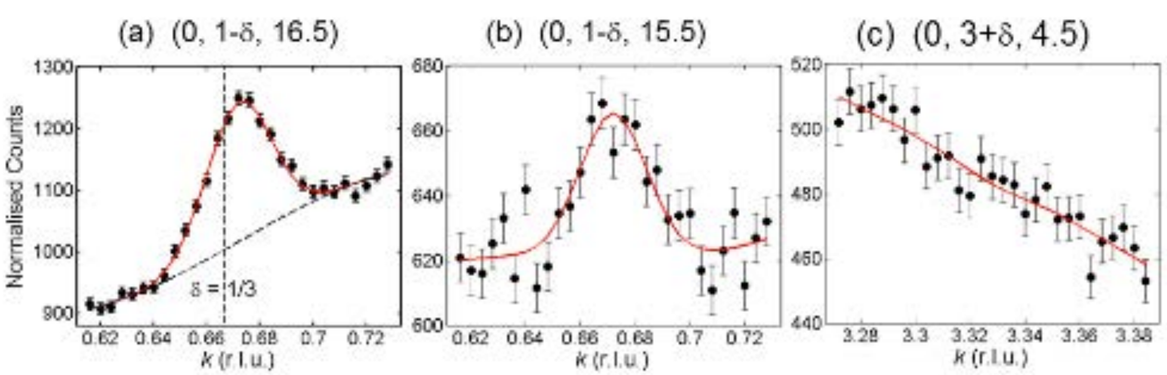
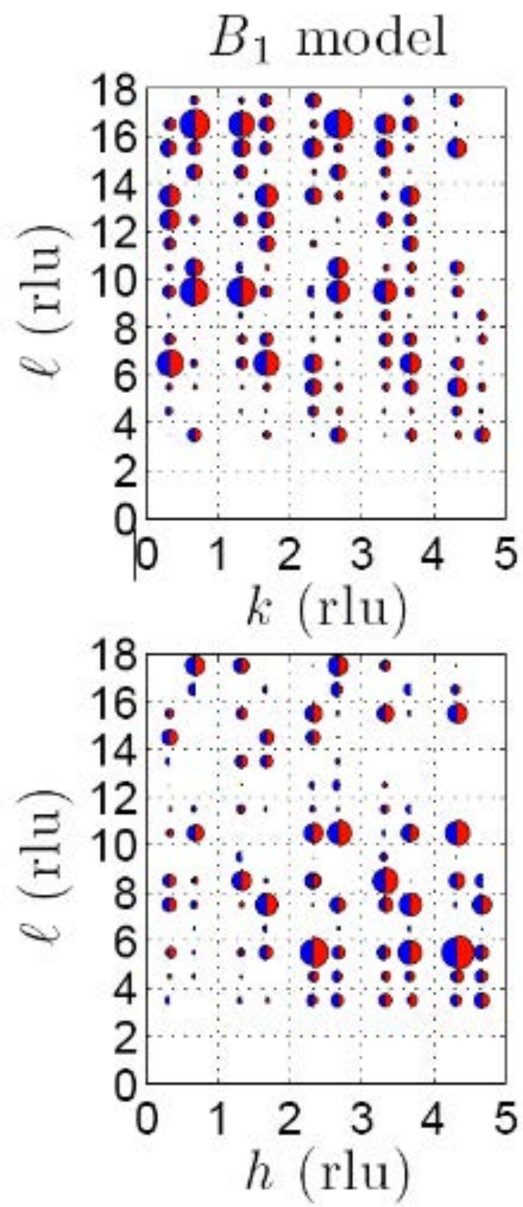
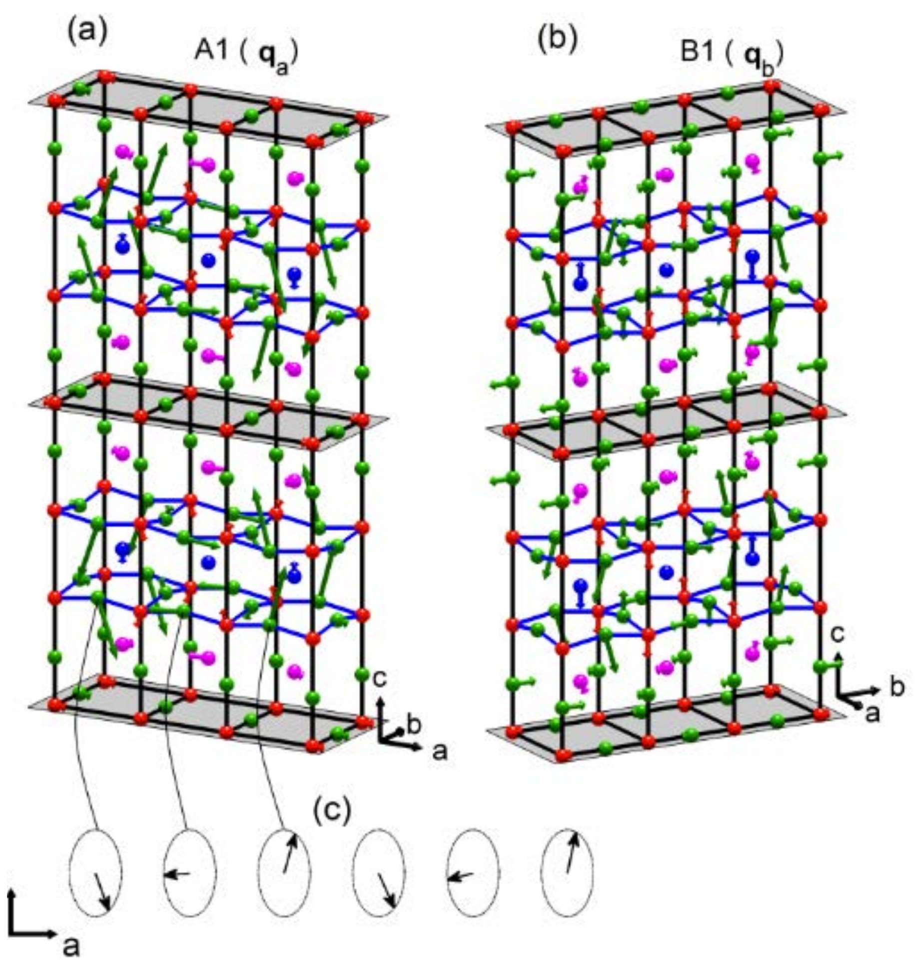
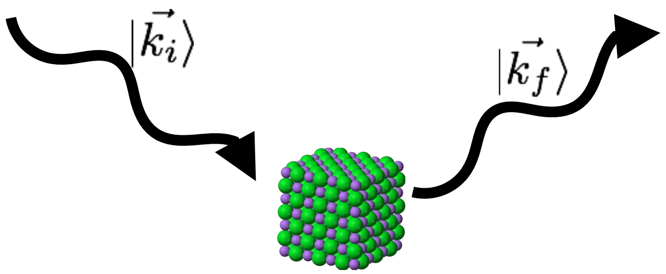


Underdoped YBCO. CDW formation causes all the ions to shift slightly in the lattice.

Forgan, Nat. Comms. 6: 10064 (2015)







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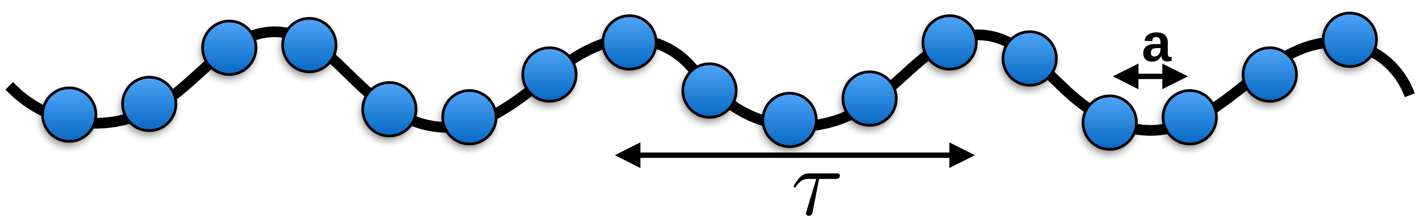
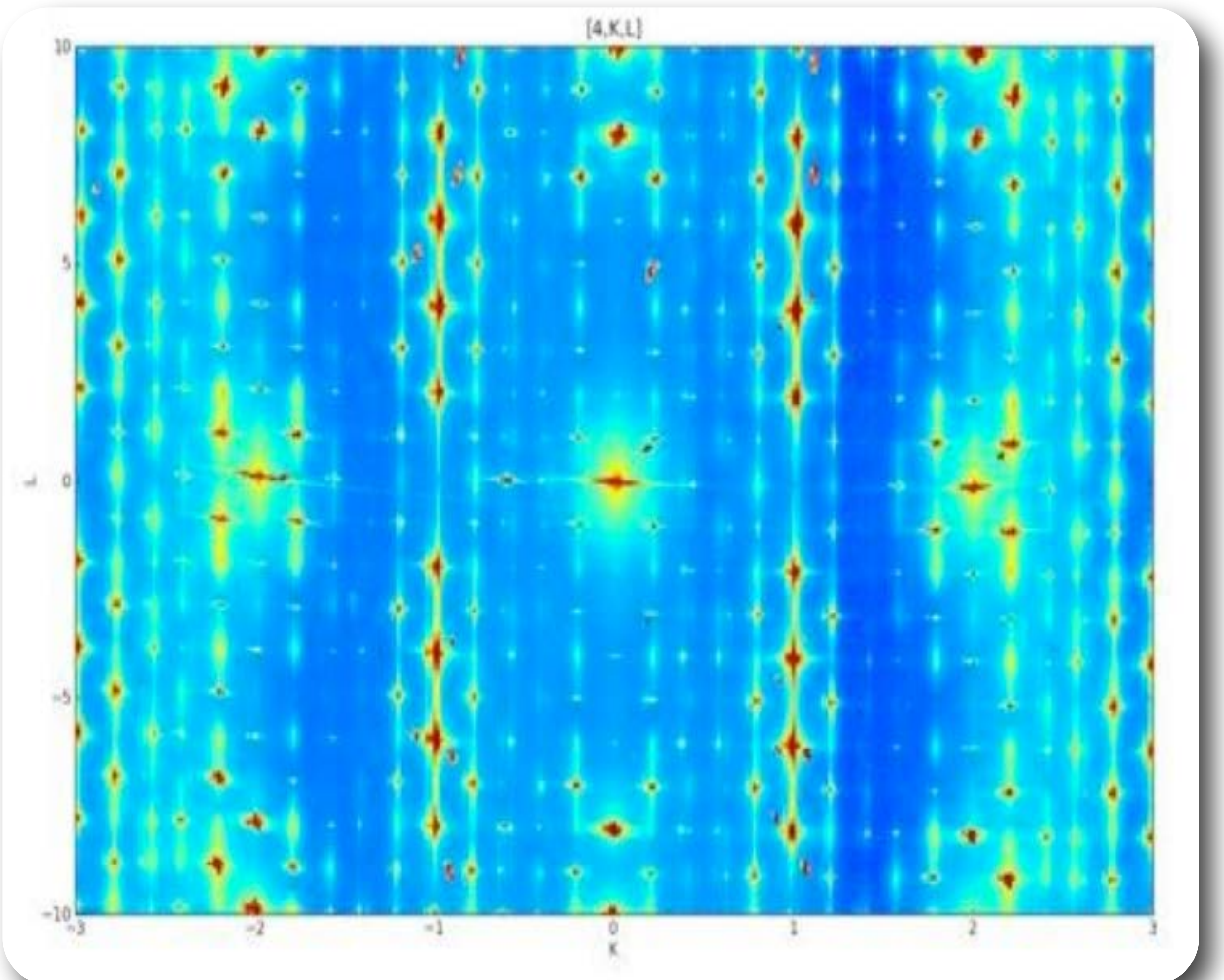
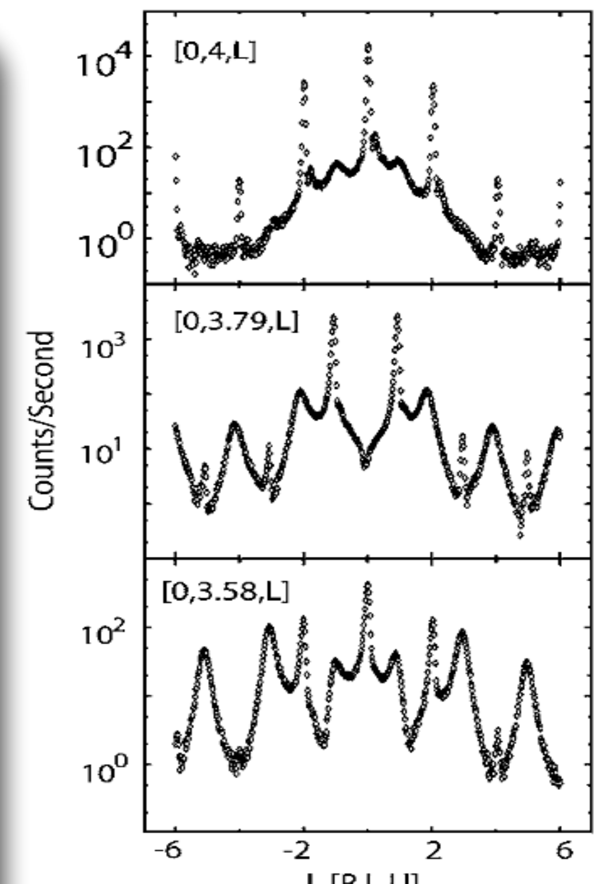
Beyond Crystallography: Incommensuration

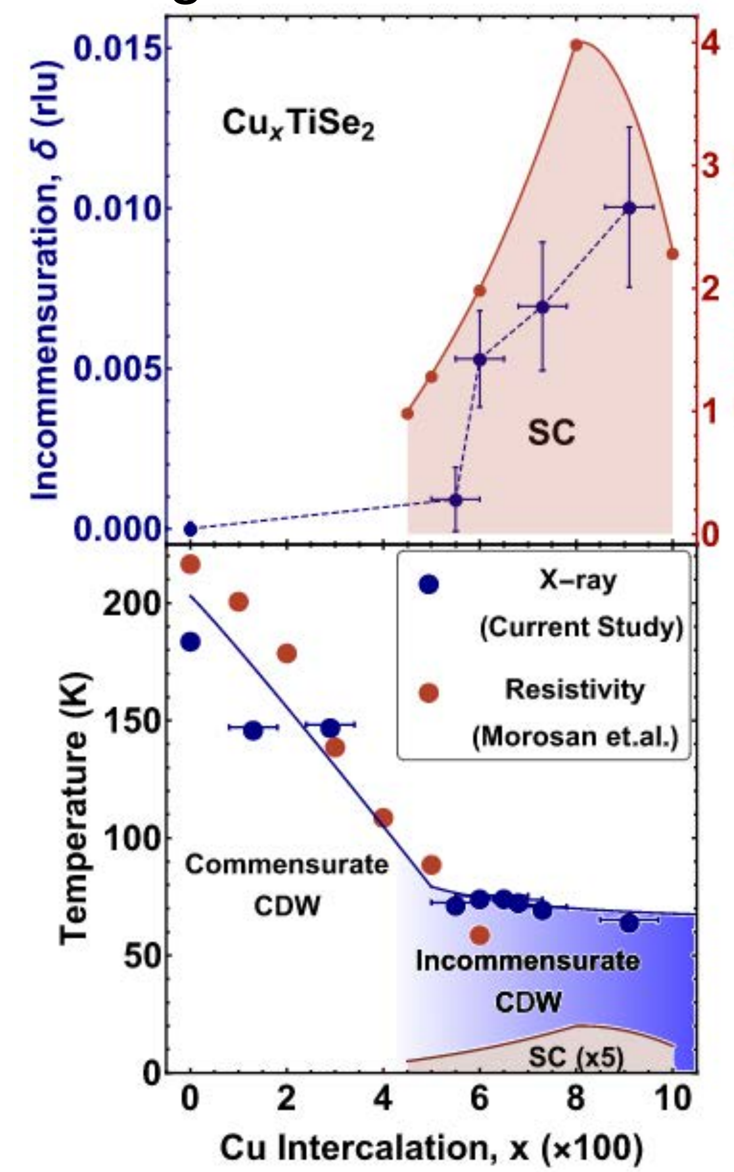
No more 3D space group or unit cell, if $n\tau \neq ma$, where m,n are integers



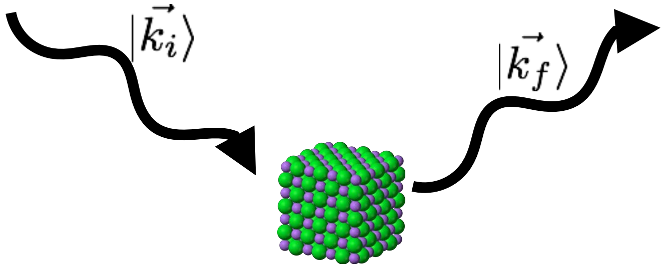




Bi-2212: Castellan
PRB 73, 174505 (2006)



Kogar
PRL 118, 027002 (2017)

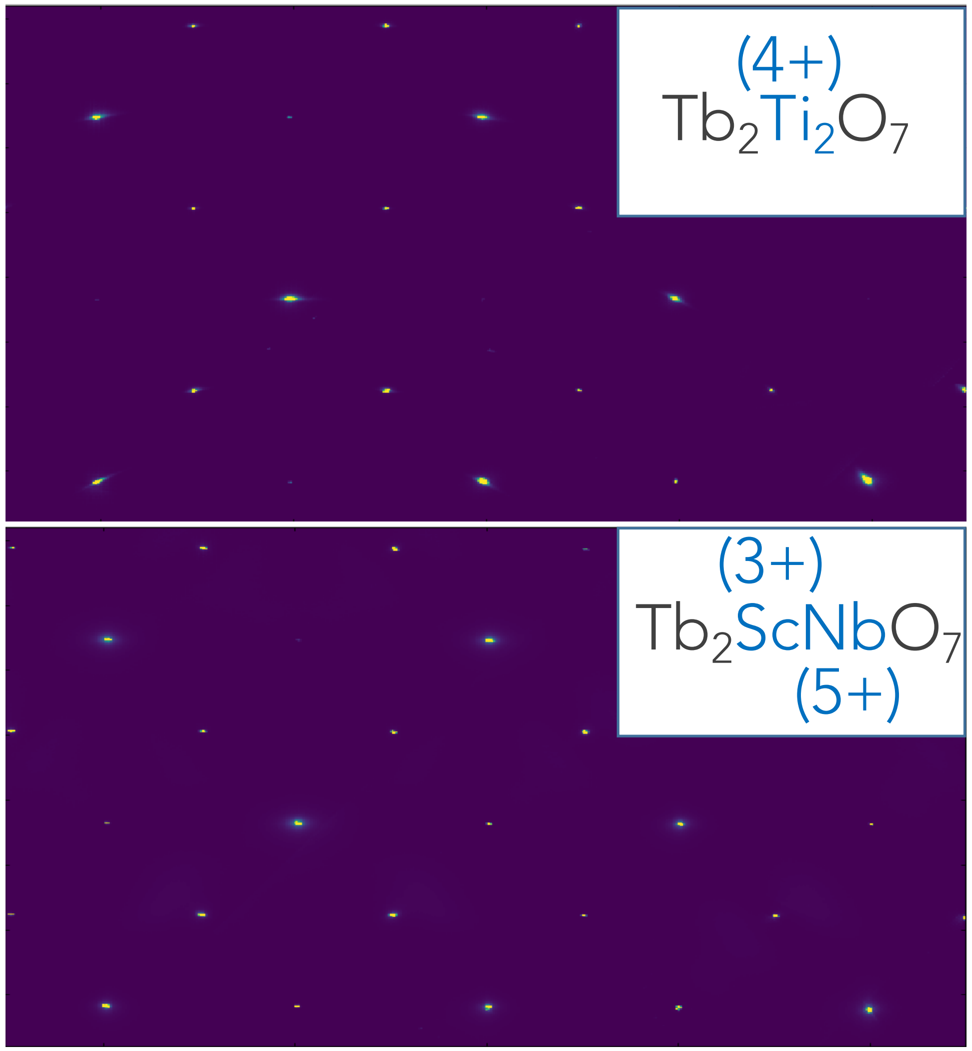


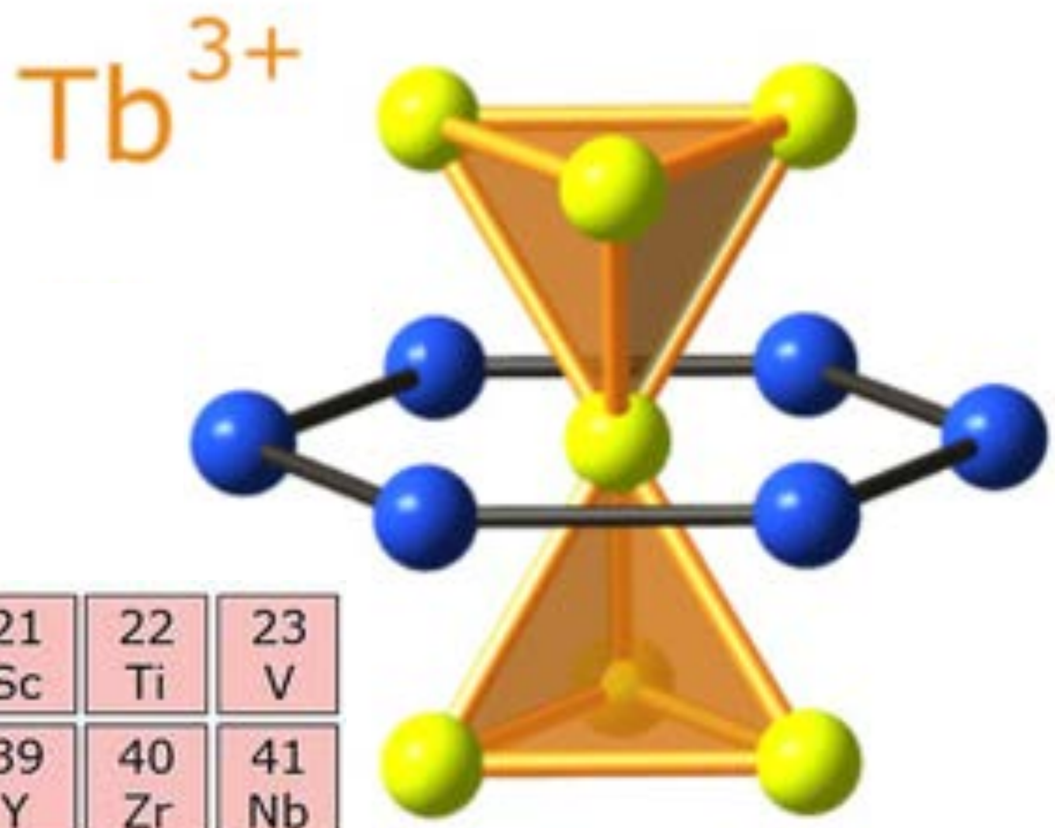
Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography: Short-ranged local order

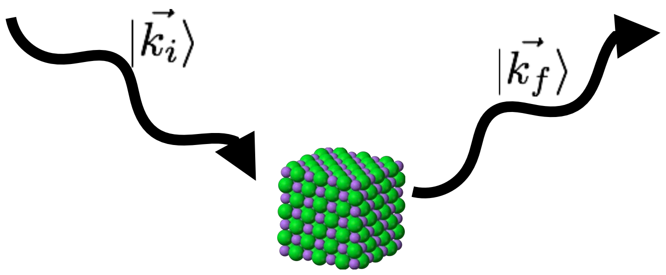
Pair correlations without Bragg Peaks, 1D and 3D PDF





21 Sc	22 Ti	23 V
39 Y	40 Zr	41 Nb

Linear scale - Similar Scattering, Avg. Structure.



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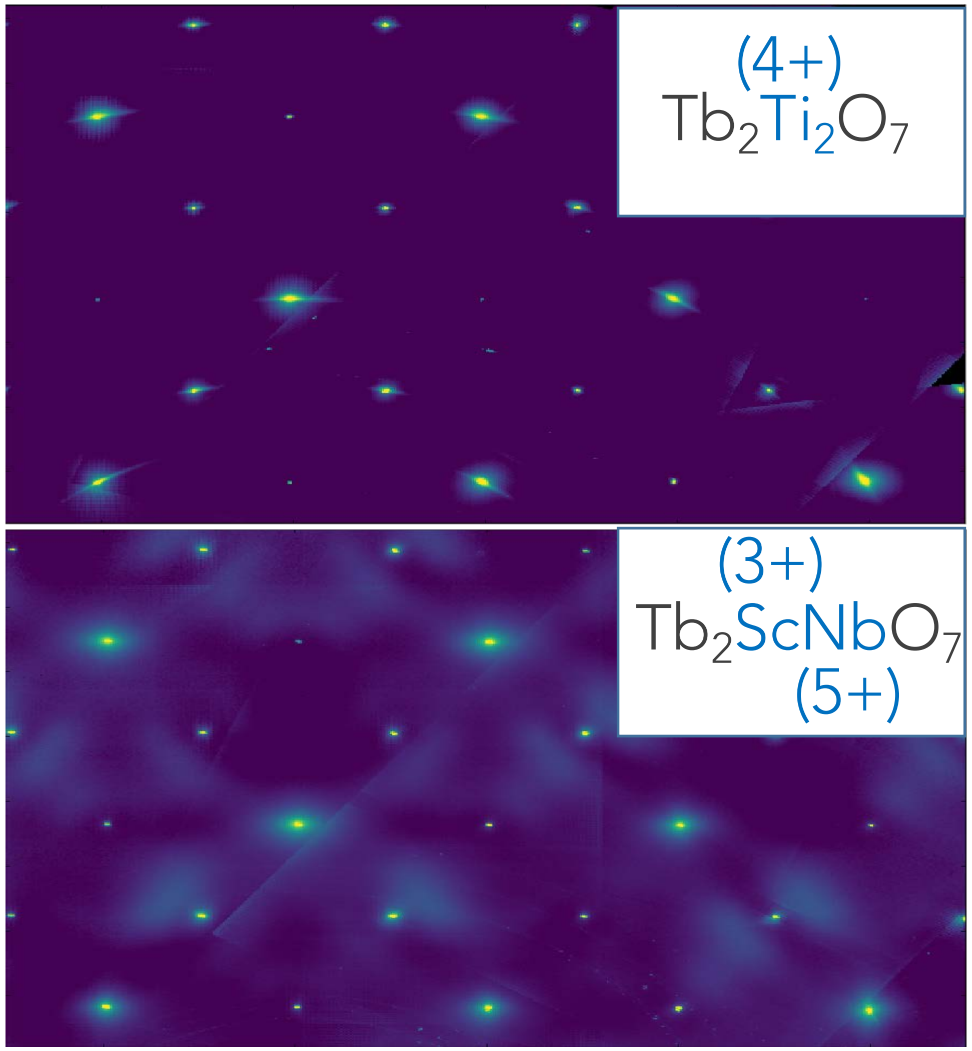
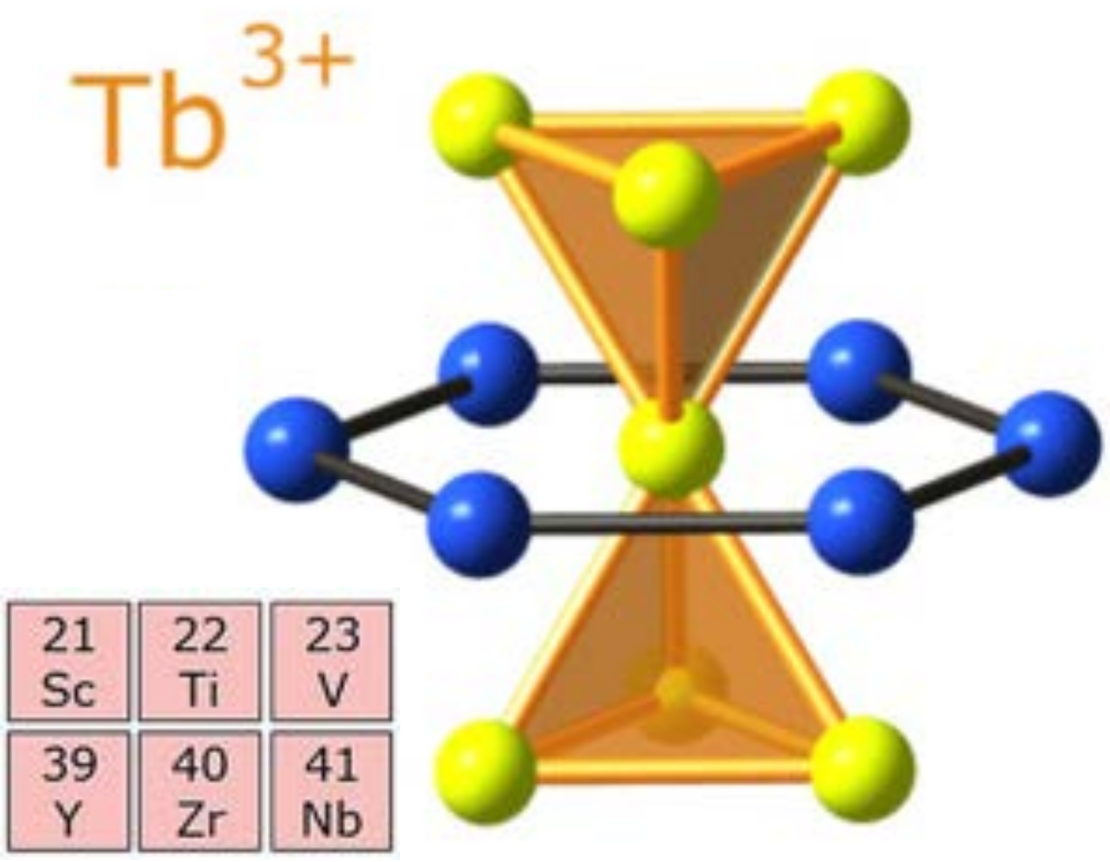
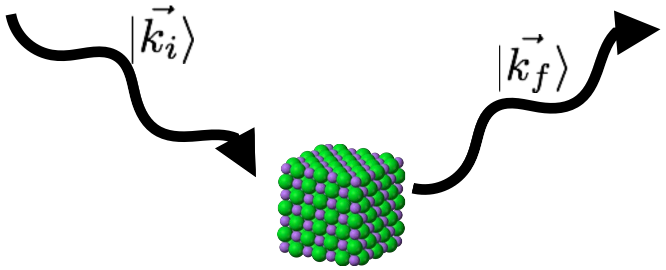




Log scale - “Charge Ice” Diffuse Scattering

Courtesy B.D. Gaulin



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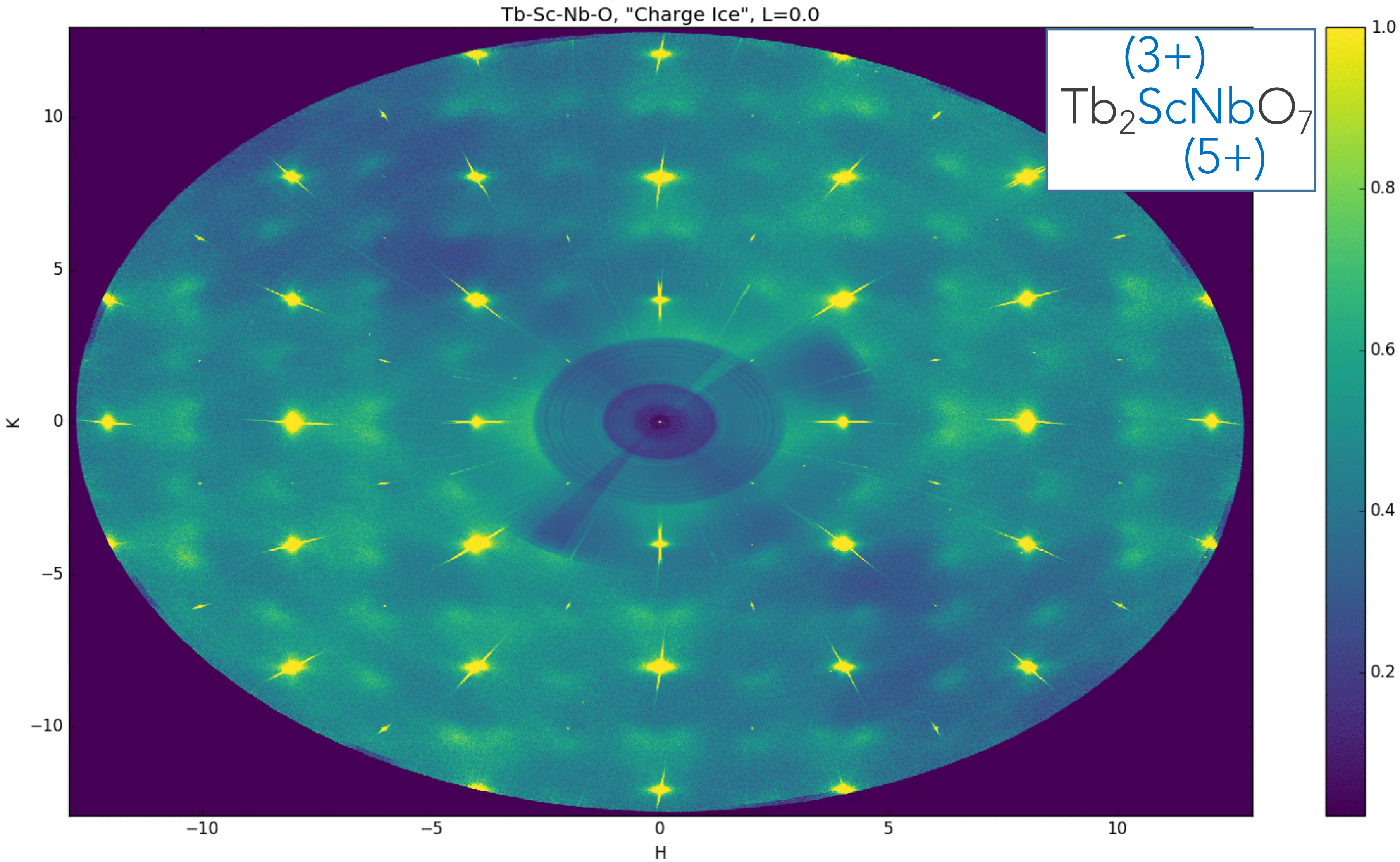
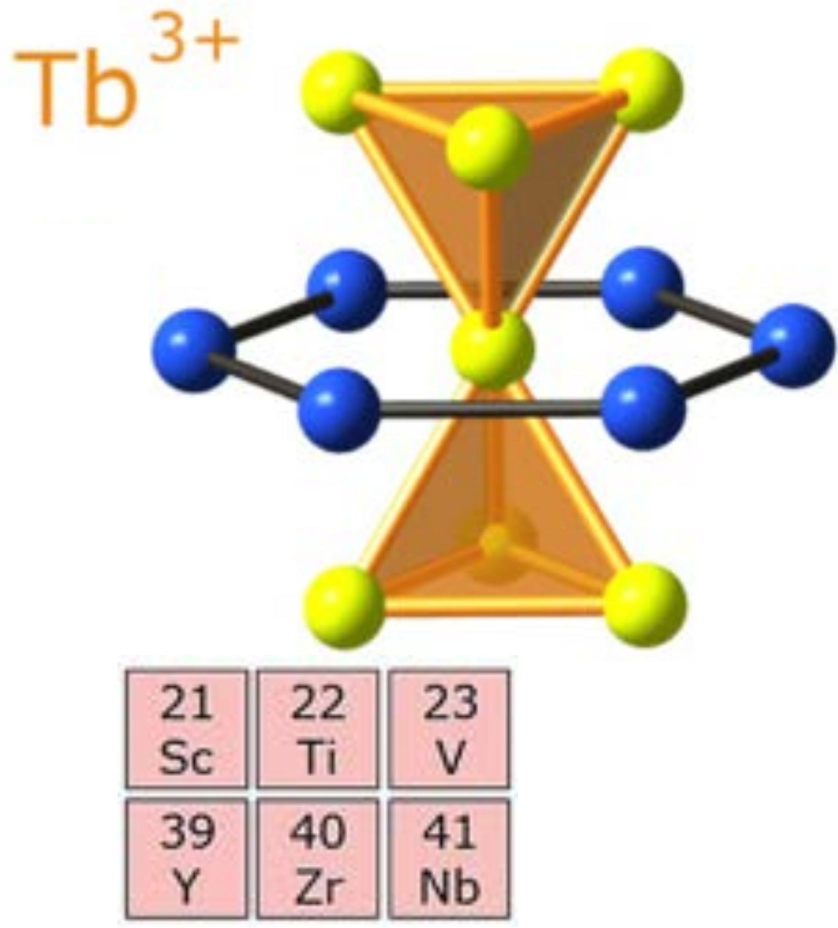
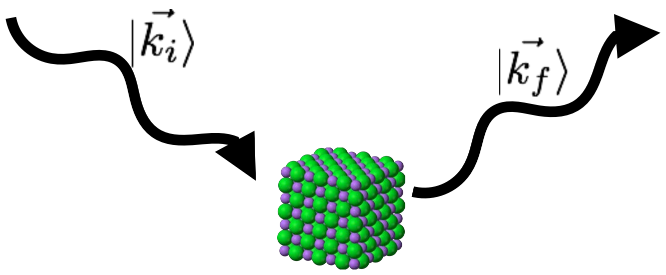




Need extensive Q coverage for PDF analysis. High energy x-rays, large detectors.



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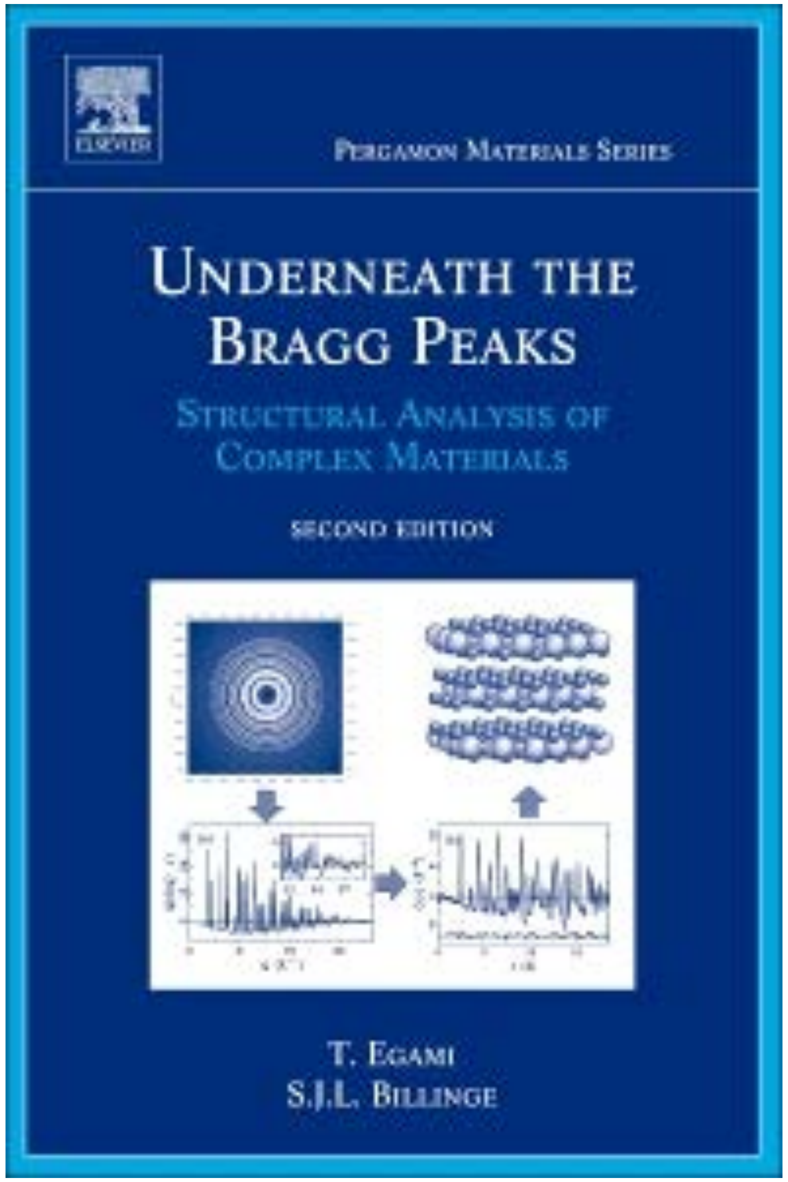
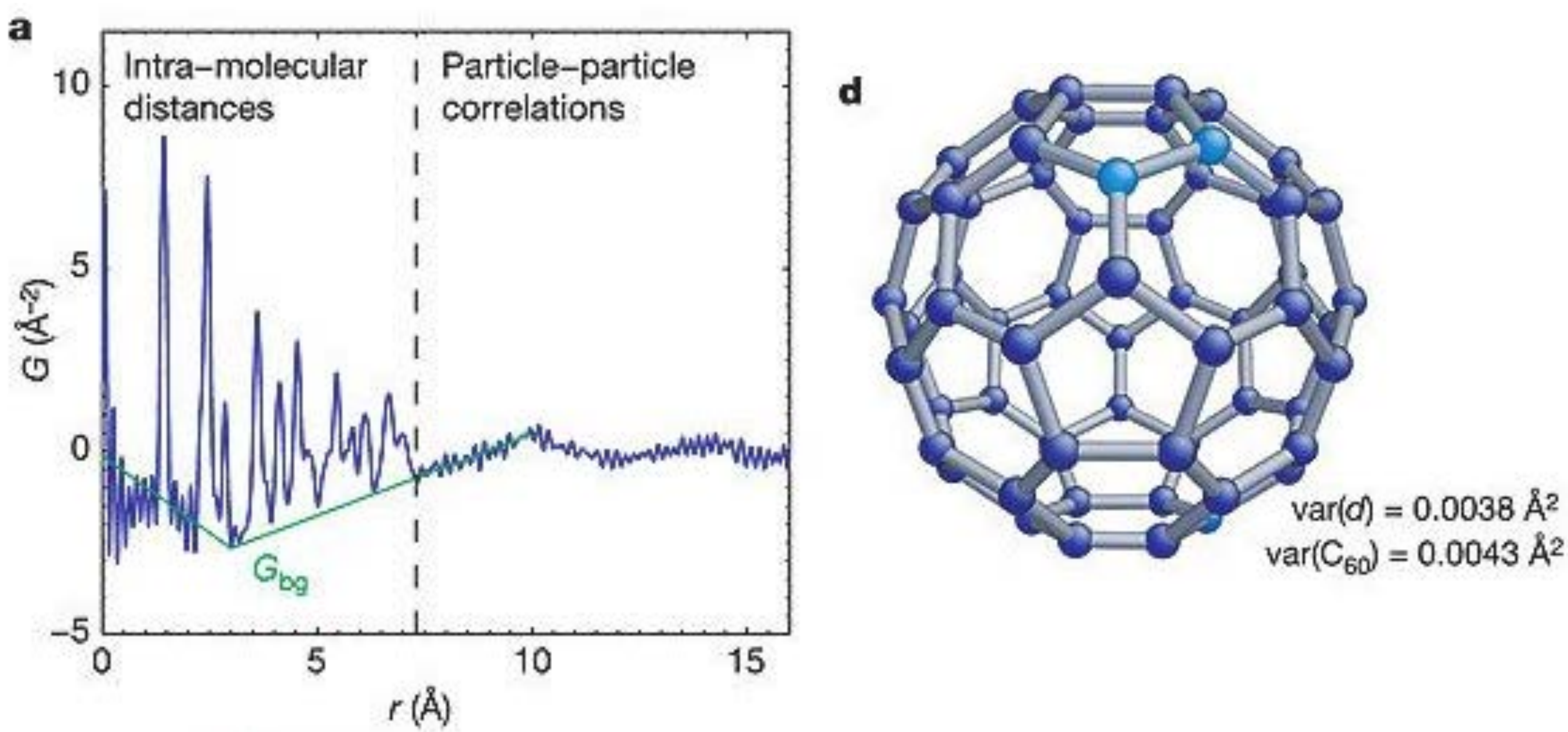
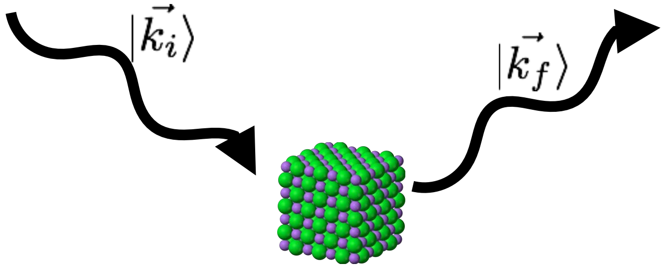
Beyond Crystallography: Short-ranged local order

PDF: Pair Distribution Function. Well established technique for amorphous materials and powders. Note the integral (and transform) spans the measured range. Q range sets real-space resolution. Juhas, Nature 440, 655 (2006)





$$G(r) = \frac{2}{\pi}\int Q[I(Q)-1]sin(Qr)dQ$$



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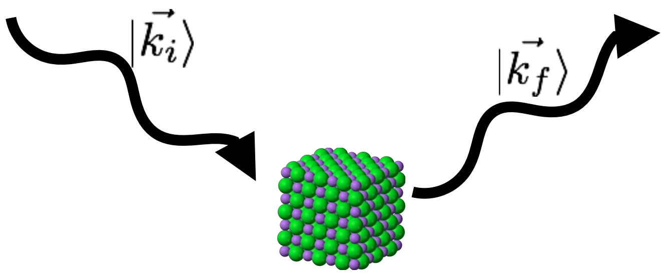
Beyond Crystallography: Short-ranged local order

3D-ΔPDF: Visualize local structures in 3D with atomic precision, if they occur in otherwise well-ordered crystals. Simonov & Weber, doi.org/10.1524/zkri.2012.1504 (2012)



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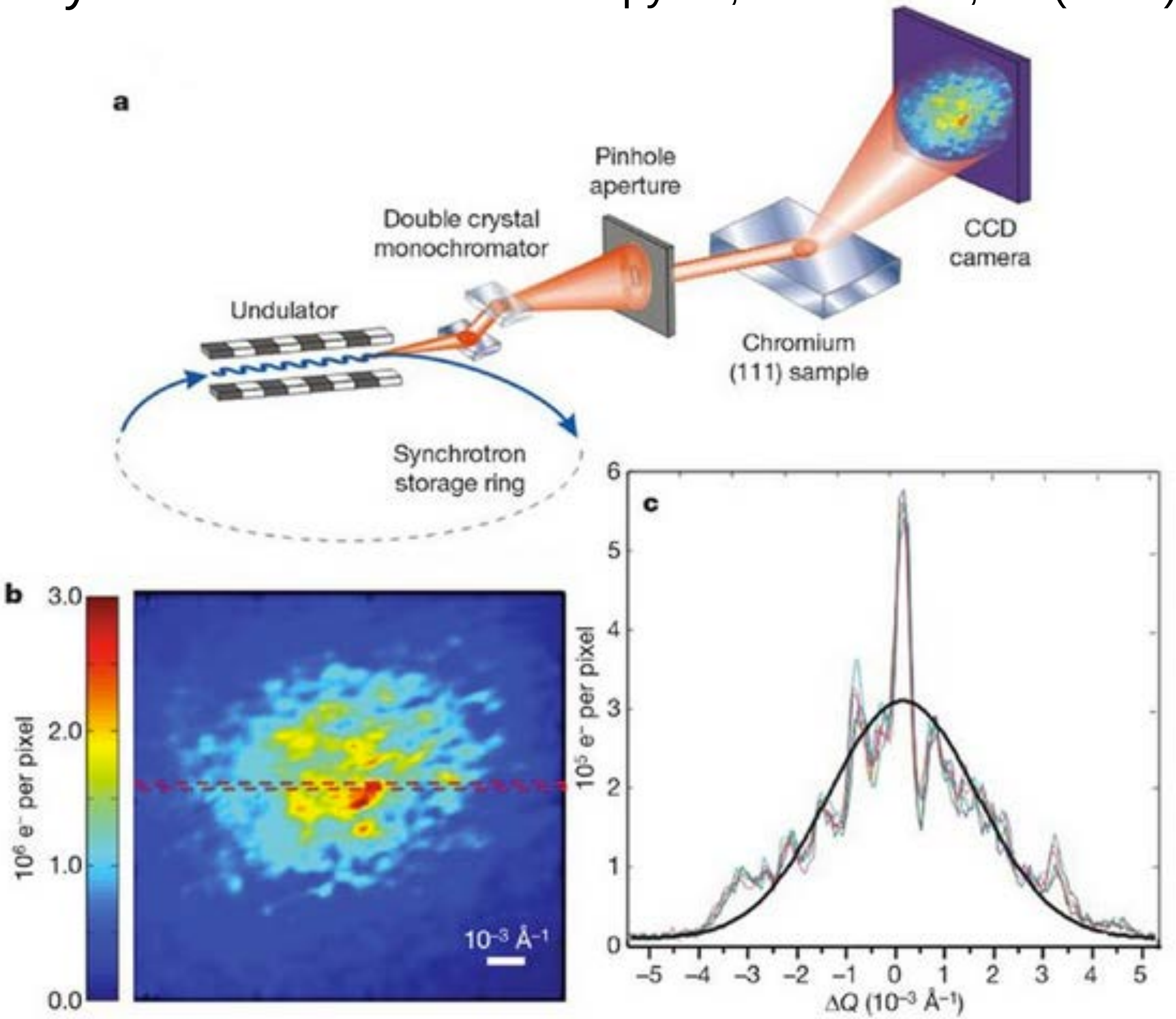
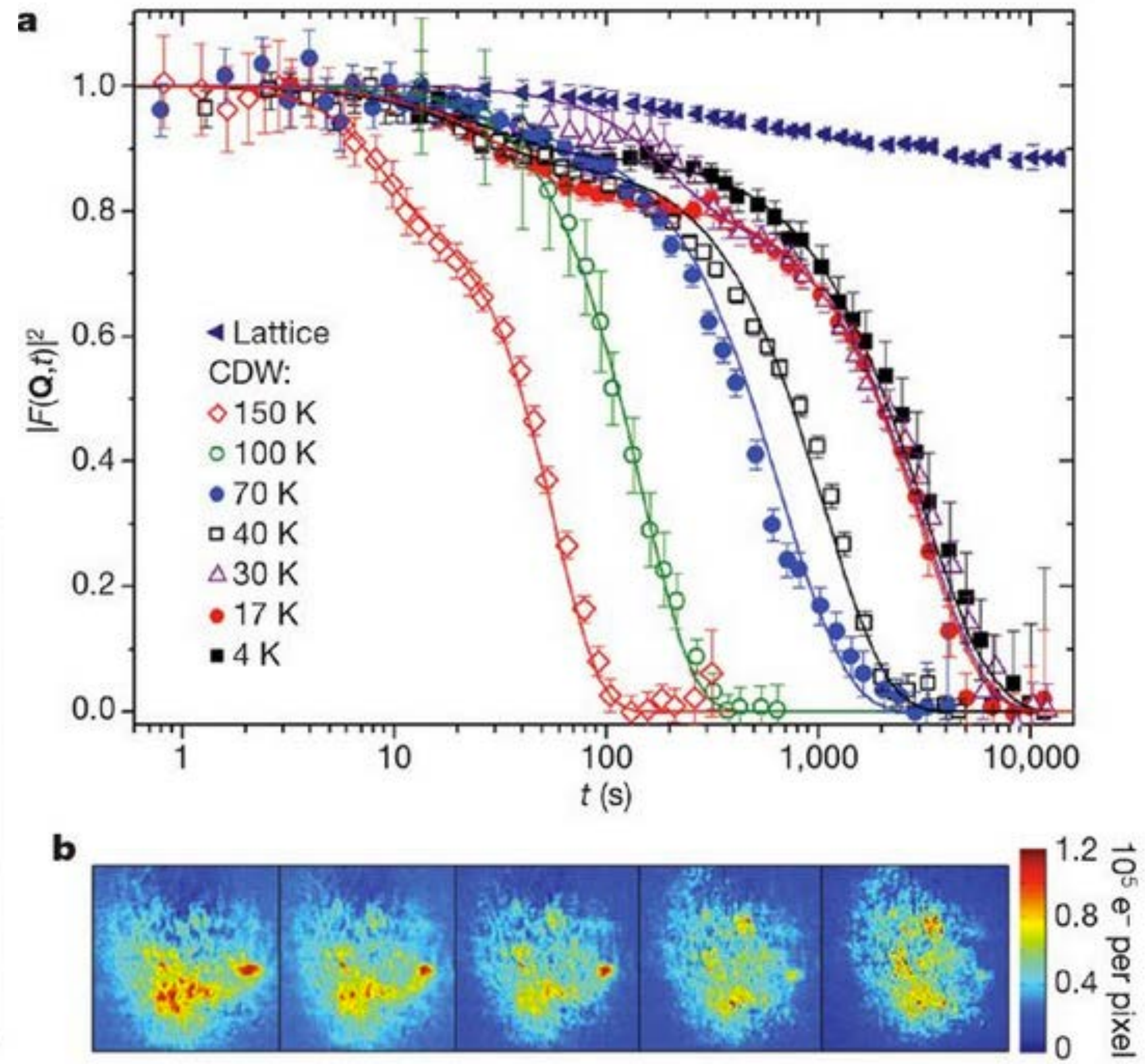
Coherent Beams: X-ray Photon Correlation Spectroscopy

Dynamics of domains Shpyrko, Nature 447, 68 (2007)





DW Domains in Cr - Speckle Dynamics vs Temp. & Time

Summary: Elastic Scattering

- Long-standing, classic technique. After 100+ years, diffraction is still the “killer app” for x-rays. Vast majority of beamlines are dedicated to this.
- Elastic x-ray scattering is a premier probe of symmetry, order, disorder, and critical phenomena.
- Looking beyond crystallography, elastic scattering exploiting high energy, high dynamic range, and high coherence can be highly informative for quantum materials research.
- Understanding structural data without a space group and unit cell remains a daunting challenge

Homework:

- Tomorrow, we will talk about resonant scattering and inelastic scattering, and possibly discuss sample environments and pumps/perturbations

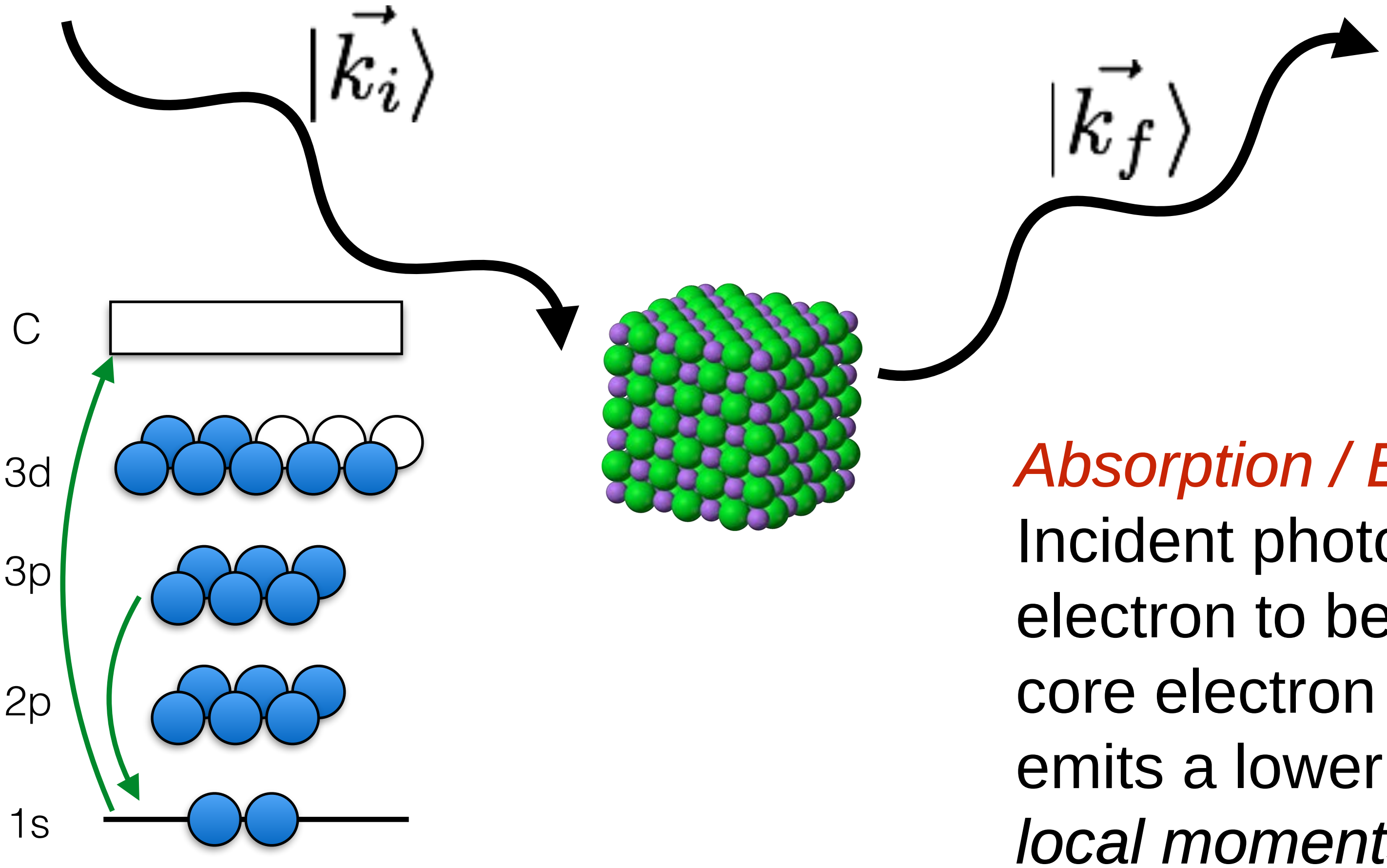
- I'd also like to open up discussion about what x-ray research at synchrotrons might have to offer to your research. I propose a Q&A.

- If you are interested, please fill out your card with the following information:

Name
Email address (optional)
Question

I will collect them before lecture tomorrow, and try to answer several of them. If we run out of time, I will email a response.

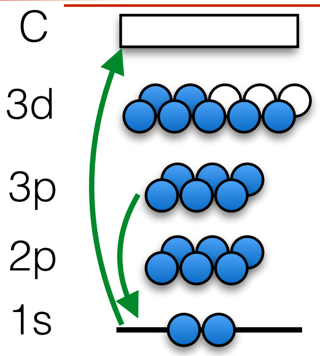
Example (made up) questions:
- "I study skyrmions. Can I use x-rays to see them?"
- "Which is the best beamline for magnetic scattering studies of Ytterbium?"
- "How do I get beam time at the LCLS?"



Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe *chemistry*, *bands, local moments.* [XANES, EXAFS, XES, XMCD]

Note: This section contains blatant theft from other talks and reviews by M. Newville, G. Bunker, and S. De Beer.



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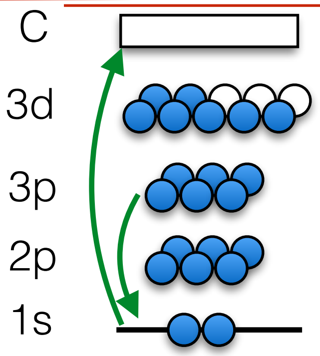
Key Ideas: High Spectral Flux, Tunable Energy, Narrow Bandwidth

For absorption / emission studies, we need bandwidth comparable to the intrinsic core-hole lifetimes in atoms.

We also need to be able to reliably tune the energy at the sub-eV level, and resolve the final energy with similar precision.

Synchrotron sources with perfect crystal optics are unique sources of such photons.



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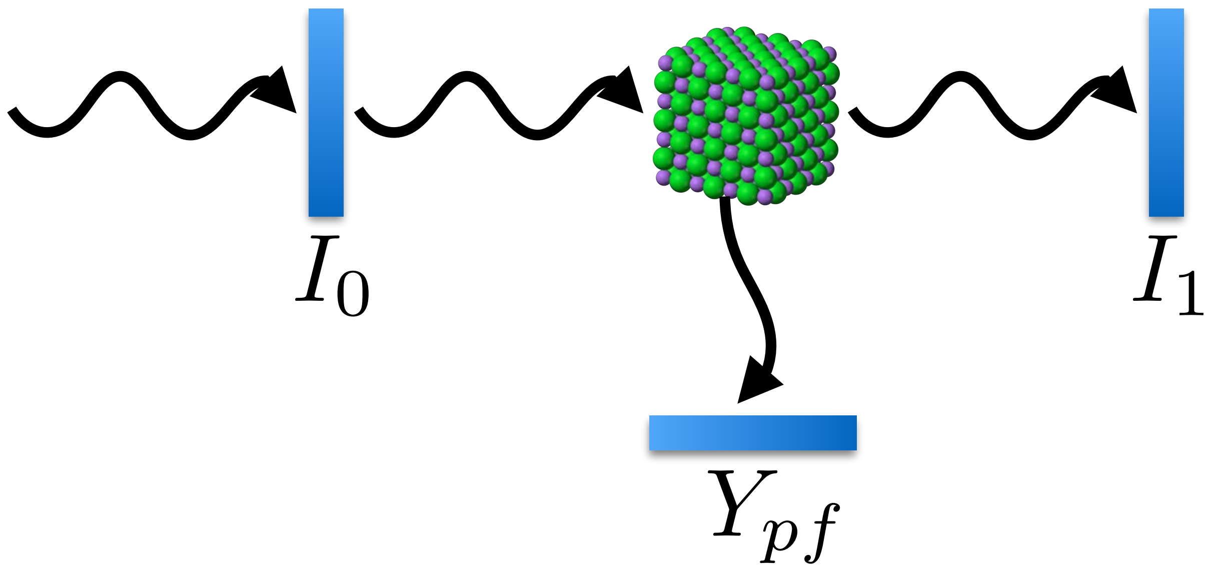


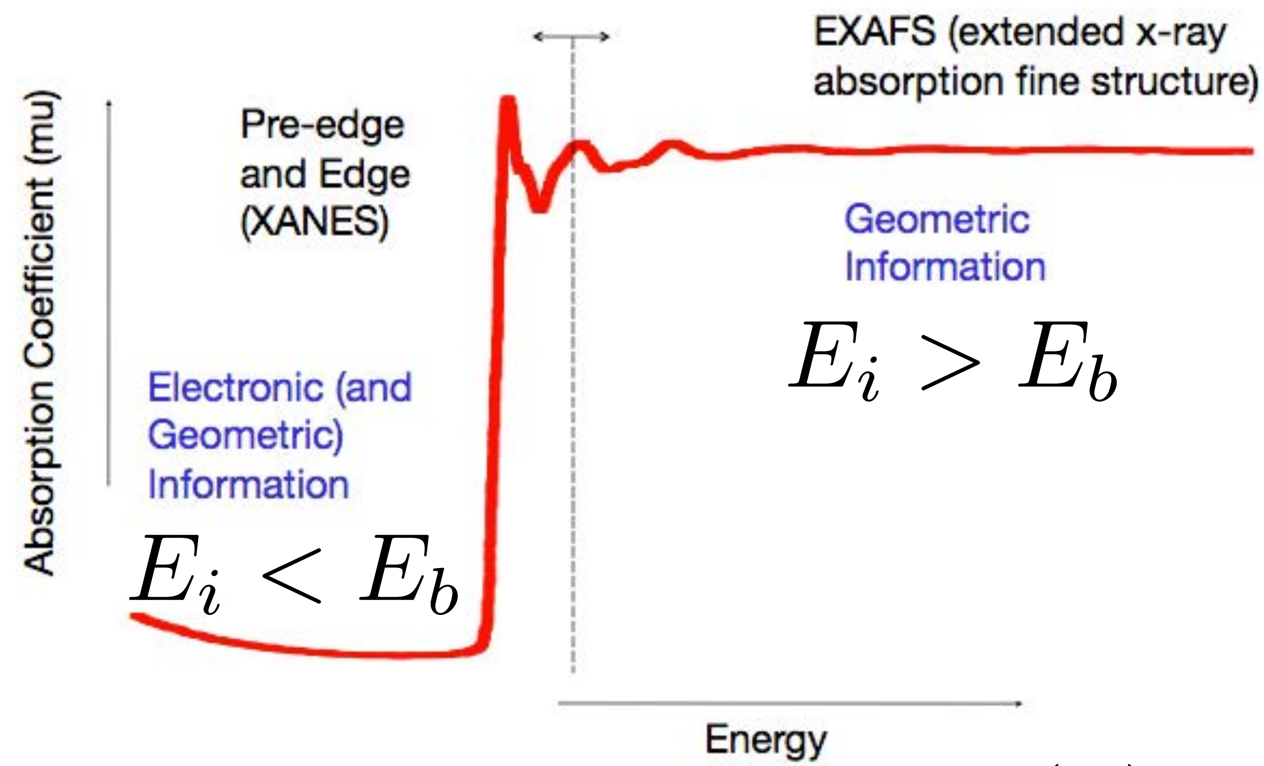
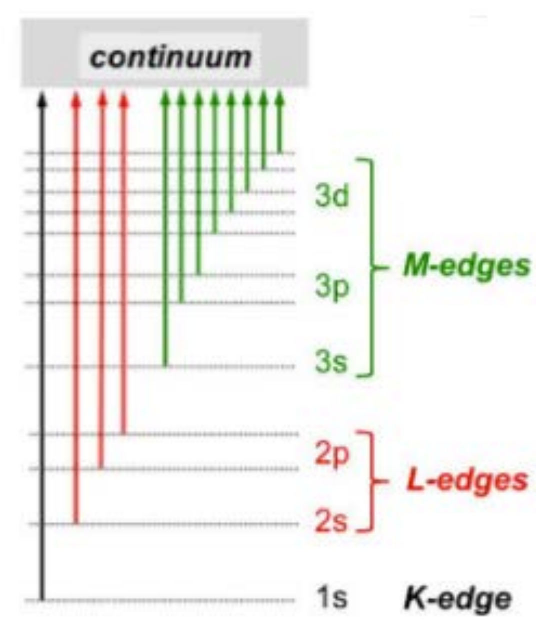


Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

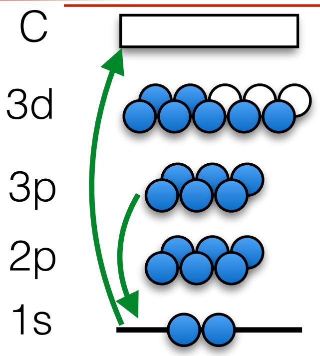
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†		
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†		
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†		
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†		
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†		
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†		
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†		
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†



$$I_1 = I_0 e^{-\mu(E)t}$$

$$\mu(E) \propto log\left(\frac{I_0}{I_1}\right)$$

$$\mu(E) \propto \left(\frac{Y_{pf}}{I_0}\right)$$



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$$\mu(E) \propto |\langle i|\hat{\epsilon}\cdot\vec{r}e^{i\vec{k}_i\cdot\vec{r}}|f\rangle|^2$$

Where initial state has (incident x-ray + core electron), final state has (core hole + photo-excited electron), and interaction is ~ the leading dipole term.

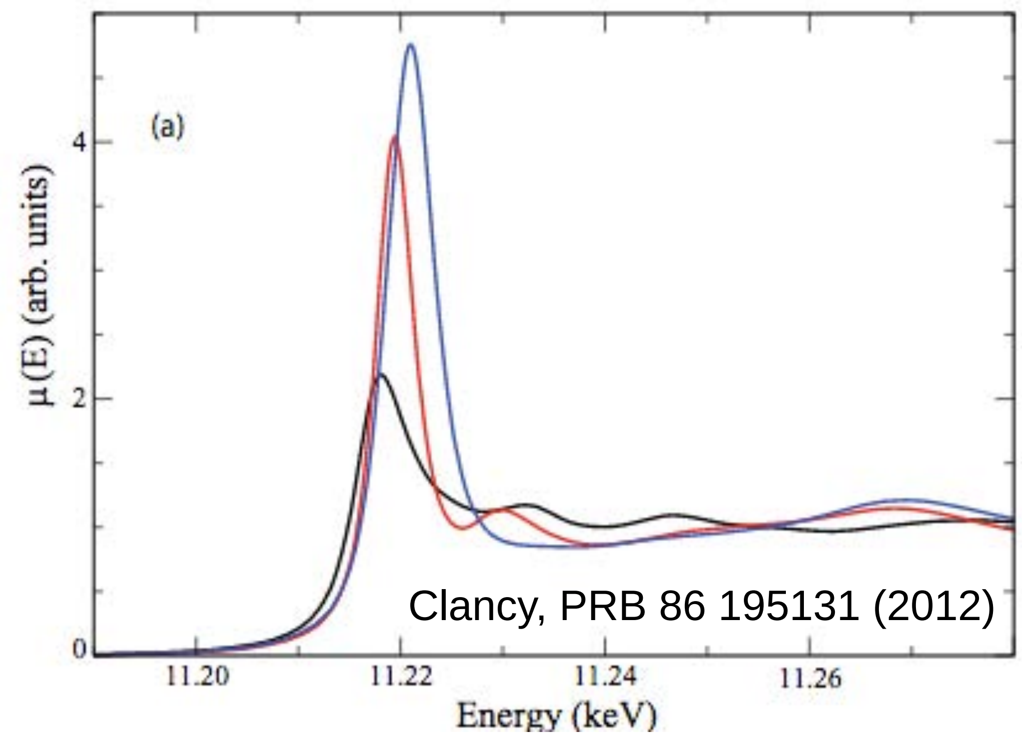
We expect low-lying density of empty final states to determine the shape and intensity of the absorption edge.

XANES: X-Ray Absorption Near-Edge Structure. Element specific, local probe. Contains information about oxidation state, spin state, ligand environment, and site symmetry.

Consider the difference between Ir L_3 spectra in the $5d^7$, $5d^6$, and $5d^5$ configurations. (Ir^0, Ir^{3+}, and Ir^{4+})

Dipole selection rules for L_3 prefer $\Delta l = \pm 1$

So, L_3 preferentially sensitive to 2p - 5d transitions.



QUESTION 3:

Which spectrum is which?
(IrO_2 is $5d^5$, Ir metal is $5d^7$, $IrCl_3$ is $5d^6$)

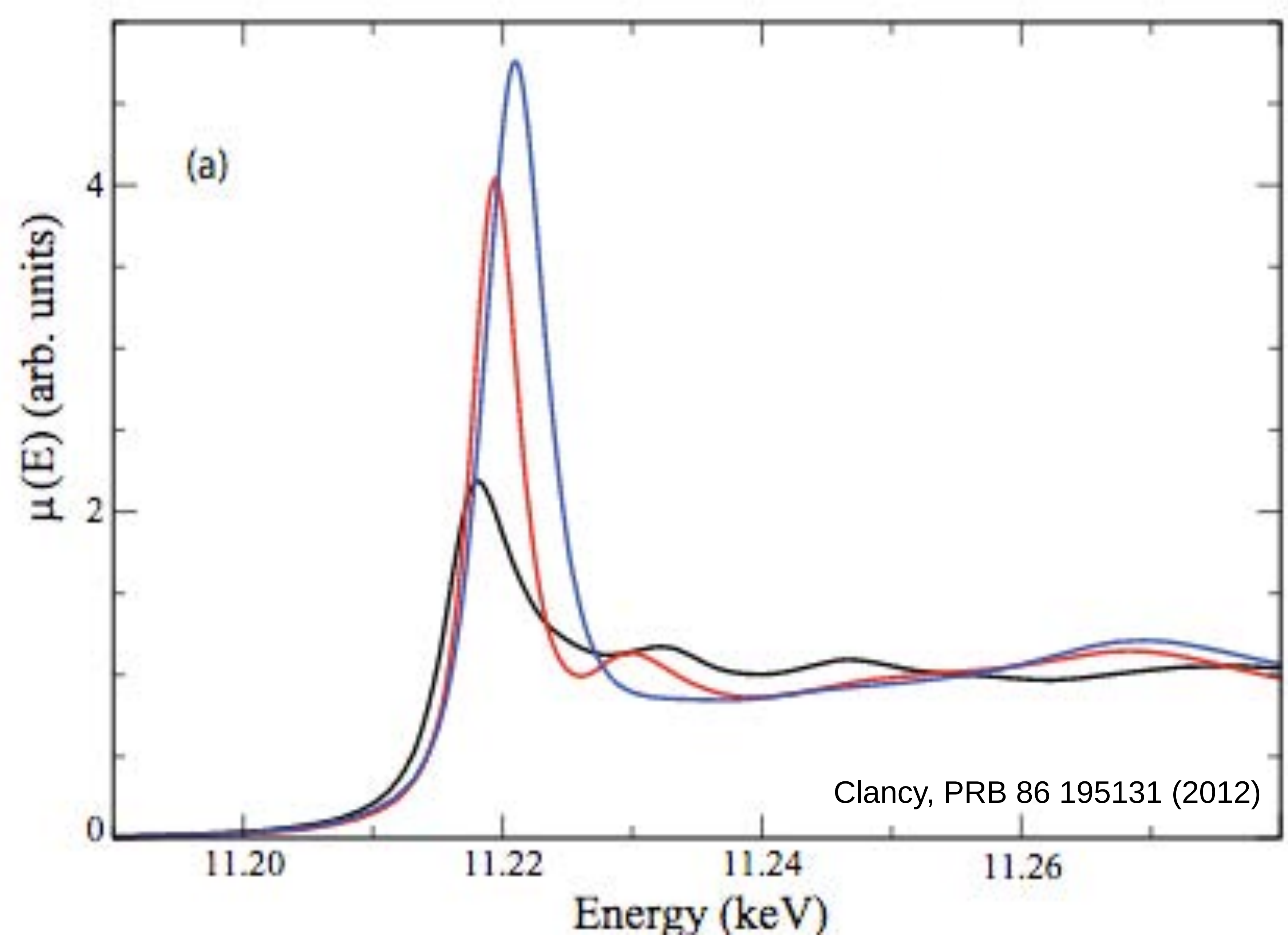
(A) $IrCl_3$, IrO_2, Ir

(B) $IrCl_3$, Ir, IrO_2

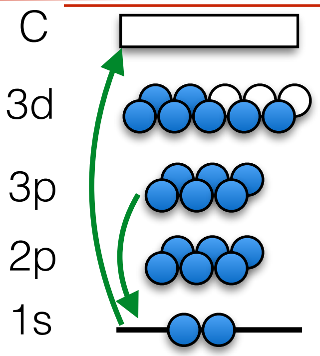
(C) IrO_2, $IrCl_3$, Ir

(D) Ir, $IrCl_3$, IrO_2

(E) Ir, IrO_2, $IrCl_3$



Clancy, PRB 86 195131 (2012)



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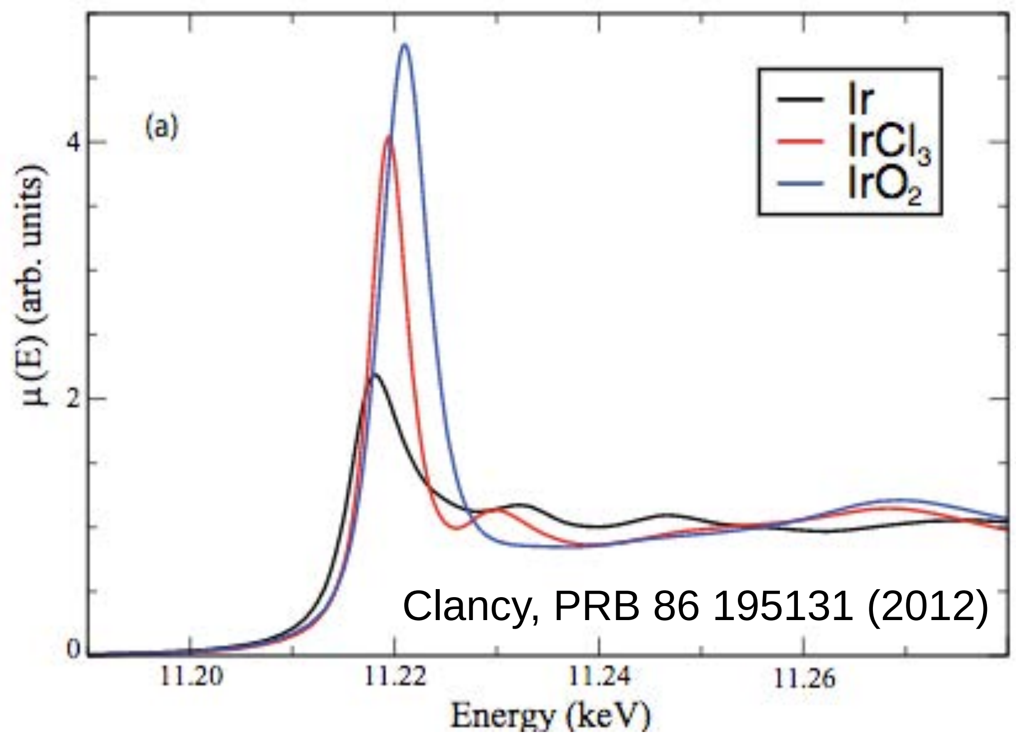

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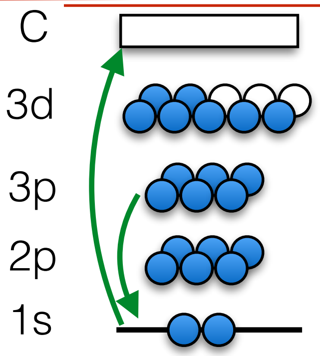

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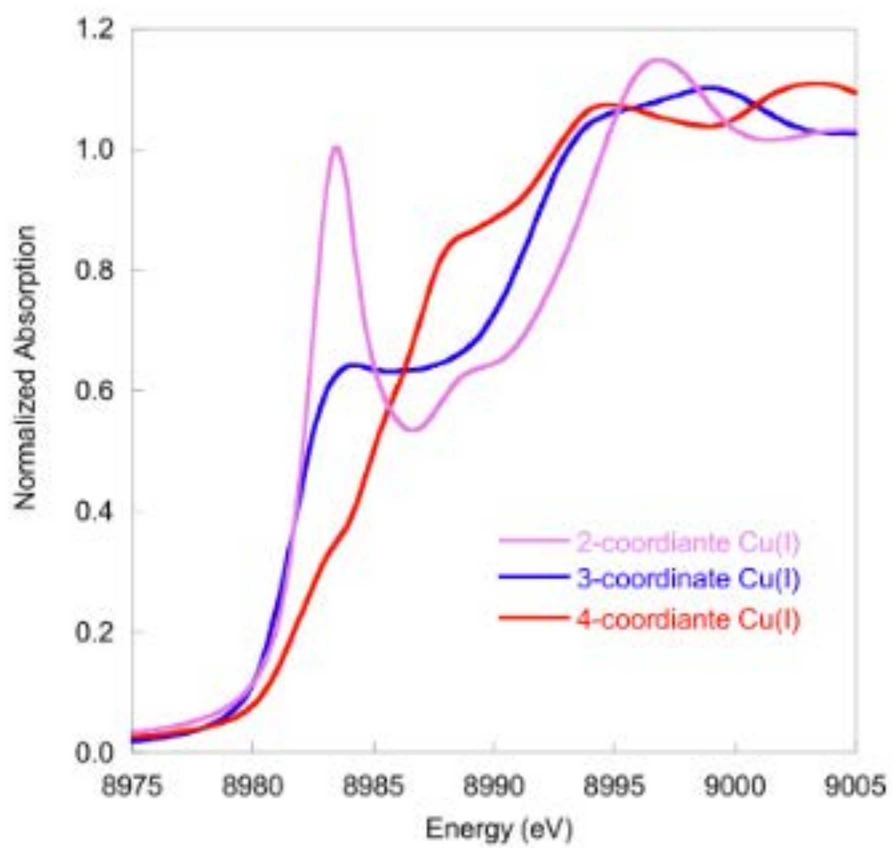
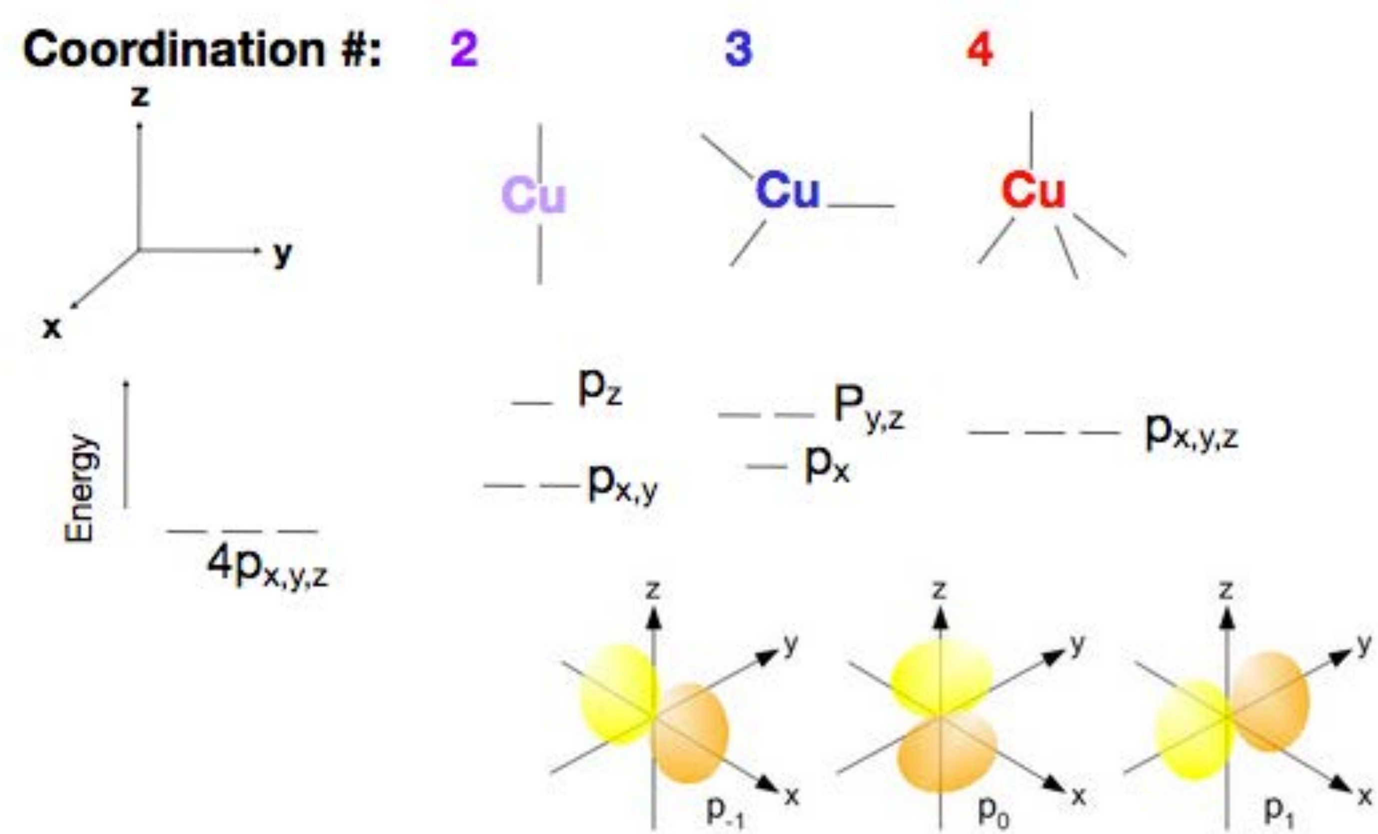
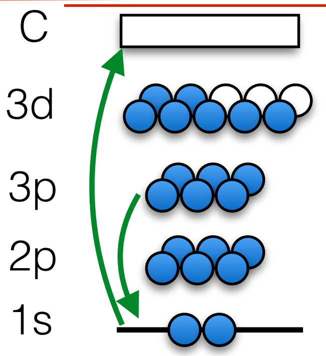


L.S. Kau et al., J. Am. Chem. Soc., **1987**, 109, 6433.



(After S. DeBeer)

Crystal environment shifts energy levels of unoccupied states.



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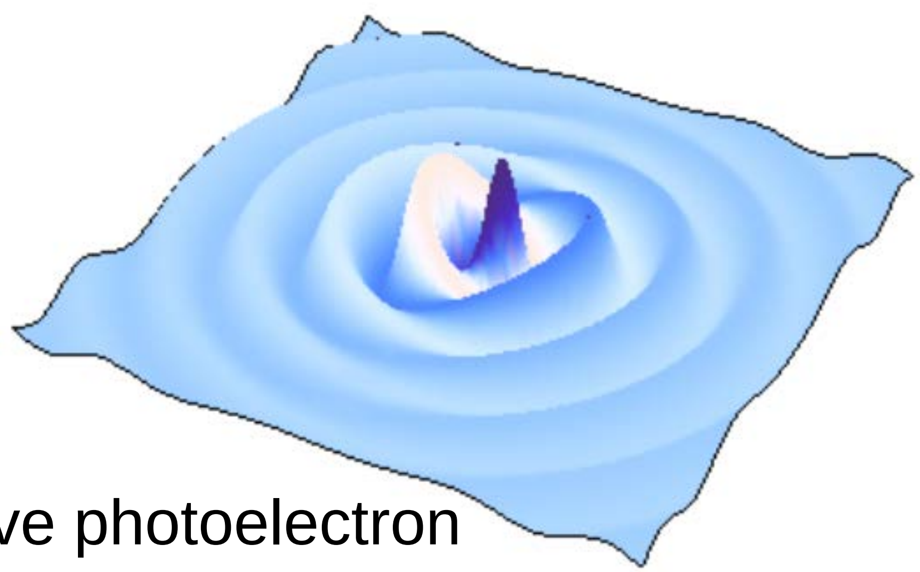
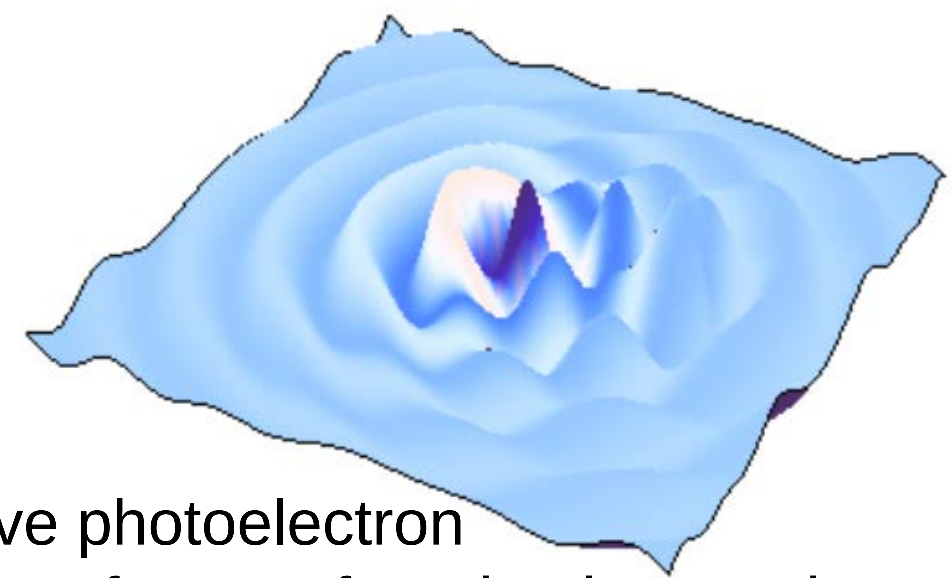
$$k_{pe} = \sqrt{\frac{2m(E_i - E_b)}{\hbar^2}}$$

Photo-electron ejected with more momentum for incident photon energies farther from the edge. These electrons can backscatter from adjacent atoms. Probe radial local environment, akin to PDF. This is EXAFS.

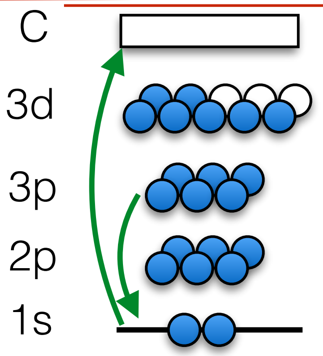


P-wave photoelectron
from isolated atom



P-wave photoelectron
with interference from backscattering neighbors

(After G. Bunker)



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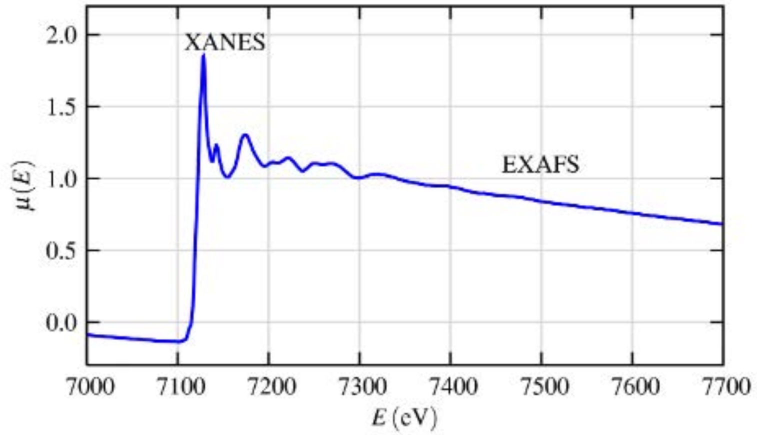
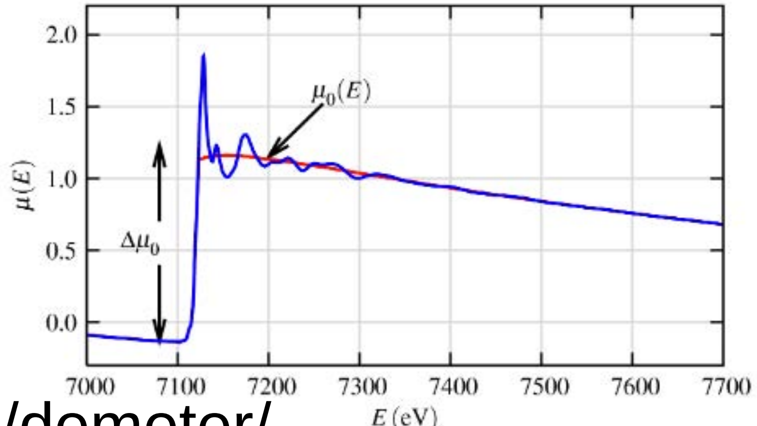
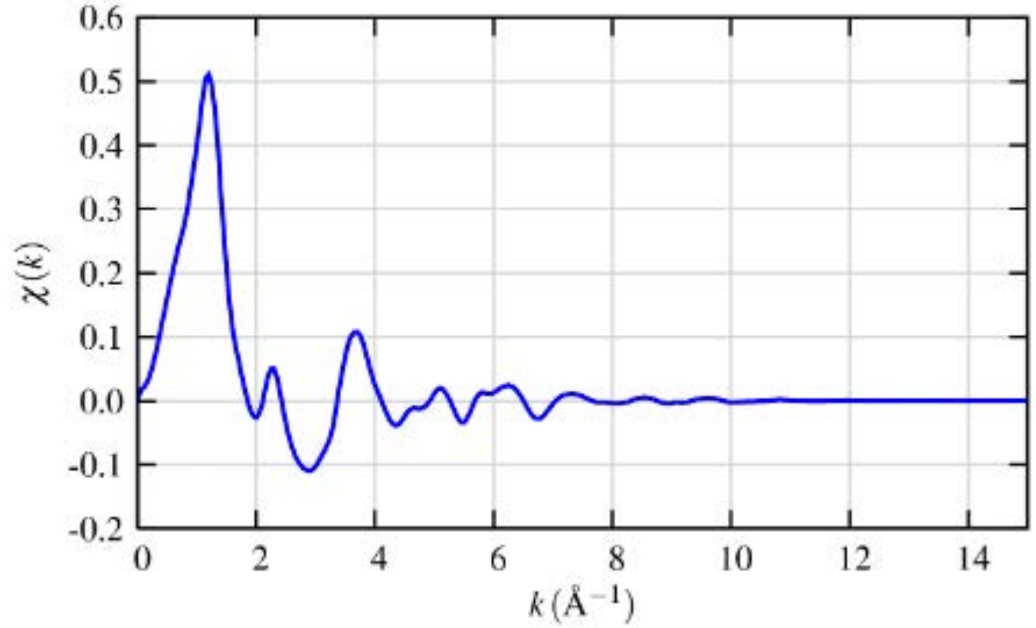
isolated atom

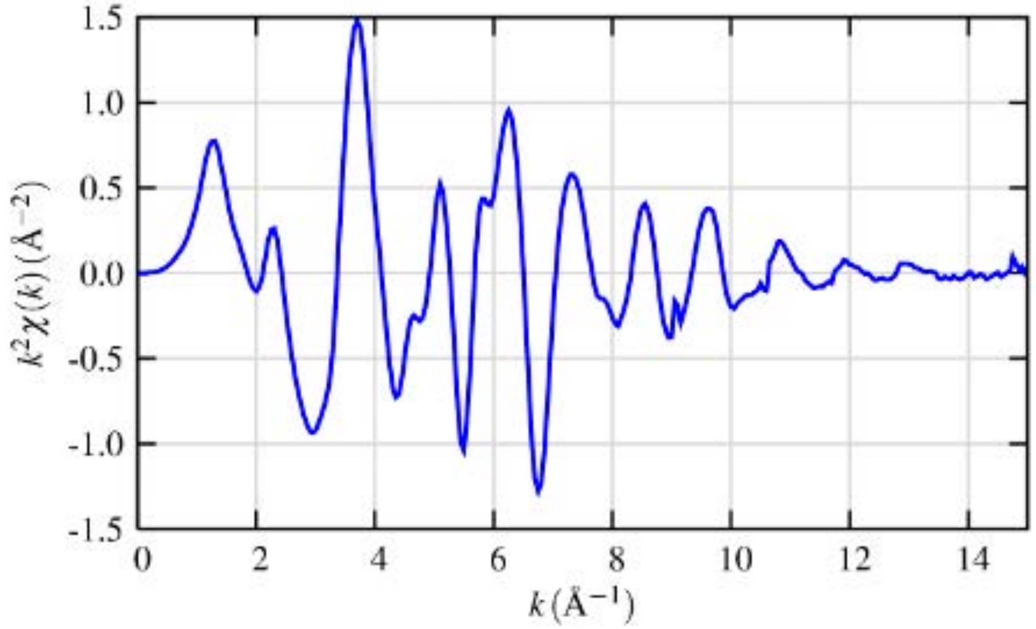
$$\mu(E) = \mu_0(E)[1+\chi(E)]$$

$$\chi(k_{pe}) = \frac{f(k_{pe})}{k_{pe}R^2} sin[2k_{pe}R + \delta(k_{pe})]$$









(After M. Newville) "Fundamentals of XAFS"

User-friendly software exists for exafs analysis.

https://bruceravel.github.io/demeter/

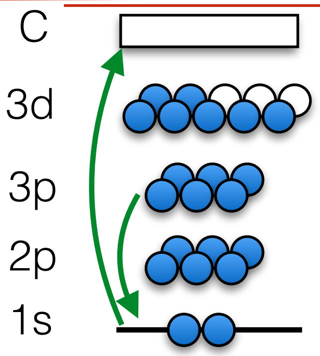


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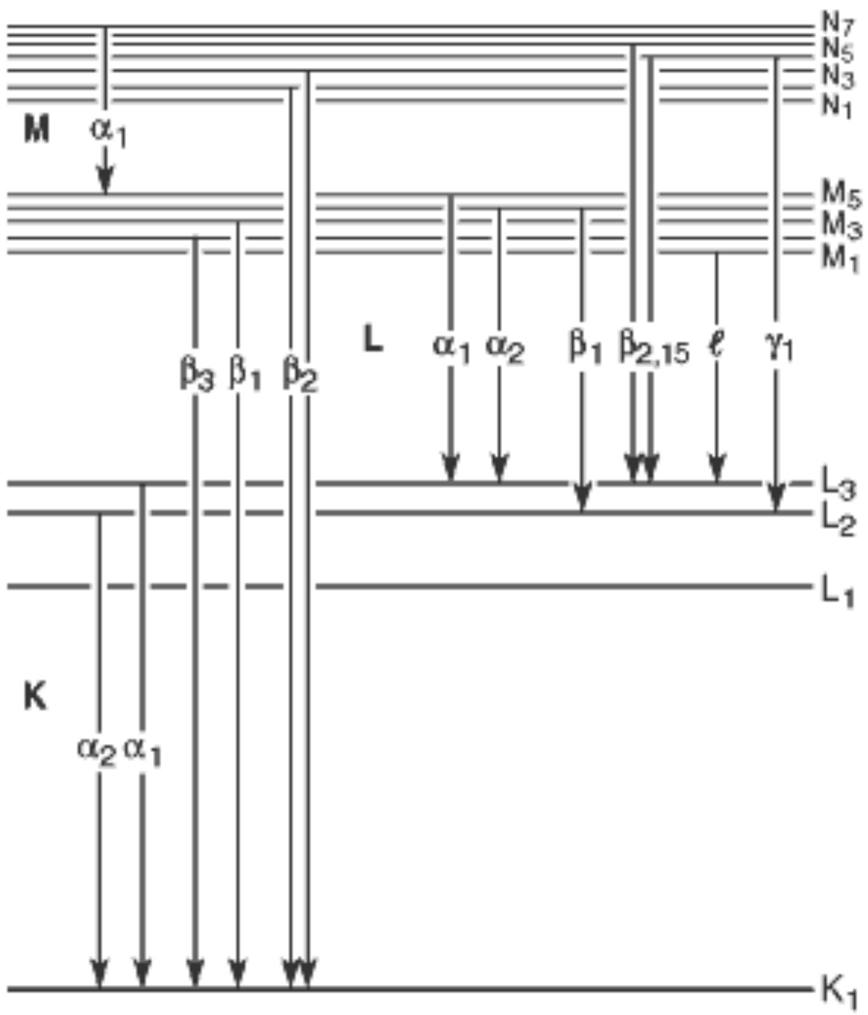
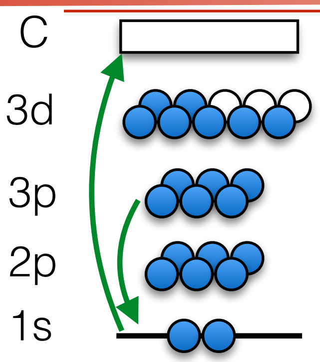
Table 1-2. Energies of x-ray emission lines (continued).

Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7
31 Ga	9,251.74	9,224.82	10,264.2	1,097.92	1,097.92	1,124.8
32 Ge	9,886.42	9,855.32	10,982.1	1,188.00	1,188.00	1,218.5
33 As	10,543.72	10,507.99	11,726.2	1,282.0	1,282.0	1,317.0
34 Se	11,222.4	11,181.4	12,495.9	1,379.10	1,379.10	1,419.23
35 Br	11,924.2	11,877.6	13,291.4	1,480.43	1,480.43	1,525.90
36 Kr	12,649	12,598	14,112	1,586.0	1,586.0	1,636.6
37 Rb	13,395.3	13,335.8	14,961.3	1,694.13	1,692.56	1,752.17
38 Sr	14,165	14,097.9	15,835.7	1,806.56	1,804.74	1,871.72
39 Y	14,958.4	14,882.9	16,737.8	1,922.56	1,920.47	1,995.84



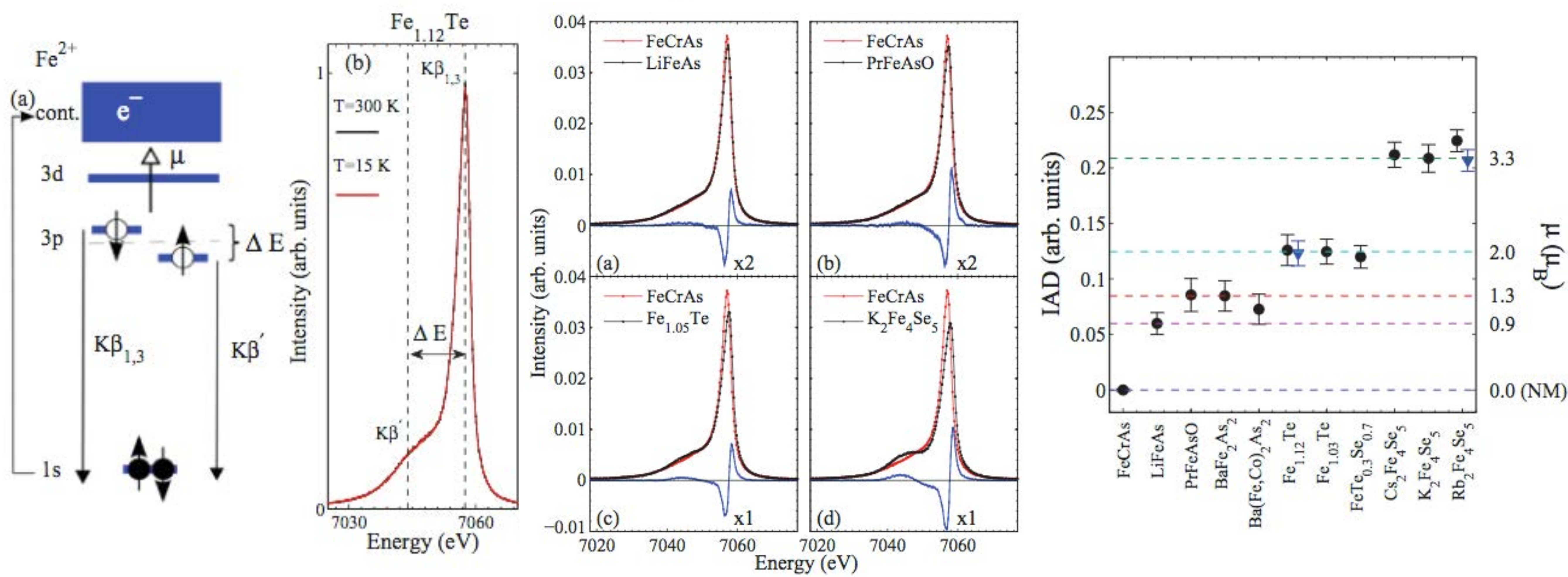
The emitted photons are not only useful as a monitor of absorption. The energy structure of x-ray emission is a powerful spectroscopy in its own right. Learn about the excited state core hole energetics in the final state. Note nomenclature for lines.



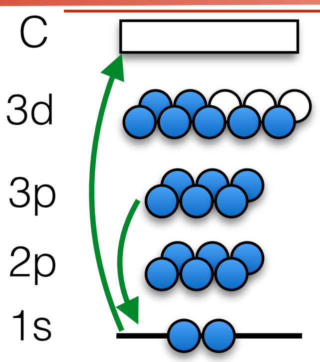
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe *chemistry*, *bands, local moments.* [XANES, EXAFS, XES, XMCD]

Local moments in Fe-SCs. [Gretarsson, PRB 84 100509 (2011)]



K_β emission can resolve the instantaneous local moment on transition metals. This is key information when trying to resolve local vs. itinerant quandaries in SDW metals.



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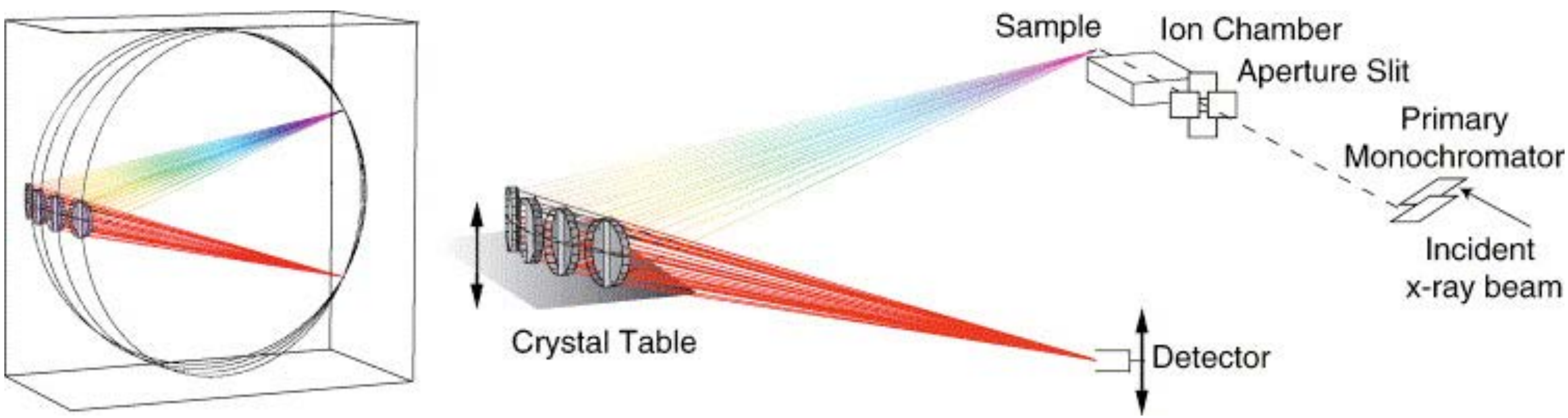
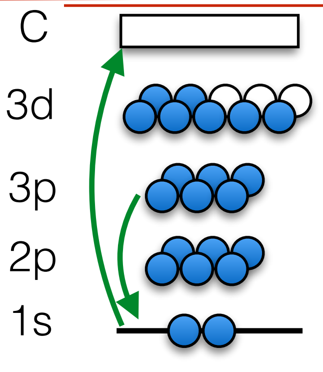
Crystal optics for emission spectroscopy. [Glatzel, Coord. Chem. Rev. 249 (2005)]



Use curved, backscattering crystal optics to collect emission over a large solid angle with fine energy resolution. (*CHESS-U - PIPOXS Beamline*)



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X-Ray Magnetic Circular Dichroism

p-d L-edge transitions with circular light, probe spin+orbital atomic moment.

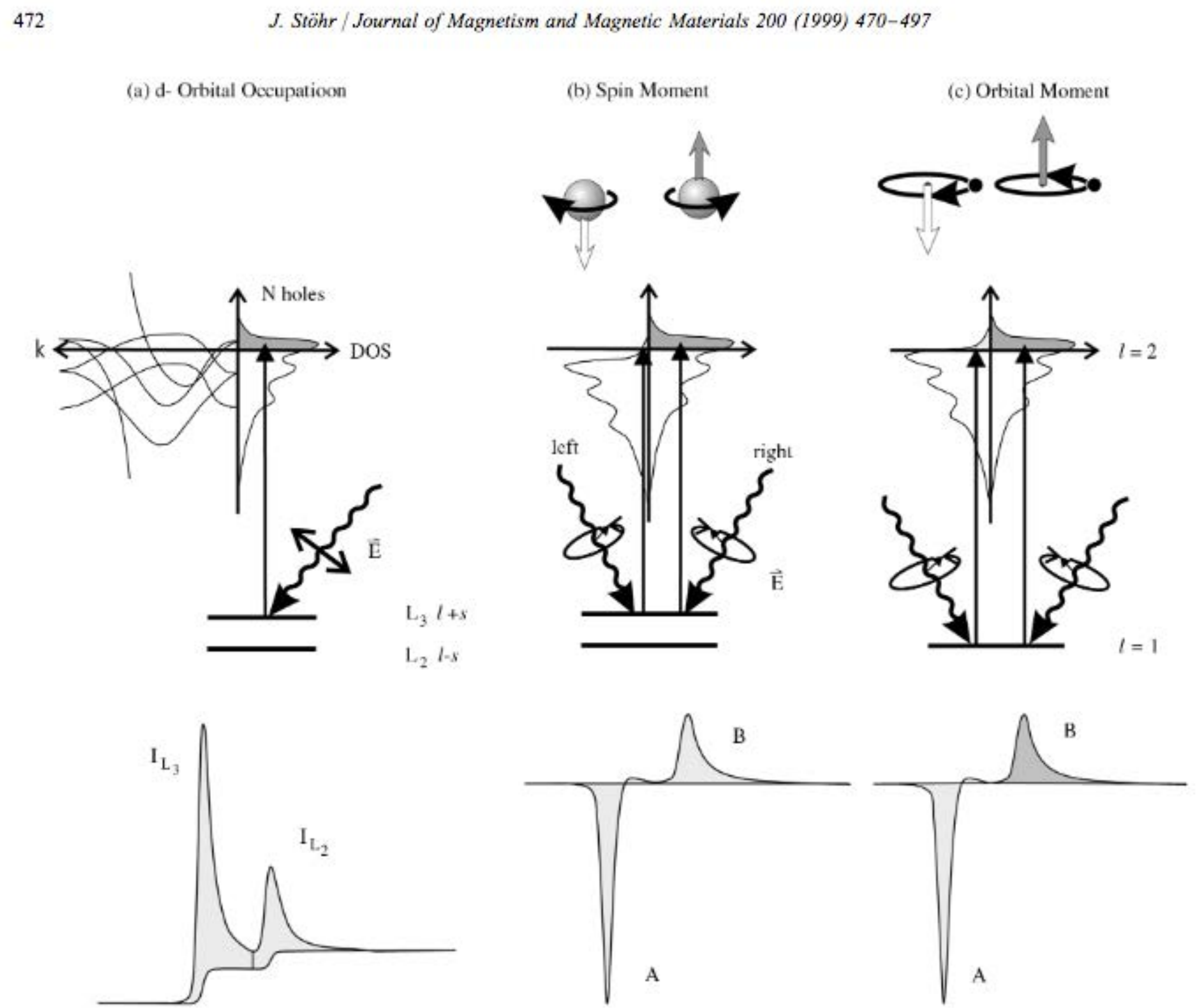
Difference in absorption when helicity is flipped.

Polarize atoms with magnetic field, measure susceptibility with atomic and orbital specificity.

Sum rules deconvolve L, S.

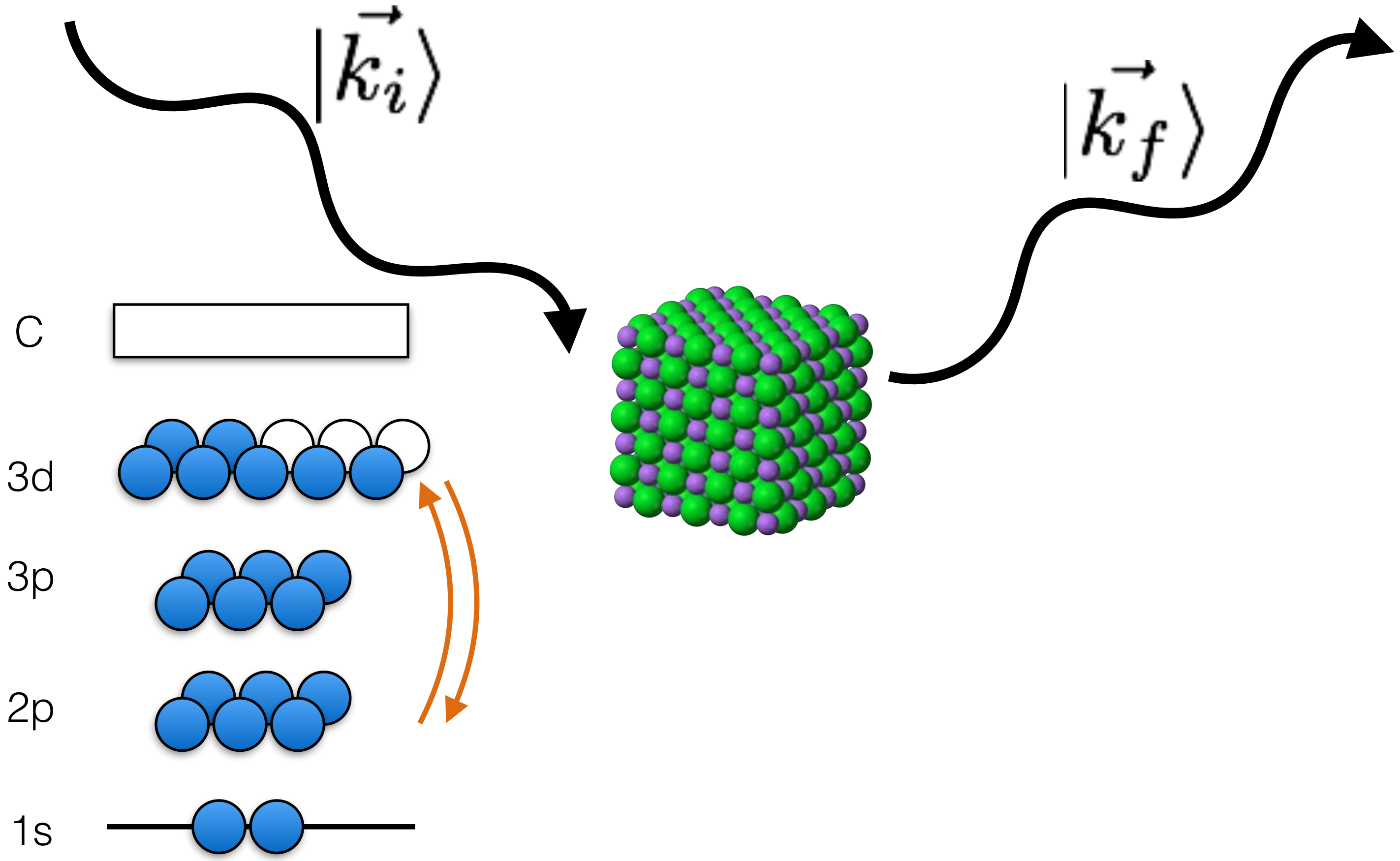
$$\langle S \rangle \propto A - 2B$$

$$\langle L \rangle \propto A + B$$



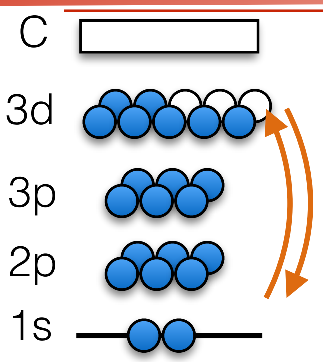
Summary: XAS/XES/XMCD

- Core electron spectroscopy can access many details of structure, chemistry, and spin/orbital configuration.
- X-rays are a uniquely appropriate probe at these energy scales.



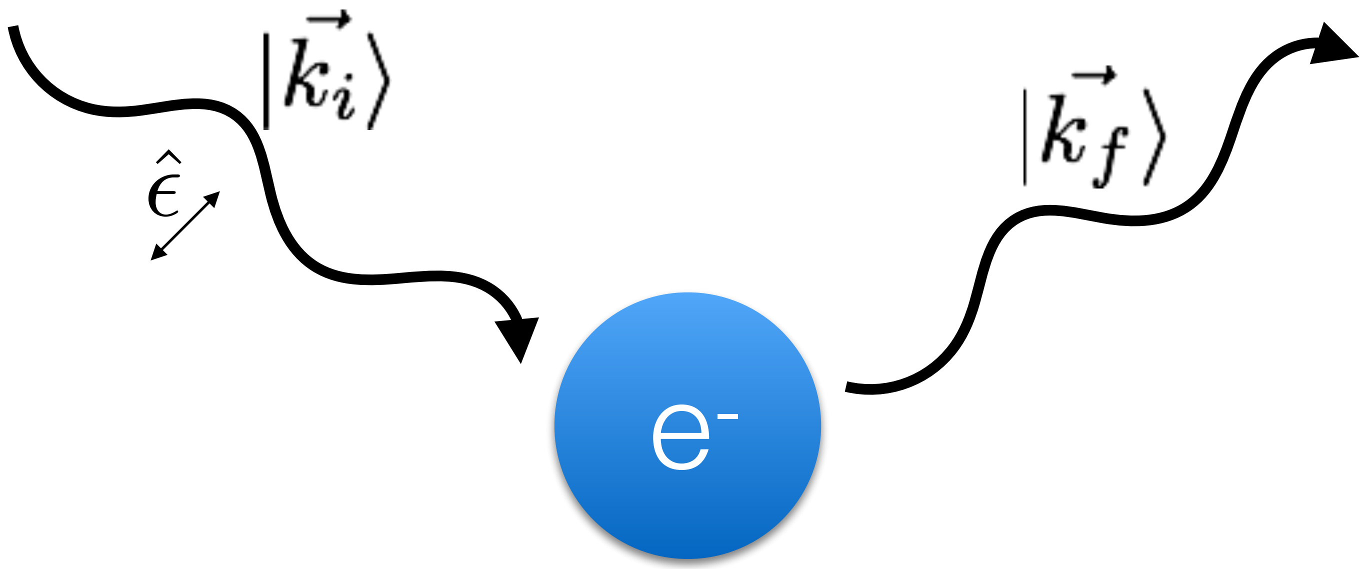
Resonant Scattering

Incident photon excites a core electron into an empty energy level. The *"same electron"* returns to (fills) the core hole, and emits a photon with close to the initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]



Resonant Scattering

Incident photon excites core electron into empty state. "*Same electron*" returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

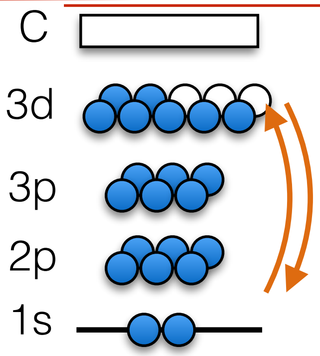


$$I = I_0 \cancel{\frac{e^4}{m^2c^4R^2}}$$

Go back to the atomic form factor, with more sophistication.
(No more taking the easy way out.)

Recall - back on slide 30 we said:
(1) There should be frequency dependence to the form factor
(2) Scattering near the edges will be complicated

We've ignored this so far…



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$$\hat{H}_1 = \sum_\alpha \frac{e^2}{2m}\left[\vec{A}(\vec{r}_\alpha, t)\right]^2,$$

$$\hat{H}_2 = -\sum_\alpha \frac{e^2}{2m^2c^2}\vec{s}_\alpha \cdot \left[\partial_t \vec{A}(\vec{r}_\alpha, t) \times \vec{A}(\vec{r}_\alpha, t)\right],$$

$$\hat{H}_3 = -\sum_\alpha \frac{e}{m}\left[\vec{A}(\vec{r}_\alpha, t) \cdot \vec{p}_\alpha\right],$$

$$\hat{H}_4 = -\sum_\alpha \frac{e}{m}\vec{s}_\alpha \cdot \left[\vec{\nabla} \times \vec{A}(\vec{r}_\alpha, t)\right].$$

$$I(\omega) \propto \left|\sum_j e^{i\vec{Q}\cdot\vec{R}_j}\left(f_j^{(0)} + f_j^{(0m)} + f_j'(\omega) + i f_j''(\omega)\right)\right|^2 \left|S(\vec{Q})\right|^2$$
$$\equiv \left|F(\vec{Q})\right|^2 \left|S(\vec{Q})\right|^2,$$

Following di Matteo - Dirac Hamiltonian, in the proper limits for elastic scattering, x-ray + bound electron. Recover Thomson term, a weak spin-scattering term, and two resonant terms.

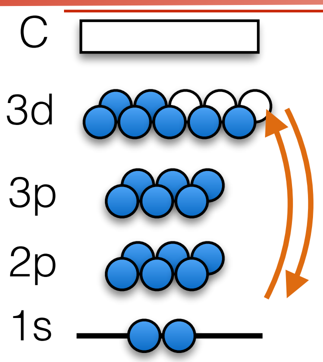
$$f_j^{(0)} = \langle \varphi_g | \hat{H}_{1j} | \varphi_g \rangle,$$

$$f_j^{(0m)} = \langle \varphi_g | \hat{H}_{2j} | \varphi_g \rangle,$$

$$f_j'(\omega) + i f_j''(\omega) = \sum_s [\langle n_{\mathrm{ph}}, \varphi_g | \hat{H}_{3j} + \hat{H}_{4j} | \varphi_s, (n \pm 1)_{\mathrm{ph}} \rangle$$
$$\times \langle (n \pm 1)_{\mathrm{ph}}, \varphi_s | \hat{H}_{3j} + \hat{H}_{4j} | \varphi_g, n_{\mathrm{ph}} \rangle][\tilde{E}_s(\omega) - \tilde{E}_g(\omega)]^{-1},$$

(Terms quadratic in vector potential are non-resonant)

Results for diffraction still hold, but now the atomic form factor is complex. Terms can interfere.



Resonant Scattering

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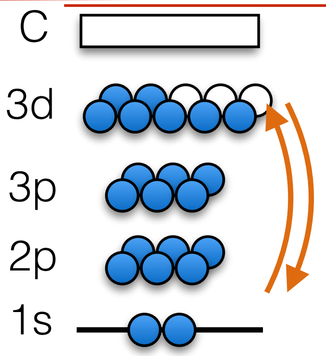
$$f = f_0 + f_{spin} + \boxed{f^{'}(\omega) + i f^{''}(\omega)}$$

As in XAS, the electric dipole ("E1") and electric quadrupole ("E2") transitions are the largest matrix elements, and give the dominant contribution to resonant scattering. Note that polarization is important now. Following Hill and McMorrow [Acta Cryst. (1996) A52 236]

$$f_{\mathrm{EL}}^{e}(\omega) = (4\pi/|k|) f_D \sum_{M=-L}^{L} [\hat{\varepsilon}'^{*} \cdot \mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}}') \mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}) \cdot \hat{\varepsilon}] F_{LM}^{(e)}(\omega)$$

$\mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}})$ are vector spherical harmonics

$$F_{LM}^{(e)}(\omega) = \sum_{\alpha,\eta} [P_\alpha P_\alpha(\eta) \Gamma_x(\alpha M \eta; \mathrm{EL})/\Gamma(\eta)]/[x(\alpha,\eta) - i]$$



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$$f = f_0 + f_{spin} + \boxed{f'(\omega) + if''(\omega)}$$

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Strength of resonance

$$f_{\mathrm{EL}}^{e}(\omega) = (4\pi/|k|) f_D \sum_{M=-L}^{L} [\hat{\varepsilon}'^{*} \cdot \mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}}')\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}) \cdot \hat{\varepsilon}] F_{LM}^{(e)}(\omega)$$

Interaction with moment direction

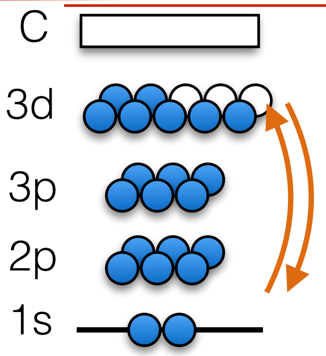
$\mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}})$ are vector spherical harmonics

$$F_{LM}^{(e)}(\omega) = \sum_{\alpha,\eta} [P_\alpha P_\alpha(\eta) \Gamma_x(\alpha M \eta; \mathrm{EL})/\Gamma(\eta)]/[x(\alpha, \eta) - i]$$

Line width ratio

Distance from resonance

Probabilities from overlap integrals



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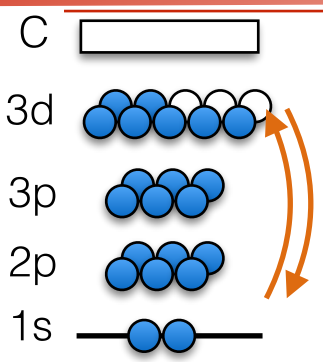
Still following Hill and McMorrow [Acta Cryst. (1996) A52 236] - an example. L3 edge magnetic scattering from holmium ion. E1 term: (plug in VSH for L=1, M= -1,0,1)

$$f_{nE1}^{\mathrm{XRES}} = [(\hat{\boldsymbol{\varepsilon}}' \cdot \hat{\boldsymbol{\varepsilon}})F^{(0)} - i(\hat{\boldsymbol{\varepsilon}}' \times \hat{\boldsymbol{\varepsilon}}) \cdot \hat{\mathbf{z}}_n F^{(1)} + (\hat{\boldsymbol{\varepsilon}}' \cdot \hat{\mathbf{z}}_n)(\hat{\boldsymbol{\varepsilon}} \cdot \hat{\mathbf{z}}_n)F^{(2)}]$$

$$F^{(0)} = (3/4k)[F_{11} + F_{1-1}]$$
$$F^{(1)} = (3/4k)[F_{11} - F_{1-1}]$$
$$F^{(2)} = (3/4k)[2F_{10} - F_{11} - F_{1-1}]$$



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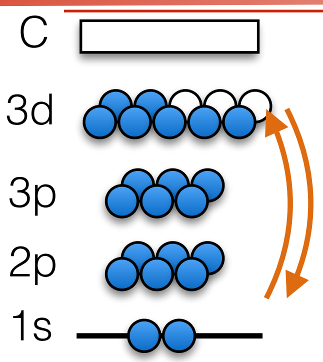
First term non-magnetic.

Second term rotates polarization, measures moment parallel to $\vec{k}_f$.

Third term maximized for non-rotating polarization, measures moment along $\hat{\epsilon}$.

Note - for vertical scattering planes, horizontal polarization is typically called σ , while polarization in the scattering plane is typically called π .



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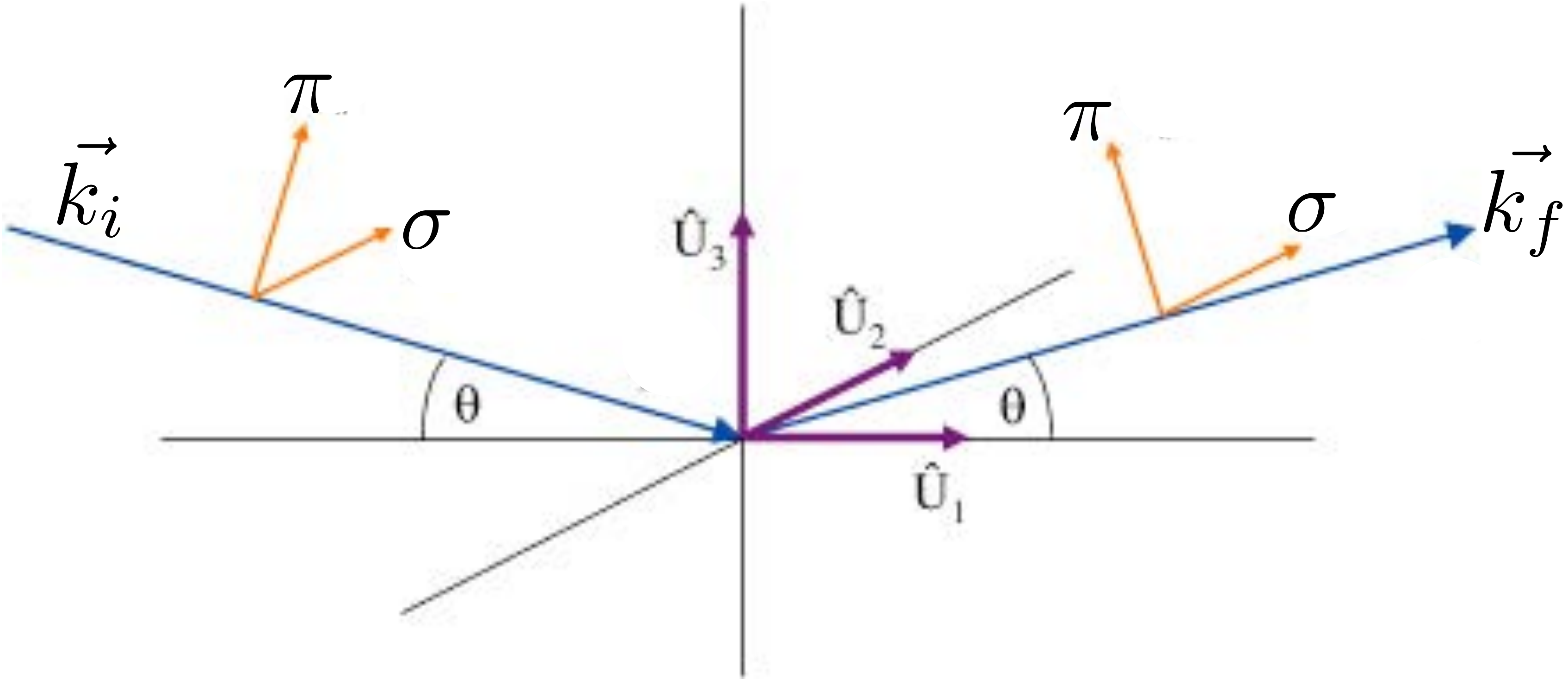
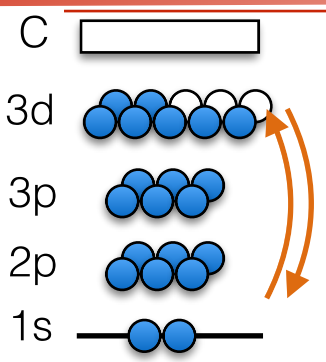


Often we prepare a beam with pure incident linear σ polarization, and analyze the π component of the scattered beam, to probe the component of magnetic moment along $\vec{k}_f$.

This makes sense - it is the leading term with the simplest explanation. However, it is worth asking why the other transitions (E2, etc) and other terms are less frequently exploited.



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Why the other transitions (E2, etc) and other terms are less frequently exploited:

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On the other hand, the second term allows $\sigma \leftrightarrow \pi$ scattering as well as $\pi \to \pi$ scattering, but $\sigma \to \sigma$ scattering is forbidden and the matrix representation is

$$(\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{z}}_n = \begin{pmatrix} 0 & \hat{\mathbf{k}} \\ -\hat{\mathbf{k}}' & \hat{\mathbf{k}}' \times \hat{\mathbf{k}} \end{pmatrix} \cdot \hat{\mathbf{z}}_n, \qquad (12)$$

where the off-diagonal elements are $\hat{\varepsilon}'_\parallel \times \hat{\varepsilon}_\perp = -\hat{\mathbf{k}}'$ and $\hat{\varepsilon}'_\perp \times \hat{\varepsilon}_\parallel = \hat{\mathbf{k}}$. The matrix representation of the third term is obtained in a similar fashion. The identities

$$\begin{aligned} \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}' &= \cos 2\theta \\ 1 - (\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}')^2 &= \sin^2 2\theta \\ \hat{\mathbf{k}}' \times \hat{\mathbf{k}} &= -\hat{\mathbf{U}}_2 \sin 2\theta \\ \hat{\mathbf{k}} + \hat{\mathbf{k}}' &= 2\hat{\mathbf{U}}_1 \cos\theta \\ \hat{\mathbf{k}} - \hat{\mathbf{k}}' &= 2\hat{\mathbf{U}}_3 \sin\theta \\ \hat{\mathbf{z}}_n &= \sum_i (\hat{\mathbf{U}}_i \cdot \hat{\mathbf{z}}_n)\hat{\mathbf{U}}_i \end{aligned} \qquad (13)$$

are used to obtain the final result:

$$f_{nE1}^{\mathrm{XRES}} = F^{(0)}\begin{pmatrix} 1 & 0 \\ 0 & \hat{\mathbf{k}}' \cdot \hat{\mathbf{k}} \end{pmatrix} - iF^{(1)}\begin{pmatrix} 0 & \hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n \\ -\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n & (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n \end{pmatrix} + \{F^{(2)}/[1 - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})^2]\} \times [\text{illegible}] \qquad (14)$$

A similar expression has also been obtained by Pengra, Thoft, Wulff, Feidenhans'l & Bohr (1994).

Next, we resolve each of the vectors $\hat{\mathbf{k}}$, $\hat{\mathbf{k}}'$ and $\hat{\mathbf{z}}_n$ into their components along $\hat{\mathbf{U}}_1$, $\hat{\mathbf{U}}_2$ and $\hat{\mathbf{U}}_3$, the coordinate system defined with respect to the diffraction plane (Fig. 1). This results in the following expression for the resonant dipole scattering amplitude:

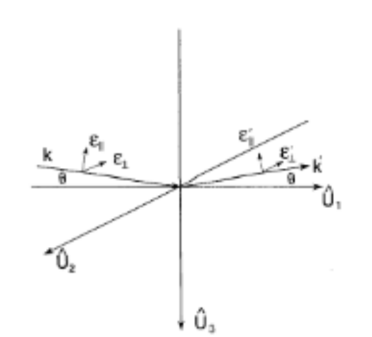

Fig. 1. The coordinate system used in calculating the polarization dependences. θ is the Bragg angle.

$$f_{nE1}^{\mathrm{XRES}} = F^{(0)}\begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} - iF^{(1)}\begin{pmatrix} 0 & z_1\cos\theta + z_3\sin\theta \\ z_3\sin\theta - z_1\cos\theta & -z_2\sin 2\theta \end{pmatrix} + F^{(2)}\begin{pmatrix} z_2^2 & -z_2(z_1\sin\theta - z_3\cos\theta) \\ +z_2(z_1\sin\theta + z_3\cos\theta) & -\cos^2\theta(z_1^2\tan^2\theta + z_3^2) \end{pmatrix}. \qquad (15)$$

where θ is the Bragg angle. From (15), it is possible to see which components of the magnetic moment contribute to the scattering for a given experimental geometry and, as we shall show in the next section, this is all that is required in many experiments. However, if a detailed comparison is to be made between (15) and a data set, then it is necessary to compute the magnitude of the coefficients F_{LM}. This is beyond the scope of this work, but the coefficients have been evaluated by Hamrick (1994) for several rare-earth elements.

2.2. *Electric quadrupole transitions (E2)*

We now carry out a similar procedure for the quadrupole contribution to the resonant cross section. An example of such a transition is the $2p_{3/2} \leftrightarrow 4f$ transition at the L_{III} edge of Ho. While the scattering from such processes is typically weaker than that due to electric dipole transitions, it can be significant. For example, in an incommensurate antiferromagnet, the quadrupole terms produce two extra resonant harmonics. These have been observed experimentally (see, for example, Gibbs *et al.*, 1988) and it is an interesting question as to what magnetic properties are being probed at these harmonics. It is hoped that the results of this section will allow such questions to be answered.

We begin, as before, with the expansion of the vector spherical harmonics (Hannon *et al.*, 1988; Hamrick, 1990). For the $L = 2$ case, 13 distinct terms are produced of various orders in the magnetic moment:

order zero

$$+(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\varepsilon}' \cdot \hat{\varepsilon})F_{E2}^{(0)};$$

order one

$$-i[(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{z}}_n + (\hat{\varepsilon}' \cdot \hat{\varepsilon})(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]F_{E2}^{(1)};$$

order two

$$\begin{aligned} &+[(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\varepsilon}' \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon} \cdot \hat{\mathbf{z}}_n) \\ &+ (\hat{\varepsilon}' \cdot \hat{\varepsilon})(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)](F_{E2}^{(2)} - F_{E2}^{(0)}) \\ &+ [(\hat{\varepsilon}' \cdot \hat{\mathbf{k}})(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon} \cdot \hat{\mathbf{z}}_n) + (\hat{\mathbf{k}}' \cdot \hat{\varepsilon})(\hat{\varepsilon}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)]F_{E2}^{(3)} \\ &- [(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n(\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{z}}_n]F_{E2}^{(4)}; \end{aligned}$$

order three

$$\begin{aligned} &-i[(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{z}}_n \\ &+ (\hat{\varepsilon}' \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n](F_{E2}^{(3)} - F_{E2}^{(1)}) \\ &- i[(\hat{\varepsilon}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{z}}_n \\ &+ (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon} \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]F_{E2}^{(3)}; \end{aligned}$$

order four

$$+(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon}' \cdot \hat{\mathbf{z}}_n)(\hat{\varepsilon} \cdot \hat{\mathbf{z}}_n)F_{E2}^{(4)};$$

where

$$\begin{aligned} F_{E2}^{(0)} &= (5/4k)[F_{22} + F_{2-2}] \\ F_{E2}^{(1)} &= (5/4k)[F_{22} - F_{2-2}] \\ F_{E2}^{(2)} &= (5/4k)[F_{21} + F_{2-1}] \\ F_{E2}^{(3)} &= (5/4k)[F_{21} - F_{2-1}] \\ F_{E2}^{(4)} &= (5/4k)[F_{22} + F_{2-2} - 4F_{21} - 4F_{2-1} + 6F_{20}]. \end{aligned} \qquad (16)$$

We now write these terms in the matrix representation of the previous section. The algebra is straightforward, if somewhat tedious. The following result for the polarization dependence of the resonant electric quadrupole terms is obtained:

$$f_{nE2}^{\mathrm{XRES}} = F_{E2}^{(0)}\begin{pmatrix} (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}) & 0 \\ 0 & (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})^2 \end{pmatrix} - iF_{E2}^{(1)}(\ldots) + \ldots \quad [\text{illegible}] \qquad (17)$$

where the matrix elements of the first second-order term are

$$\begin{aligned} M_{11}^2 &= [(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})[(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^2 \\ &\quad + [1 - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})^2](\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)](\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})^{-1} \\ M_{12}^2 &= (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n[(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n) - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)] \\ M_{21}^2 &= (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n[(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}')(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n) - (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)] \\ M_{22}^2 &= (\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})[(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)^2 + (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)^2 \\ &\quad - 2(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)] \end{aligned} \qquad (18)$$

and the matrix elements of the two third-order terms are

$$\begin{aligned} {}^1M_{11}^3 &= [(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^3 \\ {}^1M_{12}^3 &= (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)^2[1 - (\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}')^2] \\ &\quad + [(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^2[\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n - (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})] \\ {}^1M_{21}^3 &= -(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)^2(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)[1 - (\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}')^2] \\ &\quad + [(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^2[-\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n + (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})] \\ {}^1M_{22}^3 &= (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n\{[(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)^2 + (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)^2] \\ &\quad - 2(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)\}(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}) \end{aligned} \qquad (19)$$

and

$$\begin{aligned} {}^2M_{11}^3 &= (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n[2(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}')(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n) \\ &\quad - (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)^2 - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)^2] \\ {}^2M_{12}^3 &= -[(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^2(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}) \\ &\quad - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)[(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n) - (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})]^2 \\ {}^2M_{21}^3 &= [(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n]^2(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}) \\ &\quad + (\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)[(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n) - (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})]^2 \\ {}^2M_{22}^3 &= (\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{z}}_n[(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)^2 + (\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)^2 \\ &\quad - 2(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}_n)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{z}}_n)](\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}). \end{aligned} \qquad (20)$$

We are now in a position to write an expression for the dependence of the quadrupole contribution on the individual components of the spin. In the same coordinate system as before, we obtain

$$f_{nE2}^{\mathrm{XRES}} = F_{E2}^{(0)}\begin{pmatrix} c_2 & 0 \\ 0 & c_2^2 \end{pmatrix} + \ldots \quad [\text{illegible}] \qquad (21)$$

where we have used the shorthand notation $c = \cos\theta$, $c_2 = \cos 2\theta$, $c^2 = \cos^2\theta$ *etc.* Despite the apparent complexity of (21), it can be of use in interpreting resonant scattering data. For example, in recent work on Nd_2CuO_4, a large resonant enhancement was observed at the Nd L_{II} edge (Hill, Vigliante, Gibbs, Peng & Greene, 1995). Polarization analysis of the scattering revealed it to be entirely $\sigma \to \pi$ with little or no $\sigma \to \sigma$ component. For the particular geometry of the experiment, z_1, z_2 and $z_3 \neq 0$. Inspection of (21) shows that in such a situation the observed scattering cannot be due to qudrupolar excitations, since $\sigma \to \sigma$ is an allowed channel in the first-order terms. Therefore, the scattering is dipole and this in turn implies a polarization of the Nd $5d$ bands.

3. Examples

The expressions derived above are generally applicable. In order to illustrate their use, it is helpful to study some particular examples. We choose three magnetic structures common amongst the elemental rare earths.

3.1. *Basal-plane spiral antiferromagnet*

We first take the case of a basal-plane spiral, such as occurs in Ho, Tb and Dy. In this structure, the moments are confined to the *ab* plane in ferromagnetic sheets. The direction of the magnetization rotates from basal plane to basal plane, creating a spiral structure propagating along the *c* axis. The modulation vector then lies along $(00L)$. The magnetic moment takes the form

$$\hat{\mathbf{z}}_n = \cos(\boldsymbol{\tau} \cdot \mathbf{r}_n)\hat{\mathbf{U}}_1 + \sin(\boldsymbol{\tau} \cdot \mathbf{r}_n)\hat{\mathbf{U}}_2. \qquad (22)$$

Now, the full X-ray scattering cross section may be written as

$$\mathrm{d}\sigma/\mathrm{d}\Omega = \sum_{\lambda\lambda'} P_\lambda \left| \langle\lambda'|\langle M_c\rangle|\lambda\rangle - i(\hbar\omega/mc^2)\langle\lambda'|\langle M_m\rangle|\lambda\rangle + \langle\lambda'|\langle M_{E1}^{\mathrm{XRES}}\rangle|\lambda\rangle + \langle\lambda'|\langle M_{E2}^{\mathrm{XRES}}\rangle|\lambda\rangle + \ldots \right|^2, \qquad (23)$$

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where λ, λ' are incident and scattered polarization states and P_λ is the probability for incident polarization λ. $\langle M_c\rangle$ *etc.* are the expectation values of the respective operators in the initial and final state $|a\rangle$ of the solid, *i.e.* $\langle M_{E1}^{\mathrm{XRES}}\rangle = \langle a|\sum_n \exp(i\mathbf{Q} \cdot \mathbf{r}_n)f_{nE1}^{\mathrm{XRES}}|a\rangle$. For the purposes of this example, we assume that the dipole contribution is dominant and ignore any interference effects. This will be valid at resonance and away from charge Bragg peaks, then

$$M_{E1}^{\mathrm{XRES}} = \sum_n \exp(i\mathbf{Q} \cdot \mathbf{r}_n) \times \begin{pmatrix} z_2^2F^{(2)} & -iz_1\cos\theta F^{(1)} - z_2z_1\sin\theta F^{(2)} \\ iz_1\cos\theta F^{(1)} + z_2z_1\sin\theta F^{(2)} & iz_2\sin 2\theta F^{(1)} - z_1^2\sin^2\theta F^{(2)} \end{pmatrix}. \qquad (24)$$

For simplicity, we take $P_\lambda = \delta_{\lambda\sigma}$, which is a reasonable approximation for a bending magnet source at a synchrotron, then only $\sigma \to \sigma$ and $\sigma \to \pi$ terms contribute and

$$\mathrm{d}\sigma/\mathrm{d}\Omega = \left|\langle a|\sum_n \exp(i\mathbf{Q} \cdot \mathbf{r}_n)z_2^2F^{(2)}|a\rangle\right|^2 + \left|\langle a|\sum_n \exp(i\mathbf{Q} \cdot \mathbf{r}_n)(iz_1\cos\theta F^{(1)} + z_2z_1\sin\theta F^{(2)})|a\rangle\right|^2. \qquad (25)$$

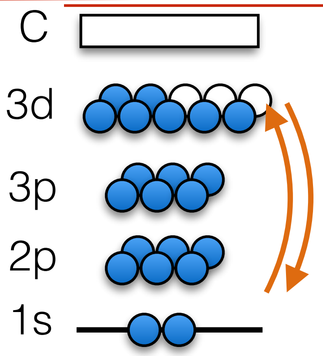
Substituting $z_1 = \cos(\boldsymbol{\tau} \cdot \mathbf{r}_n)$, $z_2 = \sin(\boldsymbol{\tau} \cdot \mathbf{r}_n)$ and writing the sine and cosine terms as the sums of complex exponentials, we obtain the cross section for a flat spiral with incident radiation perfectly polarized perpendicular to the scattering plane:

$$\begin{aligned} \mathrm{d}\sigma/\mathrm{d}\Omega|_{E1}^{\mathrm{XRES}} &= \tfrac{1}{4}F^{2(2)}\delta(\mathbf{Q} - \mathbf{G}) \\ &+ \tfrac{1}{4}\cos^2\theta F^{2(1)}(\mathbf{Q} - \mathbf{G} \pm \boldsymbol{\tau}) \\ &+ \tfrac{1}{16}(1 + \sin^2\theta)F^{2(2)}\delta(\mathbf{Q} - \mathbf{G} \pm 2\boldsymbol{\tau}). \end{aligned} \qquad (26)$$

The intensity of the observed scattering will only be proportional to the expression above if both polarization components of the scattered beam are collected with equal weight. This is the case if no analyzer crystal is employed. If one is used, then the polarization component that is in the scattering plane of the analyzer must be weighted by a factor $\cos^2 2\theta_A$, where θ_A is the Bragg angle of the analyzer crystal. From (26), we see that, in addition to producing scattering at the Bragg peak, the resonant dipole contribution produces two magnetic satellites at $\pm\boldsymbol{\tau}$ and $\pm 2\boldsymbol{\tau}$ on either side of the Bragg peak. We may calculate (Pengra *et al.*, 1994) the ratio of the factors $F^{(1)}/F^{(2)}$ in Ho using the published value for the ratio of the first two resonant harmonics (Gibbs *et al.*, 1991) and (26),

$$\frac{I(0, 0, 2 + \boldsymbol{\tau})}{I(0, 0, 2 + 2\boldsymbol{\tau})} = \left(\frac{2F^{(1)}}{F^{(2)}}\right)^2 \frac{\cos^2\theta}{(1 + \sin^2\theta)} \simeq 30 \qquad (27)$$

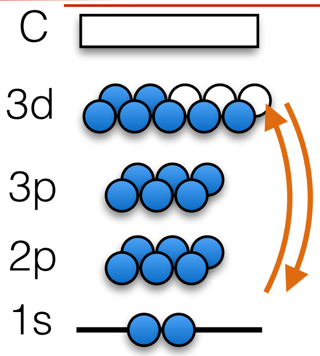
$$\Rightarrow F^{(1)}/F^{(2)} \simeq 2.7. \qquad (28)$$



Resonant Scattering

Incident photon excites core electron into empty state. "*Same electron*" returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

We spent all last lecture assuming Thomson scattering was a legit description, and did plenty of good science. So, maybe E1 in $\sigma - \pi$ isn't so bad. Some examples:



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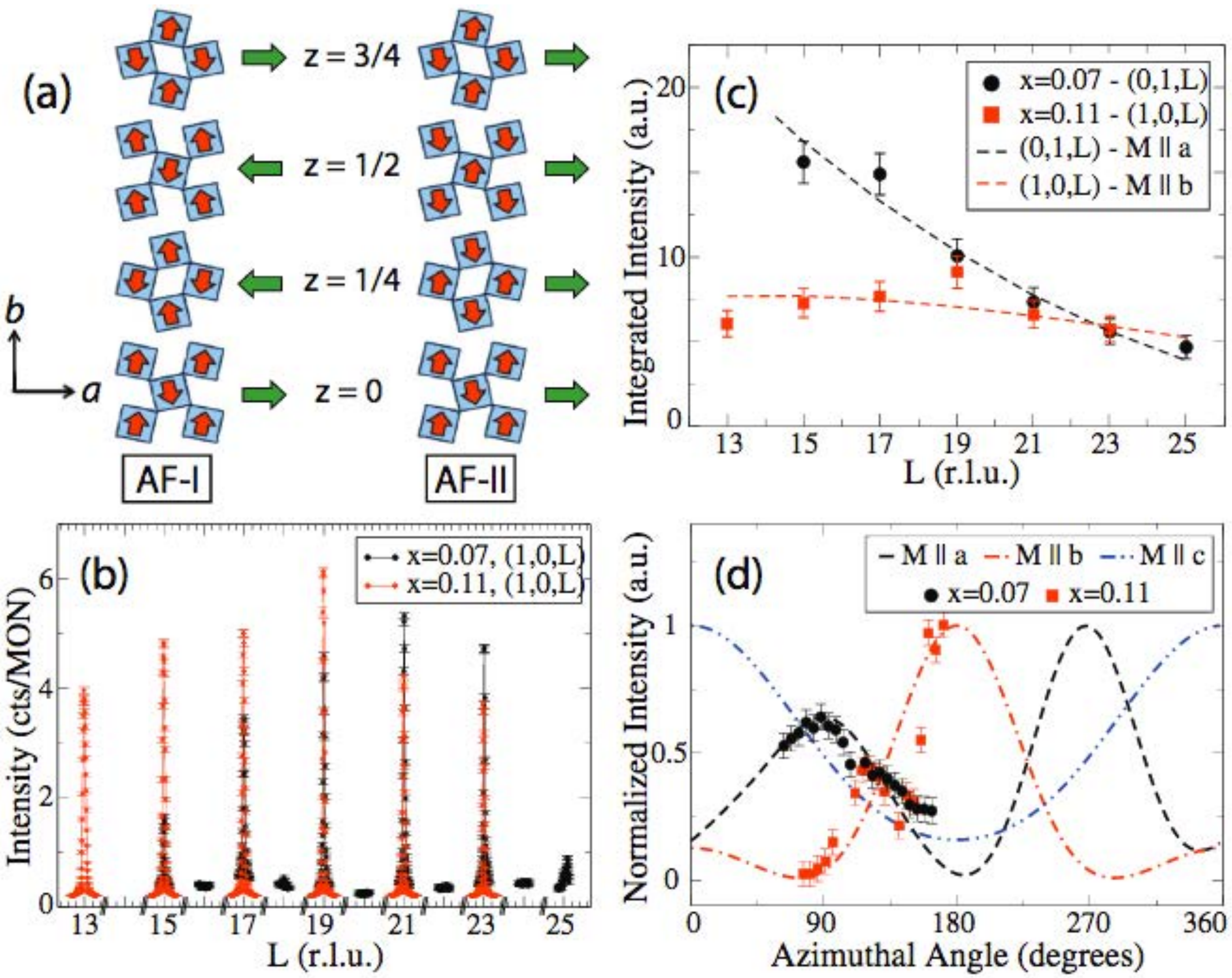
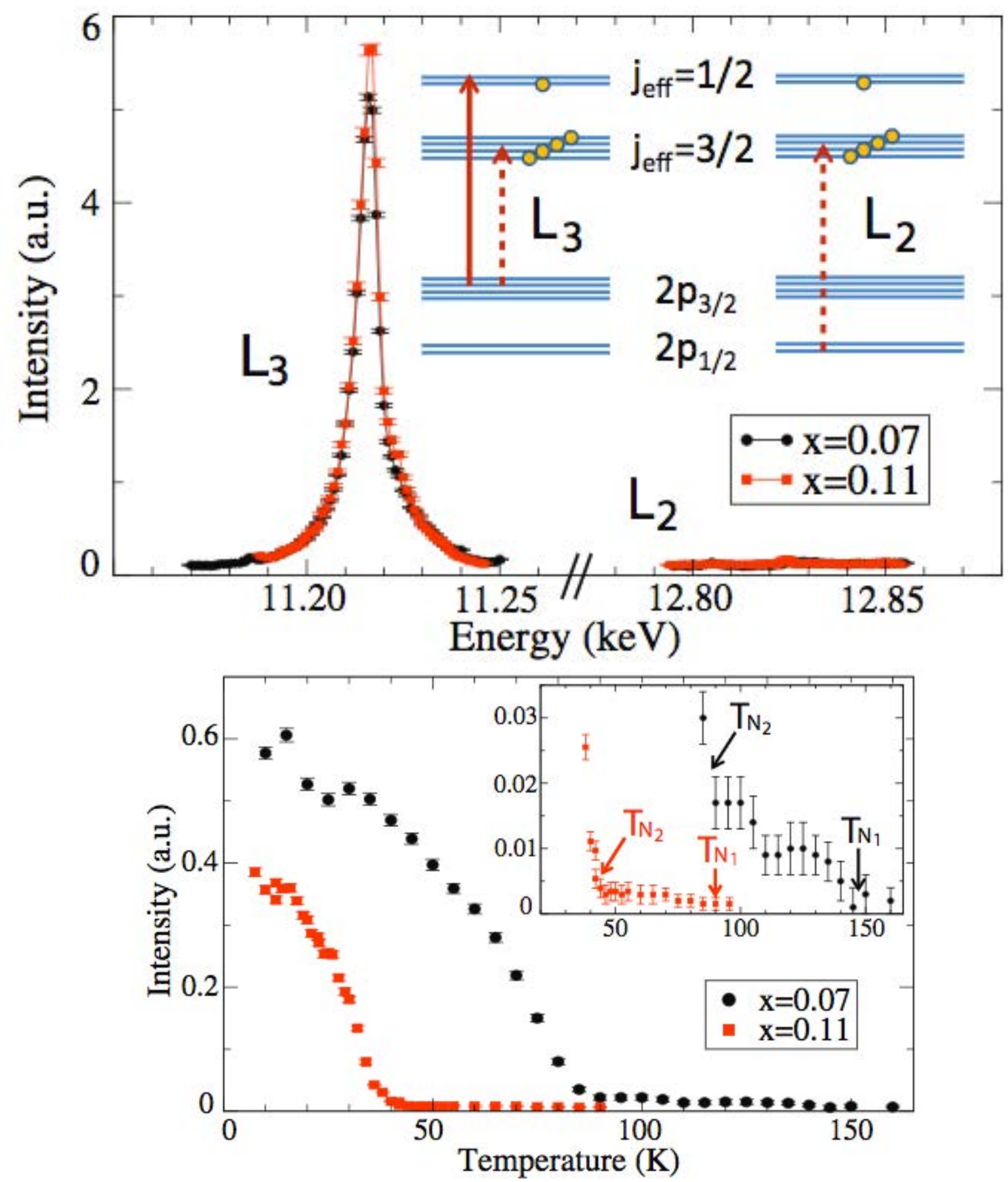
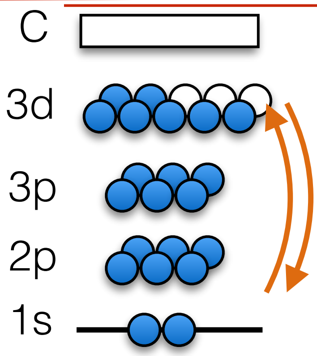




$Sr_2Ir_{1-x}Rh_xO_4$, L edges, $\sigma - \pi$

[Clancy, PRB 89 054409 (2014)]



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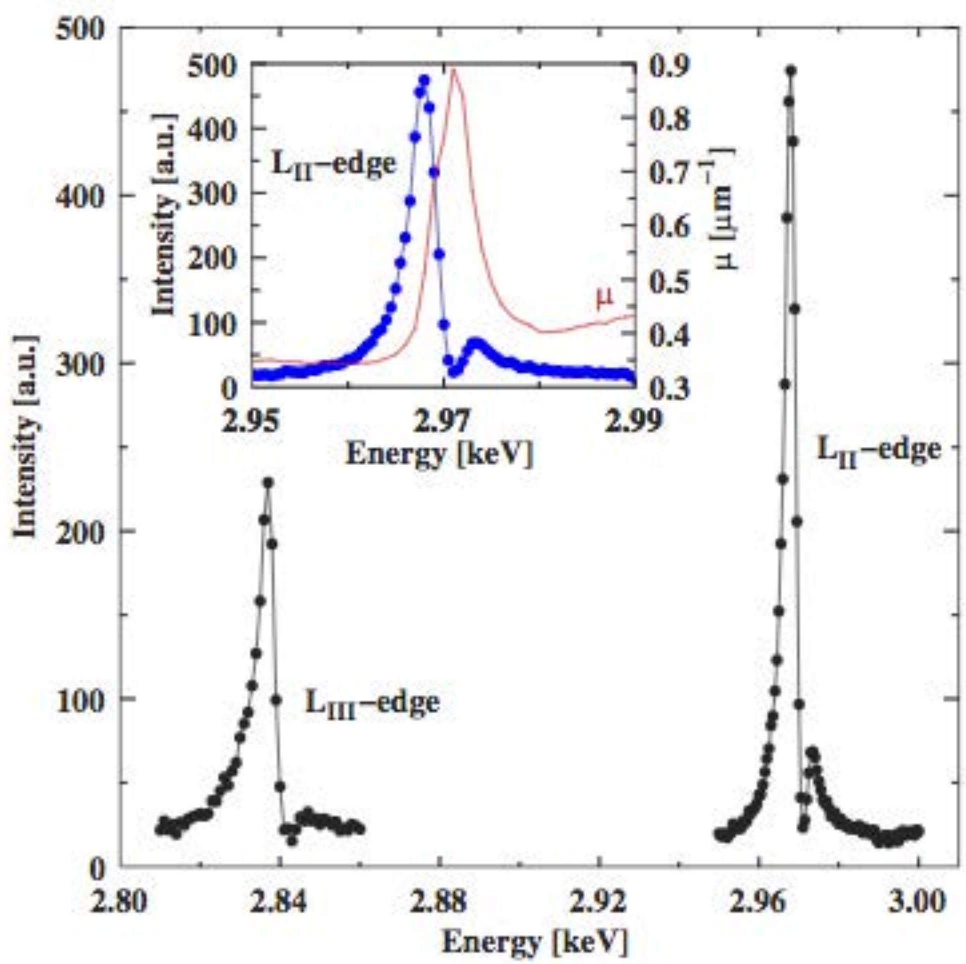
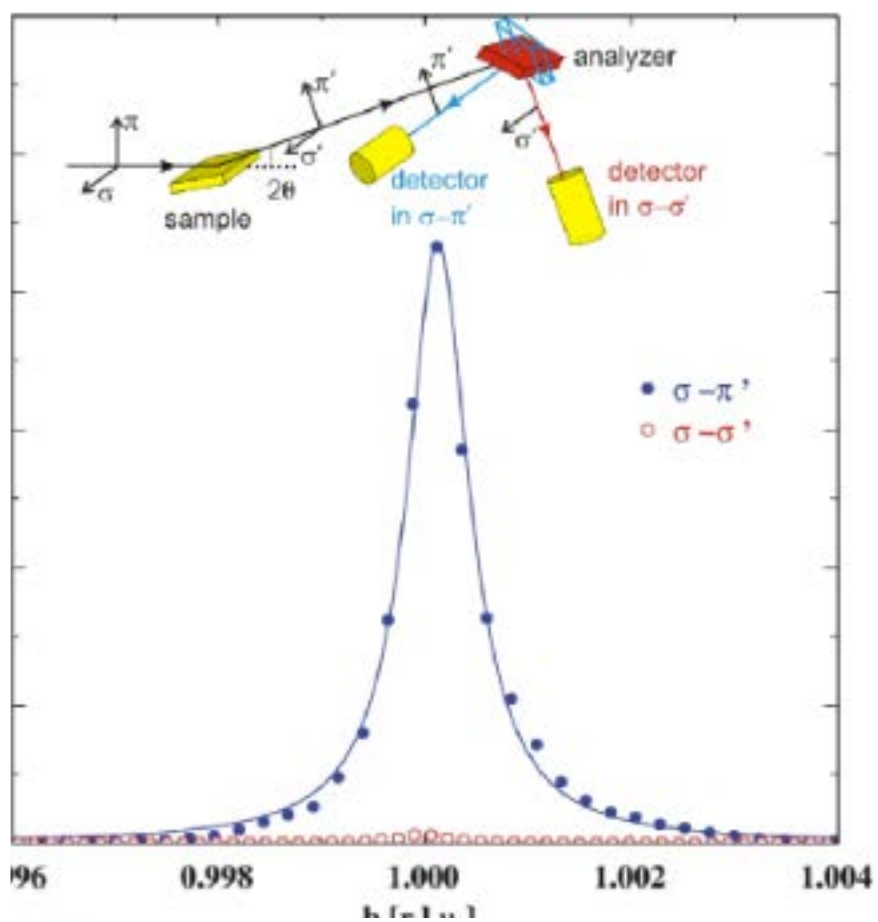
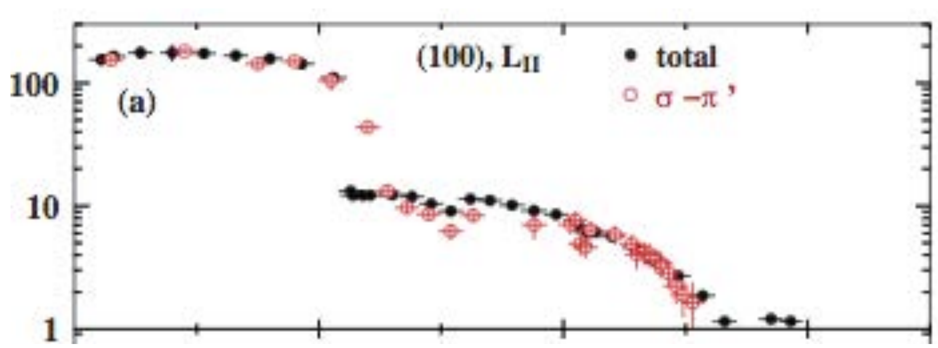
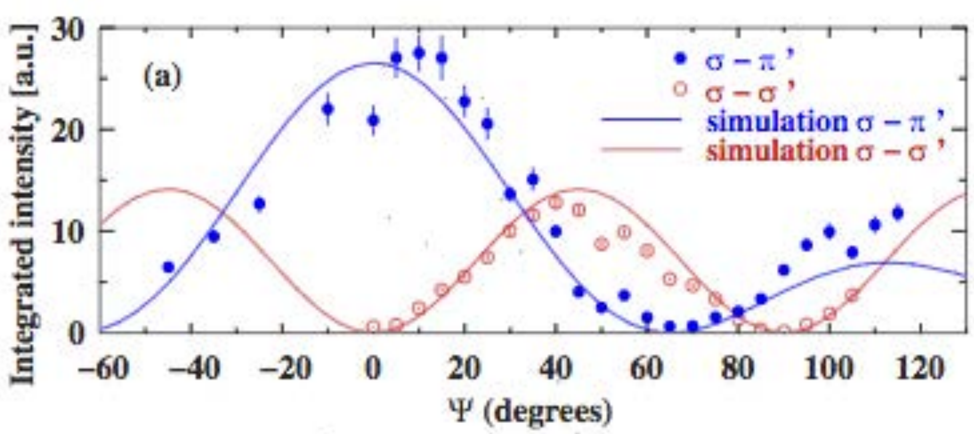




Ca$_2$RuO$_4$, L edges, $\sigma - \pi$

[Zegkinoglu, PRL 95 136401 (2005)]





QUESTION 4:

You are doing L_3 edge REXS measurements of an antiferromagnet with a simple tetragonal structure, looking at the (0,0,1/2) magnetic peak. You perform a scan of the azimuthal angle over a range from 0º to 360º. At the beginning and end of this scan the scattering plane is (H0L). What is the collinear axis of the moments?

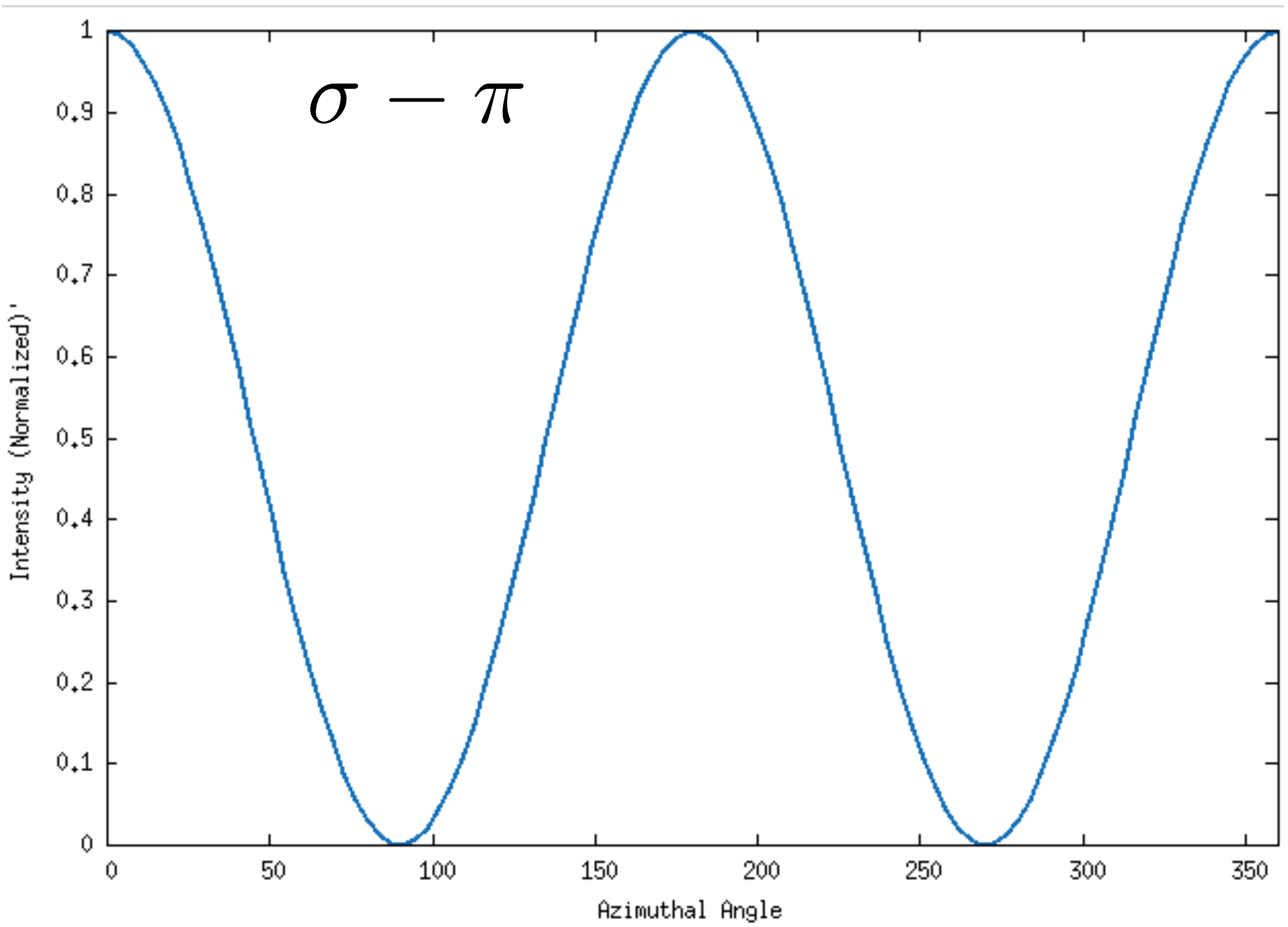
(A) a-axis

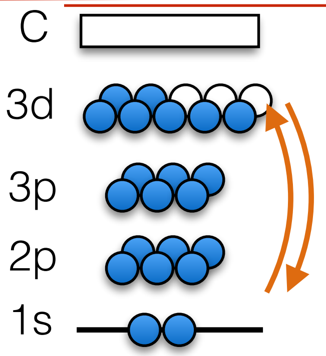
(B) b-axis

(C) c-axis

(D) mixed

(E) unknowable





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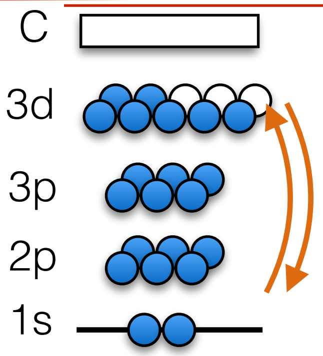
REXS to RIXS:

If we add the final-photon energy resolution from XES to our momentum-resolved resonant scattering, and narrow our incident bandwidth, we can gain sensitivity to elementary excitations in the sample (spin waves, etc). This is resonant inelastic x-ray scattering. Very precise and powerful technique, but very "photon hungry".



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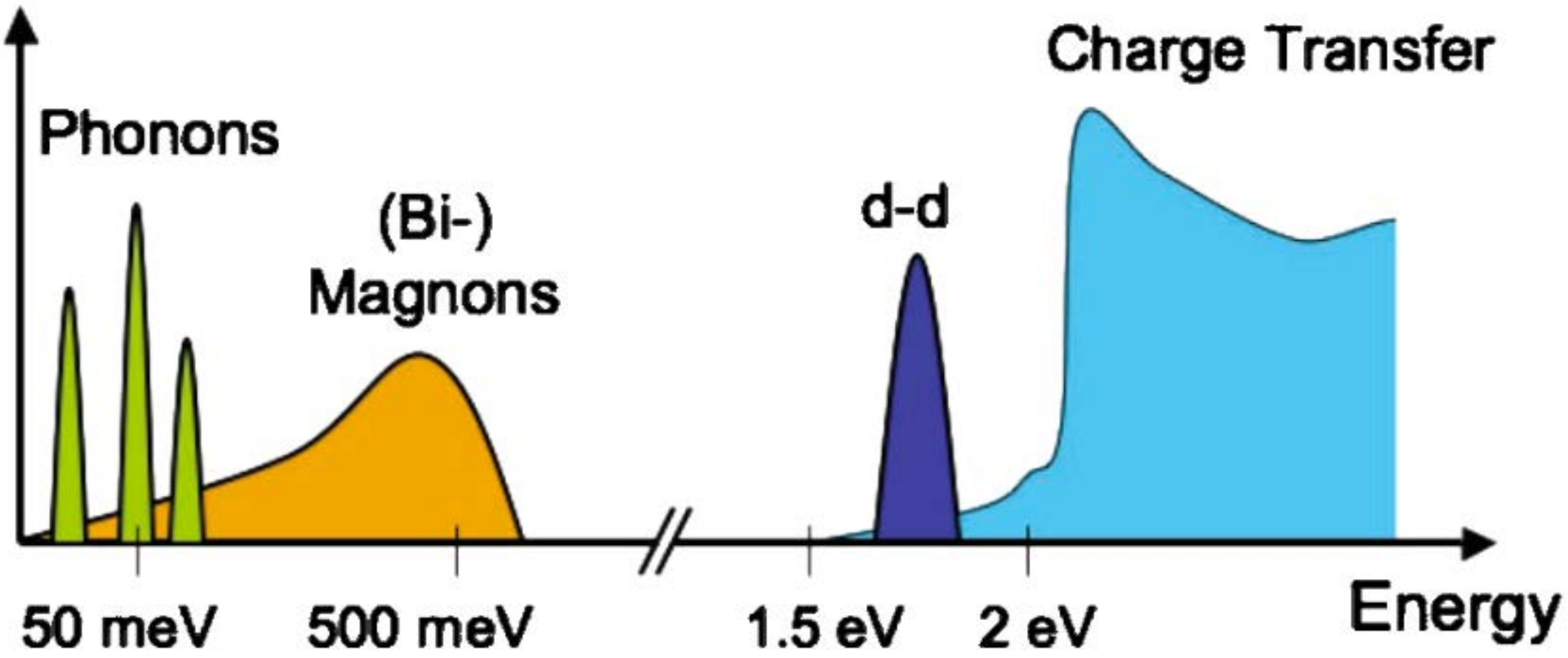
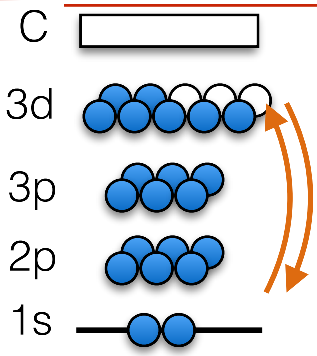


Elementary excitations to probe with x-rays.

These slides follow [Ament, Rev. Mod. Phys. 83 (2011)]



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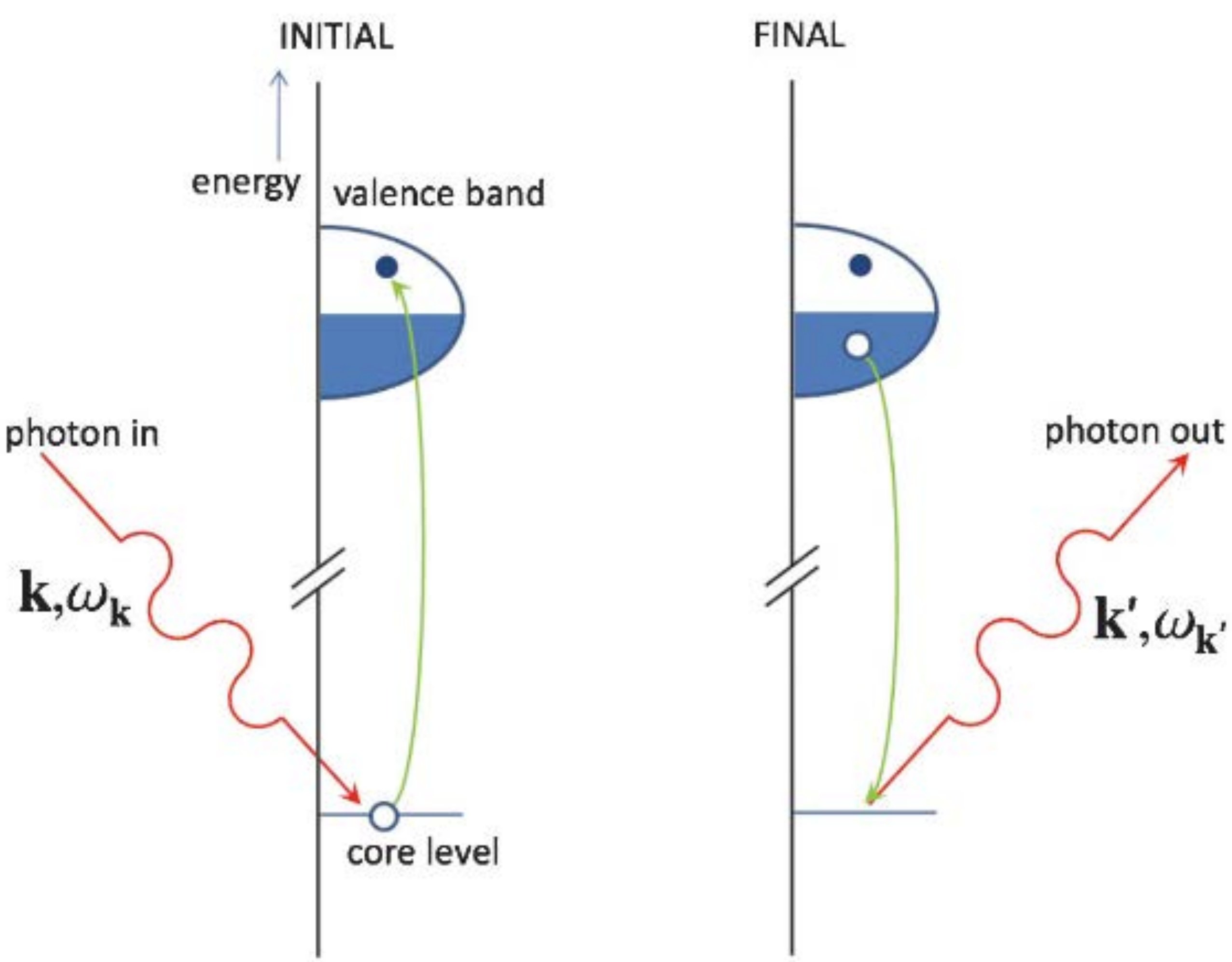
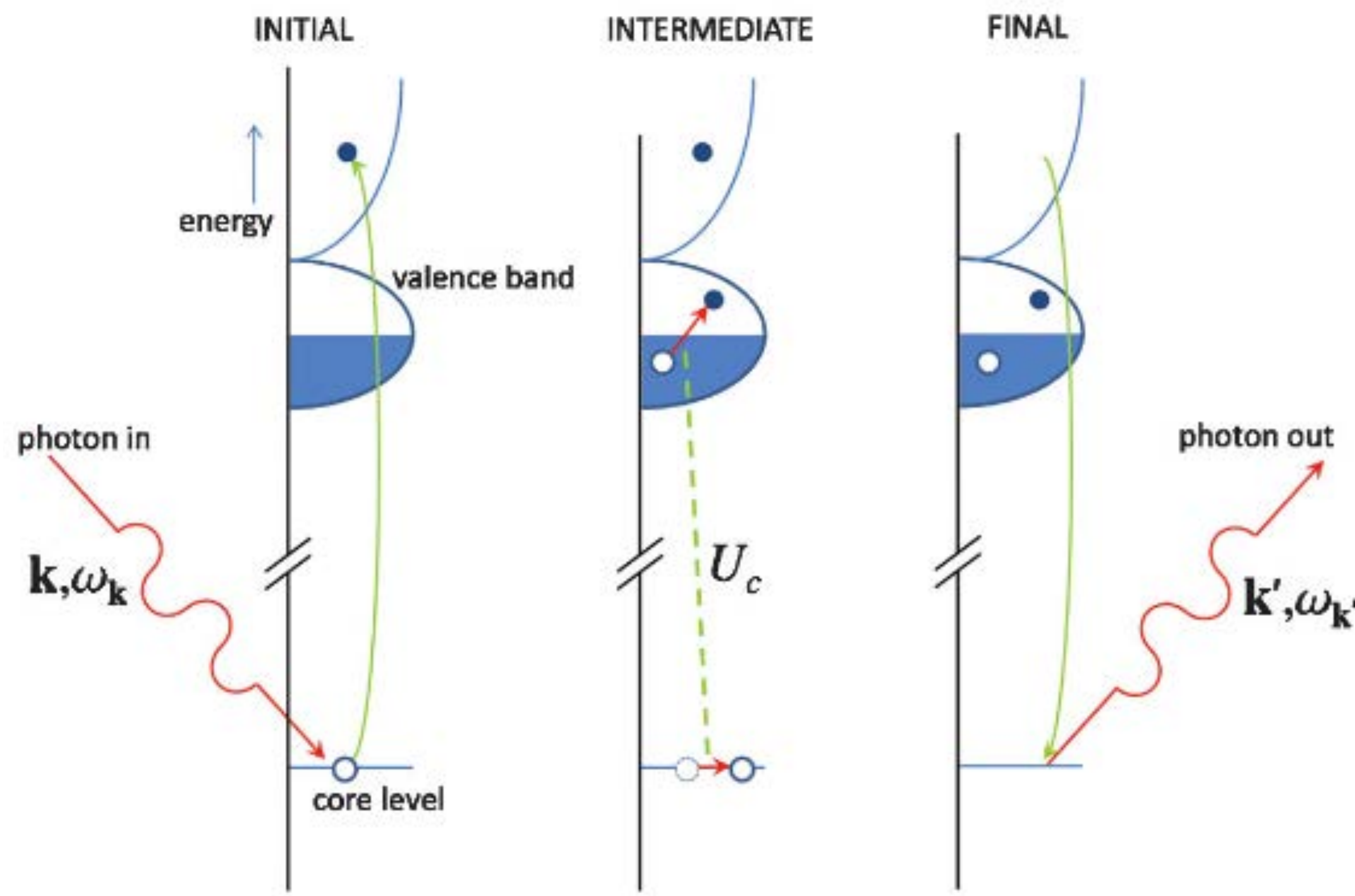
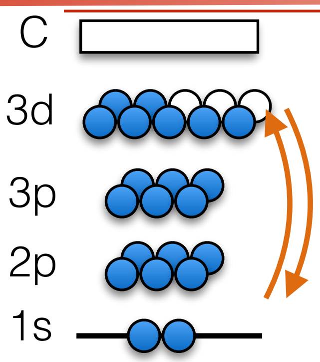


Direct RIXS - dominant process if allowed



Indirect RIXS - dominant when direct processes are forbidden.



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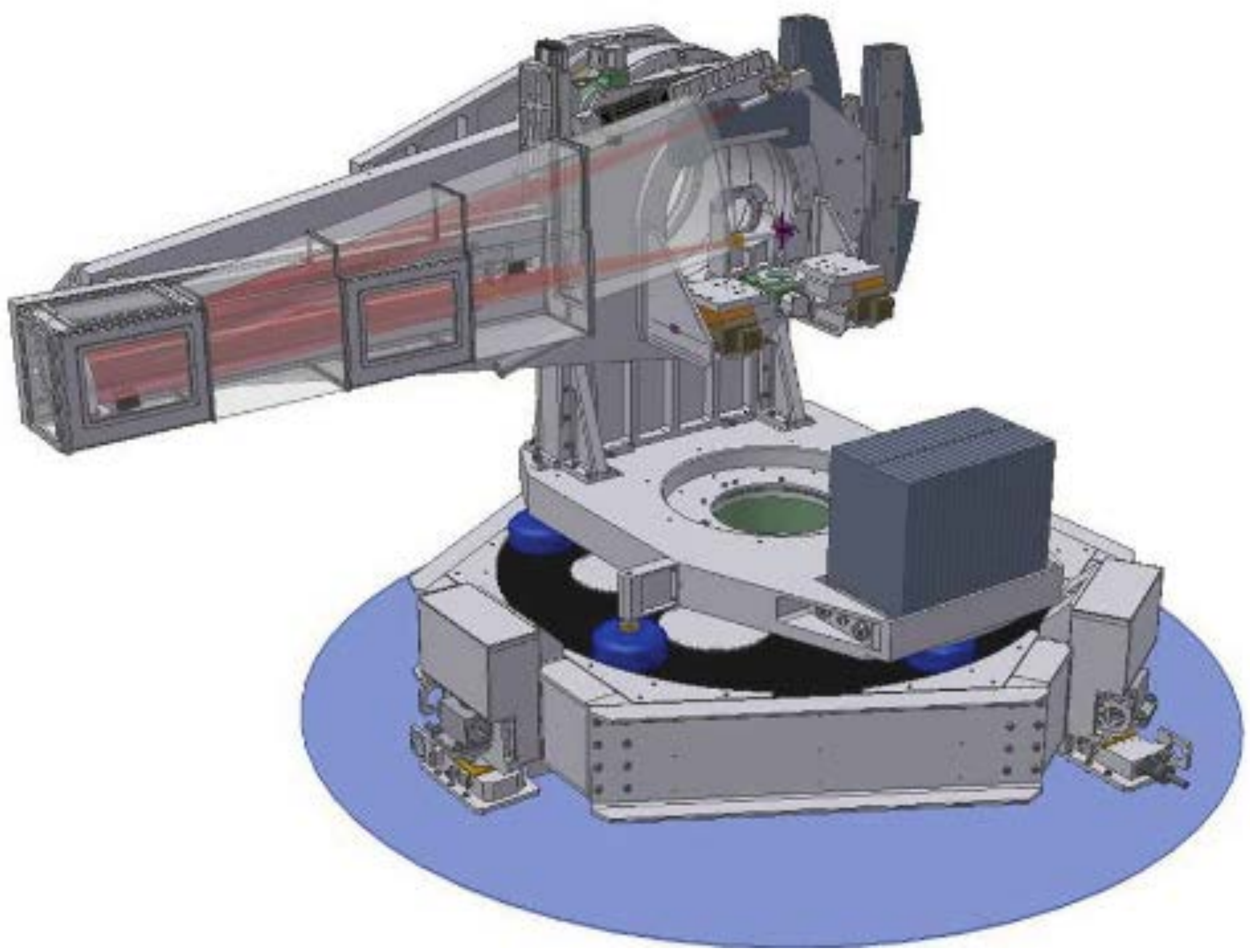
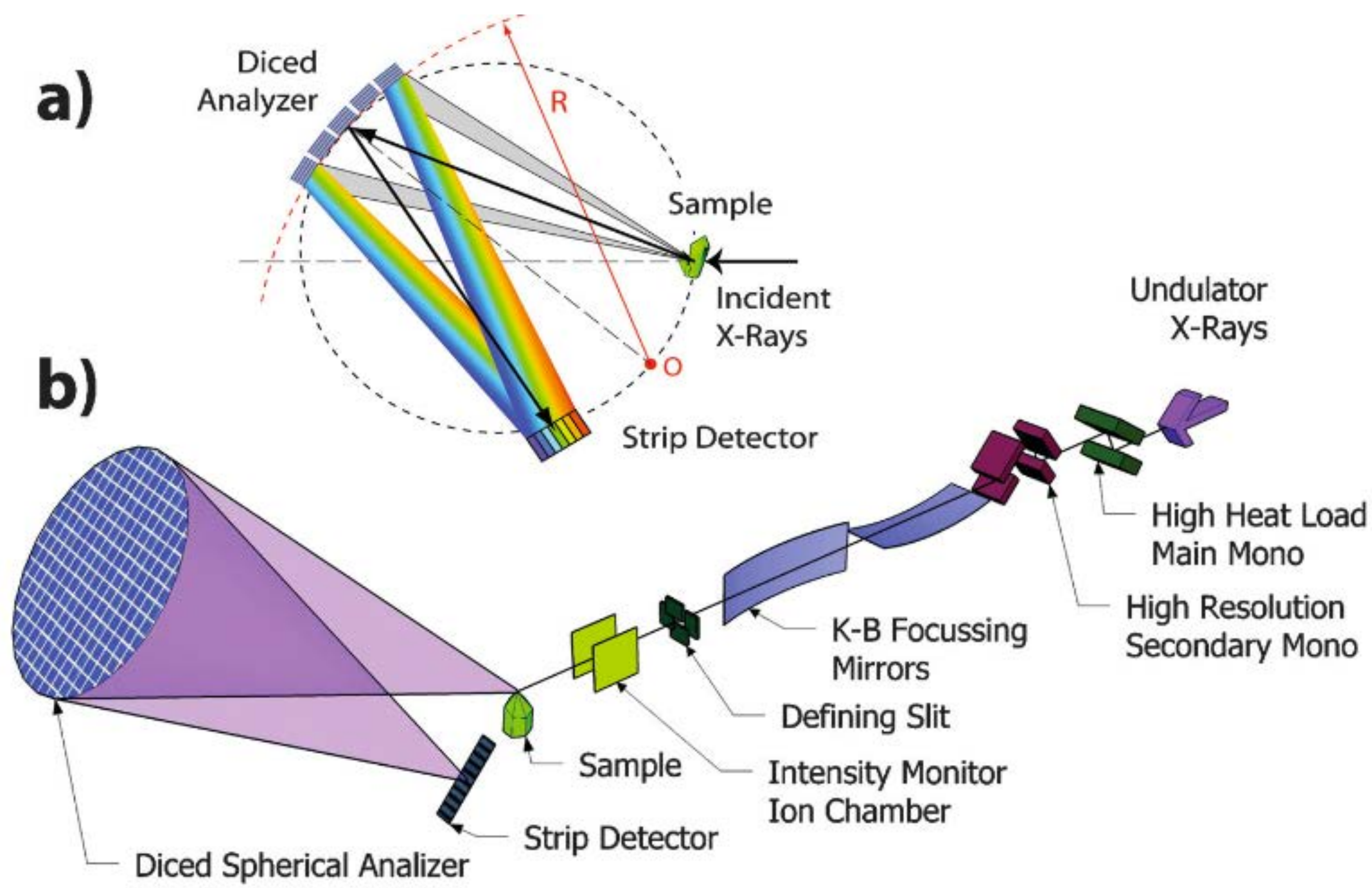
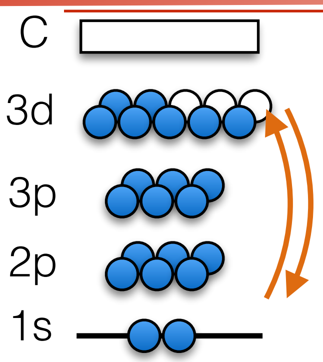




MERIX @ APS



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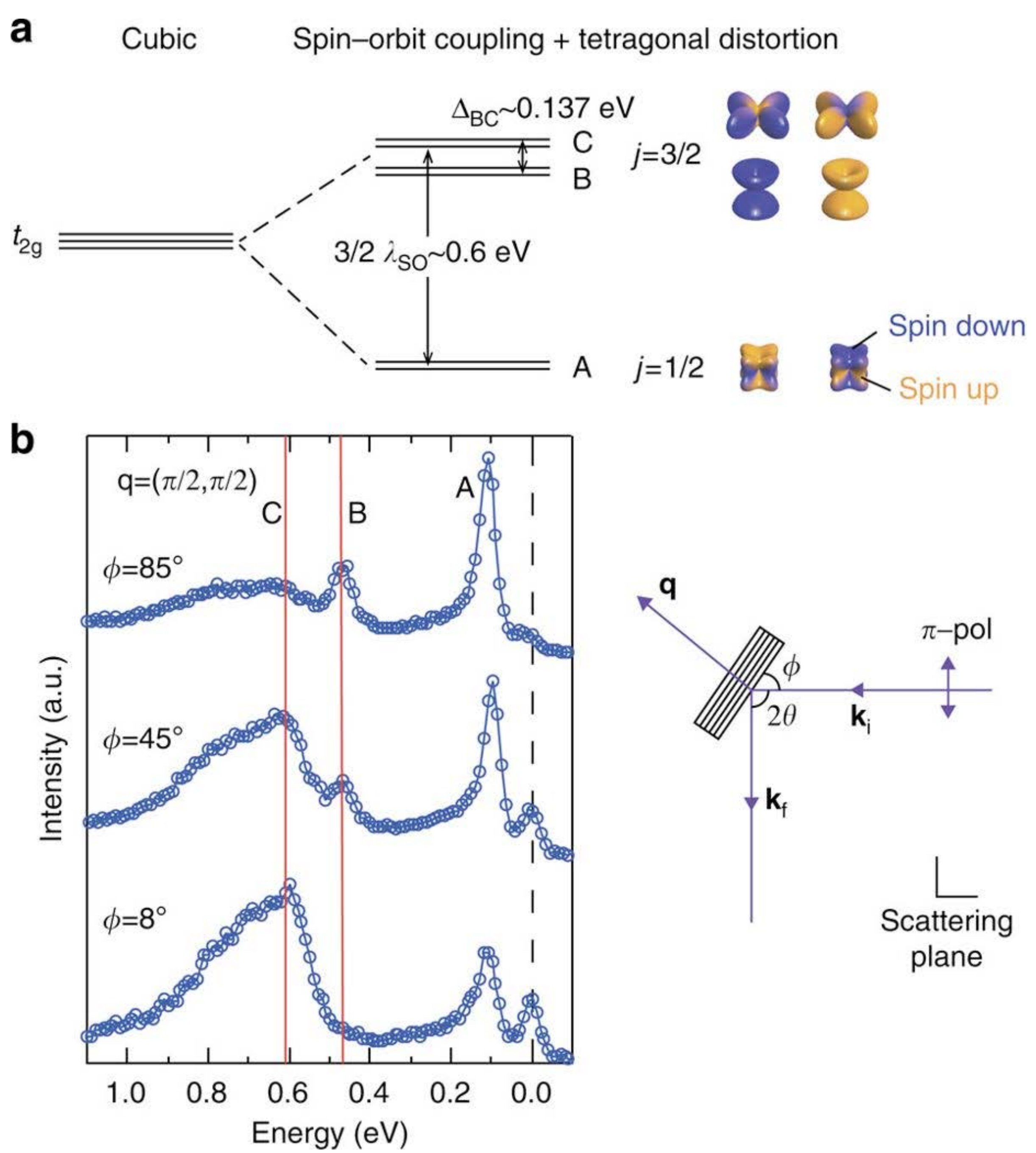
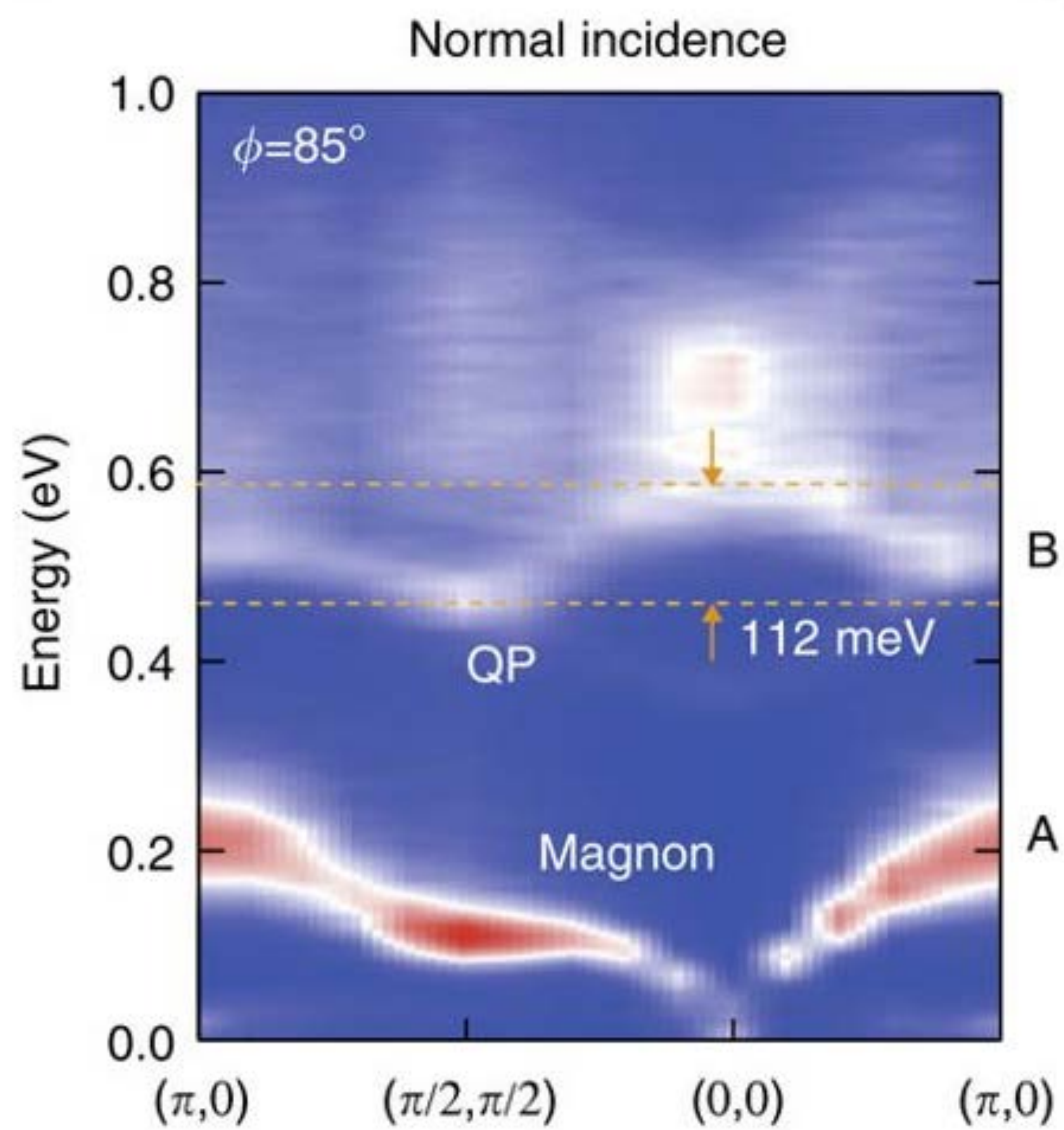
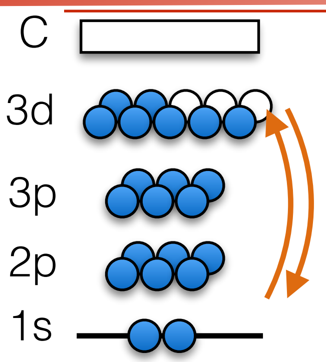
MERIX on Sr_2IrO_4

[Kim, Nat. Comm. 5: 4453 (2014)]







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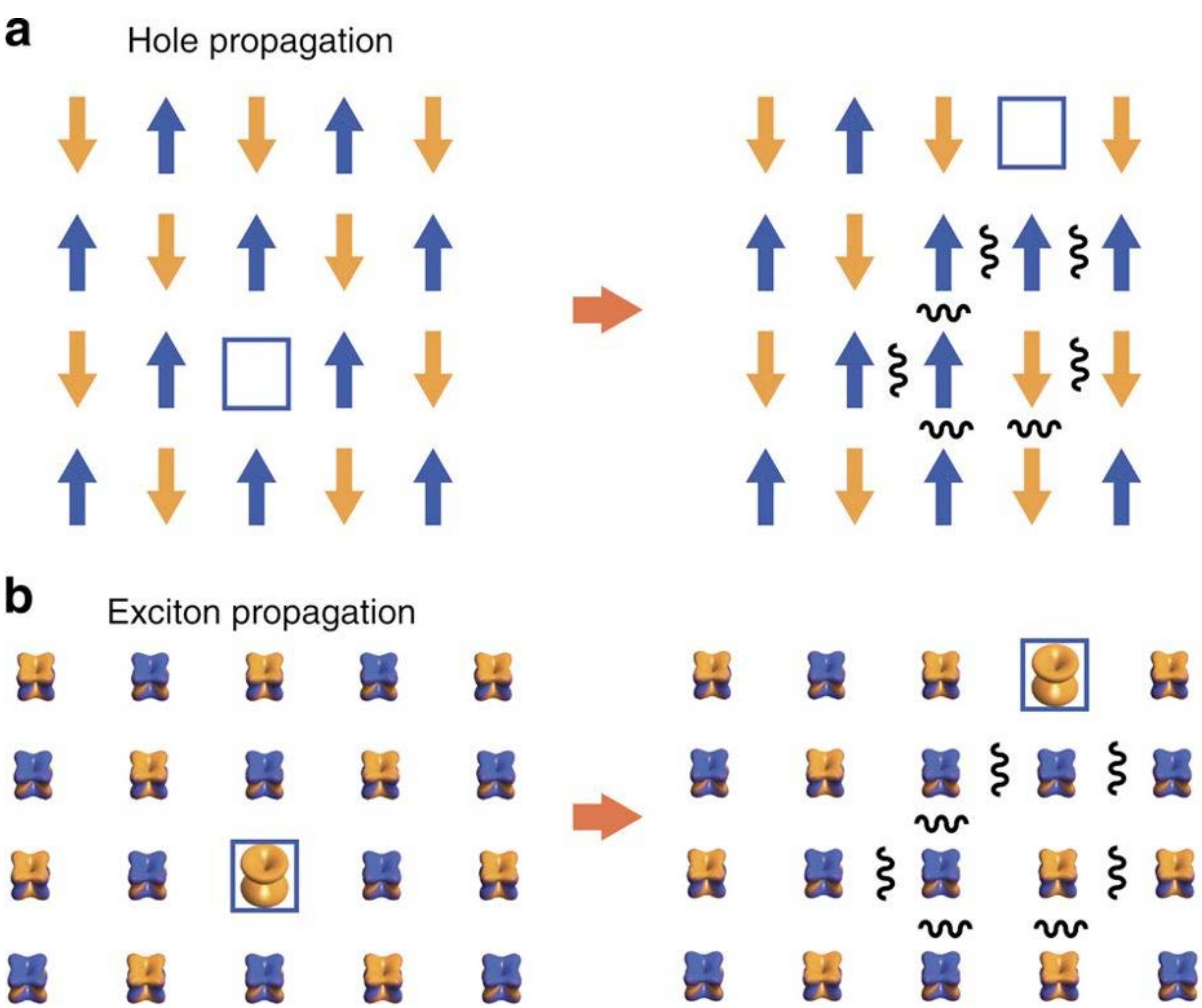

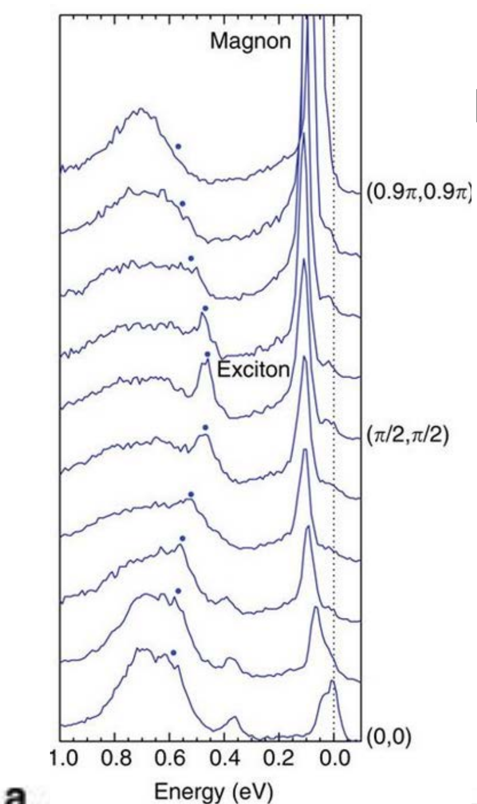

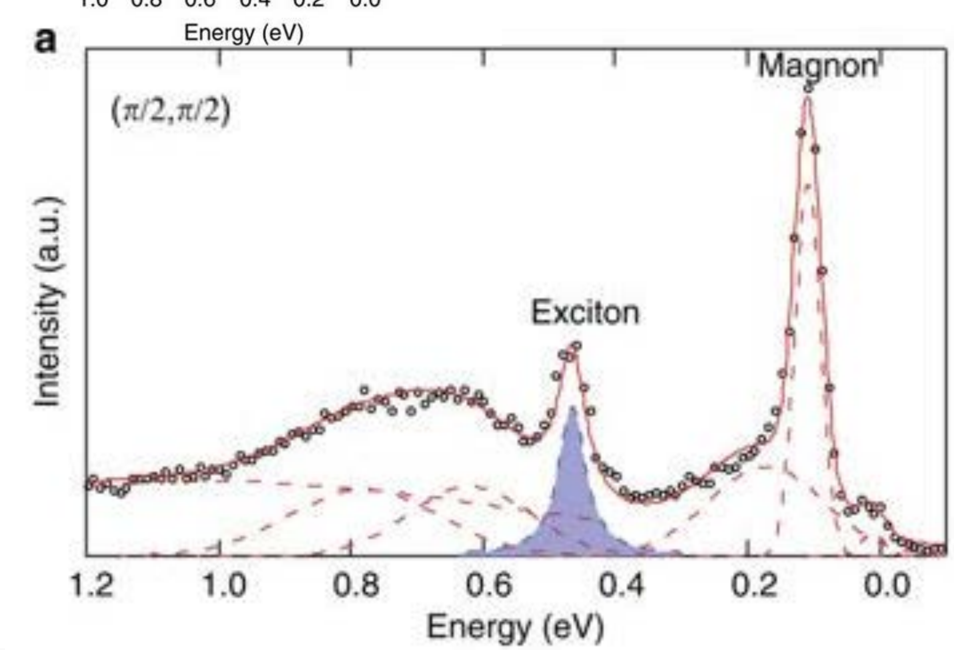

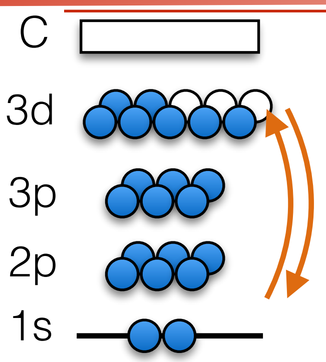

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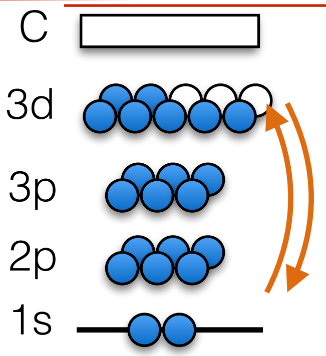
Can also do non-resonant IXS:

If we narrow the incident and final energy resolutions to the absolute limit, we can look directly at non-resonant inelastic scattering processes. This lets us measure i.e. phonon dispersions with x-rays. Caution - even more "photon hungry". Very long counting times.



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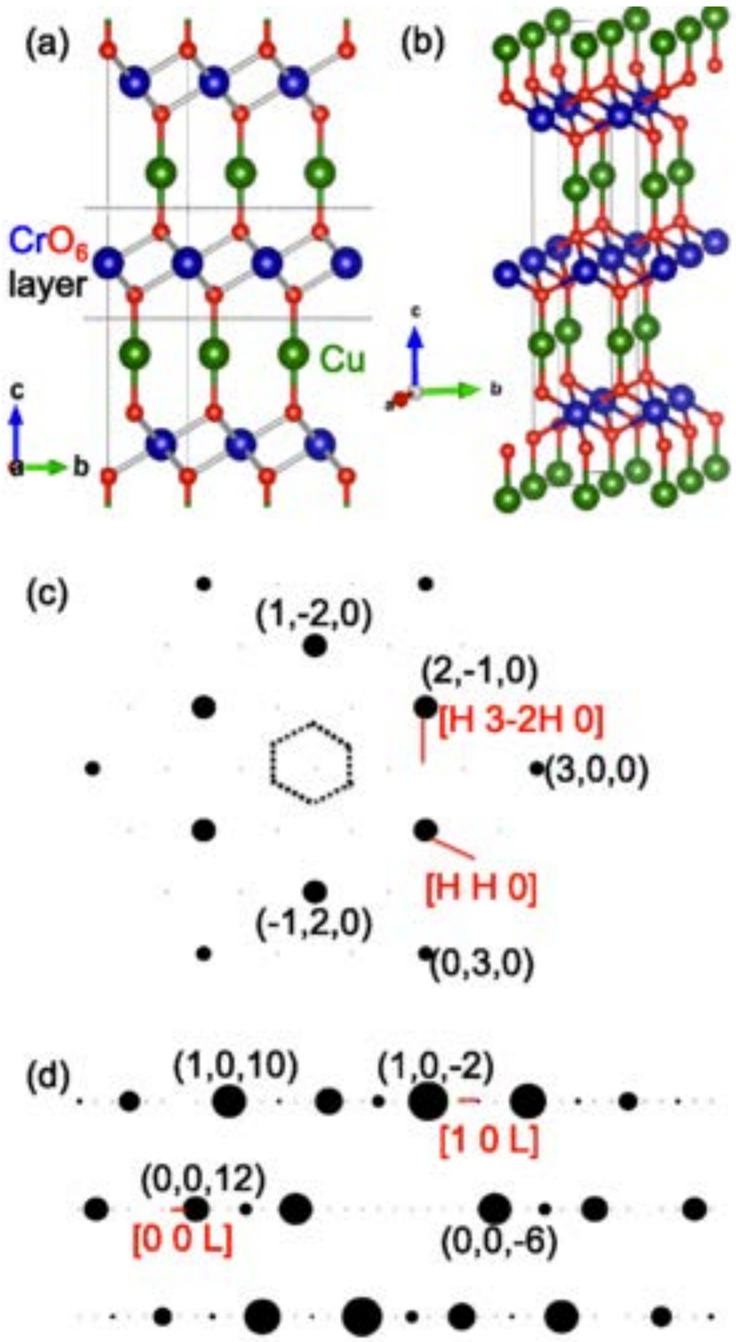
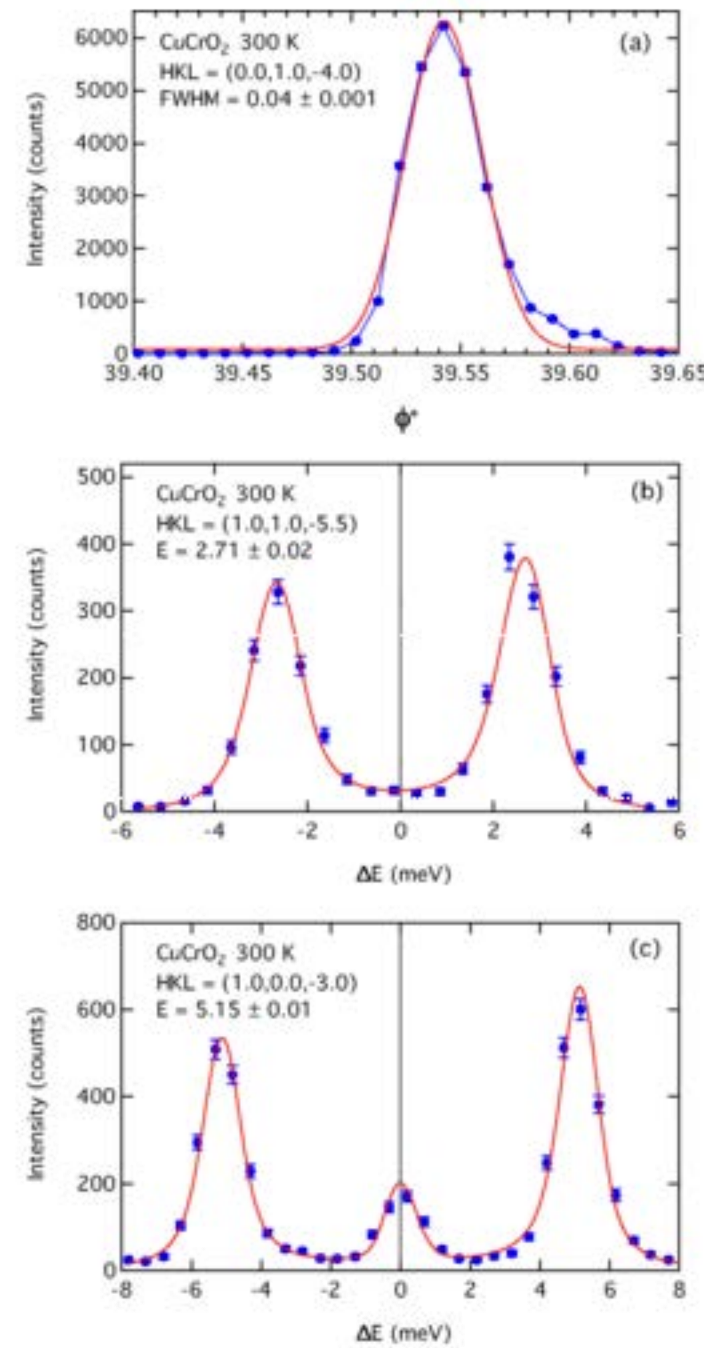
HERIX @ APS

Phonons in CuCrO2
[Bansal, PRB 95 054306 (2017)]





Question : Why not Neutrons?

- Many of the phenomena probed by resonant / inelastic scattering are also well studied by neutrons (phonons, magnetic order, spin waves).
- When neutrons work - they are often superior. Large crystals, non-absorbing elements, coherent neutron cross -sections.
- When neutrons won't work, x-rays can be the only recourse: thin films, microcrystals, short timescales, "bad" elements for neutron work.
- Different cross sections can give complimentary information. Use both!

4. Sample Environments

Synchrotrons offer a wide variety of methods to perturb your samples

- Low temperatures: T>0.5K at few beamlines, T>4K at most beamlines.
- High Pressure: Diamond Anvil Cells are transparent to high-energy x-rays, and small probe volumes facilitate very high pressures. See HPCAT, HPSync @ APS.
- Magnetic fields: Up to 7T DC fields available at SSRL, NSLS-II, APS. Up to 30T pulsed fields available at APS and LCLS.
- Optical pump-probe: Dozens of laser and THz systems set up to pump materials for time resolved measurements in the ps regime (synchrotrons) or fs regime (FELs).
- In-situ growth chambers (PLD, CVD, MBE) operating at various beamlines as well.
- Several locations also specialize in accommodating custom setups (plug and play sample environments with partner users.)