Introduction to Inelastic X-Ray Scattering

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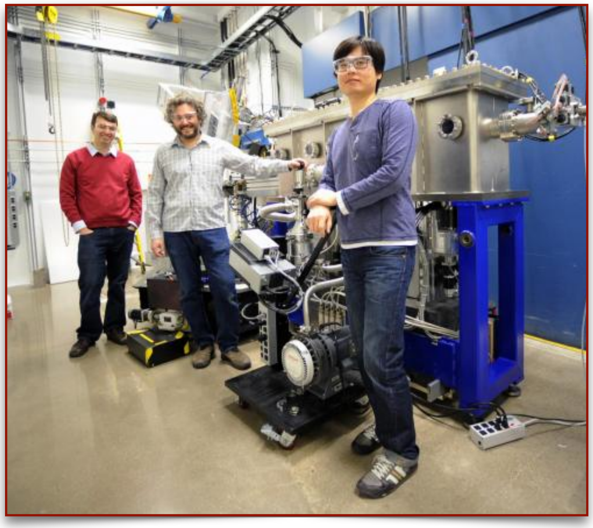
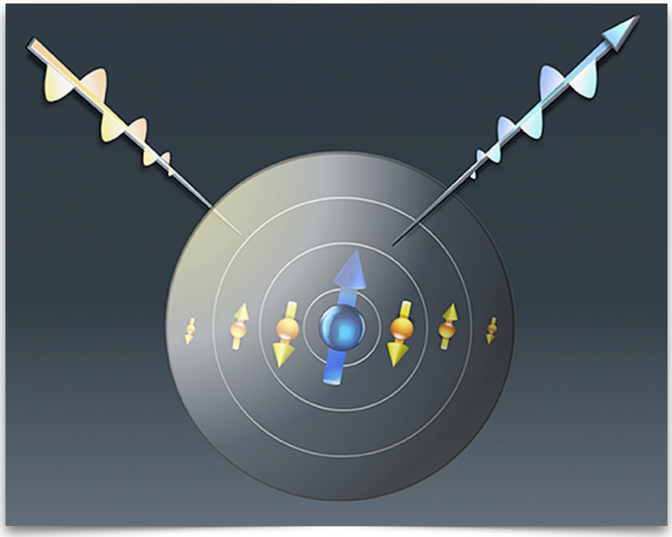




Neutron and X-ray Scattering School
Argonne National Laboratory, Argonne, IL

Outline

- Introductions
- Dispersion relations in materials physics
- Elastic waves and classification of phonons
- Phonon inelastic X-ray scattering examples
- Resonance phenomena in multi-electron atoms
- Resonant inelastic X-ray scattering examples

UConn Condensed Matter Physics

Alexander Balatsky
Theoretical physics
Superconductivity
Quantum materials

Gayanath Fernando
Theoretical physics
Electronic structure
Quantum materials

Boris Sinkovic
Thin films synthesis
Electron spectroscopy

Lea F. Dos Santos
Theoretical physics
Quantum chaos

Elena Dormidontova
Soft Matter Theory

Jason Hancock
THz, Infrared, X-ray
Applied physics

Ilya Sochnikov
Low-T transport
Scanning SQUID

Pavel Volkov
Materials theory
Twistronics

Niloy Dutta
Photonics
Applied physics

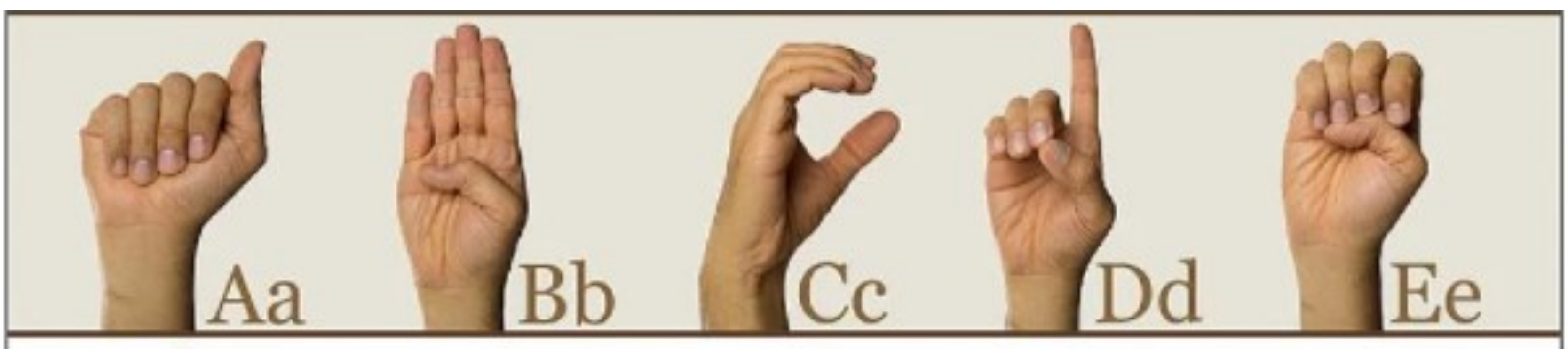
Menka Jain
Thin film synthesis

Barrett Wells
PLD films, Muons,
Neutrons, ARPES

Plus strong connections with: AMO group, UConn Institute for Materials Science, New UConn Tech Park

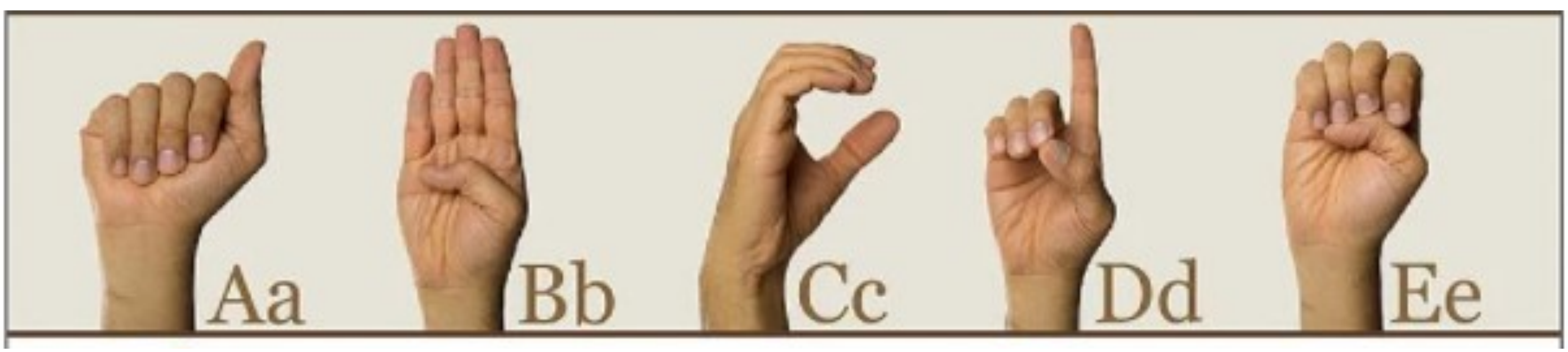
My PhD research does/will likely use…

A	B	C	D	E
X-rays	Neutrons	Both X-rays and Neutrons	Neither	I am a theorist

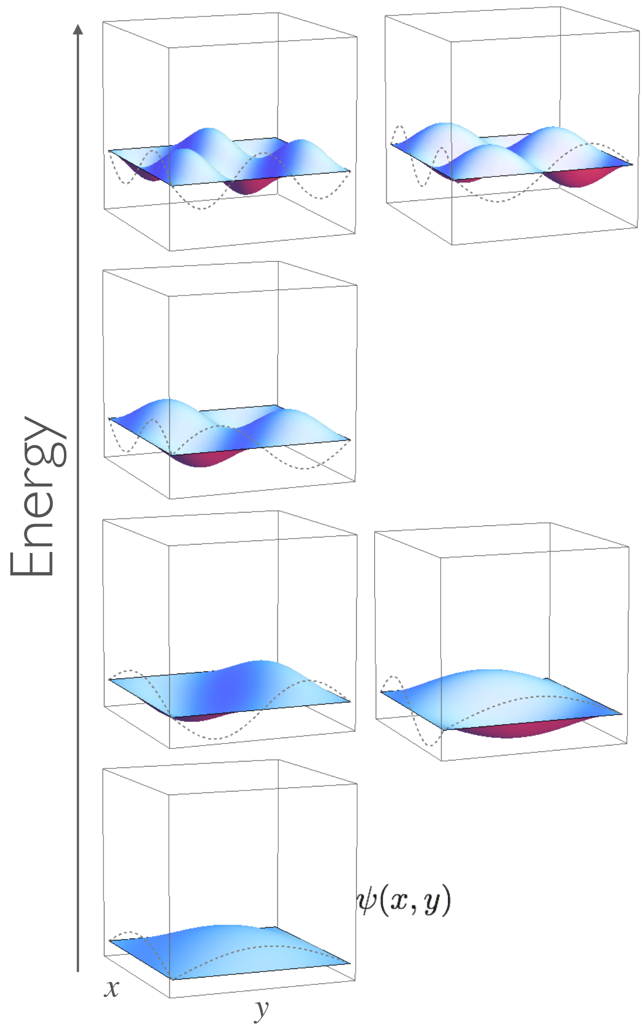


My PhD research does/will likely regard…

A	B	C	D	E
Mostly structural studies	**Spectroscopy and electronic structure**	**Advanced imaging**	**Still figuring it out**	**None of these**



Particle-in-a-box: the simplest quantum problem

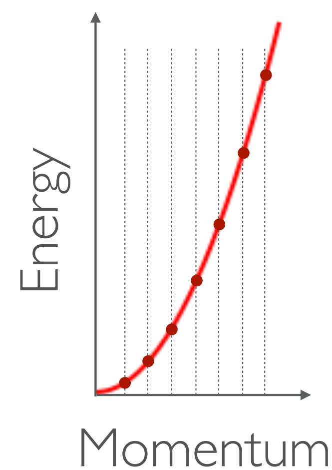


$$H\psi = E\psi$$

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Kinetic energy

$$E = \frac{\hbar^2 k^2}{2m}$$

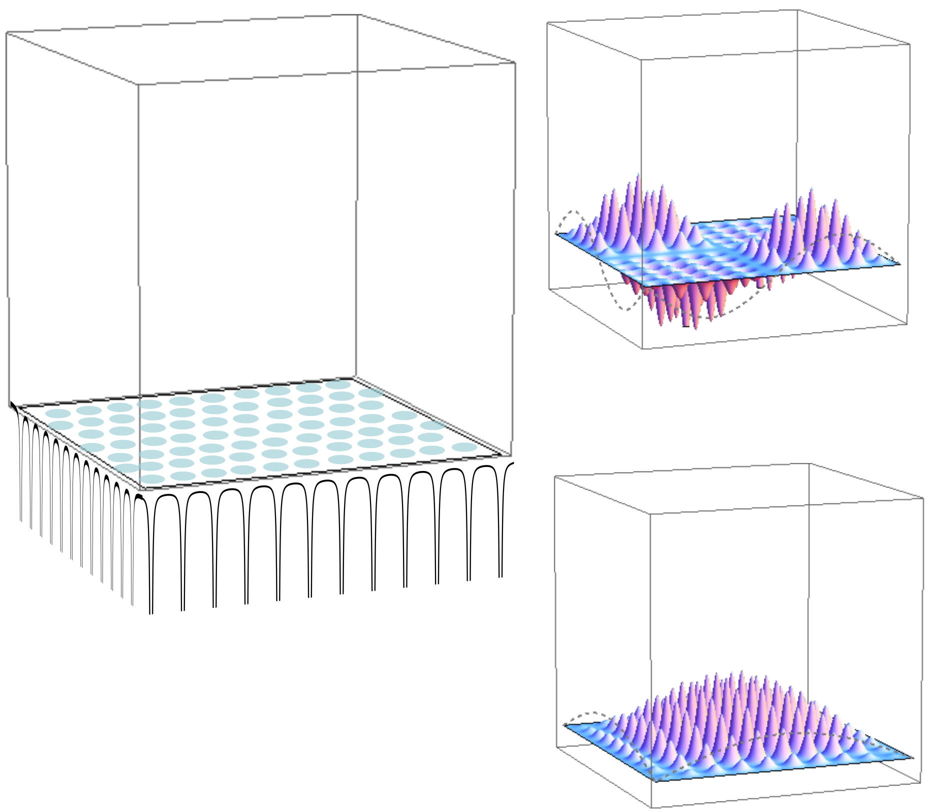


$$E \to i\hbar\frac{\partial}{\partial t}$$

$$p \to -i\hbar\frac{\partial}{\partial x}$$

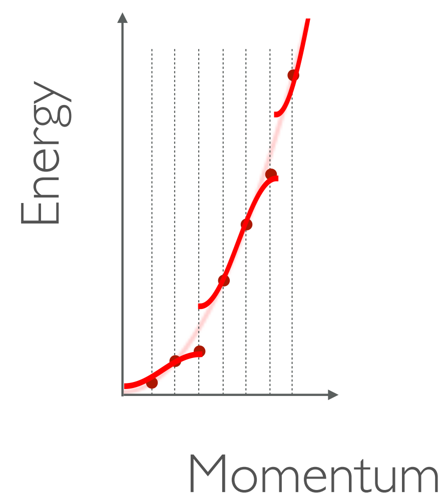
Dispersion relation

Particle in a box to the band theory of solids

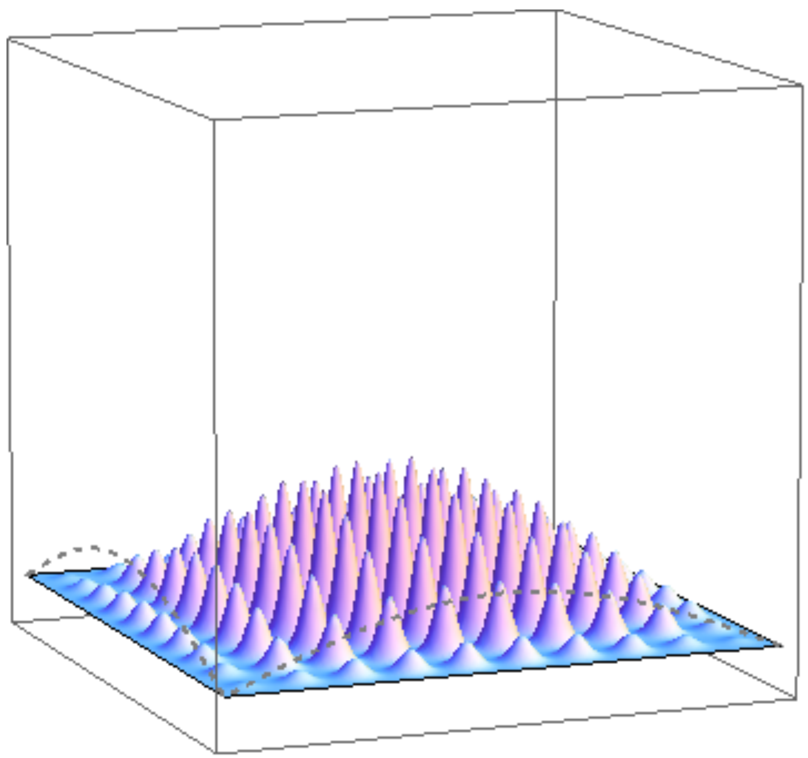


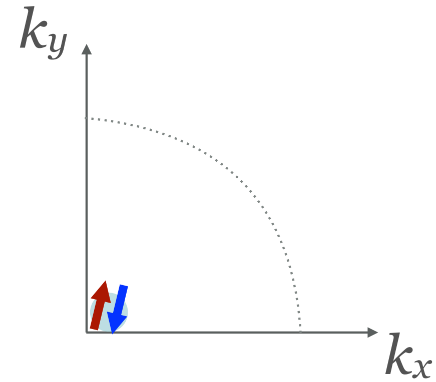
$$H\psi = E\psi$$

$$H = \frac{p^2}{2m} + V(\vec{r})$$

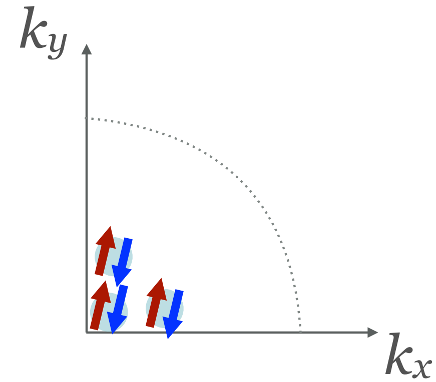


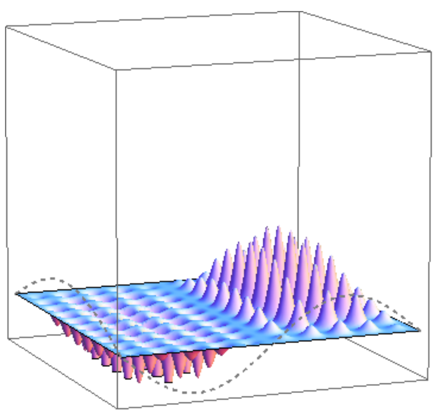
Many electron states

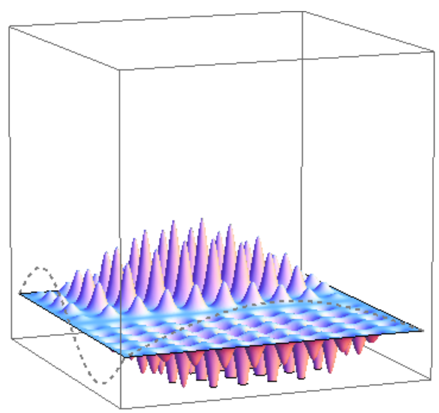


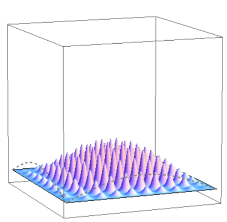


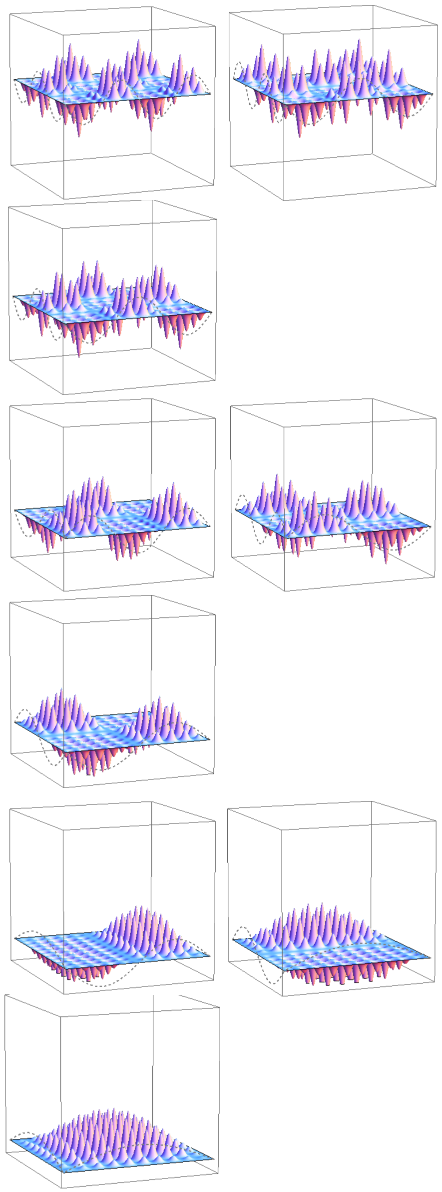
Many electron states



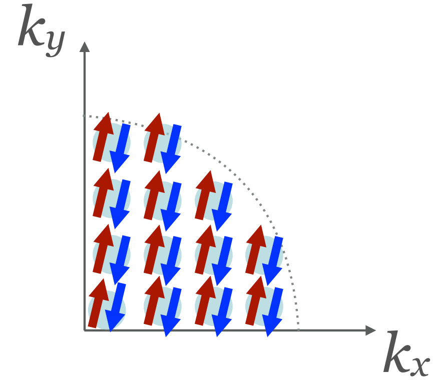


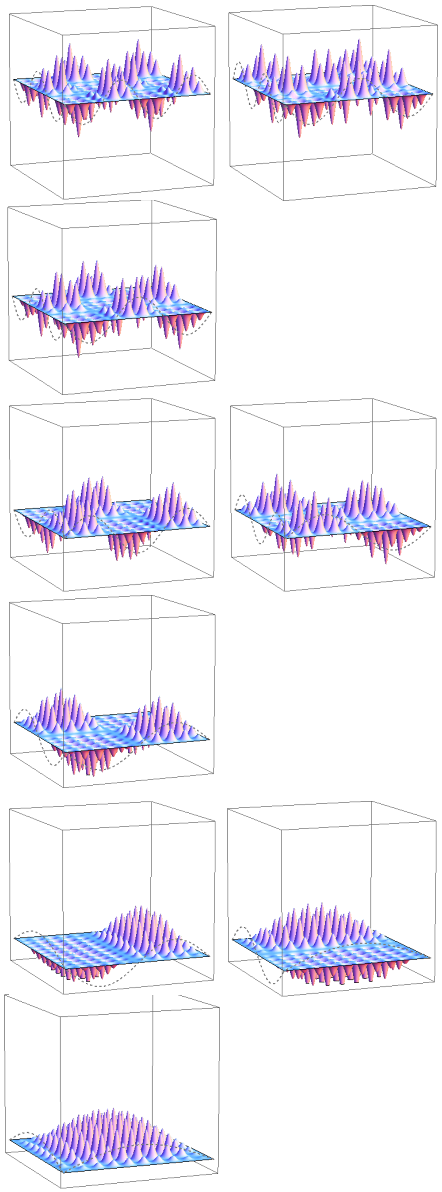




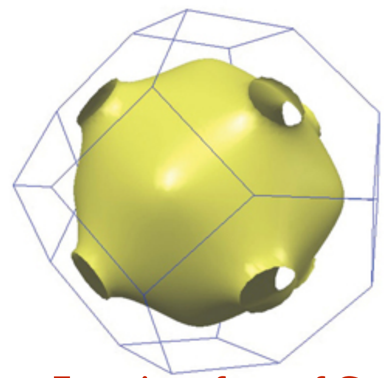


Many electron states

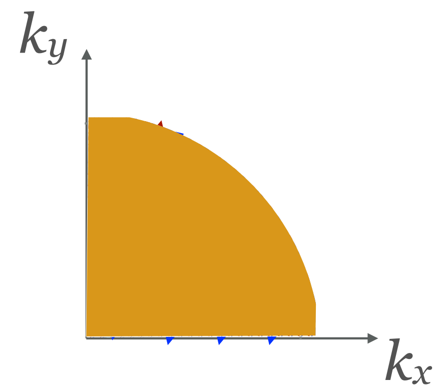


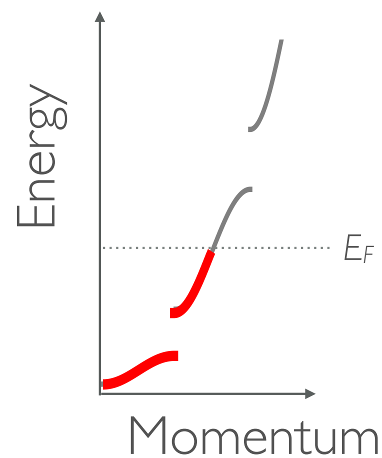


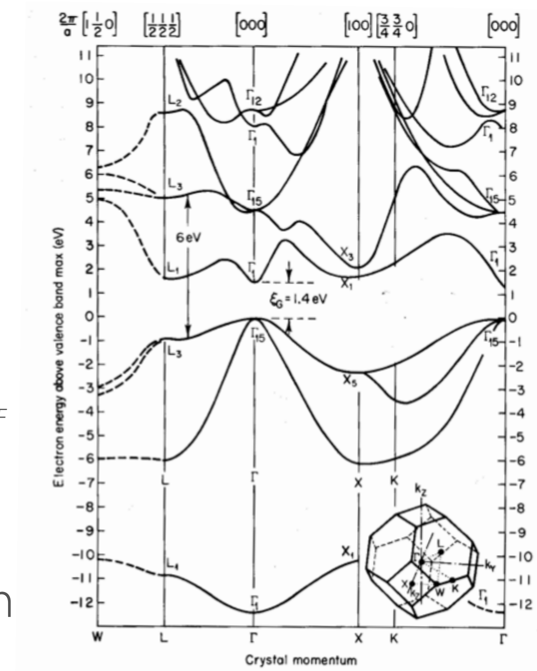
Many electron states



Fermi surface of Cu





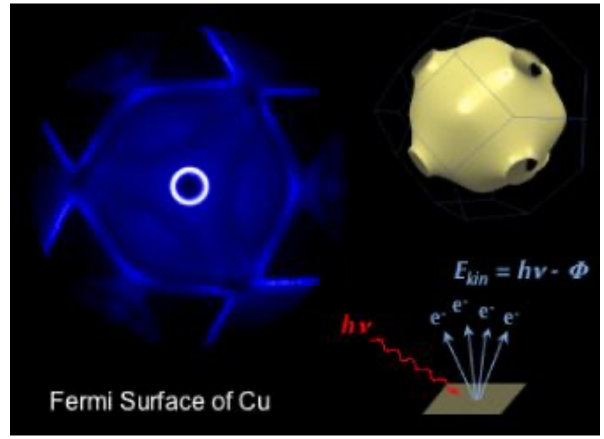


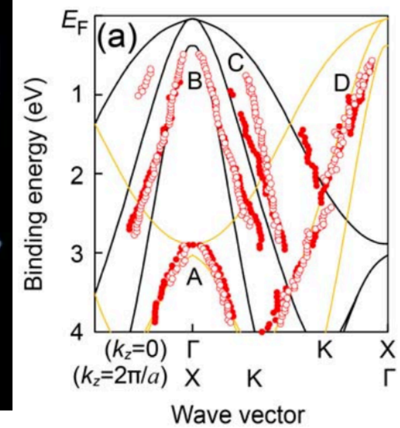
Dispersion relation of GaAs

Uncorrelated electron systems

Electron-electron interactions do not dominate material behavior

Well-established theoretical framework describes most properties of semiconductors (Si,Ge,GaAs), good metals (Cu,Ag,Al,Au)





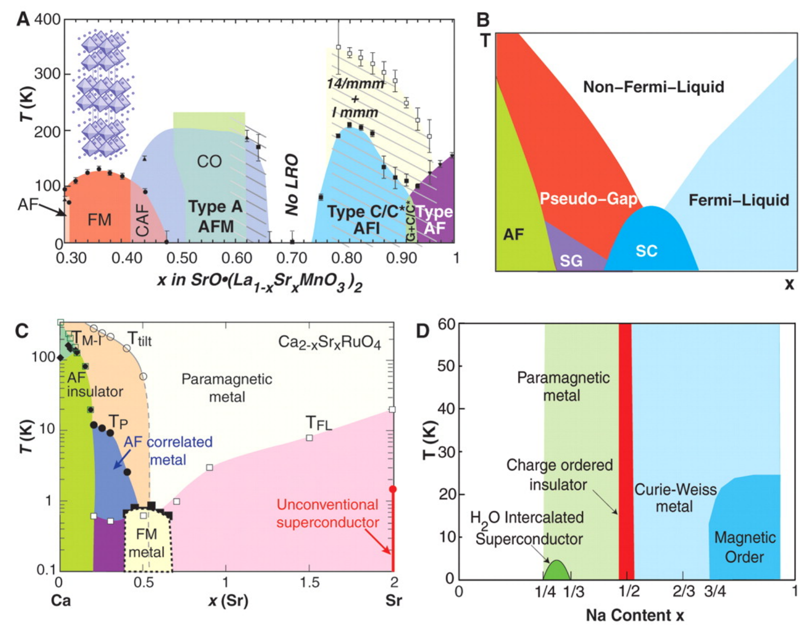
Correlated electron systems

Electron-electron interactions dominate material behavior

Often includes magnetism, more exotic behavior

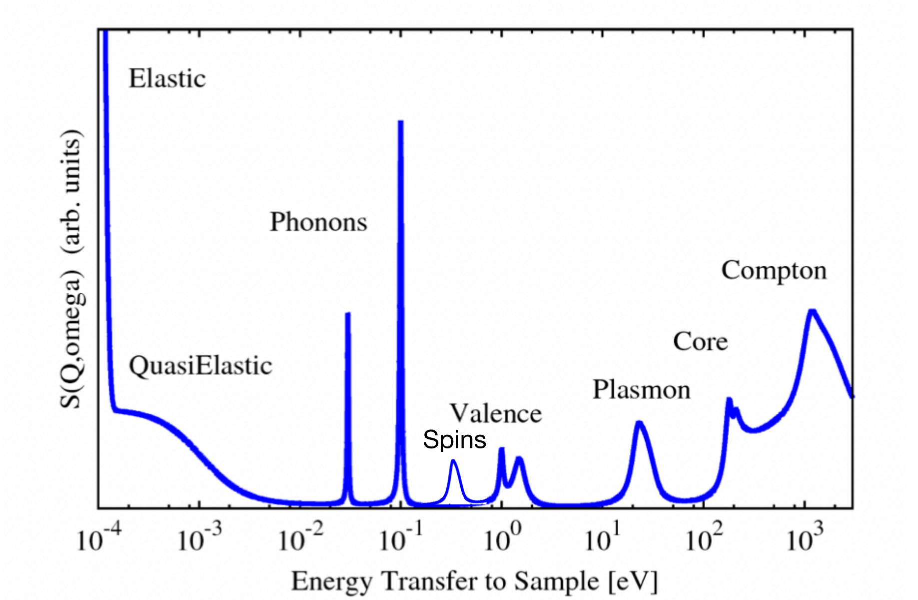
Theoretical treatment is very limited

High potential for applications and interesting basic science



Collective excitations in materials

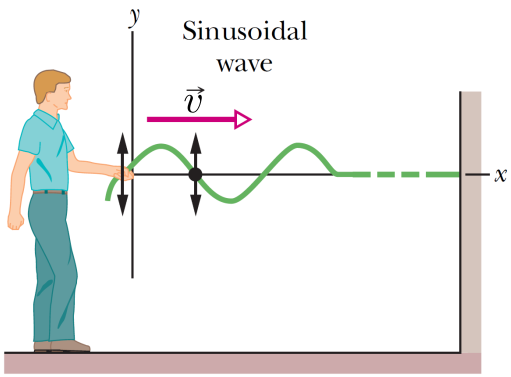
- “Fields” of spin, charge, nuclear displacement self organize according to interactions and confining potential
- Disturbances in the pattern form excited states relevant to material behavior



Inelastic X-ray scattering can probe many different fundamental excitations

Elastic waves

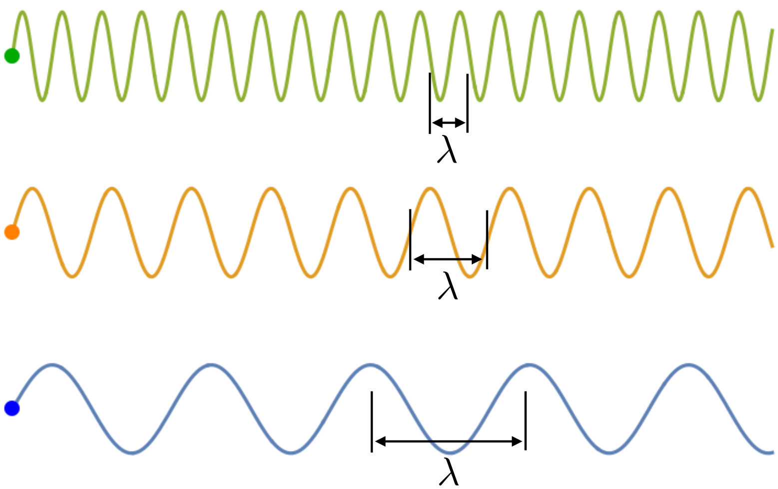
- Materials can distort in wavelike patterns, typical of transverse waves on a string



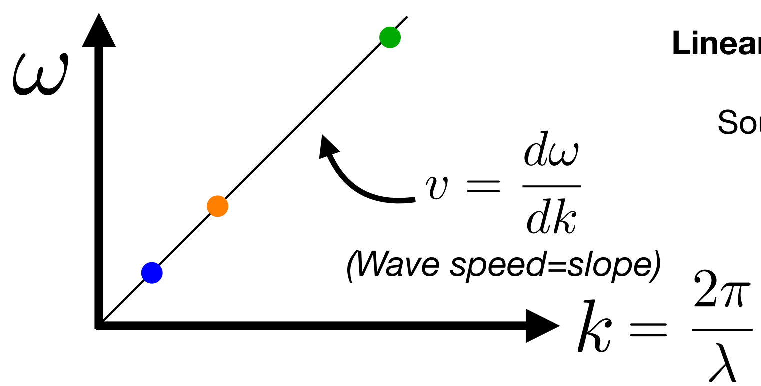
A common wave equation: $$\frac{\partial^2 f}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2}$$

permits solutions of the form: $f(x - vt)$

All waves move at the same speed, regardless of wavelength



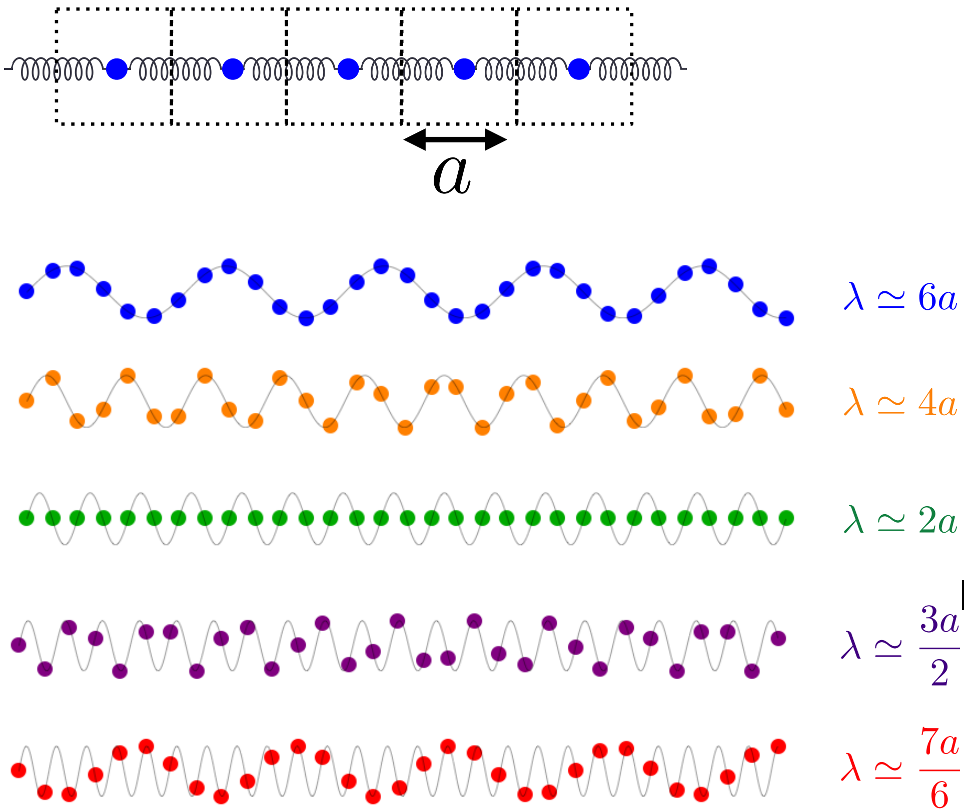
Dispersion relation for waves on a string

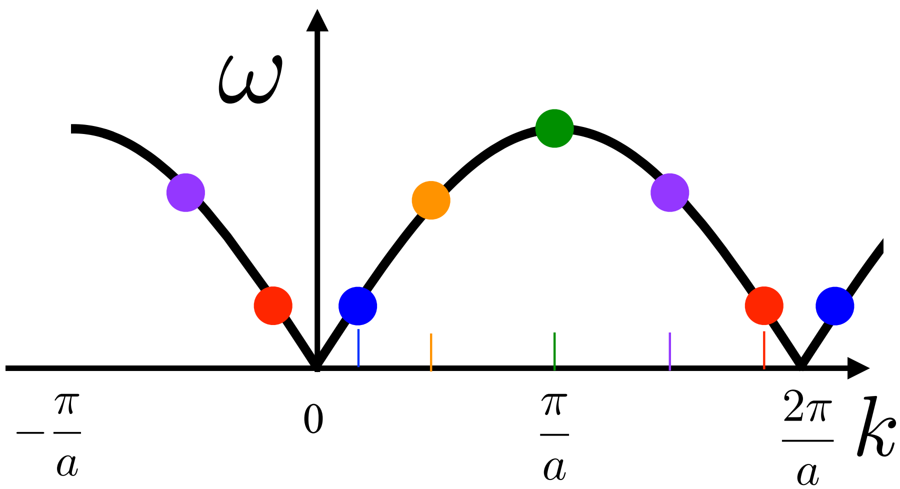


Linear dispersion also found in:
X-rays and light
Sound at long wavelengths
Shallow water waves
Gravitational waves

What about atomic scale disturbances?

- Consider *mona*tomic 1D chain and wavelengths approaching lattice parameter a



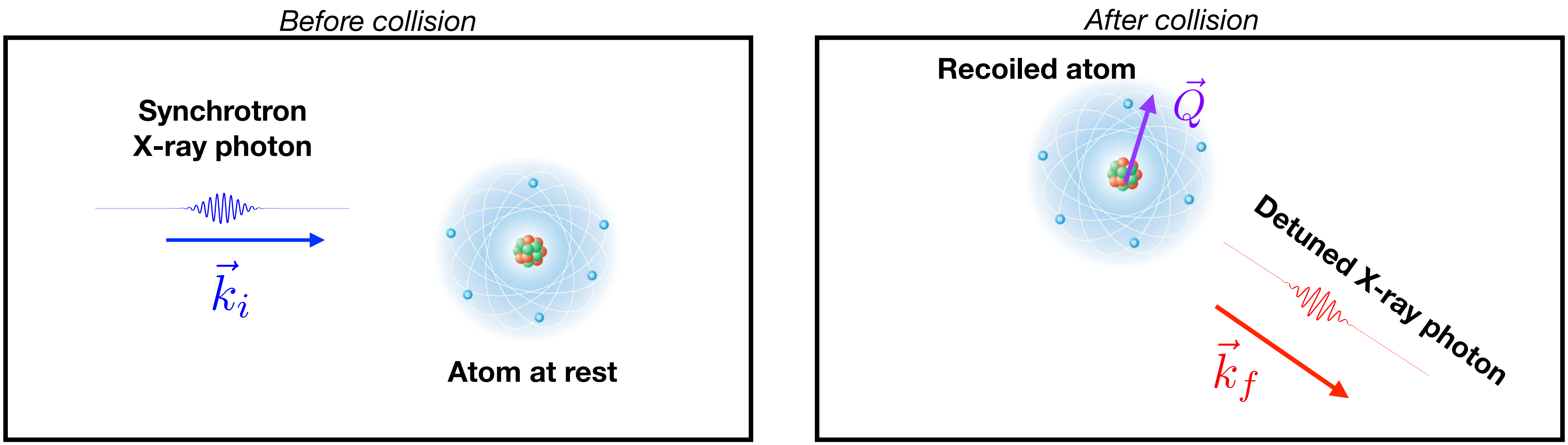


Lattice waves are periodic in momentum, just like the lattice

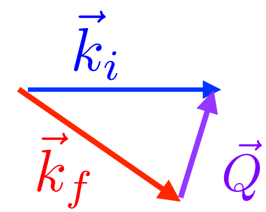
Quantum mechanics applied to lattice vibrations lead to the concept of "phonons"

Loosely, each k value refers to a different "phonon mode"

How do X-rays scatter from atoms?

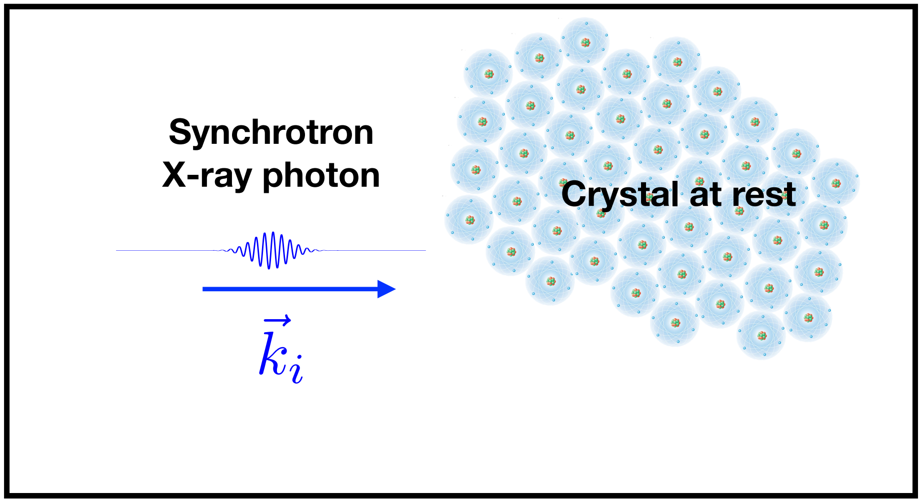


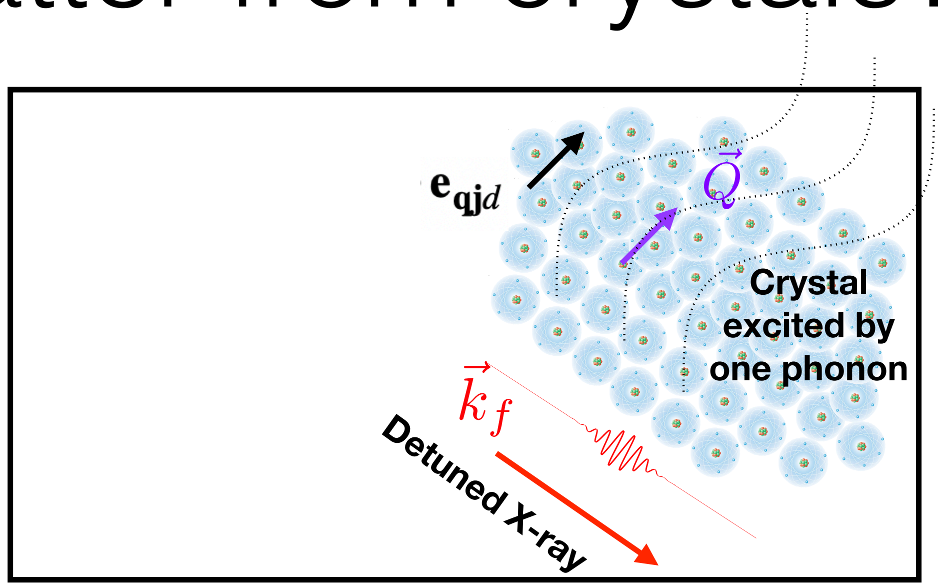
$\vec{Q} = \vec{k}_f - \vec{k}_i$ is the momentum delivered to the atom



- Off resonance, an X-ray can cause an atom to recoil in a momentum conserving collision

How do X-rays scatter from crystals?





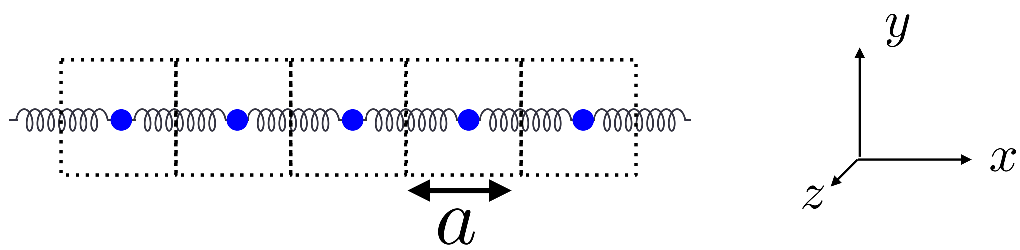
$\vec{Q} = \vec{k}_f - \vec{k}_i$ is the momentum delivered to the crystal

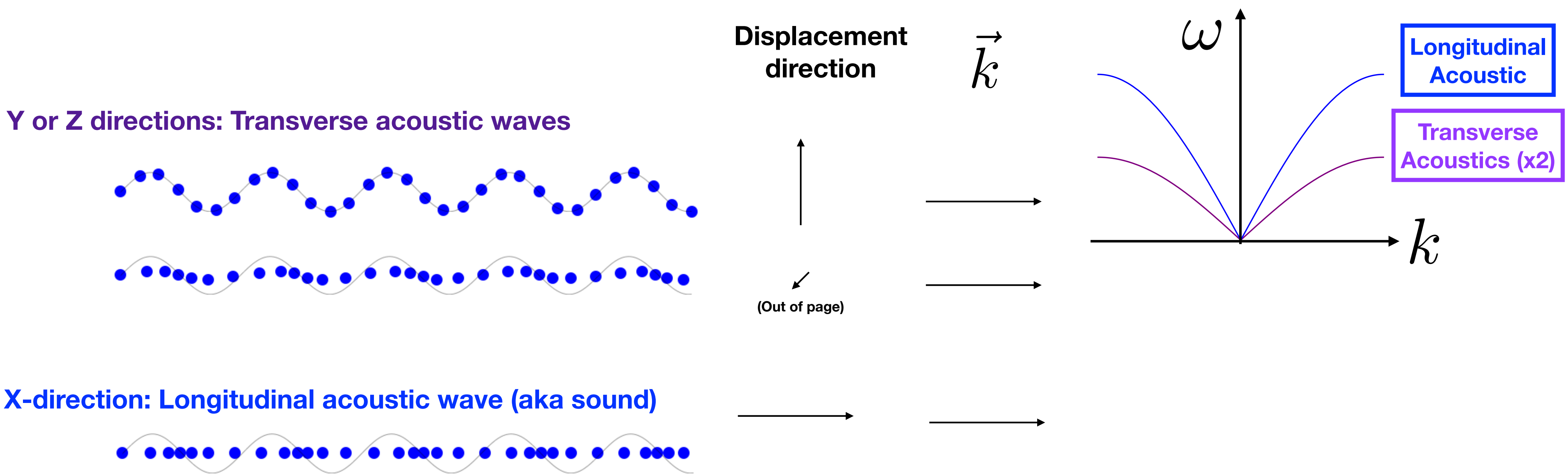
$$\left|F_{1\mathrm{p}}(\tau,\mathbf{q}j)\right|^2 = \frac{1}{\omega_{\mathbf{q}j}}\left|\sum_d \frac{f_d(\mathbf{Q})}{\sqrt{2M_d}}\, e^{-W_d}\,(\mathbf{Q}\bullet\mathbf{e}_{\mathbf{q}jd})\, e^{i\mathbf{Q}\bullet\mathbf{r}_d}\right|^2$$

- Probability of scattering off of a given phonon is strong when the displacements are along Q

Polarization of phonons

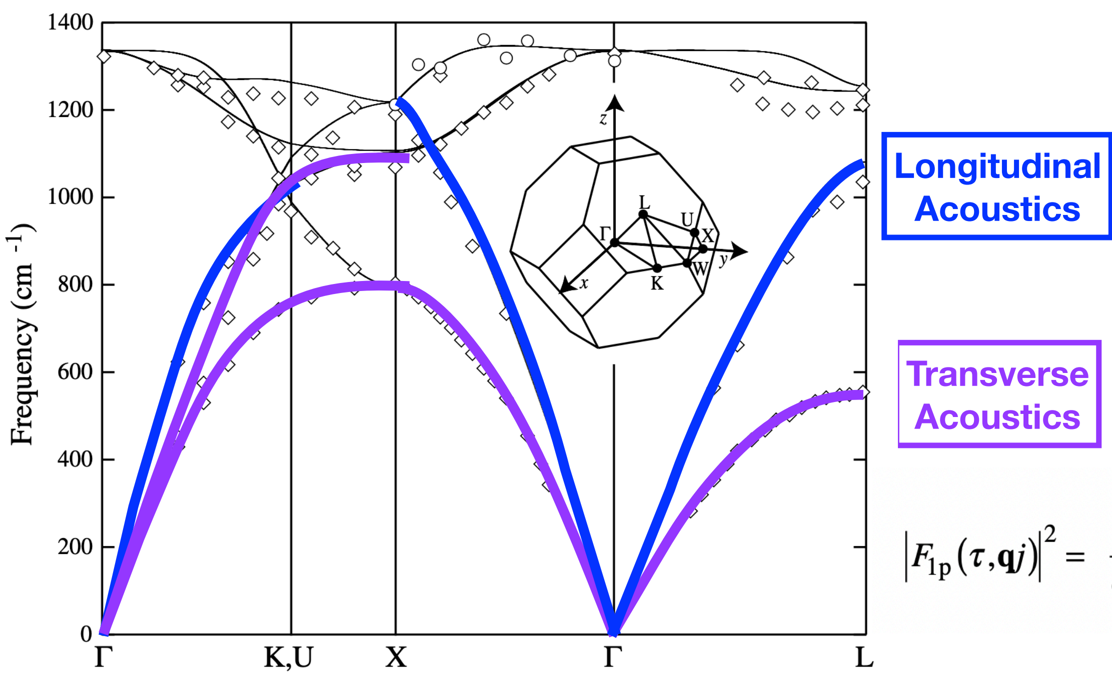
- Atoms can move in three directions, different dispersion for different directions



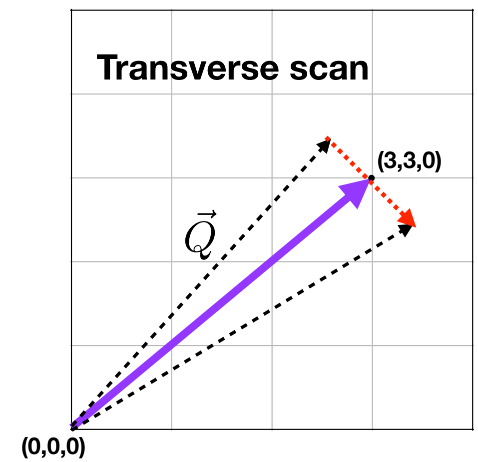


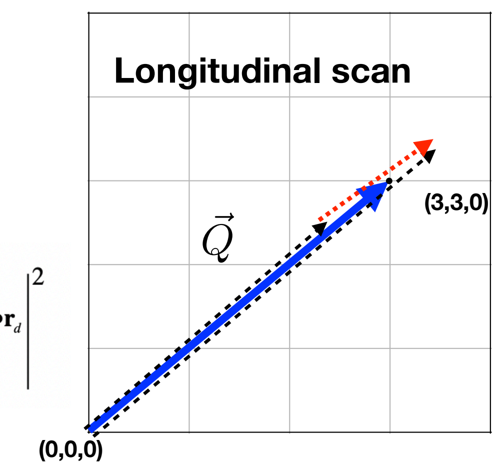
Measuring acoustic phonons with IXS

- Q sets the direction of atomic displacements
- Polarization of atomic displacement wrt reduced q can be changed by scanning different directions



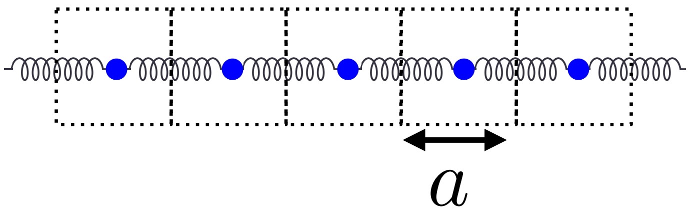
$$\left|F_{1p}(\tau,\mathbf{q}j)\right|^2 = \frac{1}{\omega_{\mathbf{q}j}}\left|\sum_d \frac{f_d(\mathbf{Q})}{\sqrt{2M_d}}\, e^{-W_d}\,\mathbf{Q}\bullet\mathbf{e}_{\mathbf{q}jd}\, e^{i\mathbf{Q}\bullet\mathbf{r}_d}\right|^2$$

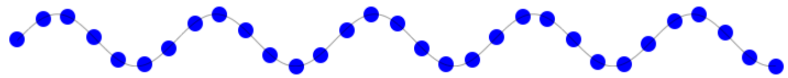


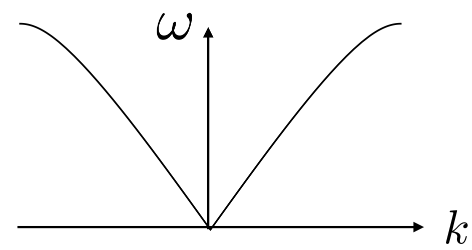


What about more complicated unit cells?

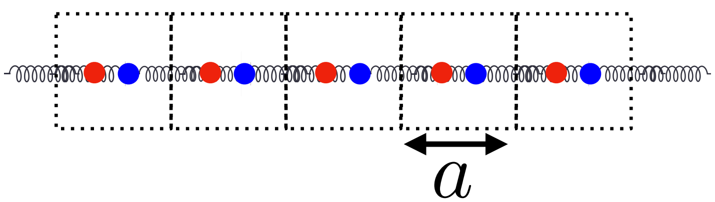
- *Mon*atomic 1D chain

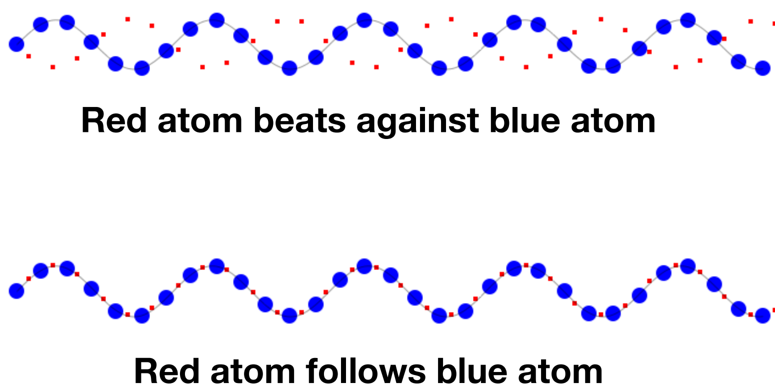


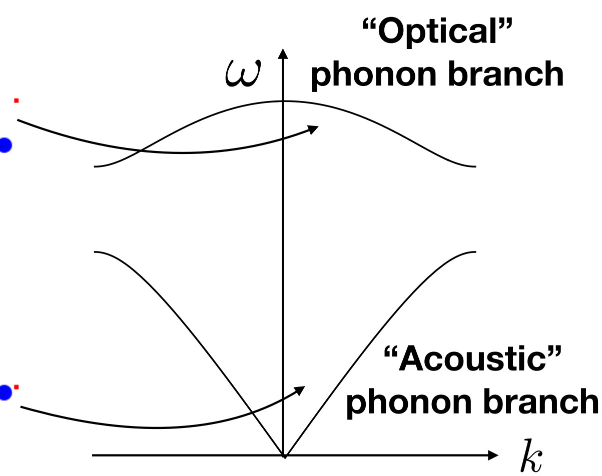




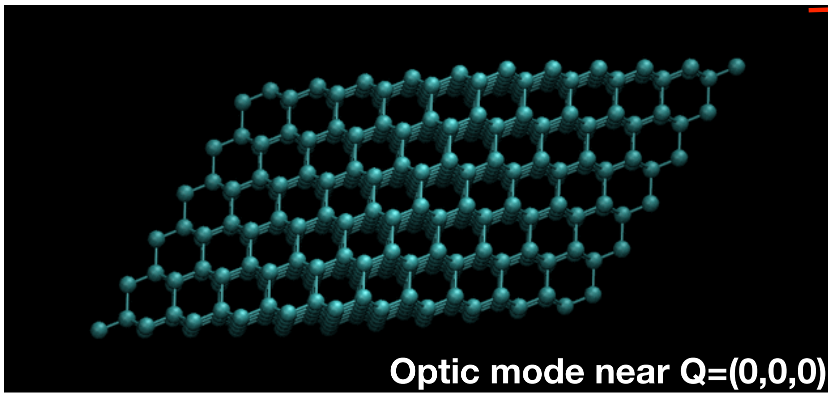
- *Di*atomic 1D chain

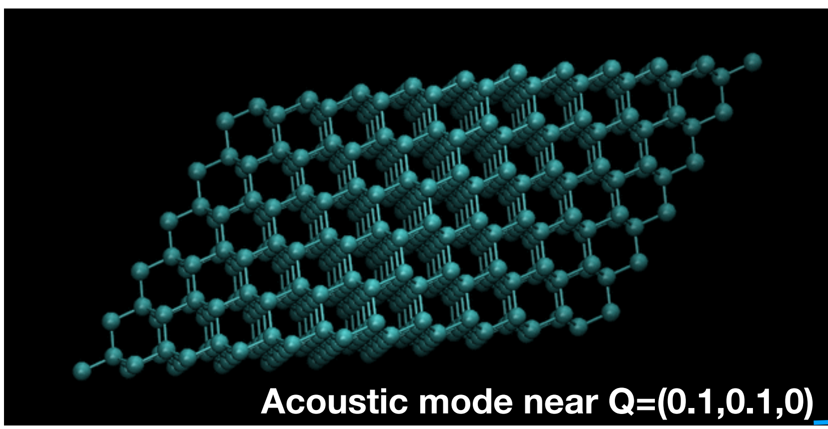


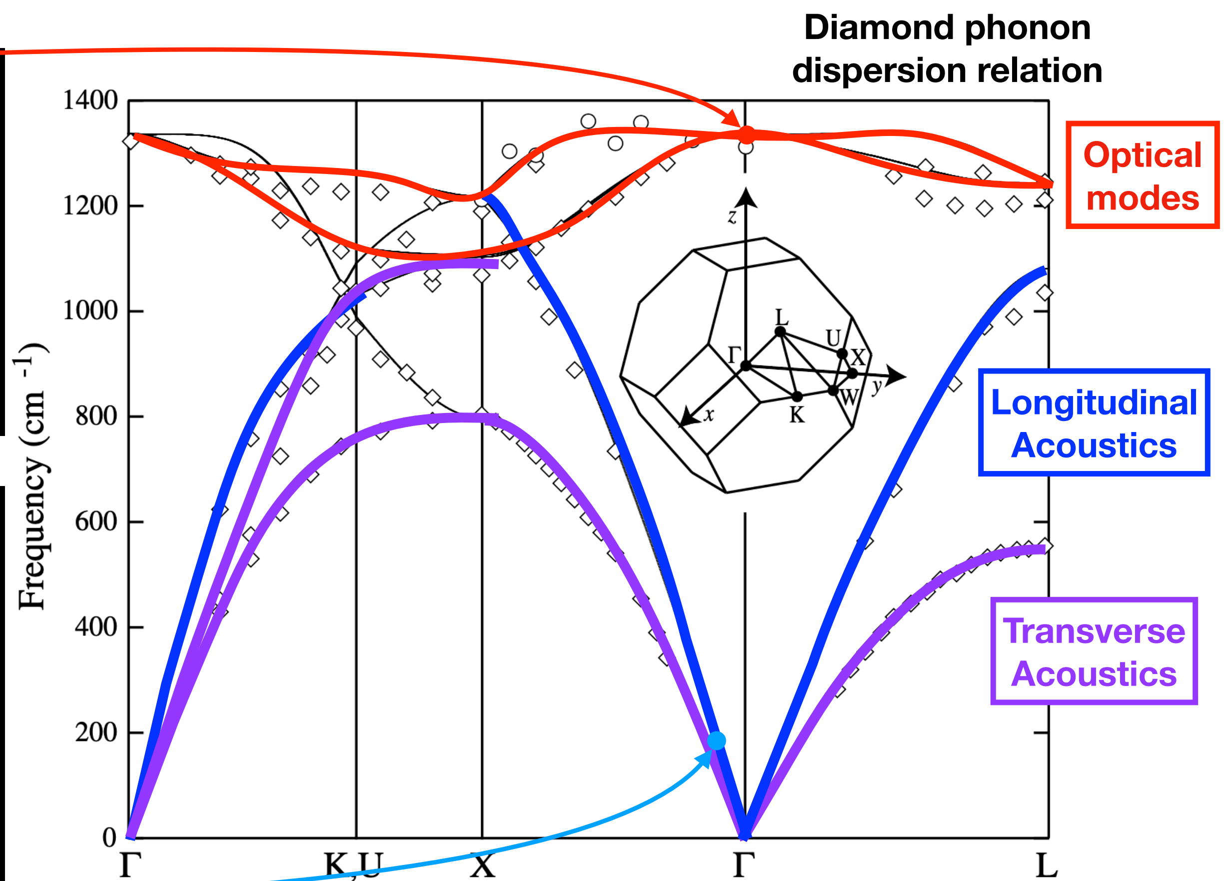




Phonons throughout the Brillouin zone

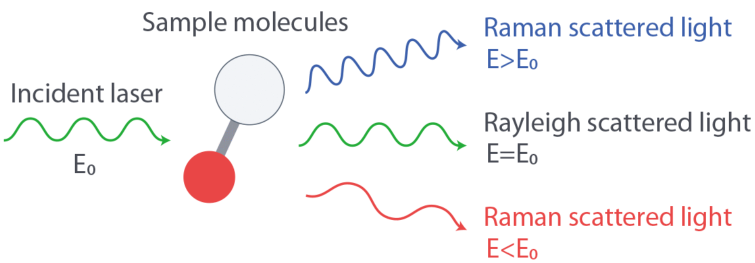


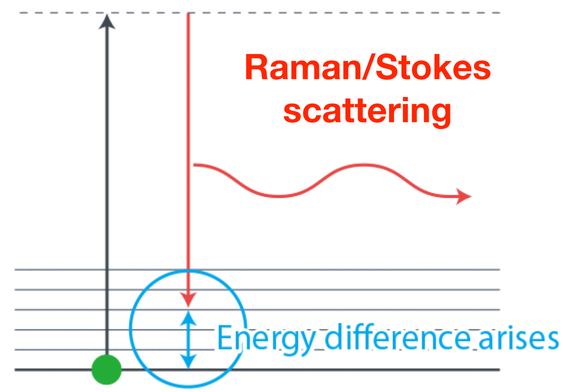




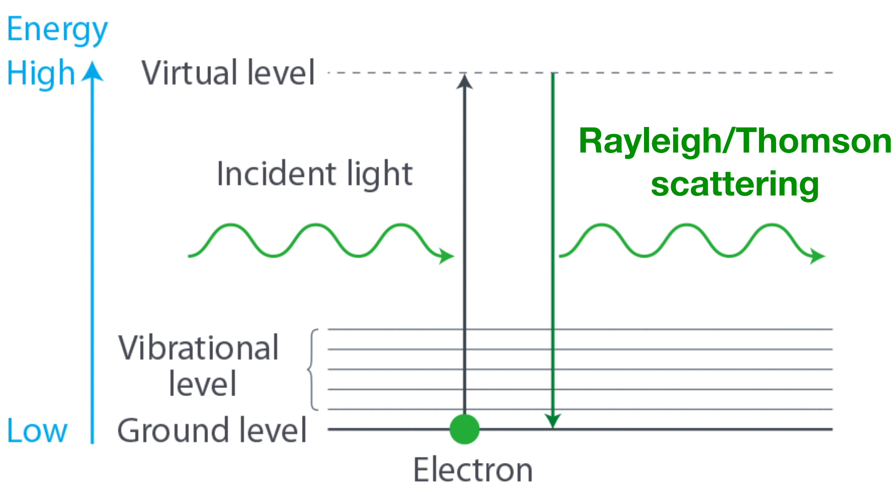
Gonze, et al, Z. Krist. 220 (2005) 458

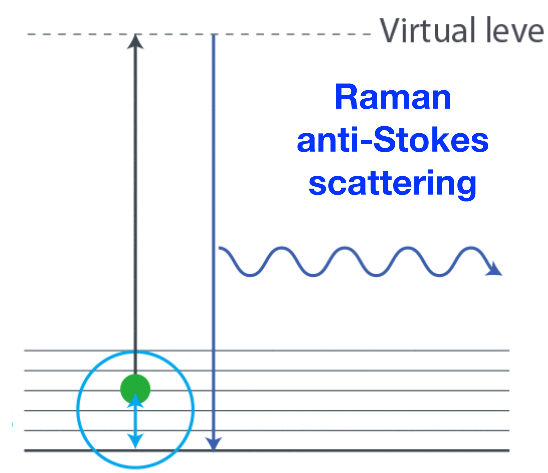
Raman=inelastic light scattering





Discovered 1928
Nobel 1930

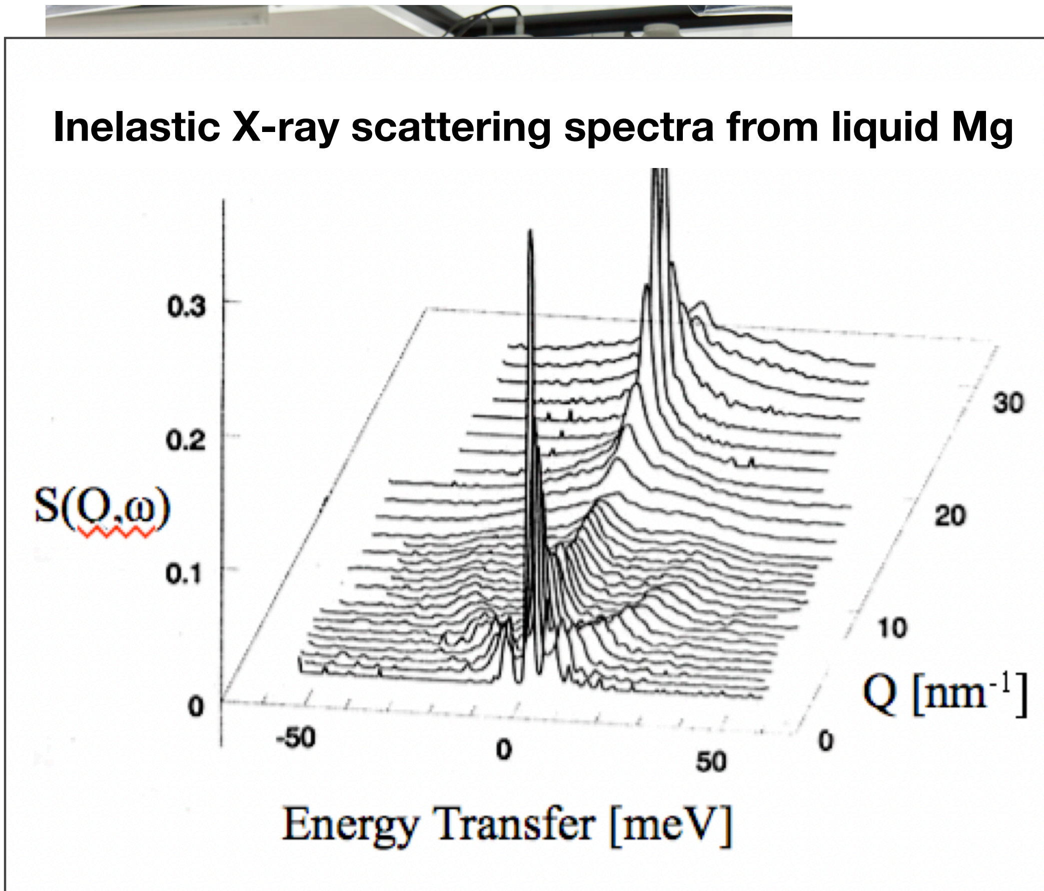


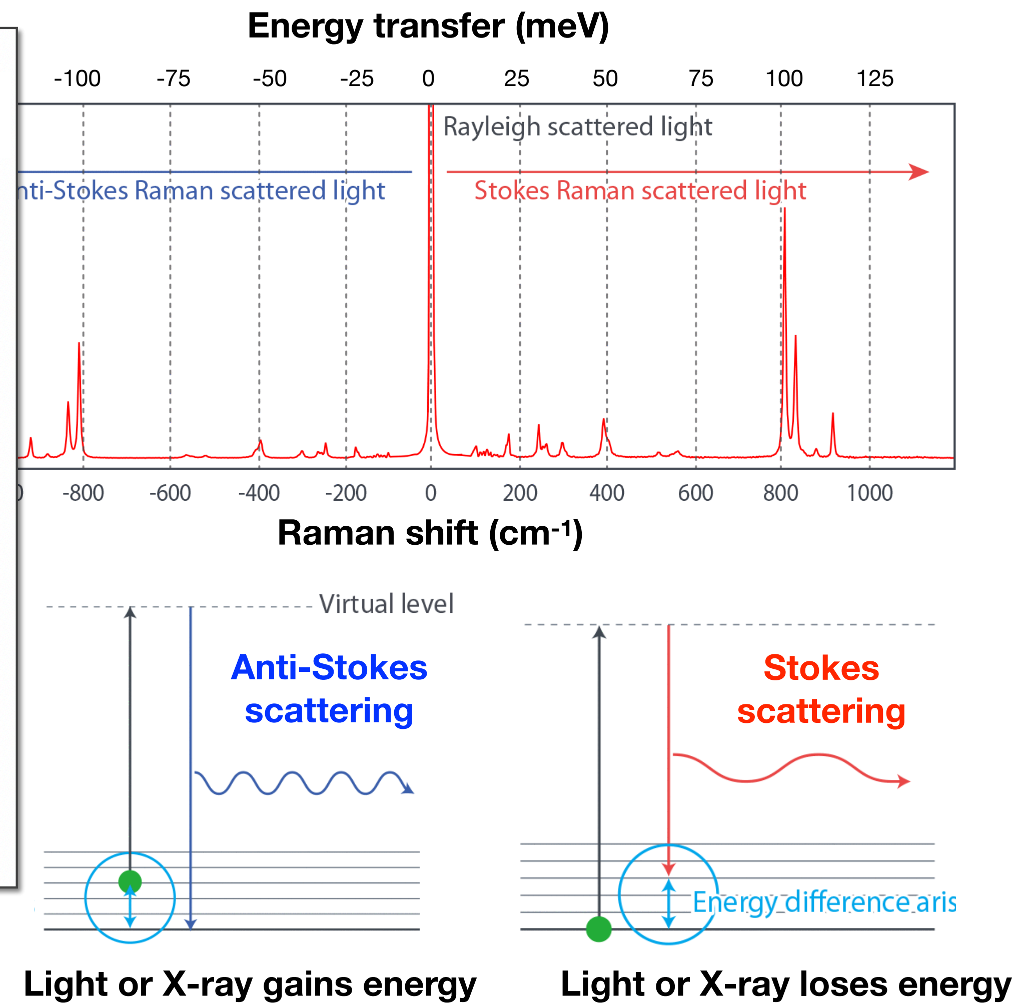


Strong limitation: momentum of light is very small

https://www.nanophoton.net/

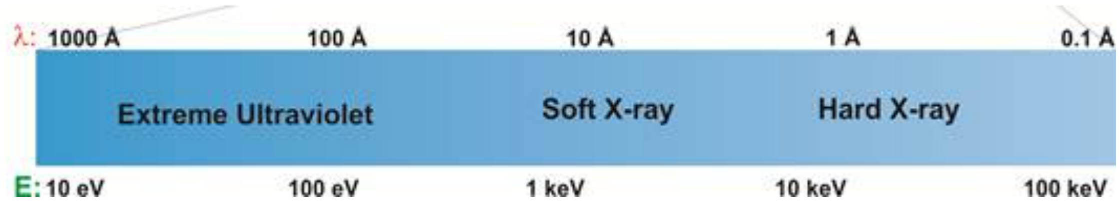
Energy transfer and Raman shift



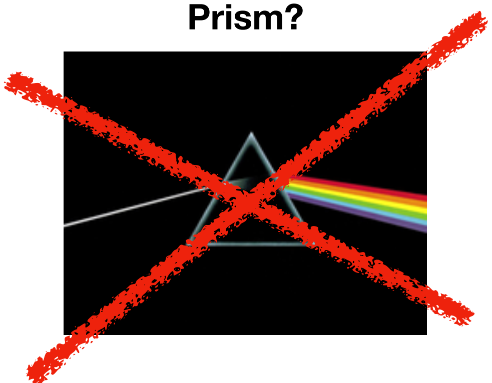


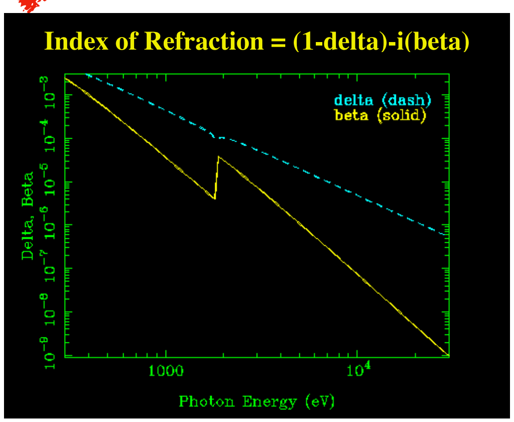
- Electronic and magnetic excitations possible

How can we disperse X-rays according to energy/wavelength?



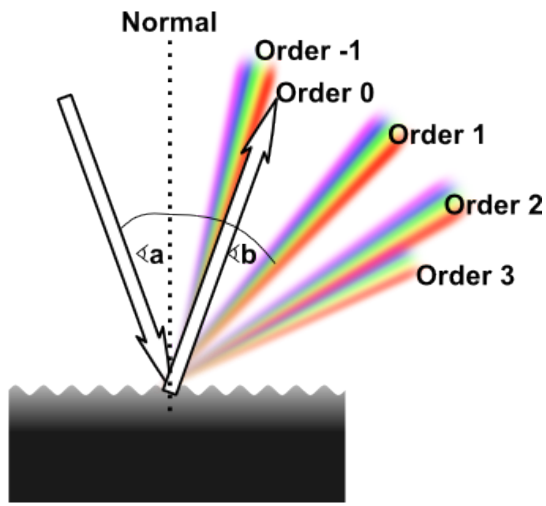
Prism?





Inefficient
Index changes too small to be effective

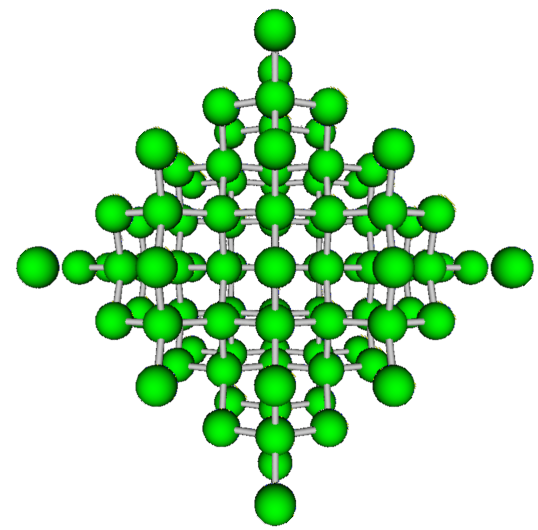
Grating?



If feature sizes can be on order wavelength

Good choice for lasers up to soft X-ray ~ 1 nm

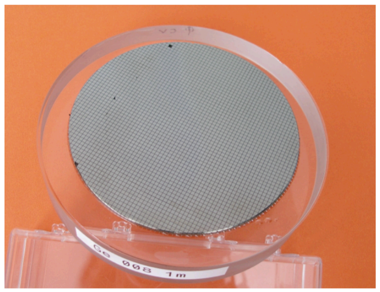
Crystal?



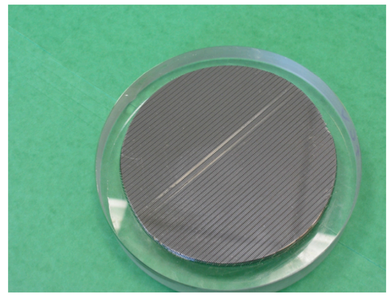
Feature size (atoms) of order X-ray wavelength

Hard X-ray << 1nm

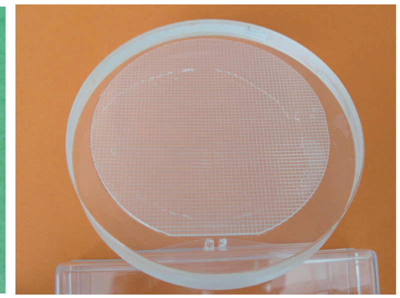
Diffracting X-rays crystals



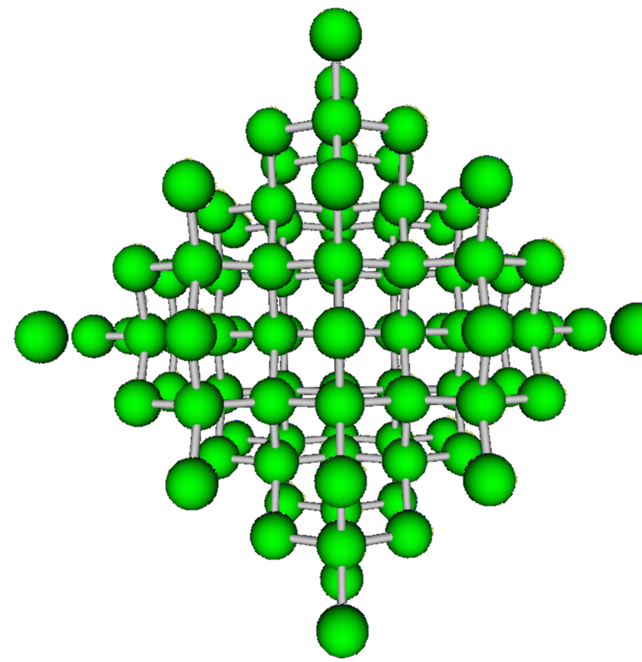
Si



Ge



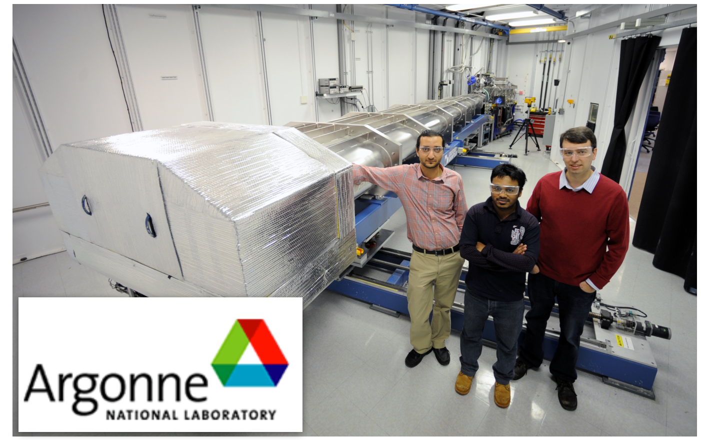
$LiNbO_3$

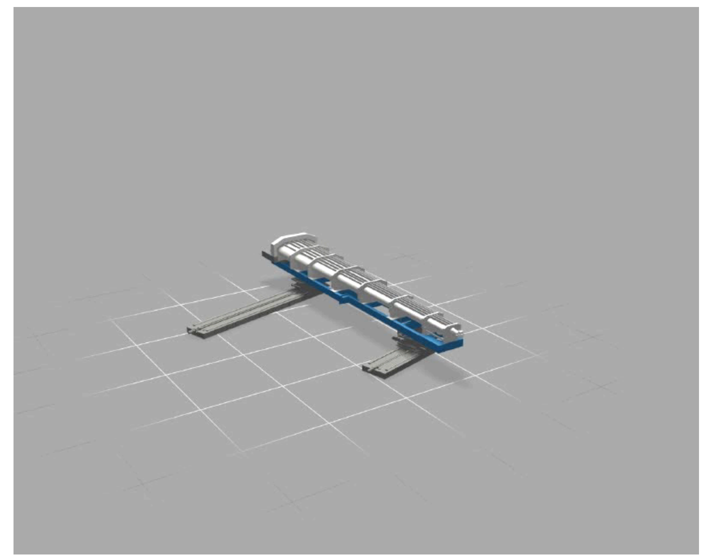


- Collecting inelastically scattered photons requires high quality, large, diced, bent crystal analyzers
- APS is a world leader in analyzer development

High **E**nergy **R**esolution **I**nelastic **X**-ray Scattering

- Sector 30, Advanced Photon Source, Argonne National Lab
- 23,724 eV incident energy
- <1 meV incident bandwidth
- Resolving power $E_i/\Delta E_i = 2\times10^7$
- 9 analyzers sample, 9 momenta transfers simultaneously, 9m arm
- 1.5 meV energy resolution
- 20μm x 5μm spot size
- Measures energy and momentum distribution of lattice vibrations $S(\vec{q},\omega)$

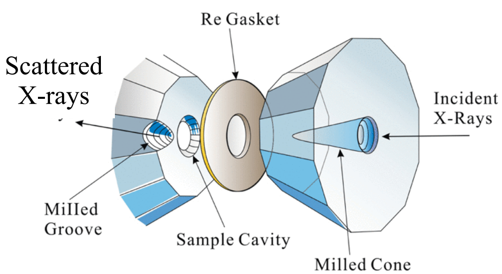


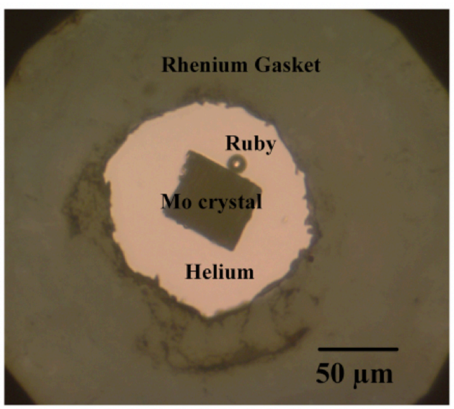


PHYSICAL REVIEW B **105**, 094105 (2022)

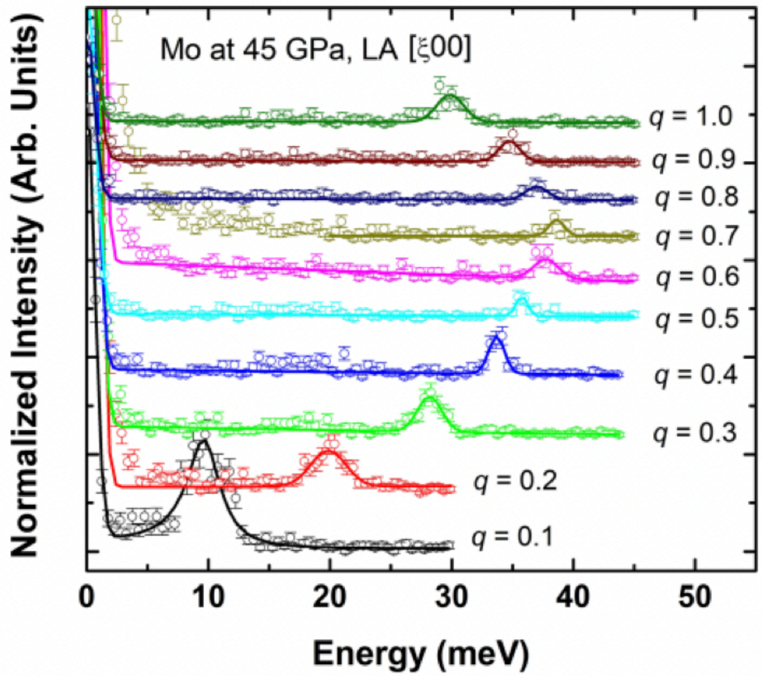
Kohn anomaly and elastic softening in body-centered cubic molybdenum at high pressure

Sample and environment

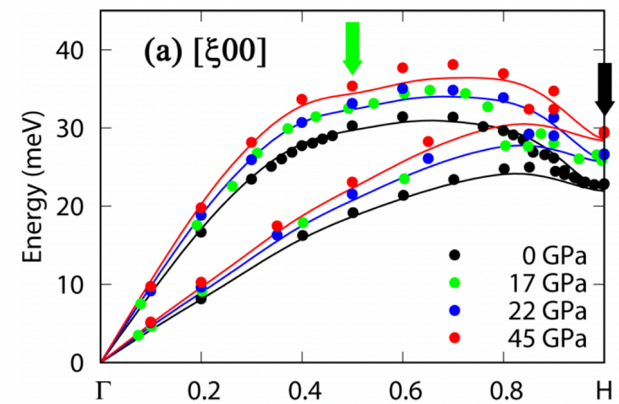




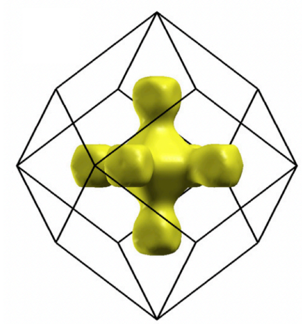
Raw IXS data



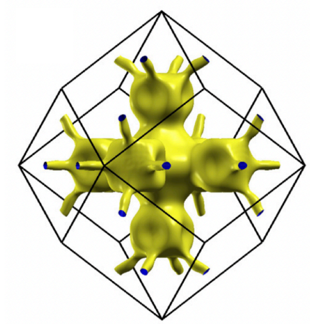
Pressure-dependent dispersion



Interpretation - fermi surface changes at high pressure



Low pressure FS



High pressure FS

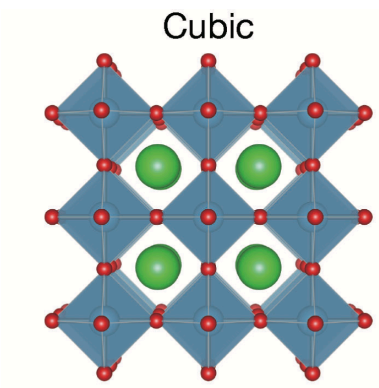
PHYSICAL REVIEW B **78**, 104121 (2008)

Central peak and narrow component in x-ray scattering measurements near the displacive phase transition in $SrTiO_3$

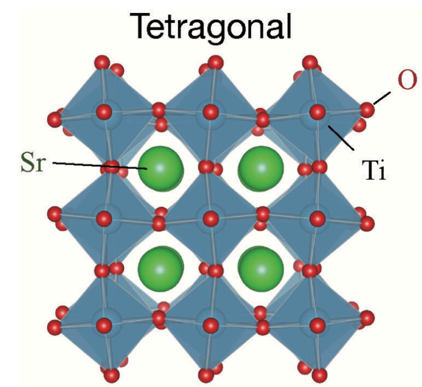
PHYSICAL REVIEW MATERIALS **1**, 070603(R) (2017)

Negative thermal expansion near two structural quantum phase transitions

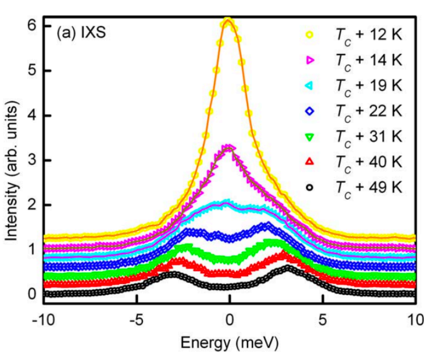
- Structural transitions can be described as the "freezing" of a phonon mode

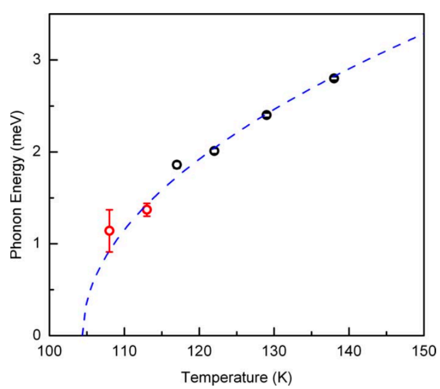


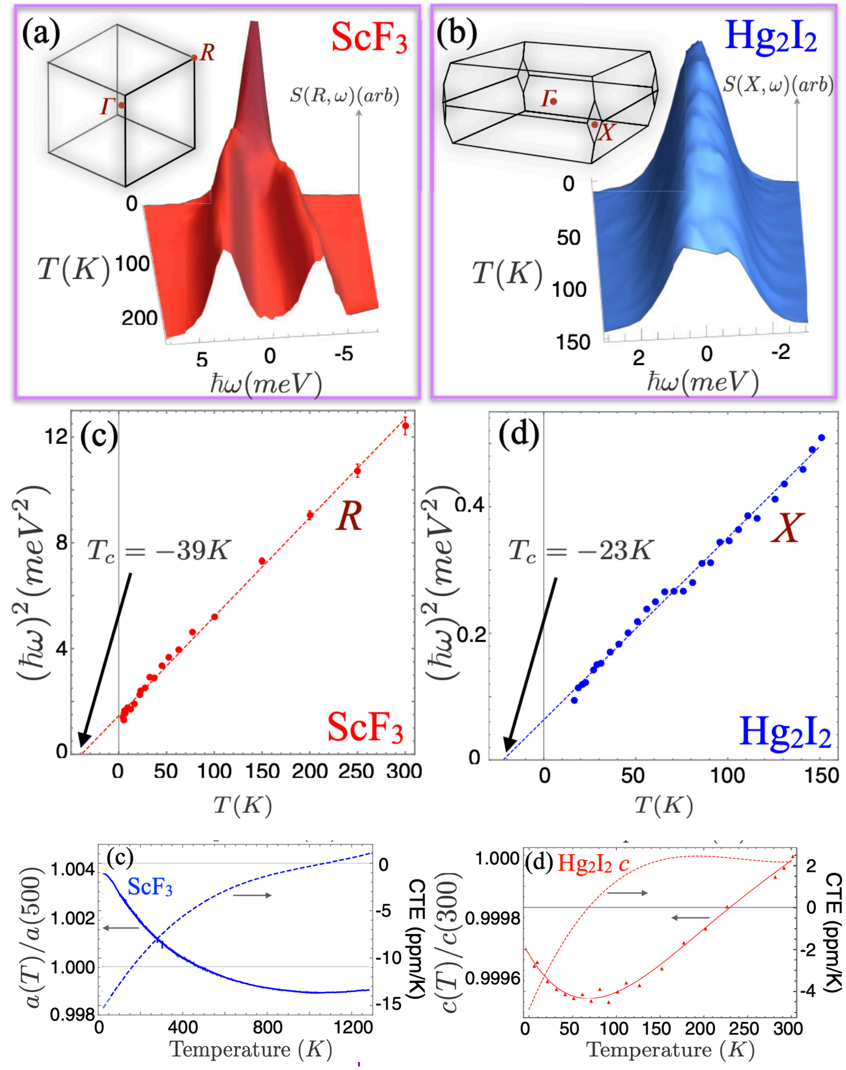
High temperature structure



Low temperature structure



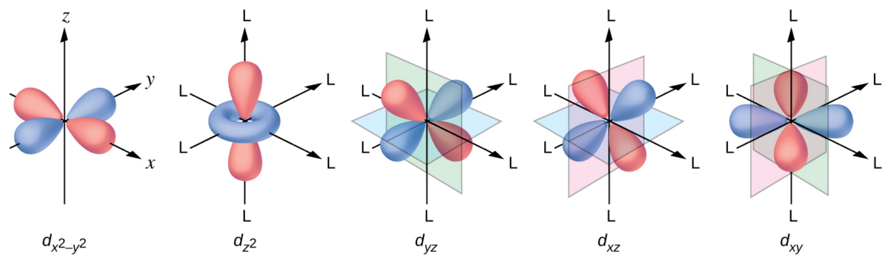


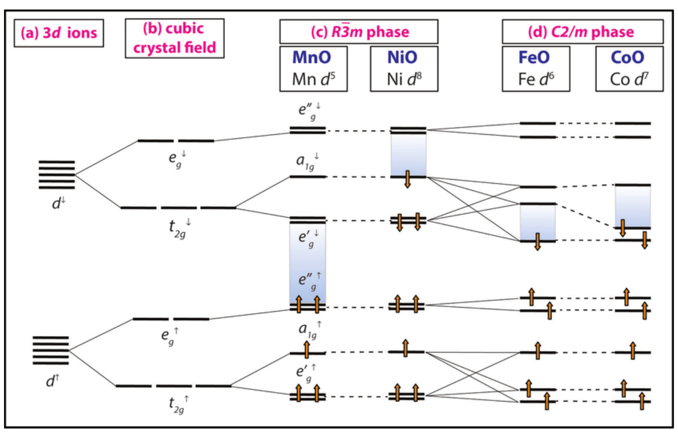


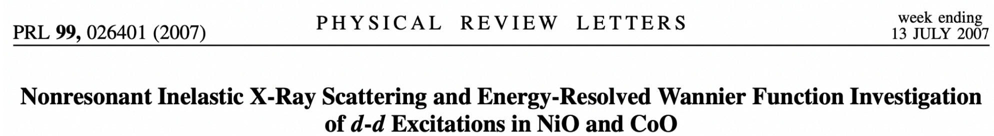
Journal of the Ceramic Society of Japan 127(6):404-408 (2019)

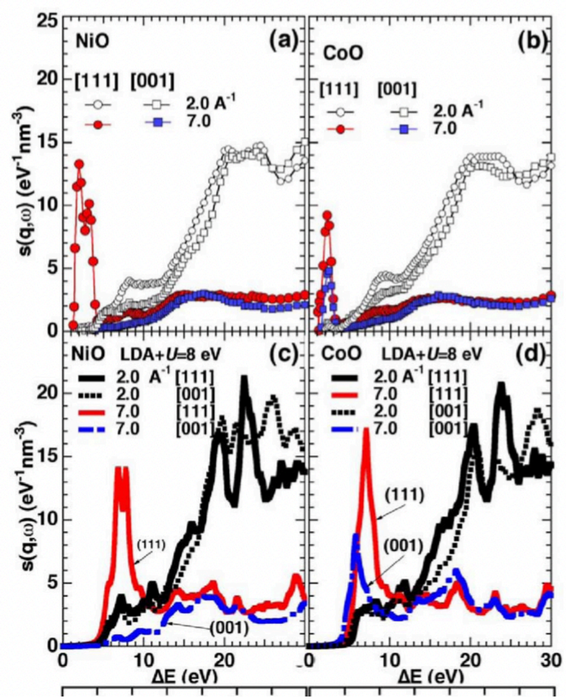
Non-phonon IXS-active excitations

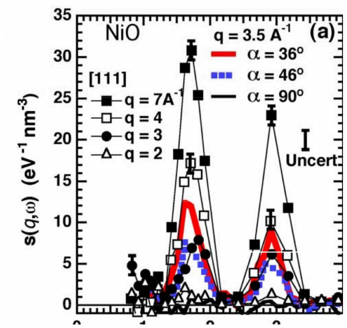
- Different d electron orbitals have different energy when placed in a crystal
- Gives rise to "crystal field excitations"

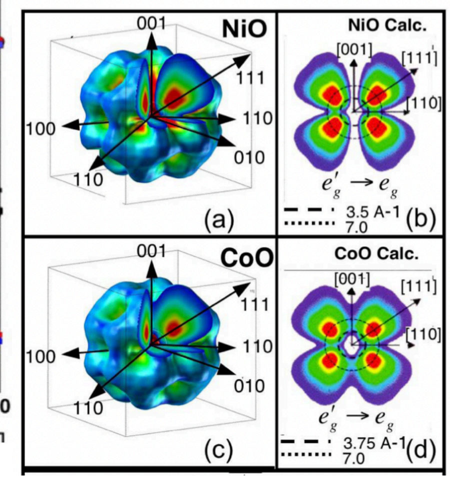






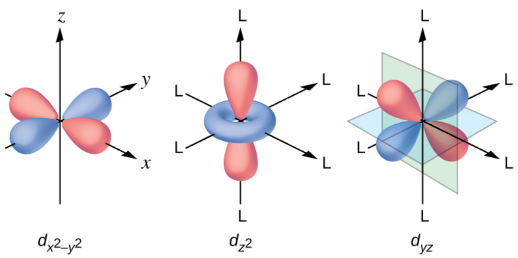


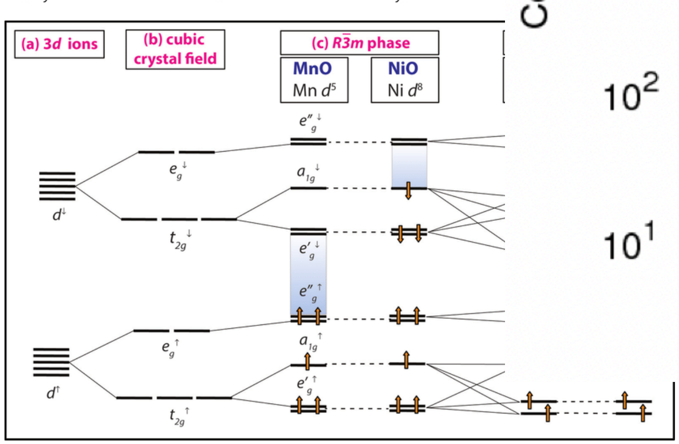


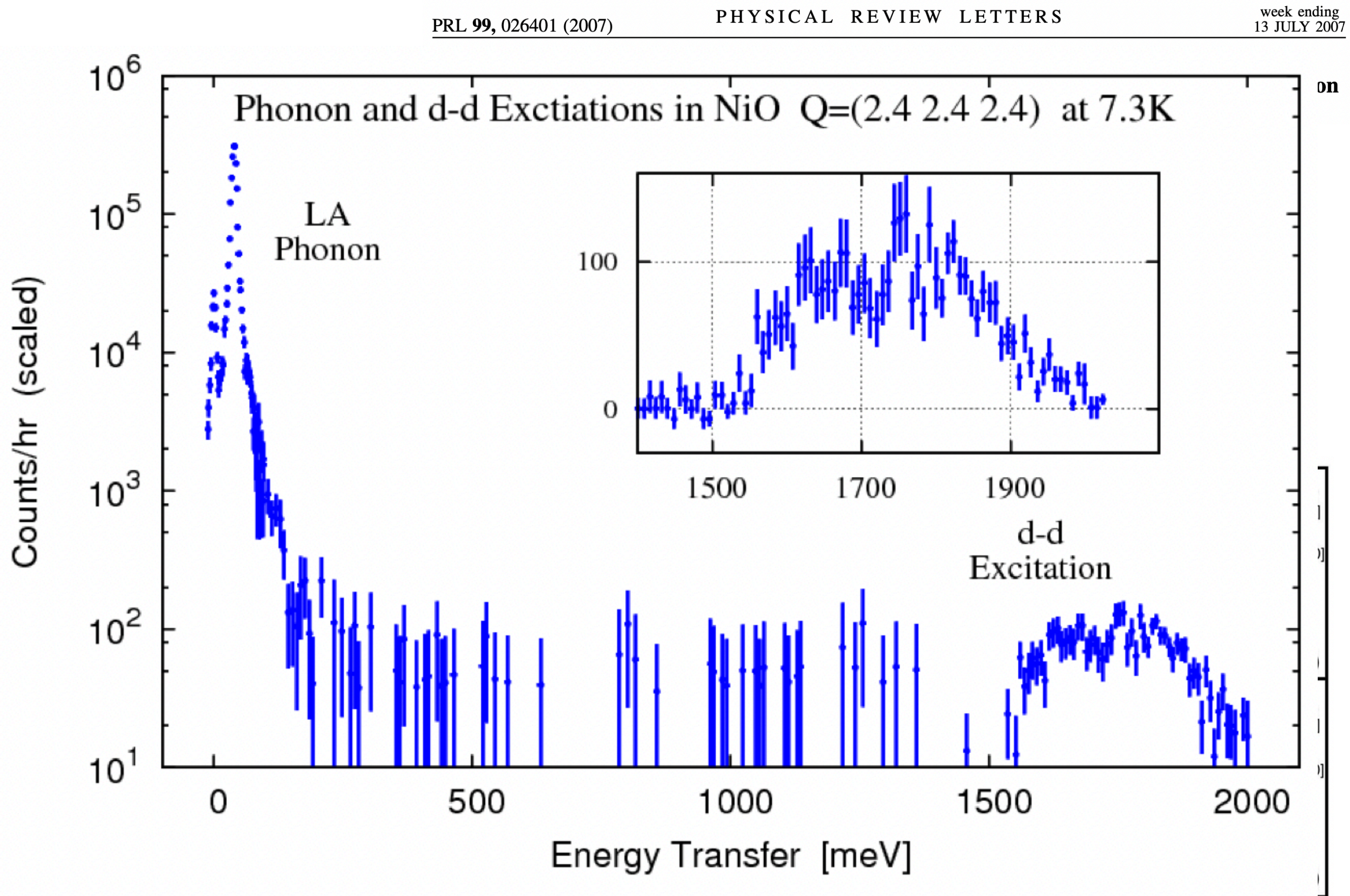


Non-phonon IXS-active excitations

- Different d electron orbit energy when placed in a
- Gives rise to “crystal fiel



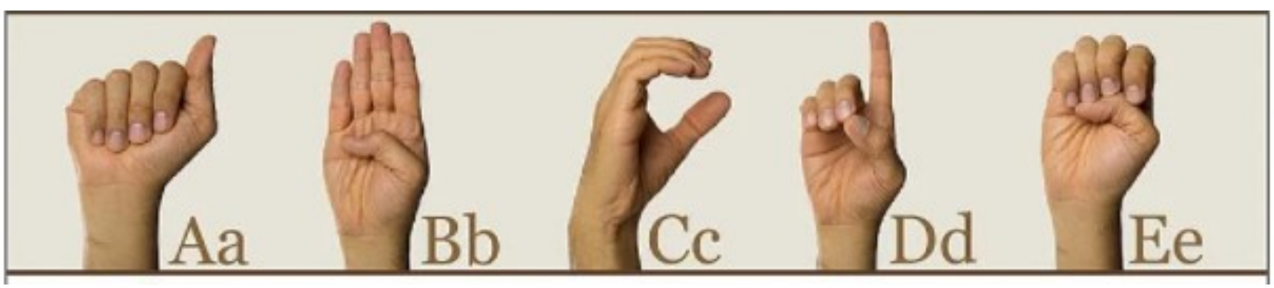




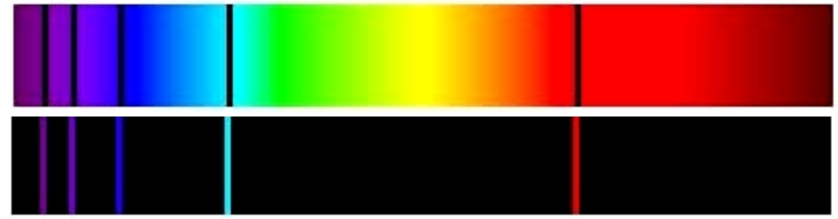
arXiv:1504.01098v7

What is this?

A	B	C	D	E
The emission spectrum of a star at z=0 redshift	A flat rainbow snake	A fashionable belt	Balmer series of emission by hydrogen	There is more than one correct answer

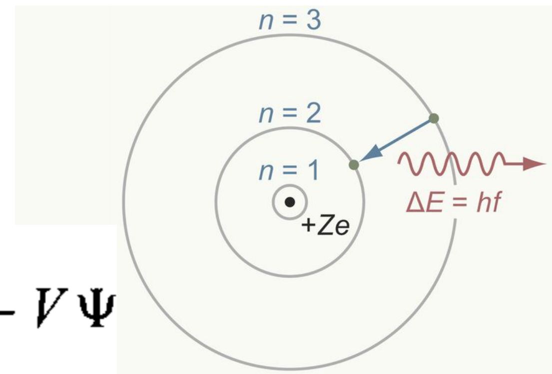


Balmer series



- Describes transitions between quantized energy levels in hydrogen (one proton, one electron)

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$



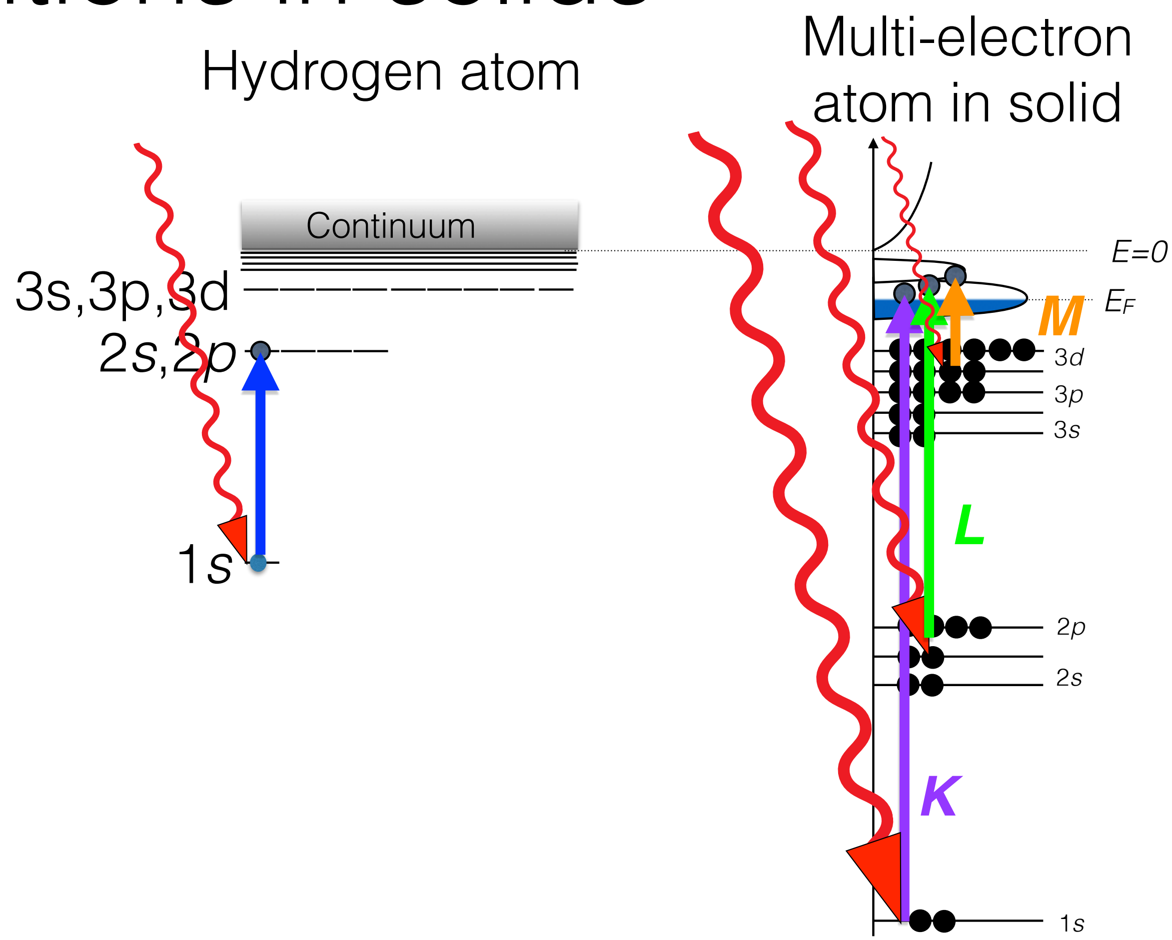
Schrodinger equation for 1/r potential: $$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

Hydrogen wavefunctions: $$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta, \phi)$$

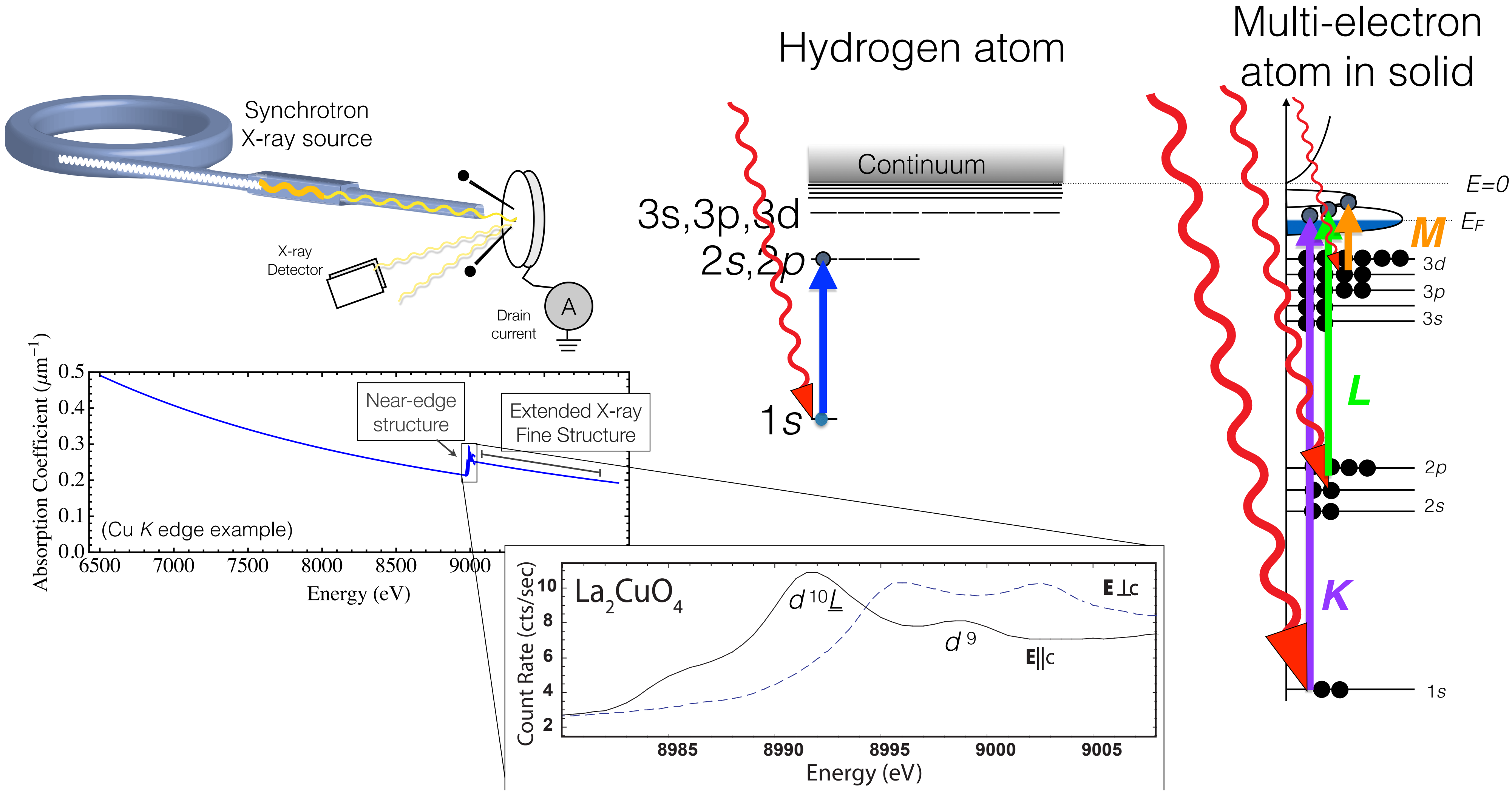
Energy levels: $$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

Bohr radius: $$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \times 10^{-10}\ \mathrm{m}$$

Atomic transitions in solids

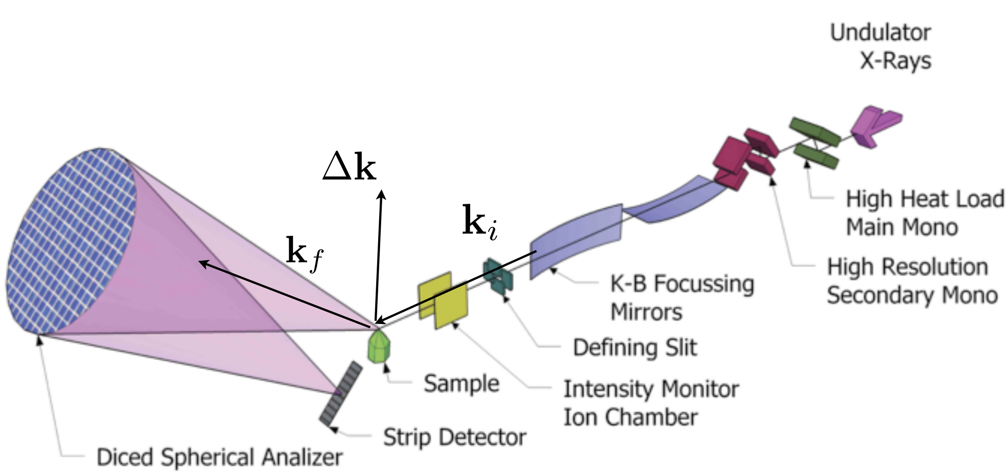


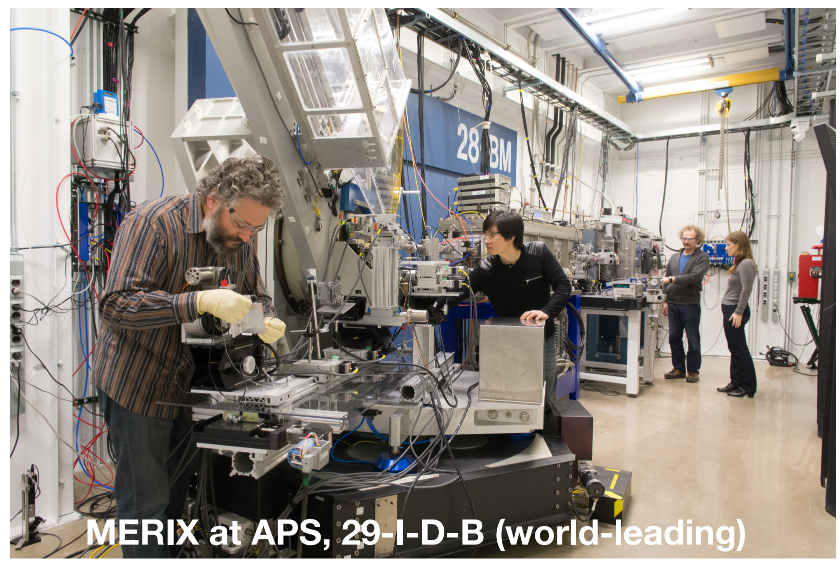
Atomic transitions in solids



RIXS - Resonant IXS

- Like IXS, but uses a resonant edge to enhance electronic signal
- Can excite electrons and things they couple to (phonons, magnons, excitons)
- Understanding resonances topic of next talk, some intro here

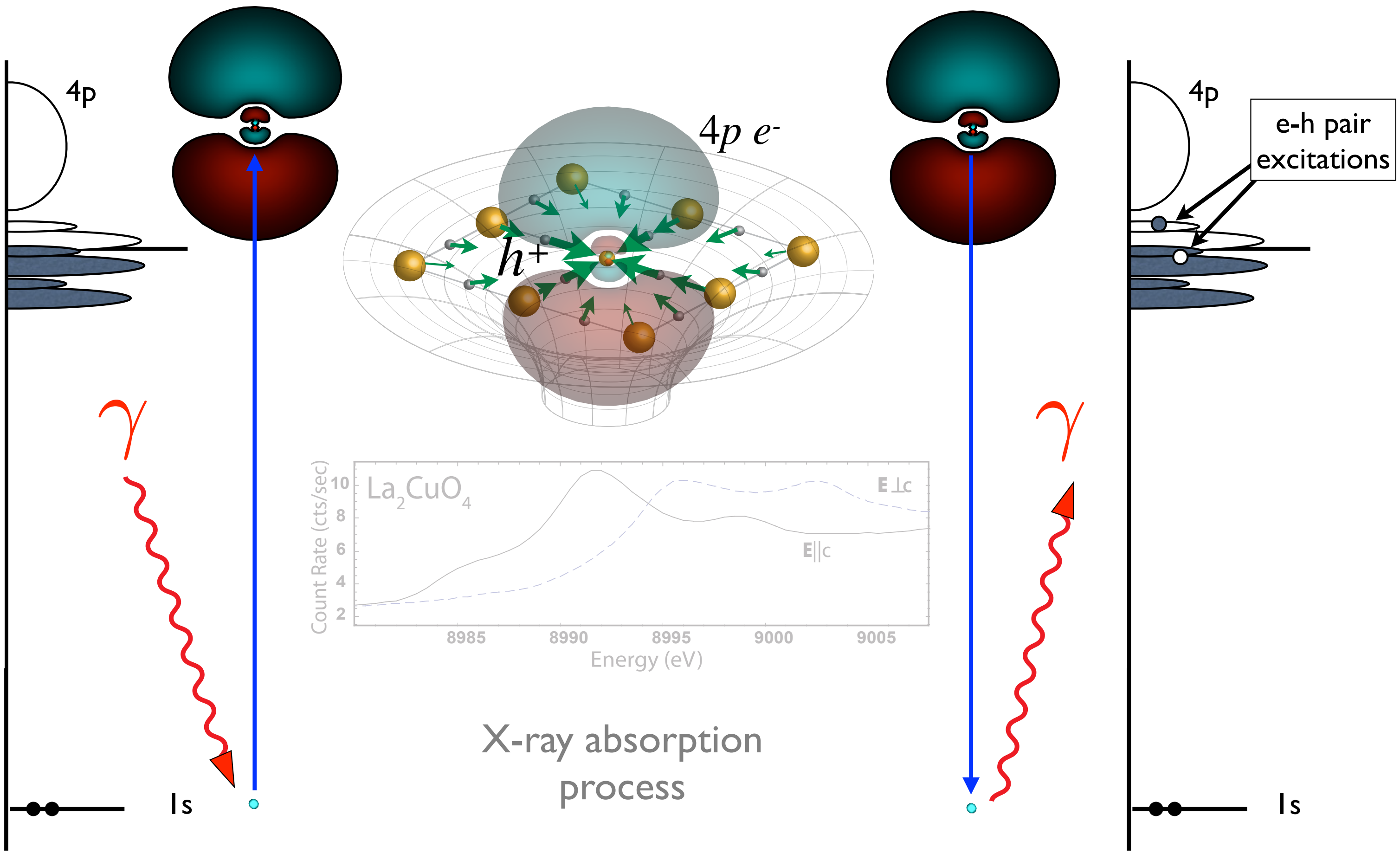




MERIX at APS, 29-I-D-B (world-leading)

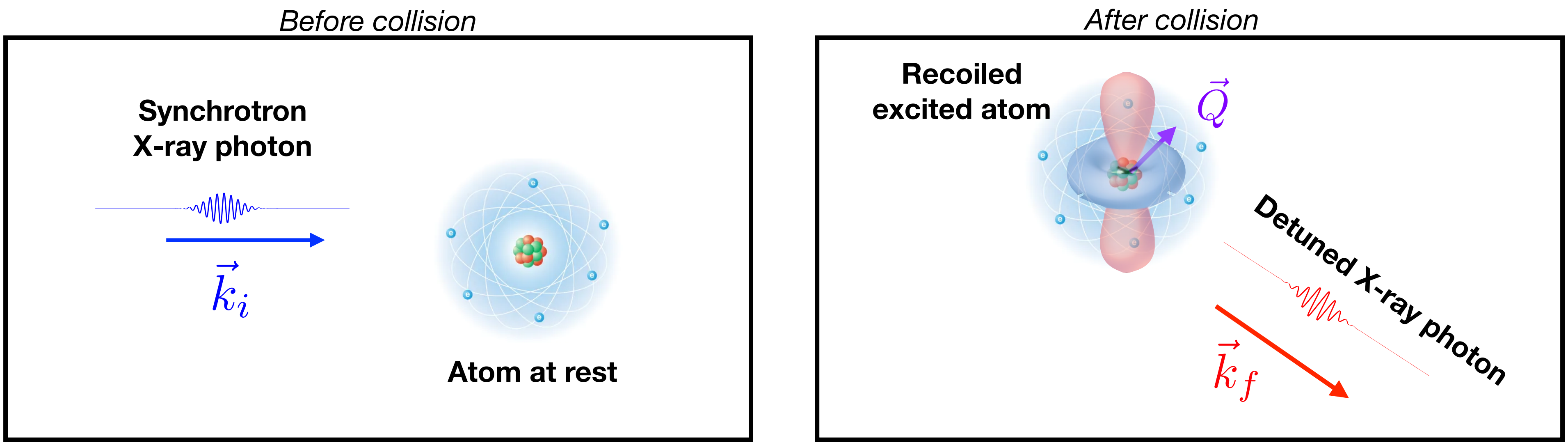
Kramers-Heisenberg:
$$\frac{d^2\sigma}{d\Omega_{k'} d(\hbar\omega_k')} = \frac{\omega_k'}{\omega_k} \sum_{|f\rangle} \left| \sum_{|n\rangle} \frac{\langle f|T^\dagger|n\rangle\langle n|T|i\rangle}{E_i - E_n + \hbar\omega_k + i\frac{\Gamma_n}{2}} \right|^2 \delta(E_i - E_f + \hbar\omega_k - \hbar\omega_k')$$

X-ray edge absorption… and RIXS



Copper *K* (example)

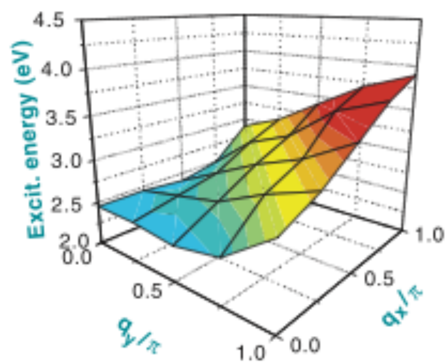
How do X-rays scatter from atoms… ….when they are tuned to an atomic resonance?



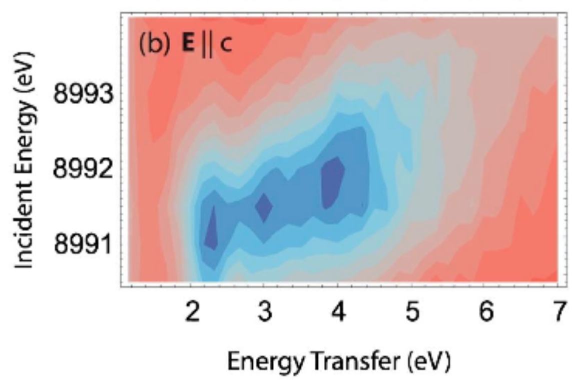
$\vec{Q} = \vec{k}_f - \vec{k}_i$ is the momentum delivered to the atom

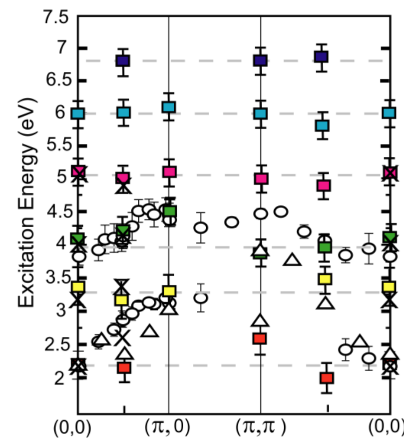
- On resonance, an X-ray can cause an atom to recoil ***and*** become electronically or magnetically excited in a momentum conserving collision

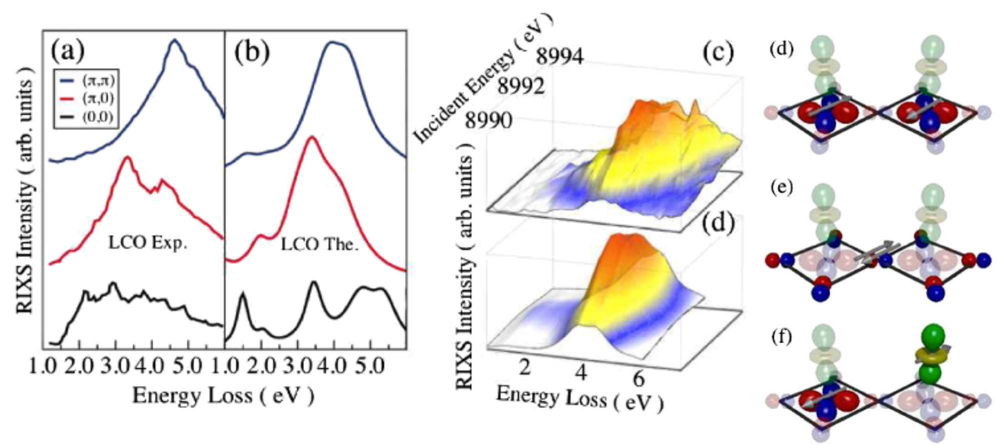
Mott gap dispersion in high-Tc cuprates



from Hasan, Science 288, 1811 (2000)

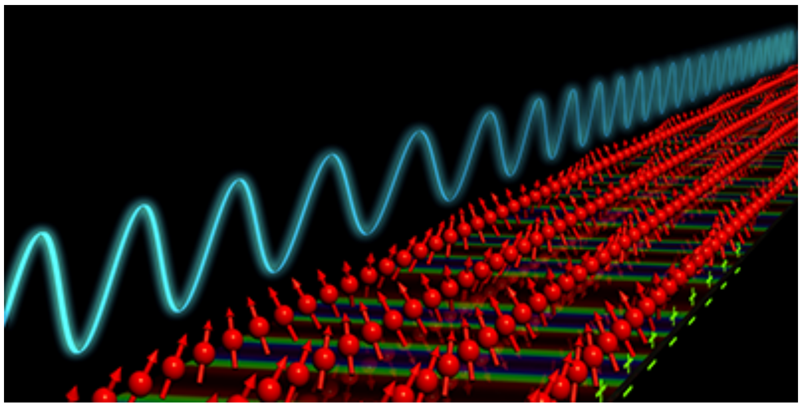


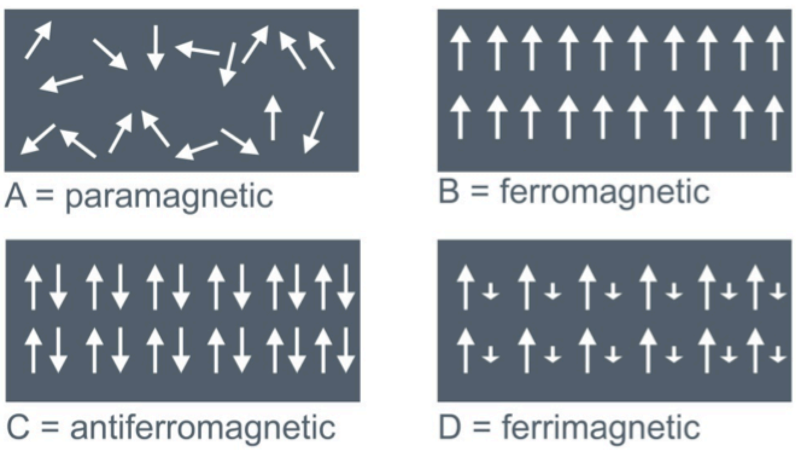




Lu *et al.* *PRL* **95**, 217003 (2005)
Lu *et al.* *PRB* **74**, 224509 (2006)
Chen *et al.* *PRL* **105**, 177401 (2010)
Chabot-Couture *et al.* *PRB* **82**, 035113 (2010)

Magnetically-ordered states

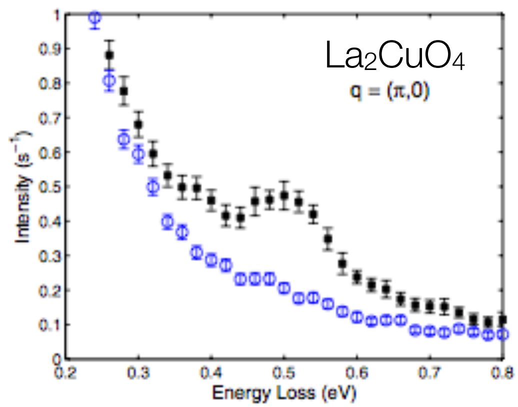




- Magnetic interactions between magnetic ions can lead to ordered states
- Disturbance in order forms “spin waves” or “magnons”
- Like sound, magnons carry momentum and energy
- Dispersion relation is important

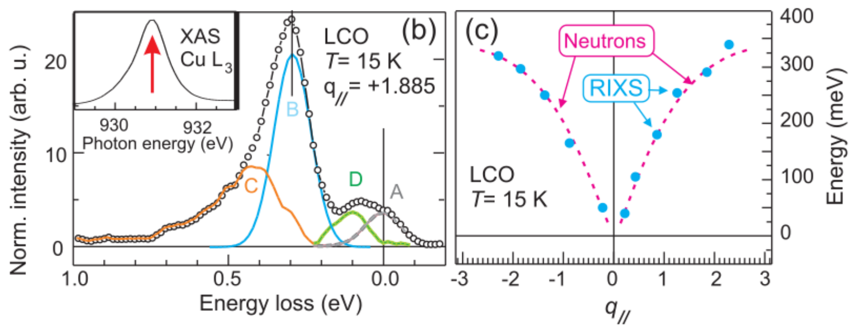
Magnetic excitations via RIXS

- 2008 Cu K edge RIXS showed bi-magnon feature, consistent with Raman q=0 result



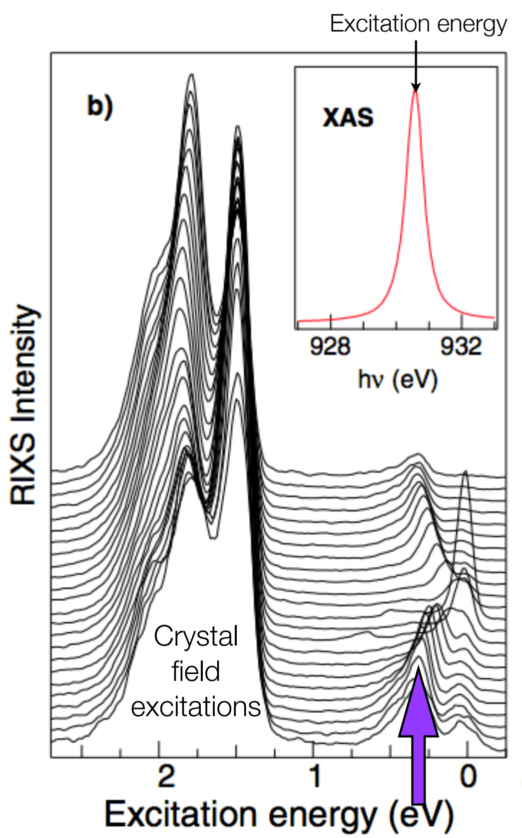
Hill, Blumberg, et al, PRL 100 097001 (2008)

- 2009 Cu L edge (soft X-ray) RIXS showed a shoulder of elastic line consistent with *single*-magnon excitation

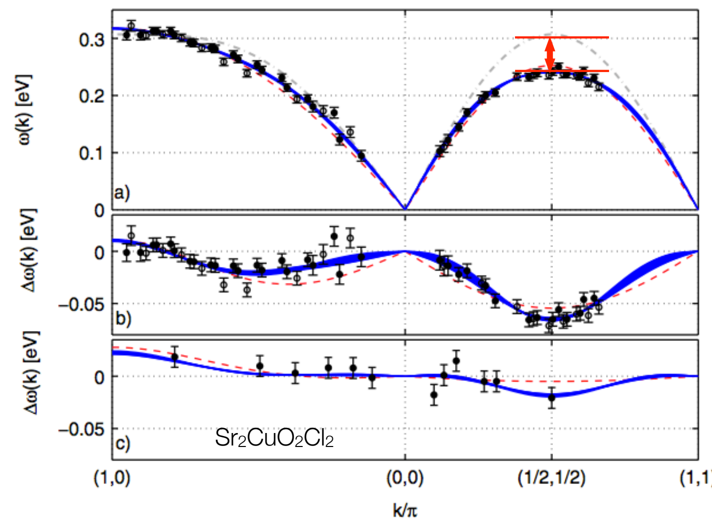


Braicovich, Ghiringhelli, et al, PRL 102 167401 (2009)

Extended interactions in a Mott insulator $Sr_2CuO_2Cl_2$



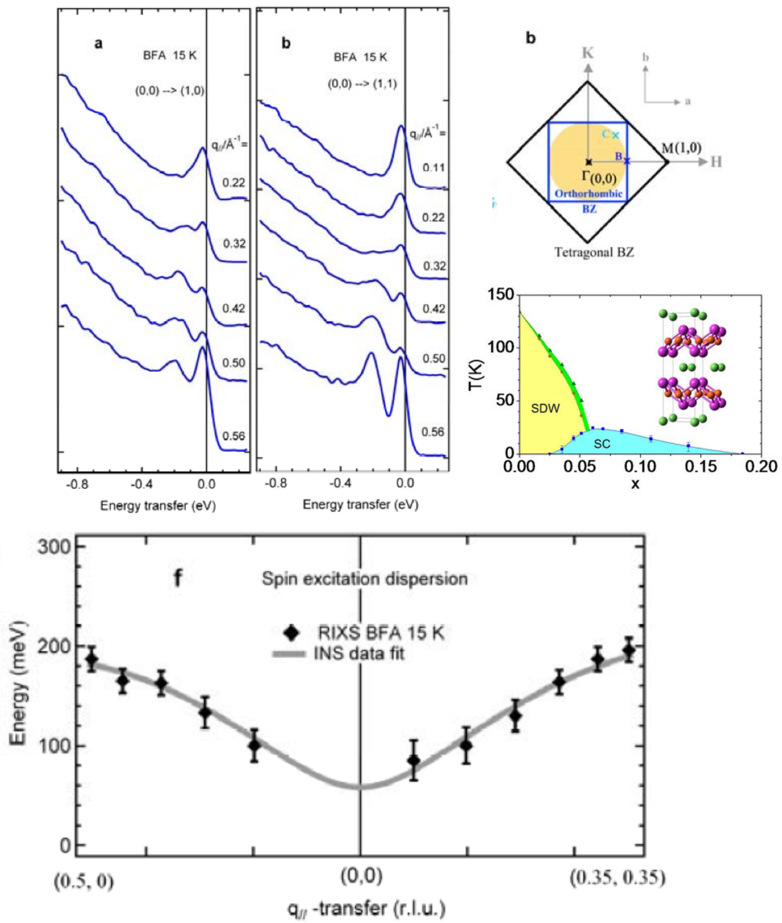
Guarise, ...JNH,... *et al. PRL* **12**, 033001 (2010)



- Suggestive of extended magnetic interactions in 2D Mott insulator

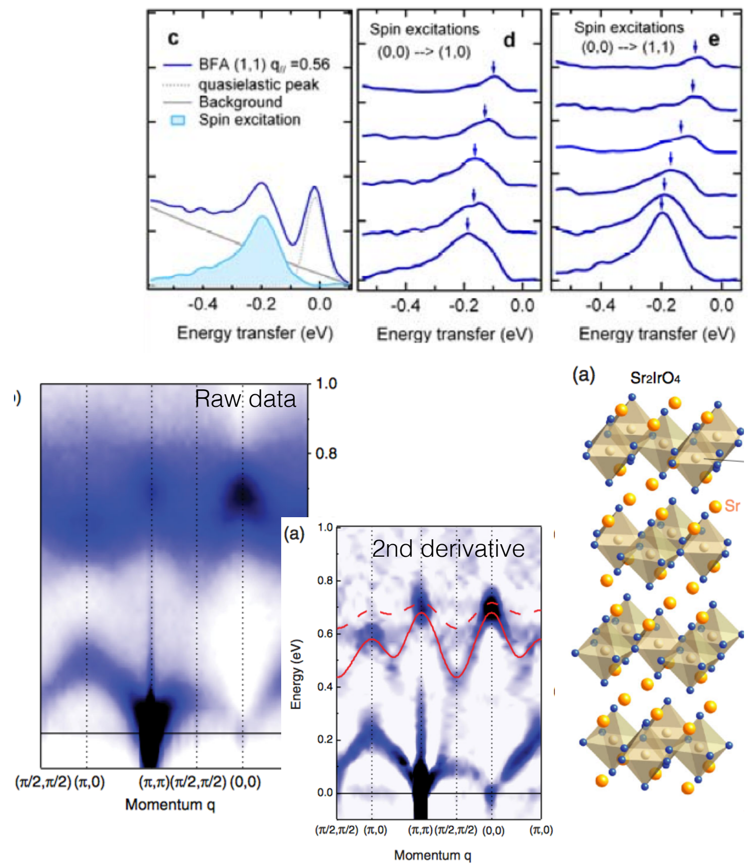
Iron pnictide superconductors and Correlated 5d systems

$BaFe_2As_2$



Zhou, et al, *Nature Comm.* **4**, 1470 (2013)

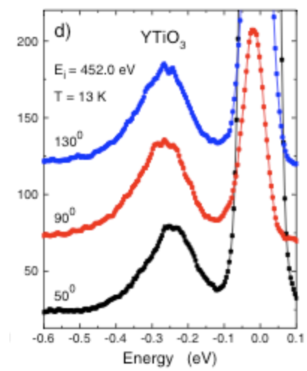
$SrIr_2O_4$



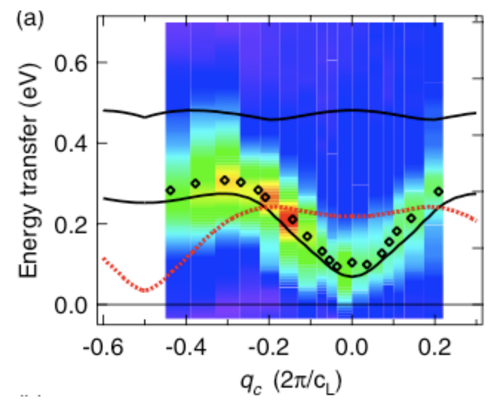
Kim, et al, Phys. Rev. Lett. **108**, 177003 (2012)

Other RIXS highlights

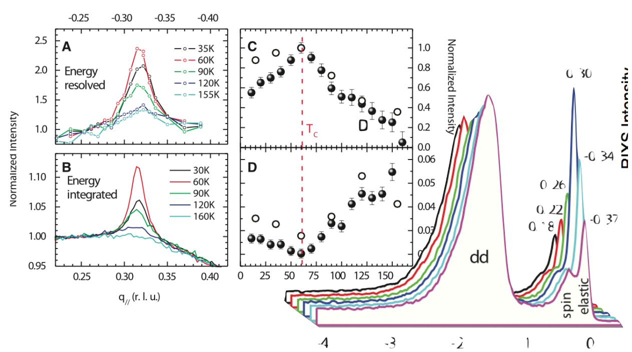
- **Orbiton** dispersion
- **Phonons** excited through core hole intermediates
- **Spin-2** (triplon) excitations
- **Incipient CDW** effect at Tc in YBCO
- **Paramagnon fluctuations** in doped cuprates



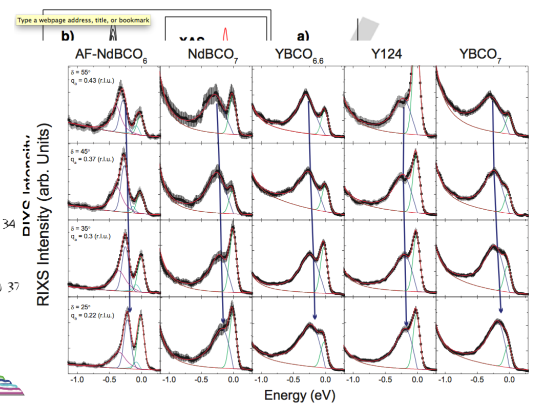
Ulrich, *et al PRL* **103**, 107205 (2009)



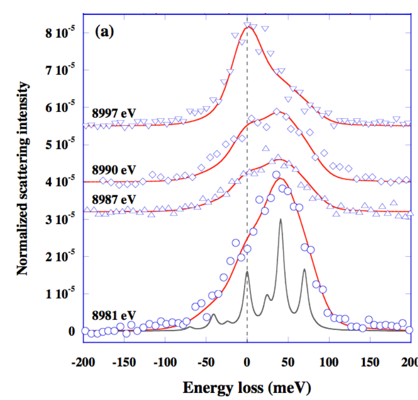
Schlappa, *et al PRL* **103**, 047401 (2009)



Ghiringhelli, et al Science 337, 821 (2012)



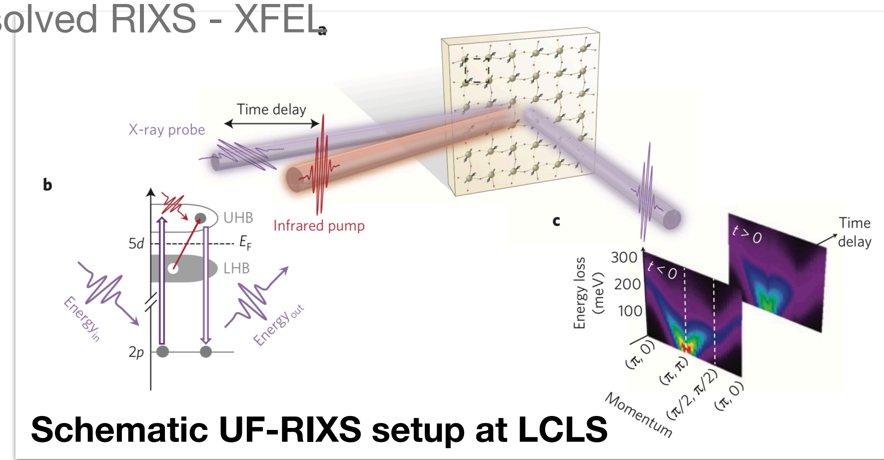
Le Tacon, et al, *Nat. Phys.* 2011



Yavas, et al JPCM **22**, 485601 (2010)

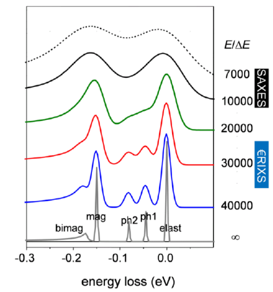
Future technique directions with RIXS

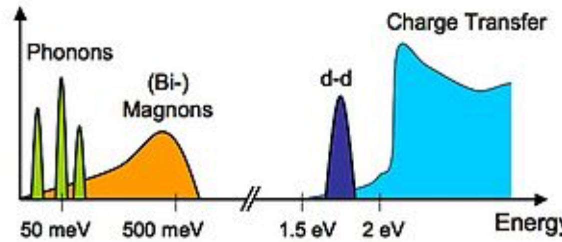
- Time-resolved RIXS - XFEL



Schematic UF-RIXS setup at LCLS

- Higher energy resolution

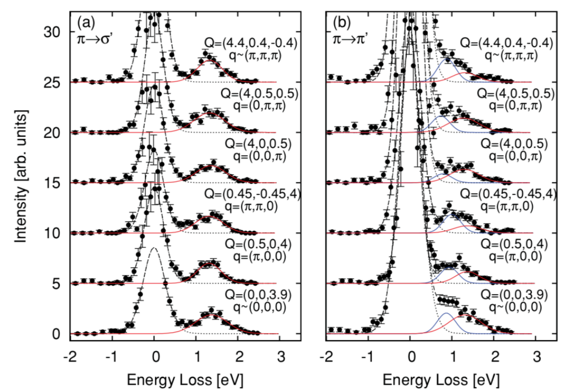




Energy scales in correlated electron systems

- Tender X-ray RIXS - new edges and opportunities

- Polarization analysis of scattered photon



High potential to resolve subtle changes, identify excitation channels

Thank you!

jason.hancock@uconn.edu