X-rays and Neutrons for the study of structure and dynamics:

Complementarity and Competition

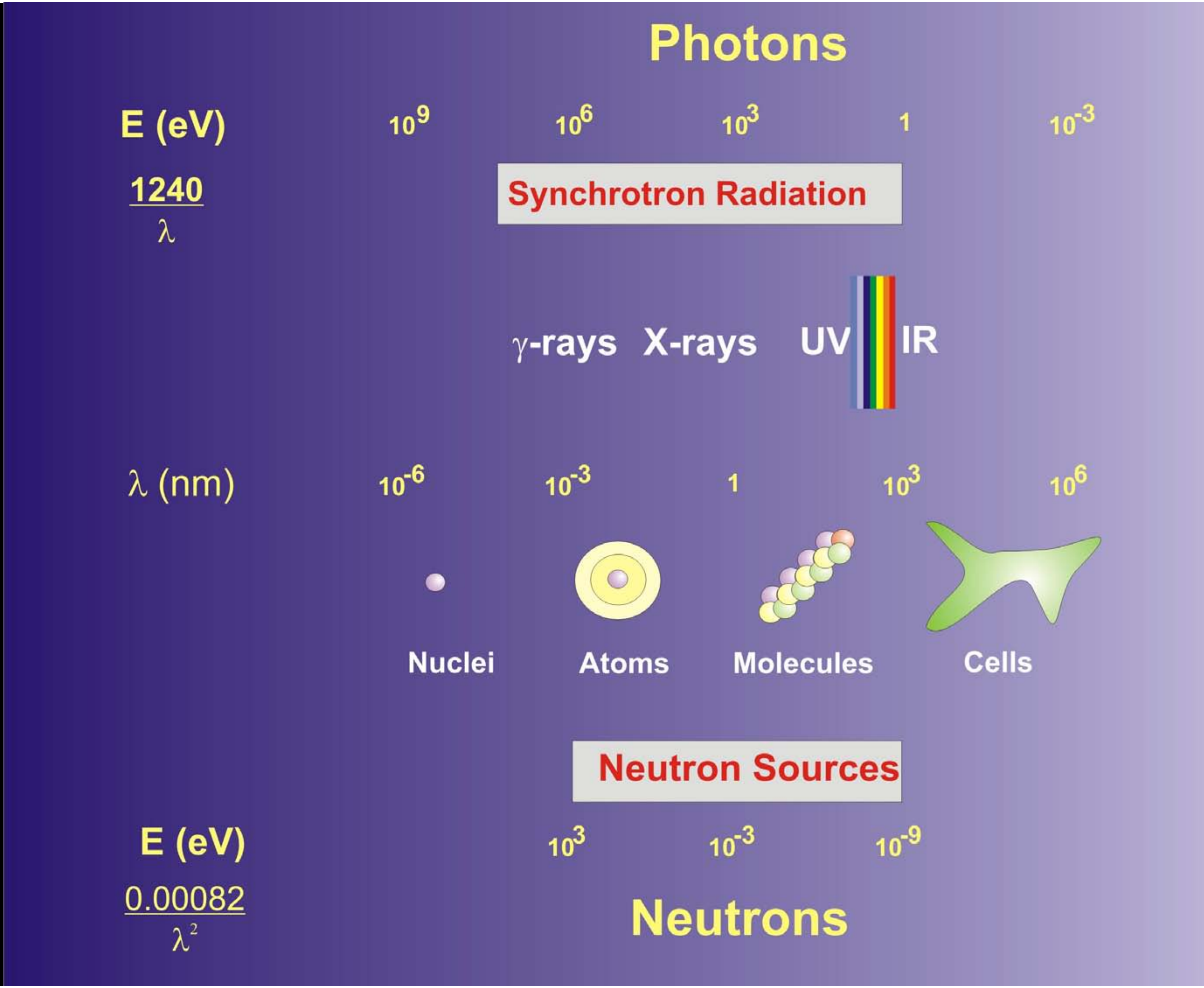
Des McMorrow

University College London/ISIS


DASH

Outline

- General considerations
  - Basic properties of probes
  - Interactions
  - Sources
- Lattice dynamics
  - Primer
  - Classical determination of phonons by neutron scattering
  - Inelastic X-ray scattering
  - Superconductivity in MgB_2
  - Phonon dispersion in superconducting CaC_6
- Magnetism
  - Magnetic structure of the rare earths: neutrons and x-rays
  - Development of x-ray resonant scattering (XRS) techniques
  - Application of XRS to $PrBa_2Cu_3O_{6+x}$
  - Orbital and Multipolar order
- Conclusions



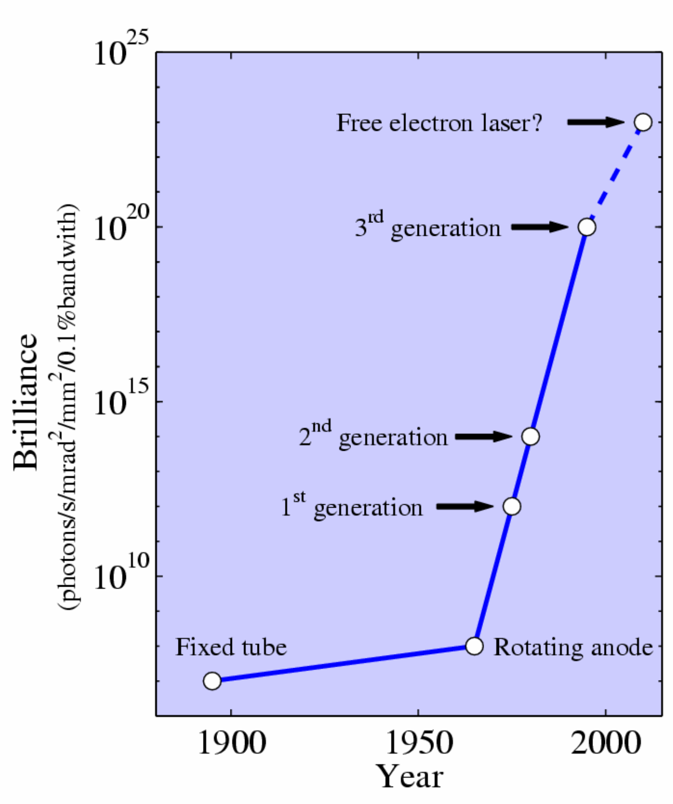
Photons
E (eV)
10^9
10^6
10^3
1
10^{-3}
$\frac{1240}{\lambda}$
Synchrotron Radiation
γ-rays
X-rays
UV
IR
λ (nm)
10^{-6}
10^{-3}
1
10^3
10^6
Nuclei
Atoms
Molecules
Cells
Neutron Sources
E (eV)
10^3
10^{-3}
10^{-9}
$\frac{0.00082}{\lambda^2}$
Neutrons

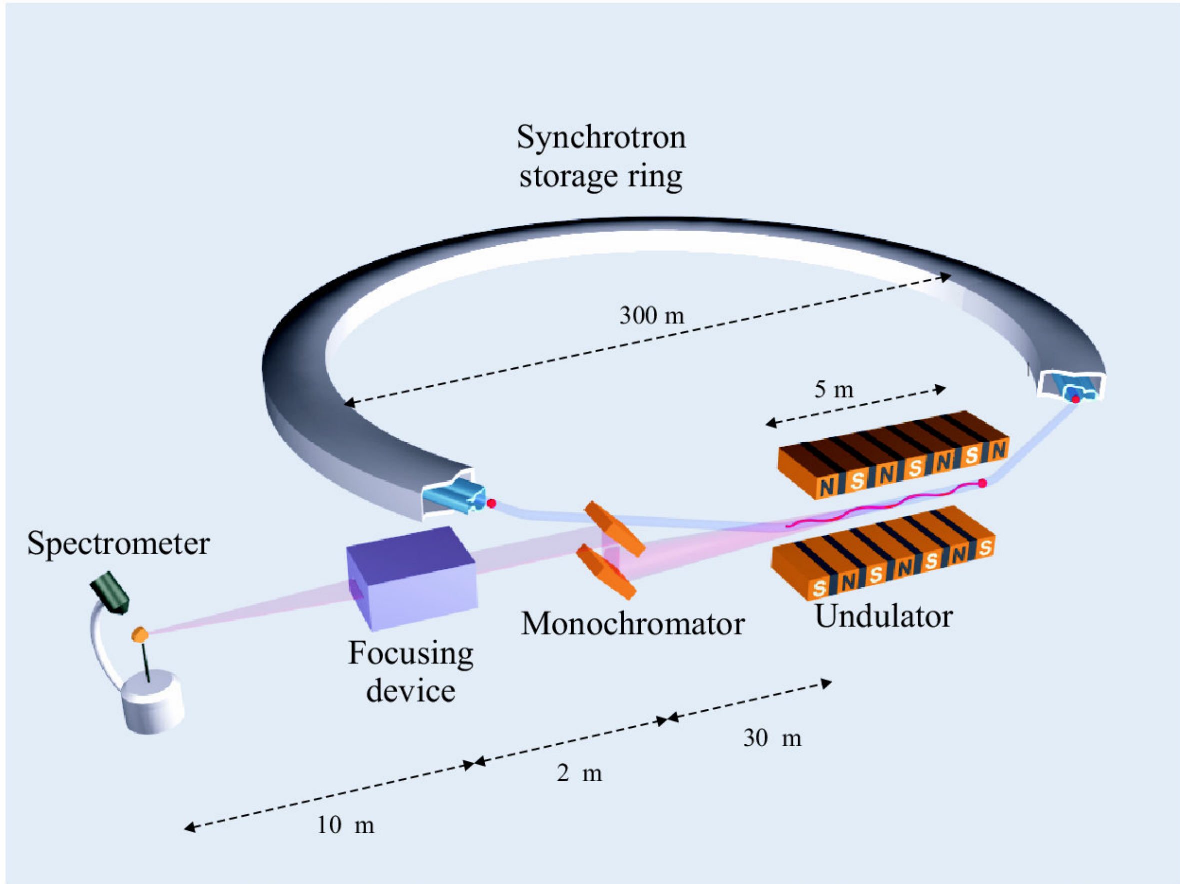
Basic Properties and Interactions

	Neutron	Photon
Charge:	0	0
Mass:	1.675×10^{-27} Kg	0
Spin:	½	1
Magnetic Moment:	$-1.913\ \mu_N$	0
Momentum:	$m\underline{v} \equiv \hbar k$	$\hbar k$
Energy:	$\frac{1}{2} mv^2 \equiv \hbar^2 k^2/2m$	$\hbar\omega = hc/\lambda$
Sensitivity to Structure:	$b \sim O(r_0)$ (Short range nuclear forces)	$r_0 = 2.82 \times 10^{-5}$ Å (E field photon and e)
Sensitivity to Magnetism:	$b_{mag} \sim r_0$ $(\mu_n.B_{dipp})$	$r_0(\hbar\omega/mc^2)$ (E, H field photon and e and μ_B)

X-ray and Neutron Sources

Modern X-ray Sources: Synchrotron Radiation





Importance of Lattice Dynamics

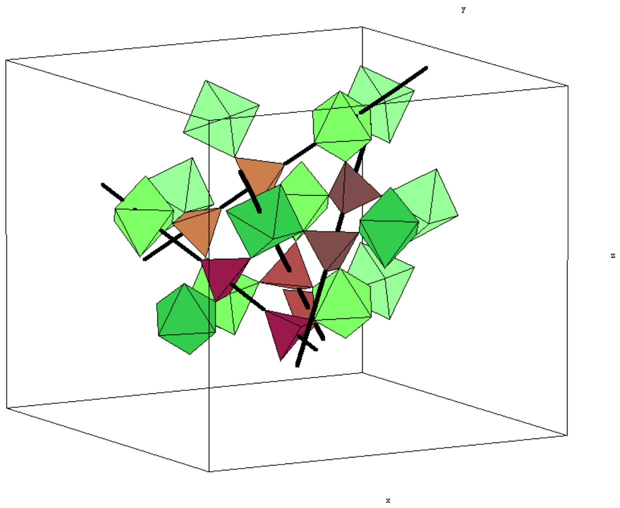
•Basic thermodynamic properties of solids

•“What atoms do” (Brockhouse), i.e. how they interact

•Phase transitions: Soft modes, etc.

•Anomalous properties of Matter, e.g. negative thermal expansion

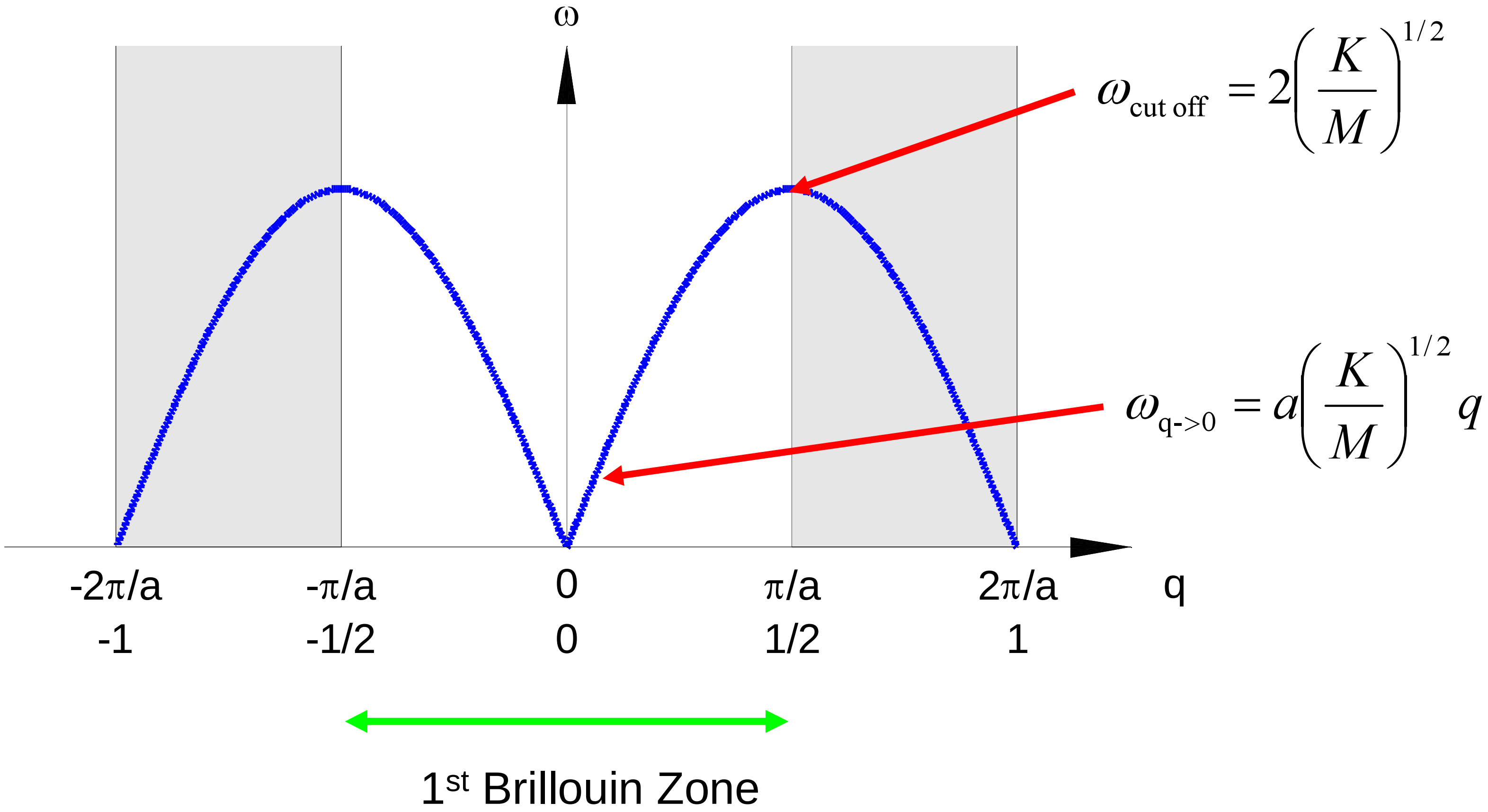
•Electron-phonon interactions, e.g. superconductors



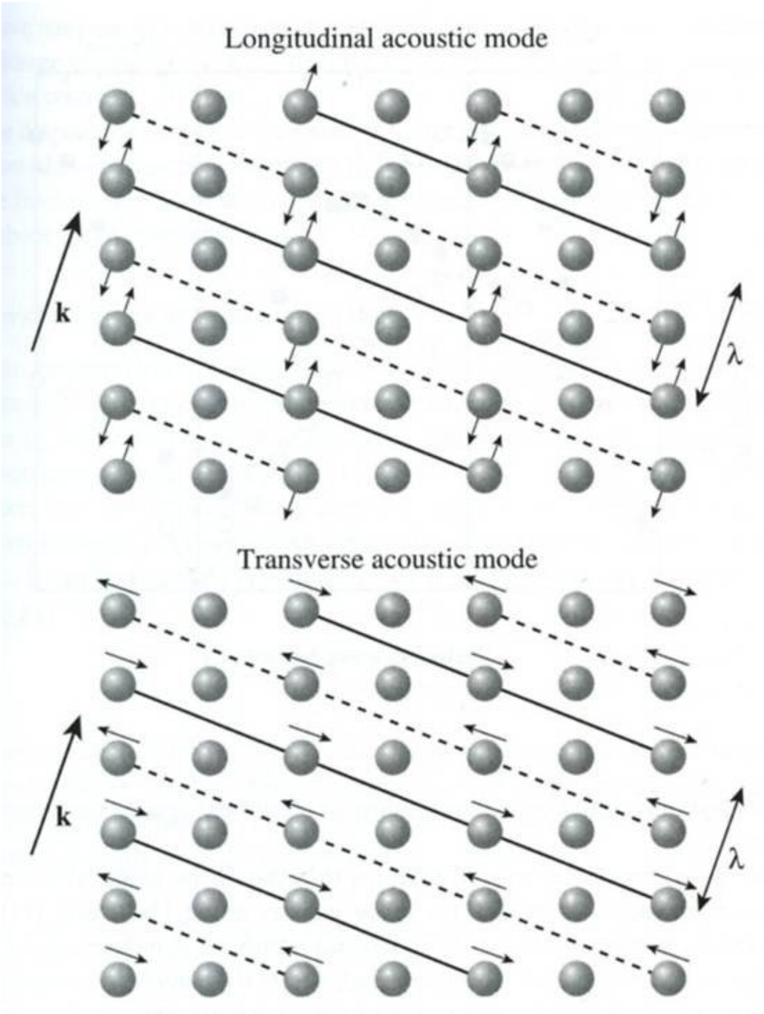
Lattice Dynamics

Harmonic approximation for a 1D Monoatomic Chain

$$\hbar\omega = 2\left(\frac{K}{M}\right)^{1/2} \left|\sin(qa/2)\right| \qquad \text{with} \quad K = \left(\frac{\partial^2 V}{\partial r^2}\right)_{r=a}$$



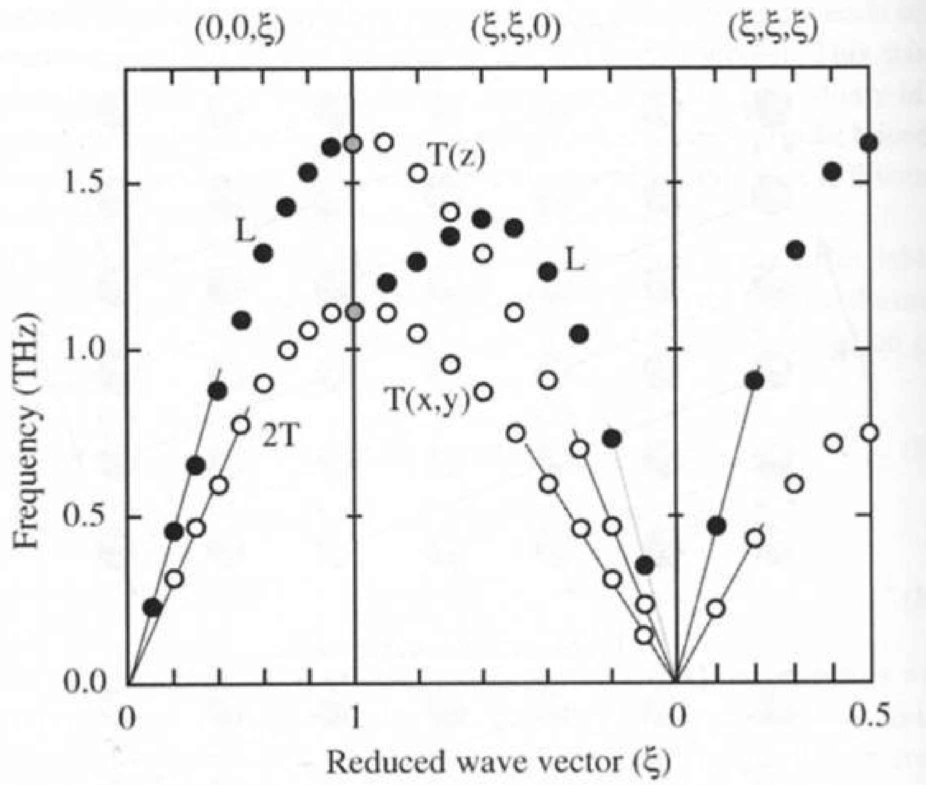
Dispersion Curves in 3D Monoatomic Crystals



- Displacements *u* now refer to planes of atoms
- Motion both Transverse and Longitudinal to direction of propagation, both described by same type of equation
- Expect in general 2 TA modes and 1 LA mode
- Degeneracies can arise along specific directions (3, 4 and 6-fold rotation axes)

Dispersion Curves in FCC Crystals

Neutron Spectroscopy

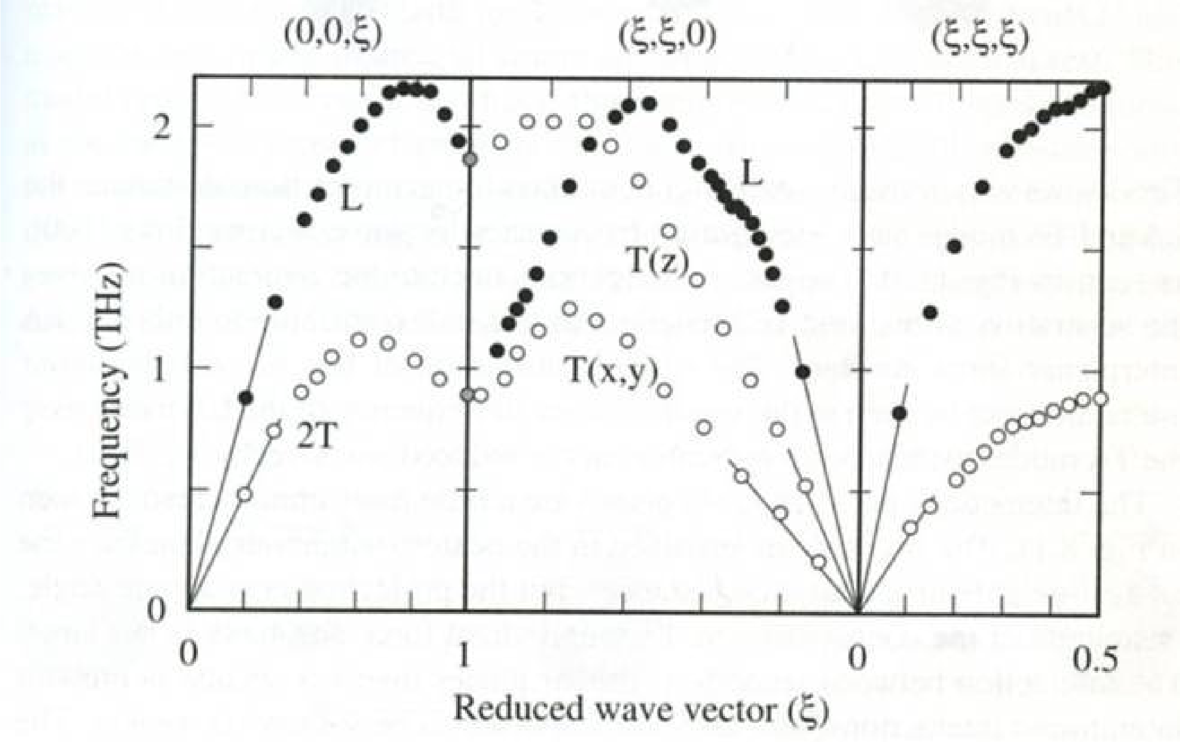


Neon

- •TA modes for [001] (4-fold) and [111] (3-fold) are degenerate
- •TA modes along [110] (2-fold) are split
- •Dispersion along [001] and [111] follow simple sinusoidal dispersion
- •Dispersion along [110] more complex due to 2nd nn coupling
- •Special symmetries exist: LA and one TA mode become degenerate at ZB along [110]. Why?

Dispersion Curves in FCC Crystals

Lead (Metal)

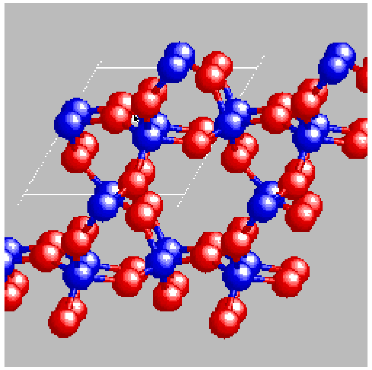


- Similar to dispersion in rare gas solids

•[001] shows indication of NNN interaction

•[110] displays glitches when q=(1/3,1/3,0) due to Kohn anomalies, when q matches that of the Fermi surface. Indication of electron-phonon coupling.

3D Crystals with Polyatomic Basis



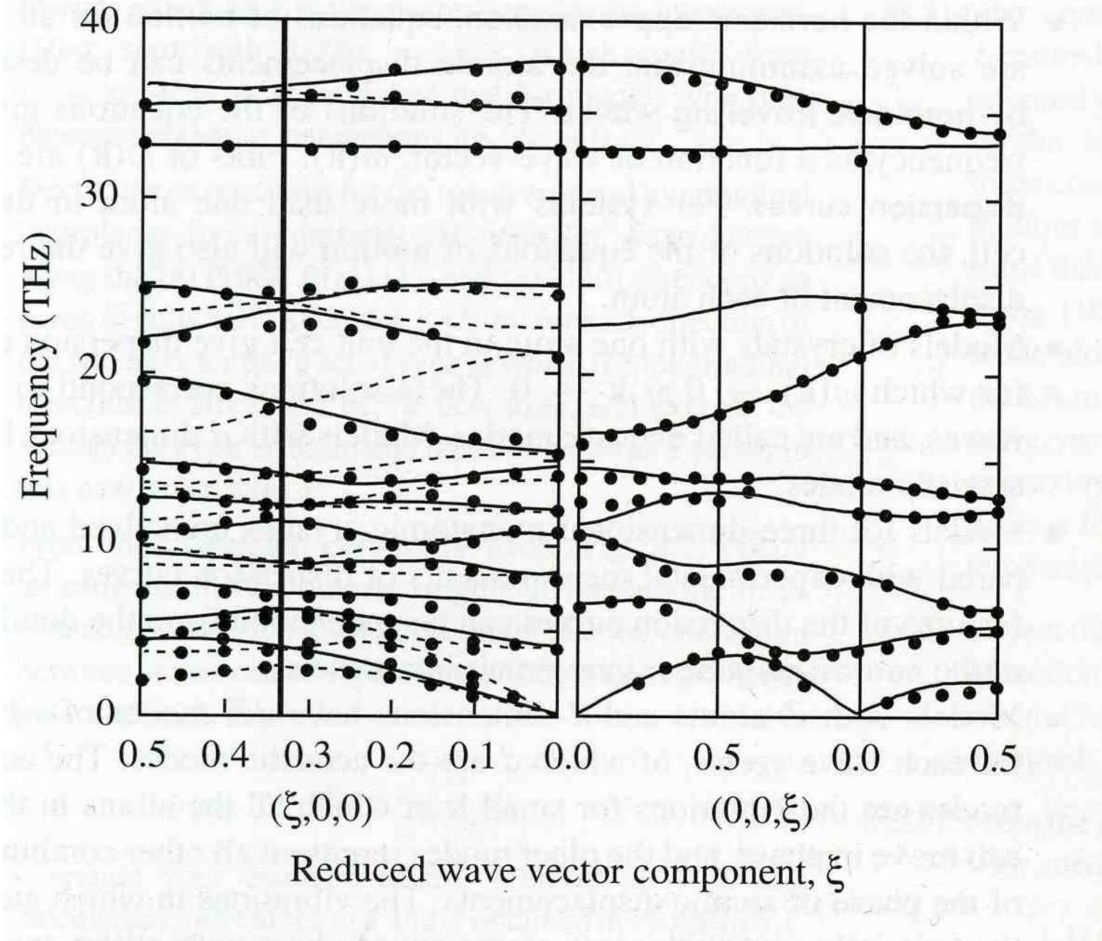
•Quartz, SiO_2, has 9 atoms per unit cell

•27 branches:
3 acoustic, 24 optic

•Spectrum extends to 40 THz, reflecting the strong covalent bonding, especially stretching of Si-O bonds

•Forces are 25 times greater than in NaCl ($\omega^2 \propto K$)

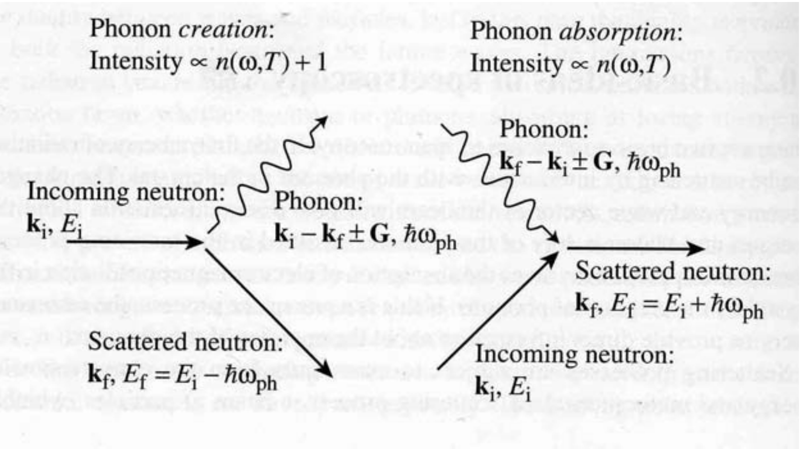
Quartz



Measurement of Phonon Dispersion Curves

Conservation of Energy

$$\pm\hbar\omega = E_i - E_f$$



Conservation of *Crystal* Momentum

$$\pm\hbar\mathrm{q} = \hbar\mathrm{k}_\mathrm{i} - \hbar\mathrm{k}_\mathrm{f} \pm \hbar\mathrm{G}$$
$$= \hbar\mathrm{Q} \pm \hbar\mathrm{G}$$

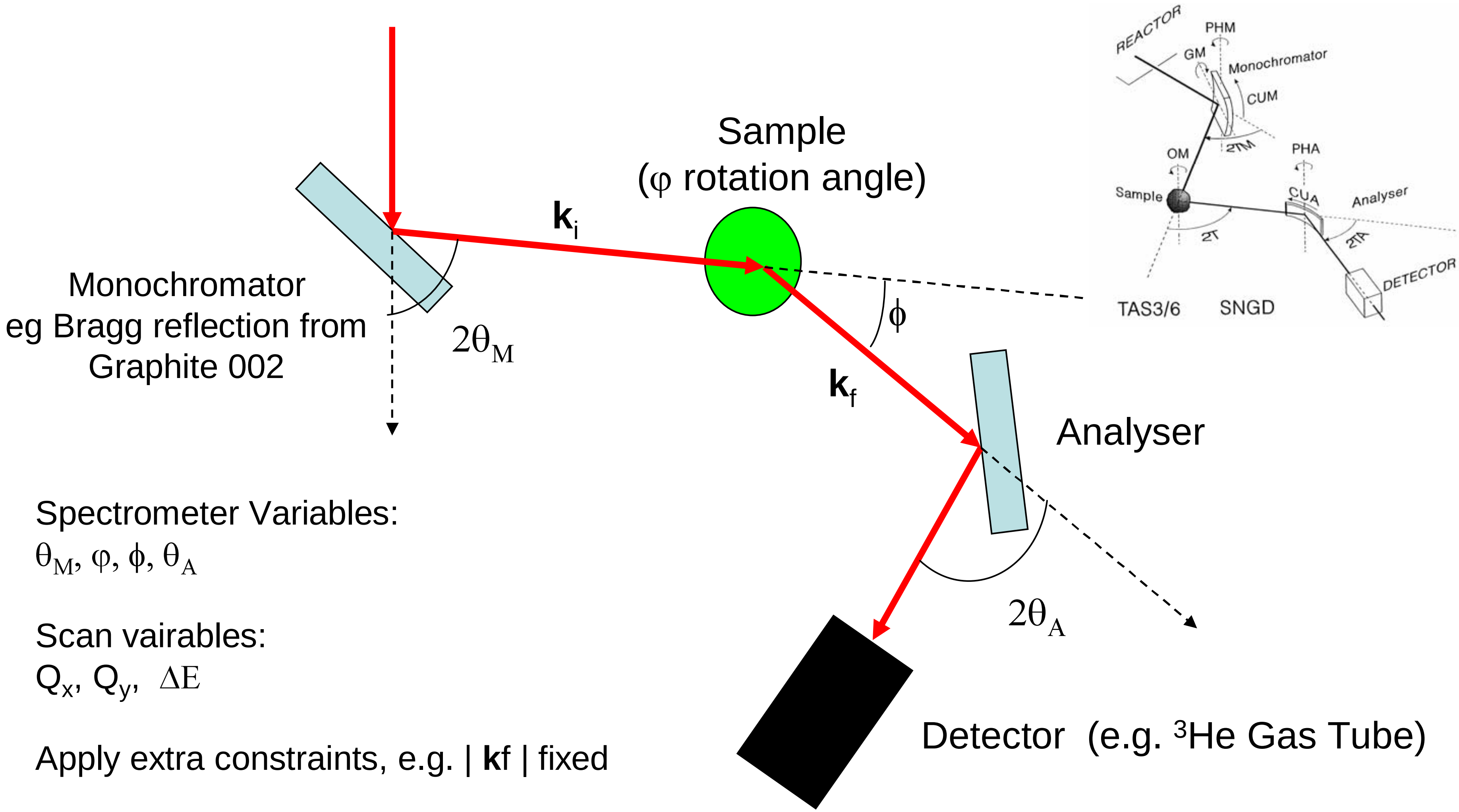
Existence of two conservation laws mean that we can map out dispersion relations

$$\hbar\omega = \frac{\hbar^2}{2m}(k_i^2 - k_f^2) = \frac{\hbar^2}{2m}(k_i^2 - |\mathrm{k}_\mathrm{i} - \mathrm{Q}|^2)$$
$$= \frac{\hbar^2}{2m}(2\mathrm{k}_\mathrm{i} \cdot \mathrm{Q} - Q^2)$$

For fixed k_f, conservation laws are satisfied by adjusting k_i and angle between **Q** and $\mathbf{k_i}$

Neutron Scattering Techniques

Triple Axis Spectrometer is a highly flexible instrument for determining phonon dispersion relations

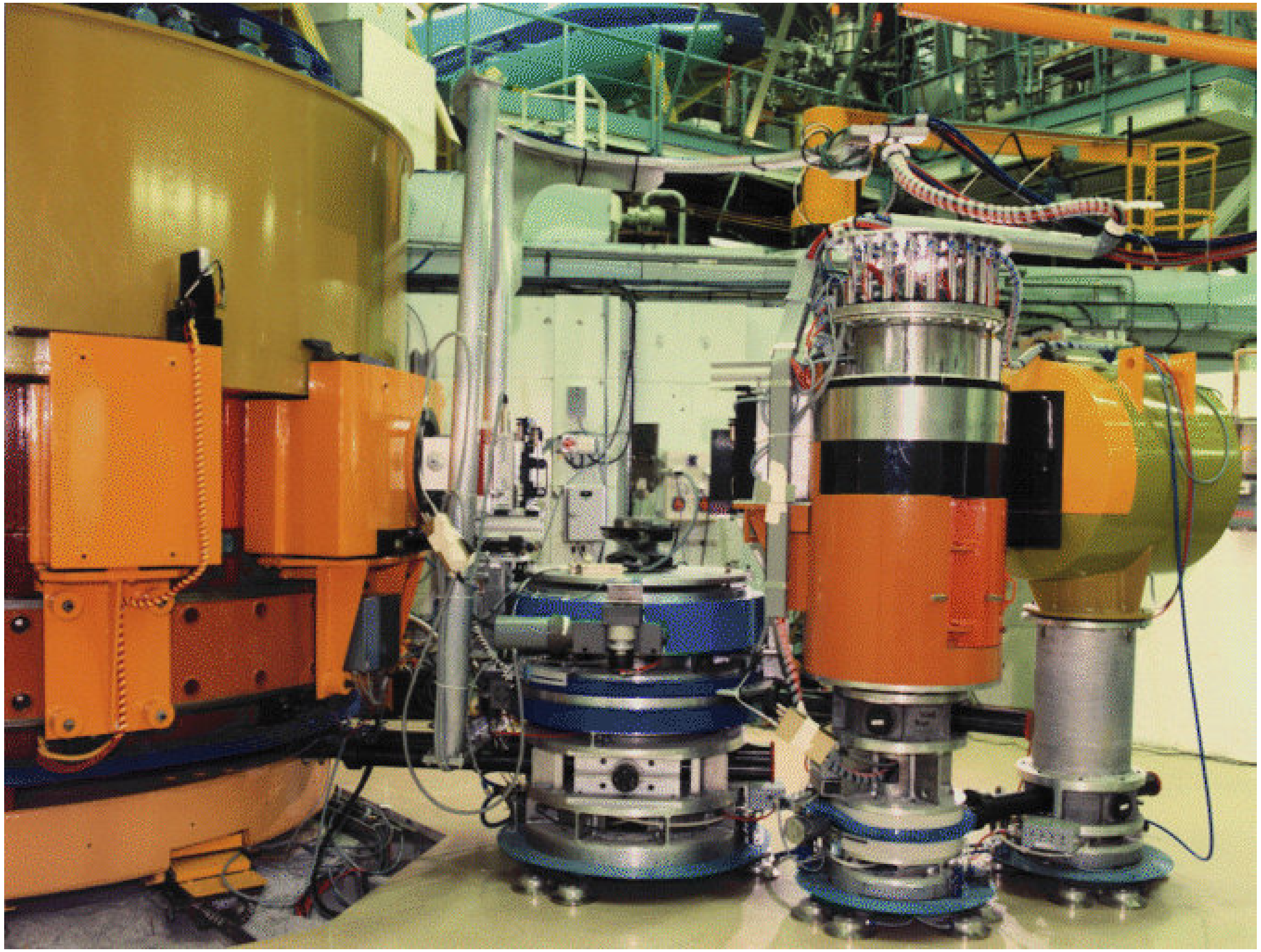


Spectrometer Variables:
θ_M, φ, ϕ, θ_A

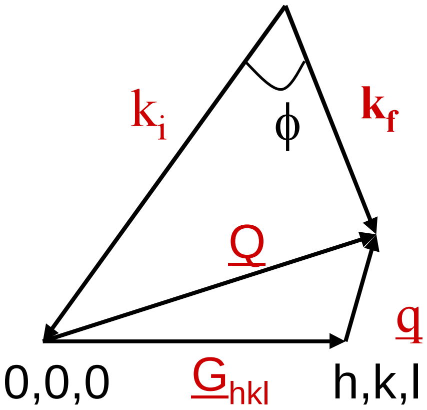
Scan vairables:
Q_x, Q_y, ΔE

Apply extra constraints, e.g. | **kf** | fixed

The triple axis spectrometer



Example: Constant Q Scan with k_f fixed

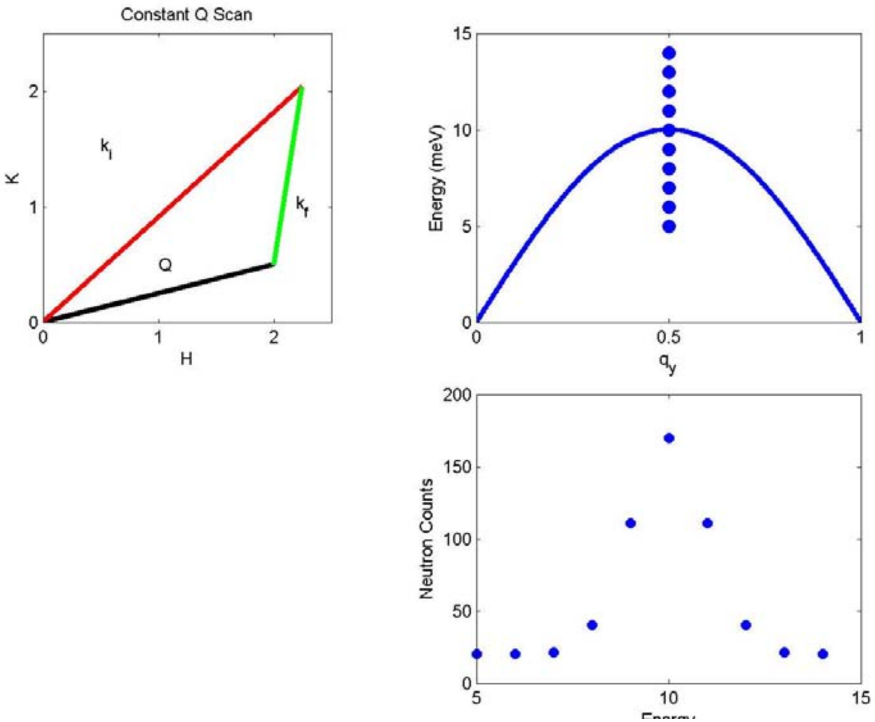


$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos\phi$$

$$\frac{\hbar^2 Q^2}{2m} = E_i + E_f - 2(E_i E_f)^{1/2}\cos\phi$$

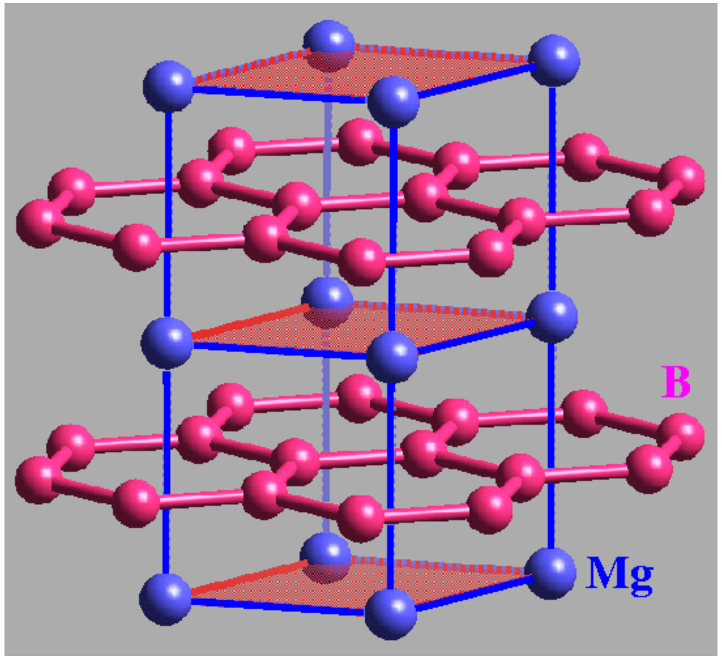
$$= 2E_i - \hbar\omega - 2(E_i(E_i - \hbar\omega))^{1/2}\cos\phi$$

Procedure:
- k_f (E_f) and **Q** are fixed
- For a given $\hbar\omega$ can find (E_i) k_i and ϕ from above
- Hence can plot scattering triangle
- Similar technique gives contstant $\hbar\omega$ scans

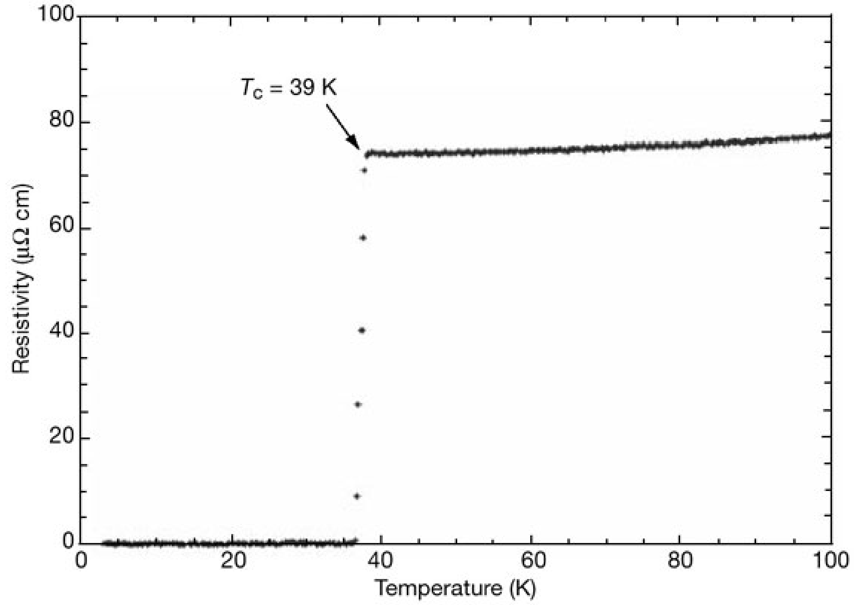


Width of observed peak is determined by Resolution which is a complicated function of E_i, E_f and collimators used to define angular divergence of beams

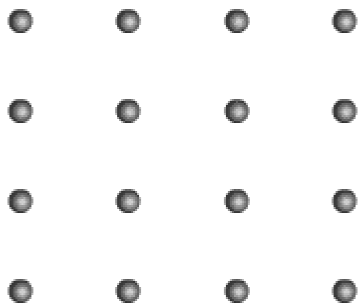
Case Study: Superconductivity in MgB_2



NAGAMATSU et al Nature (2001)



Can the high value of Tc be explained by conventional phonon mediated coupling of the electrons or is it more exotic?

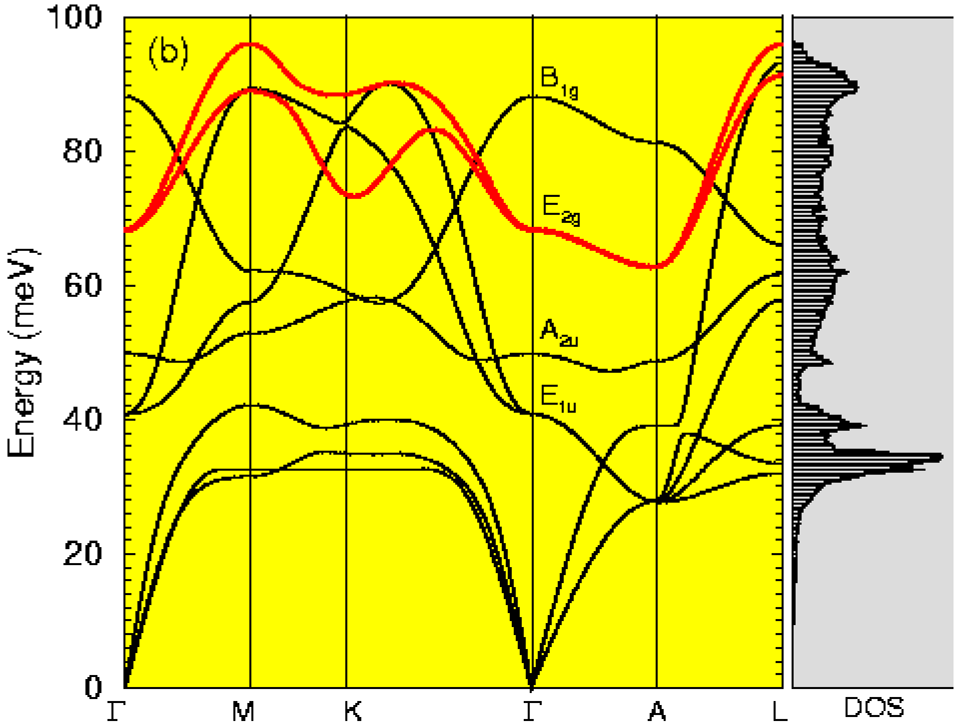


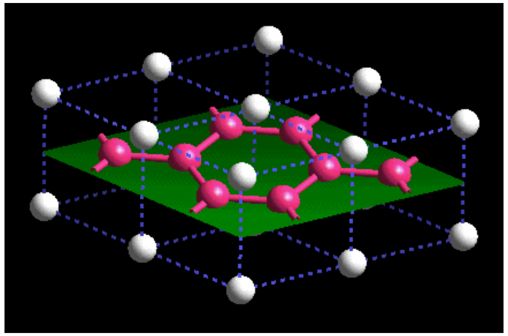
http://superconductors.org/oxtheory.htm

Lattice Dynamics in MgB_2

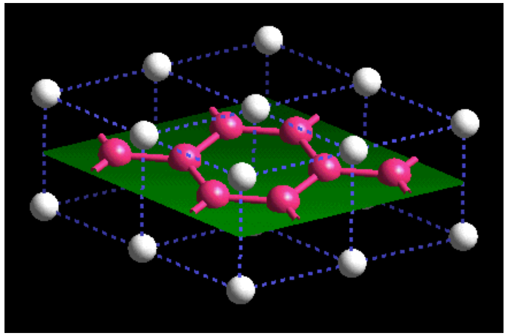
Phonon density of states

Neutron spectroscopy on Powders

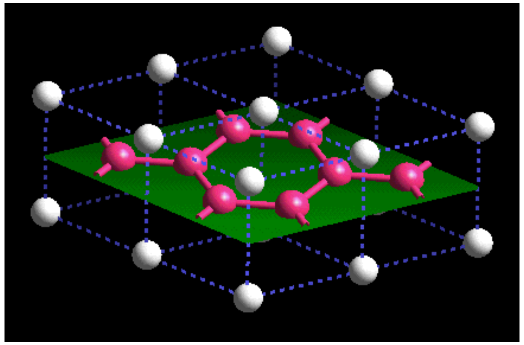




E1u



A2u

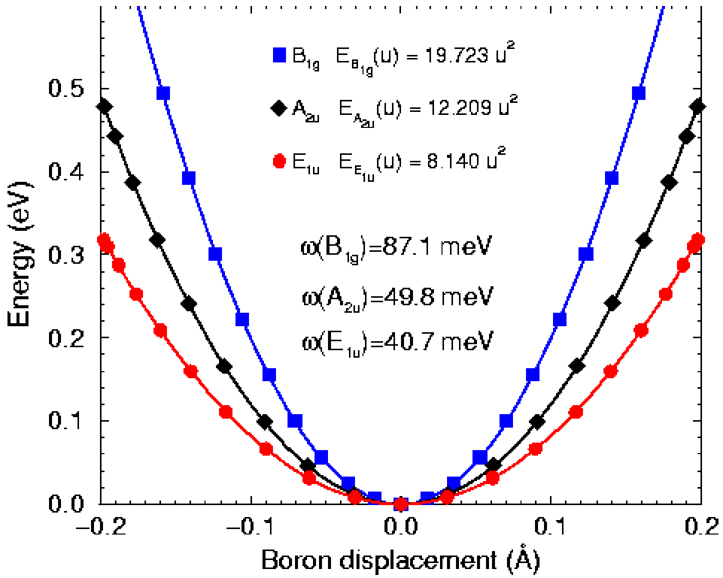


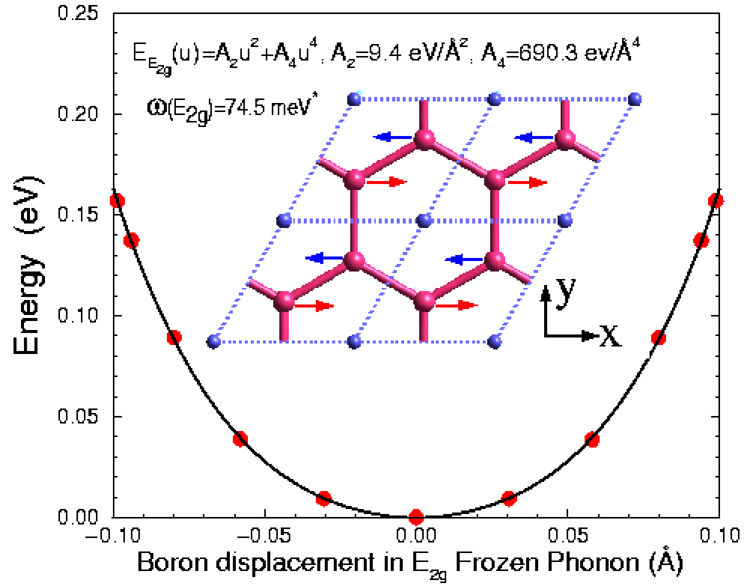
B1g

Combined neutron measurements of the phonon density of states and lattice dynamics calculation
Yildiirm et al PRL (2001)

http://www.ncnr.nist.gov/staff/taner/mgb2/mgb2home.html

Anharmonic Phonons in MgB_2

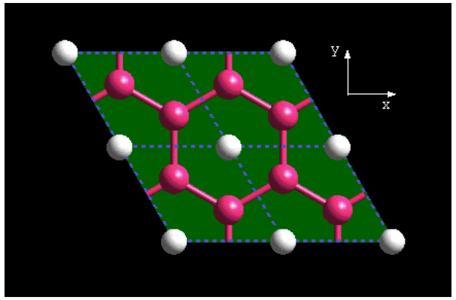




•B1g, A2u, E1u harmonic

•E2g mode strongly anharmonic with a large electron-phonon coupling

•Calculated value of Tc in agreement with experiment.



Conclusion:

MgB2 is a conventional electron-phonon superconductor in the strong-coupling regime.

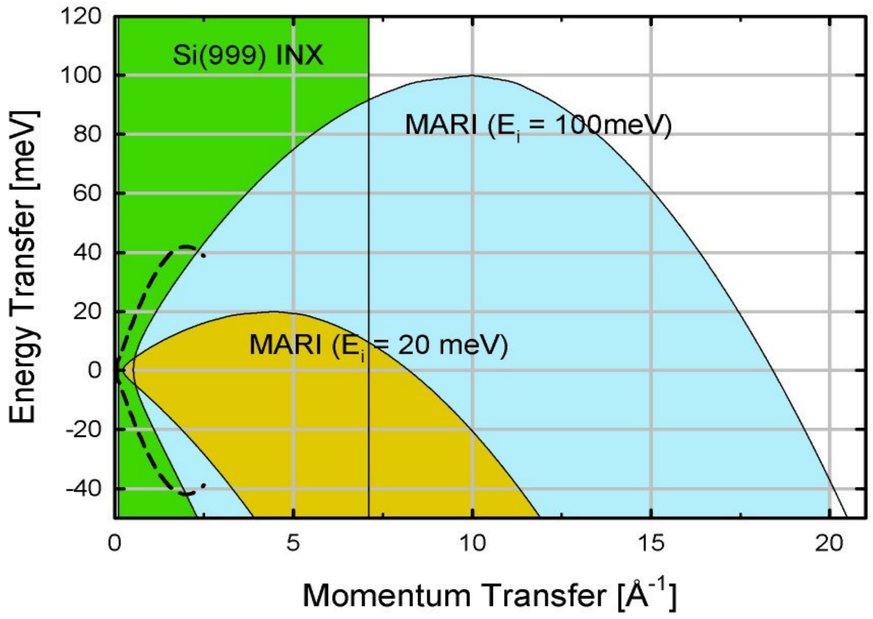
Inelastic X-ray Scattering

Disadvantages:

- Great demands on mononchromator system as require $\Delta\lambda/\lambda \sim 10^{-7}$
- Lower sensitivity to light atoms
- Resolution is non-Gaussian

Advantages:

- Open up a new kinematical window at small Q and high E (shown below).
- Extremely powerful for disordered systems where low Q and high energy transfer required
- Can work with very small samples down to 10 microns
- Resolution is independent of energy transfer (not true for neutrons) due to decoupling of E and Q



Inelastic X-ray Scattering

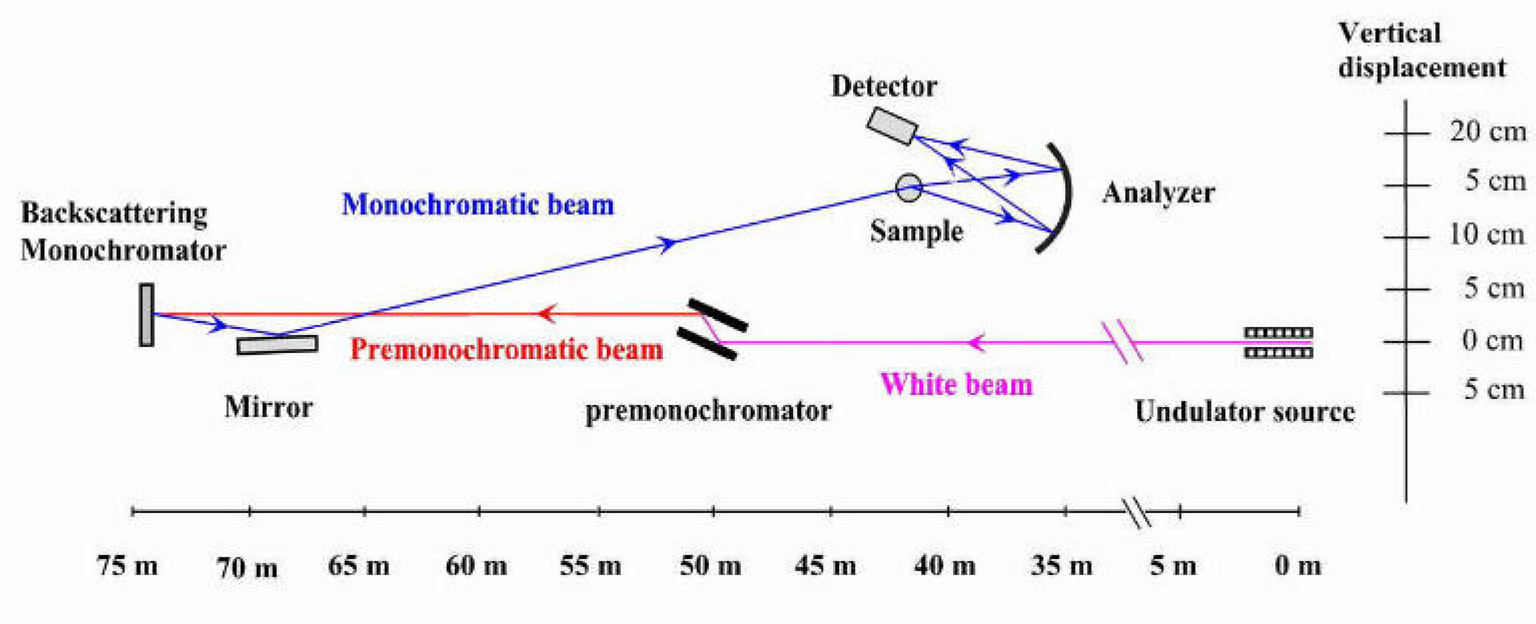
Beamline built around monochromator and analyser systems close to backscattering.

Bragg's law =>

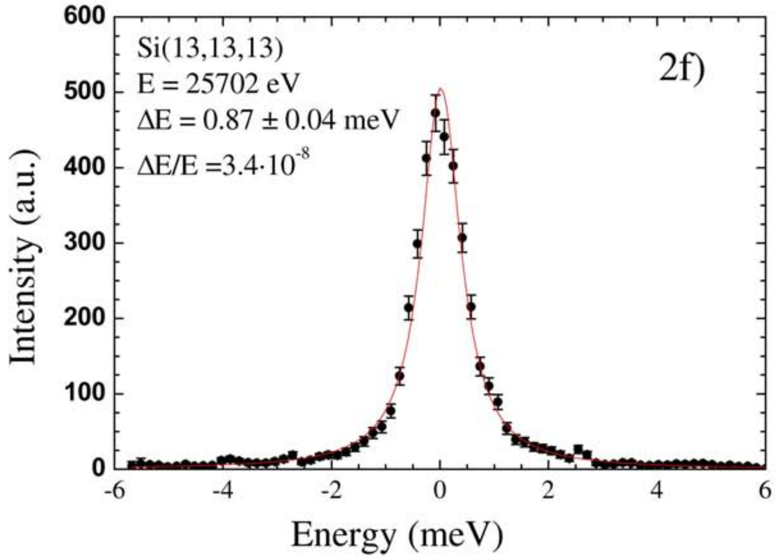
$$\frac{d\lambda}{\lambda} = \frac{dE}{E} = \cot\theta d\theta$$

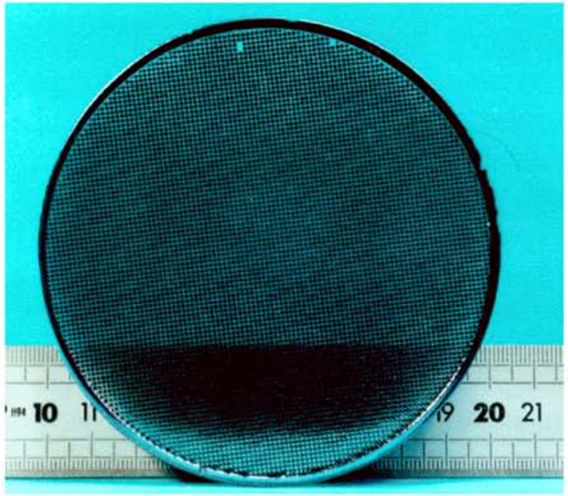
$$\rightarrow 0 \text{ as } \theta \rightarrow \pi/2$$

Reflection	Energy[keV]	E [meV]	dE/E
Si(7,7,7)	13.840	5.30	$3.8 \cdot 10^{-7}$
Si(8,8,8)	15.817	4.40	$2.8 \cdot 10^{-7}$
Si(9,9,9)	17.794	2.20	$1.2 \cdot 10^{-7}$
Si(11,11,11)	21.747	0.83	$4.7 \cdot 10^{-8}$
Si(12,12,12)	23.725	0.73	$3.1 \cdot 10^{-8}$
Si(13,13,13)	25.704	0.50	$1.9 \cdot 10^{-8}$



Inelastic X-ray Scattering





Spherical analyser formed from 10,000 0.6x0.6x3 mm^3 Si cubes

To maintain back scattering condition, energy scans are achieved by scanning the temperature of the monochromator

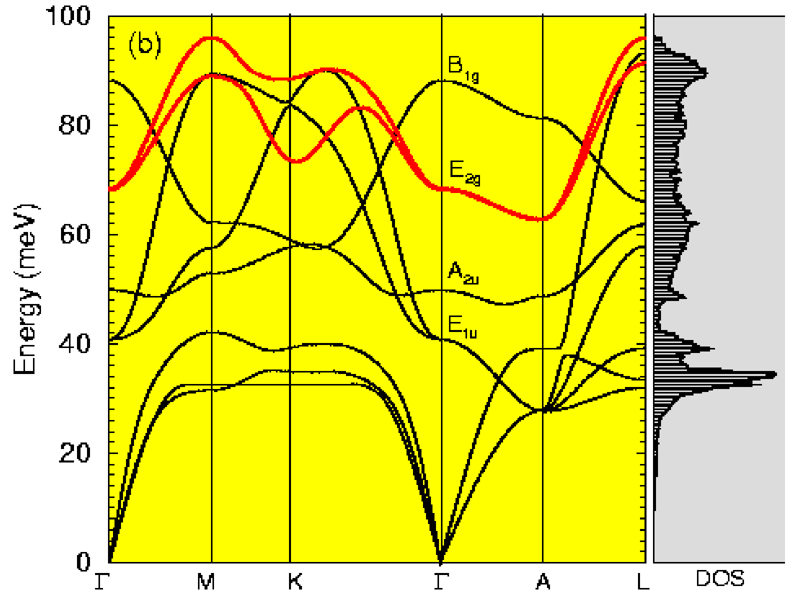
$$n\lambda = 2d(T)\sin\theta$$

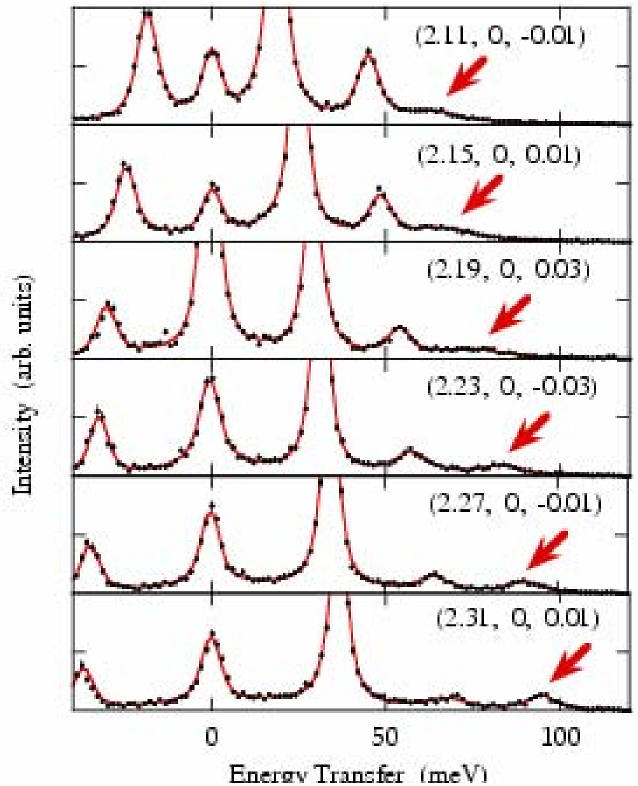
Control monochromator temperature with precision of 0.25 mK

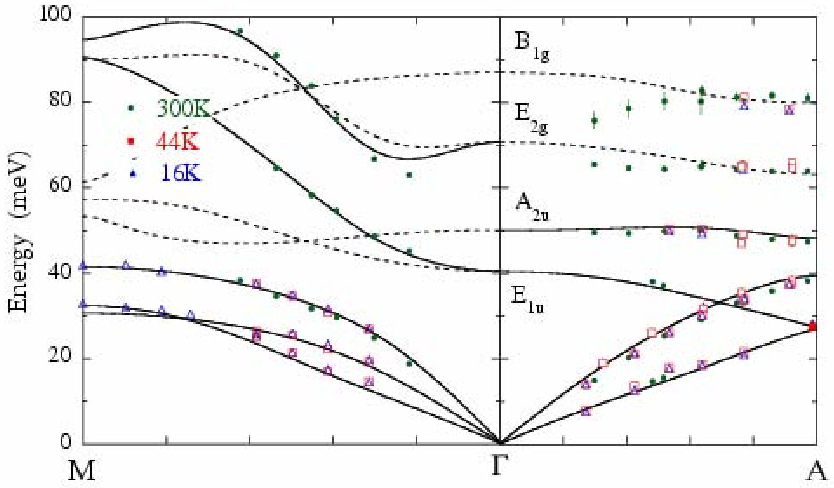
Inelastic X-ray scattering on MgB_2

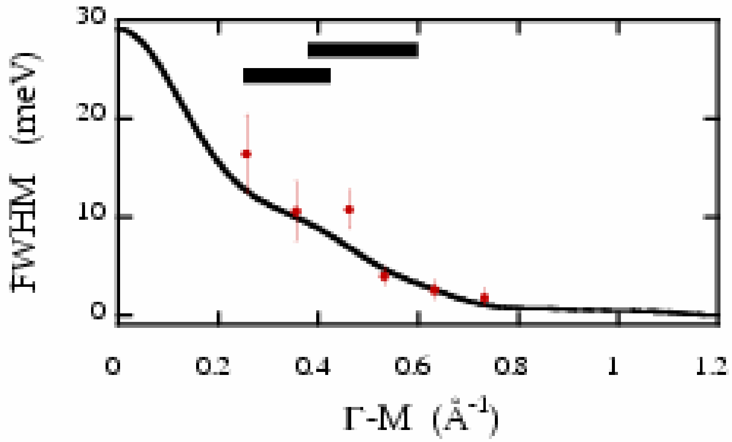
Baron et al., SPRING-8

Single Crystal MgB_2 50x70 microns^2





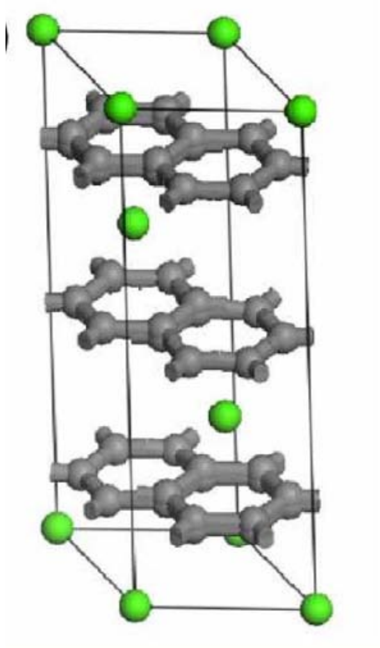


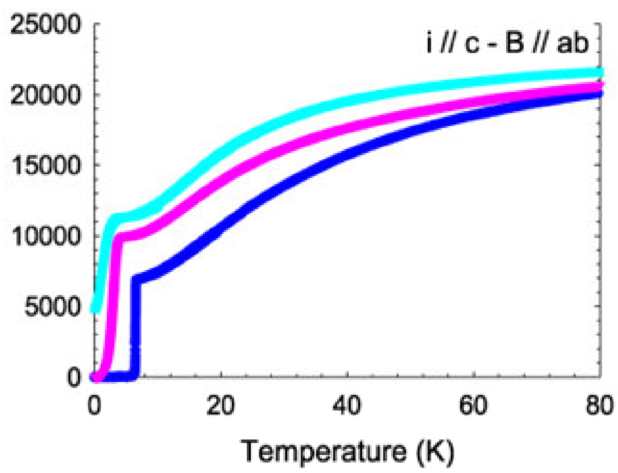


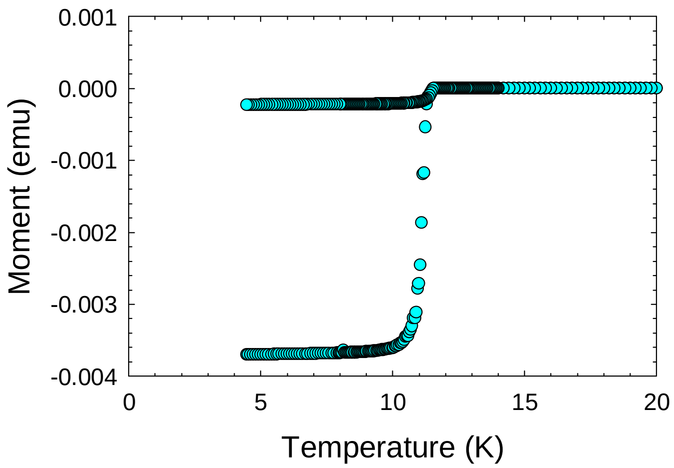
Superconductivity in the intercalated graphite compounds C_6Yb and C_6Ca

THOMAS E. WELLER[1], MARK ELLERBY[1]*, SIDDHARTH S. SAXENA[2]*, ROBERT P. SMITH[2] AND NEAL T. SKIPPER[1]

Nature Phys, **1** (2005) 39: Rec. 18 Mar 2005c





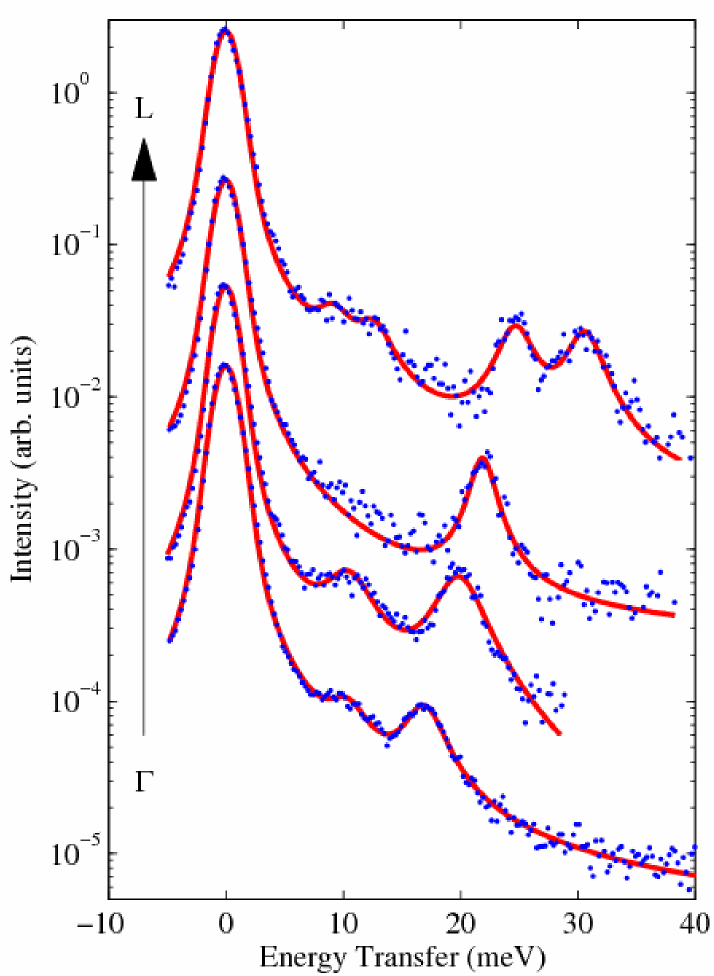


Nature of the pairing mechanism: plasmons? phonons?

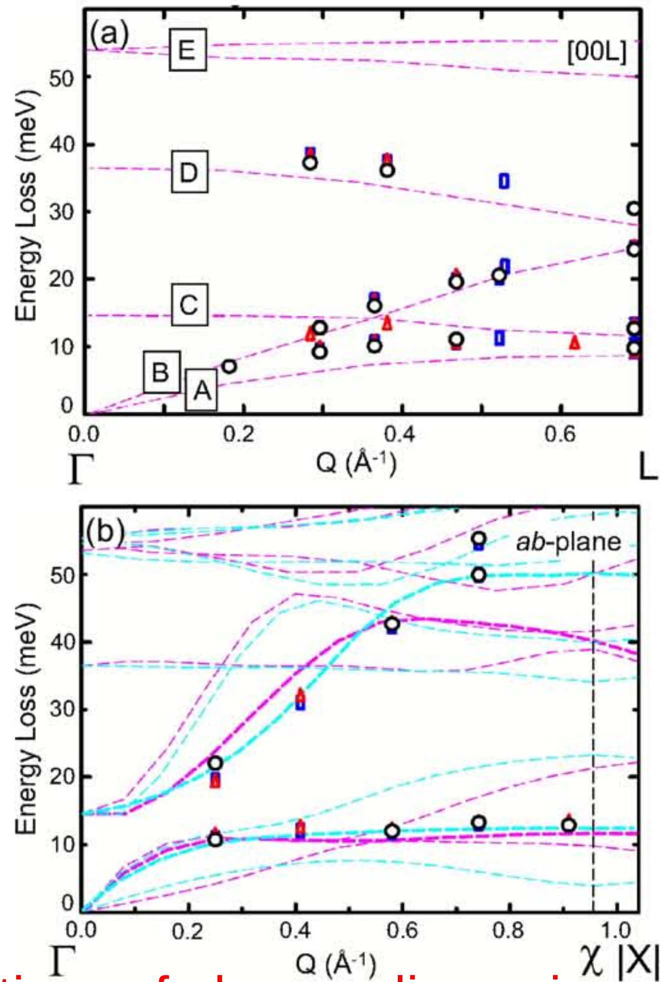
For the latter scenario: Broad agreement over predicted phonon dispersion relations, disagreement over electron-phonon coupling

Inelastic X-ray scattering study of superconducting CaC_6

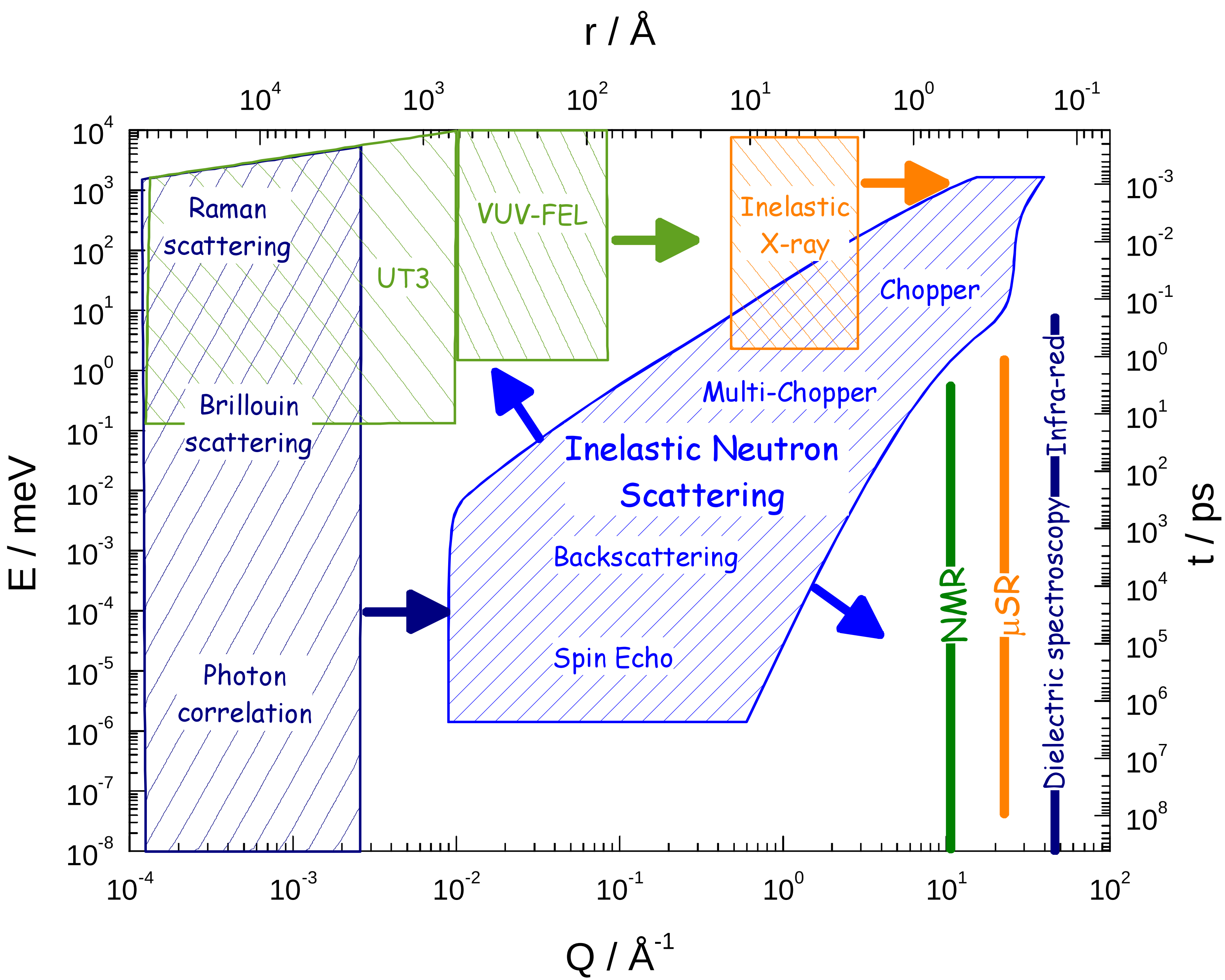
M.H. Upton, A.C. Walters, C.A. Howard, K.C. Rahnejat, M.E. Ellerby,
J.P. Hill, D.F. McMorrow, A. Alatas, B.M. Leu and W. Ku



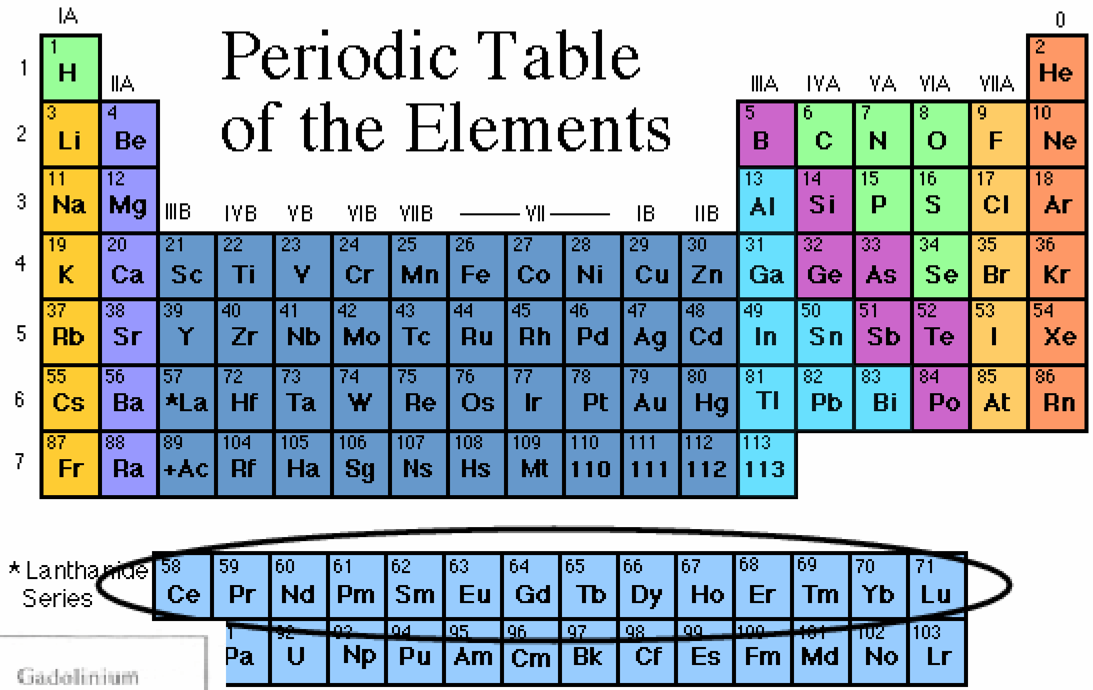
DFT calculations, Calandra and Mauri

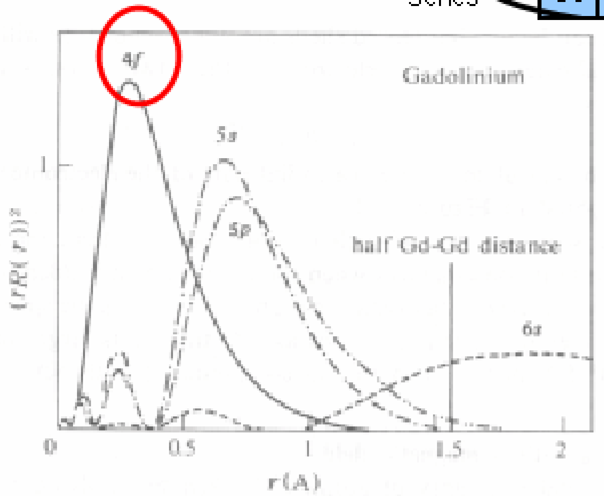


Good agreement with DFT calculations of phonon dispersion
=> electron-phonon coupling not properly understood


r / Å
10^4
10^3
10^2
10^1
10^0
10^{-1}
E / meV
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
t / ps
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^8
Q / Å^{-1}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
Raman scattering
Brillouin scattering
Photon correlation
UT3
VUV-FEL
Inelastic X-ray
Chopper
Multi-Chopper
Inelastic Neutron Scattering
Backscattering
Spin Echo
NMR
µSR
Dielectric spectroscopy
Infra-red

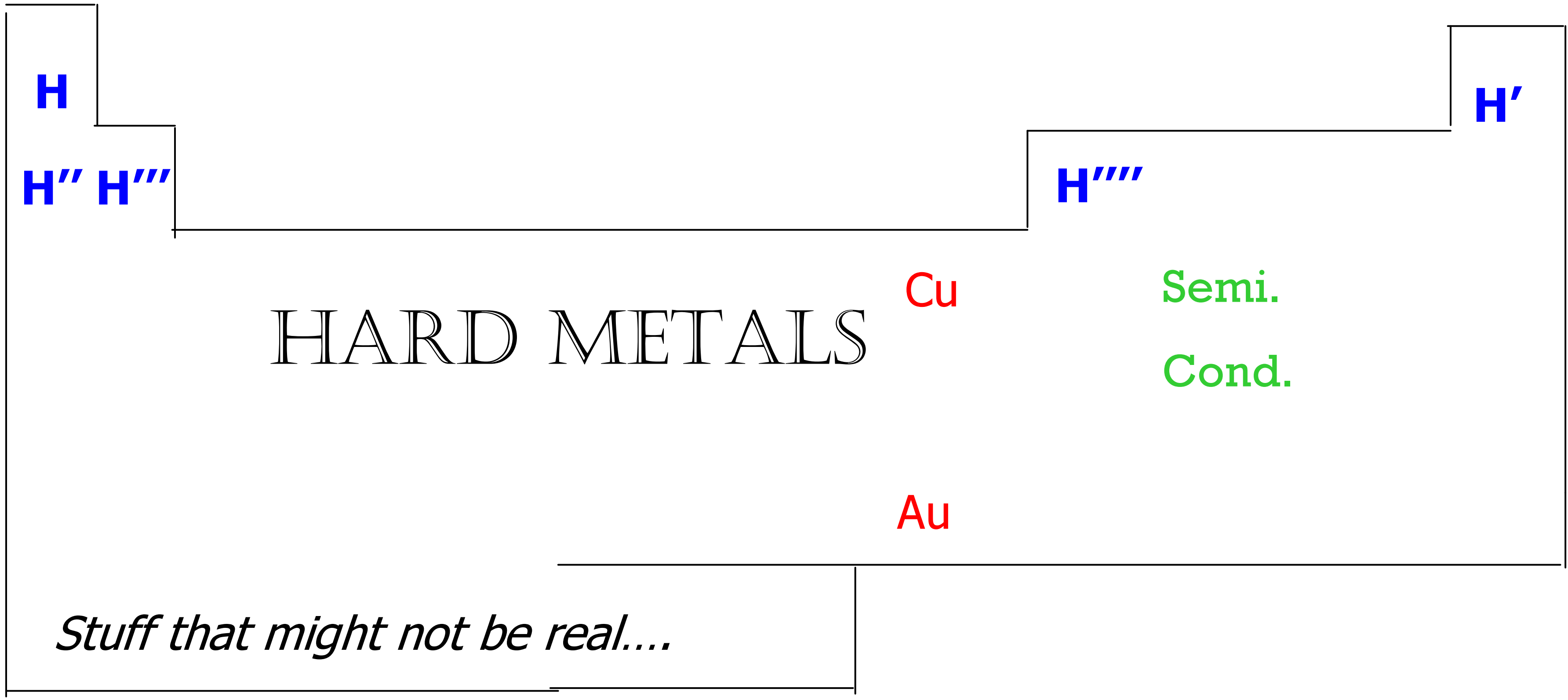
Magnetism of the Rare Earth Series





- localized 4f orbitals (no overlap)
- partially filled orbitals → L, S
- local magnetic moments
- 6s responsible for metallic bonding

Many scientists' version of the Periodic Table



Won't Be On the Final Exam

BOMBS AND OTHER NASTY STUFF

By Paul C. Canfield

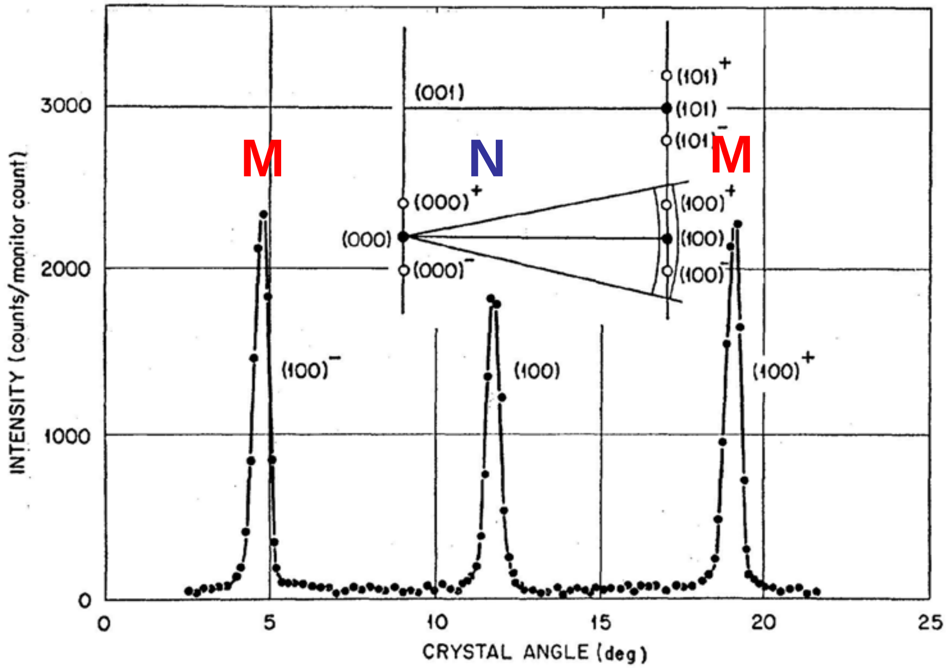
PHYSICAL REVIEW VOLUME 151, NUMBER 2 11 NOVEMBER 1966

Magnetic Structures of Holmium. I. The Virgin State*

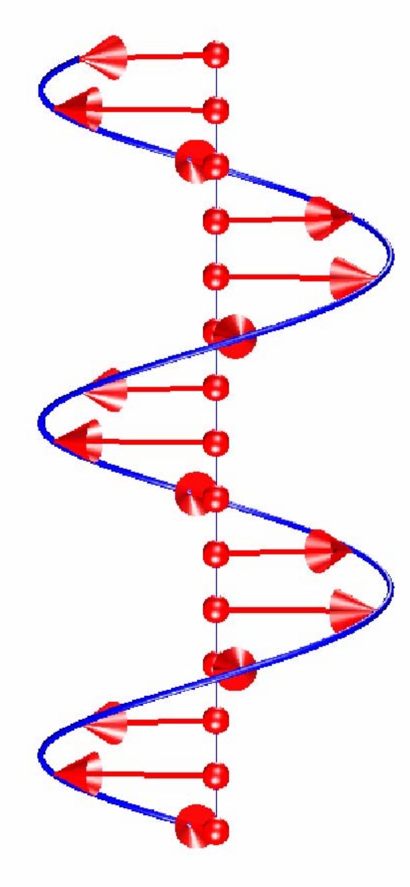
W. C. Koehler, J. W. Cable, M. K. Wilkinson, and E. O. Wollan
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 1 June 1966)

Neutron Scattering



Holmium T_N=132 K Basal Plane Spiral



- Nuclear and Magnetic scattering yield similar intensities
- Incommensurate magnetic satellite reflections observed
- From Q dependence conclude that moments form basal plane spiral below T_N and a cone below T_c

PHYSICAL REVIEW VOLUME 151, NUMBER 2 11 NOVEMBER 1966

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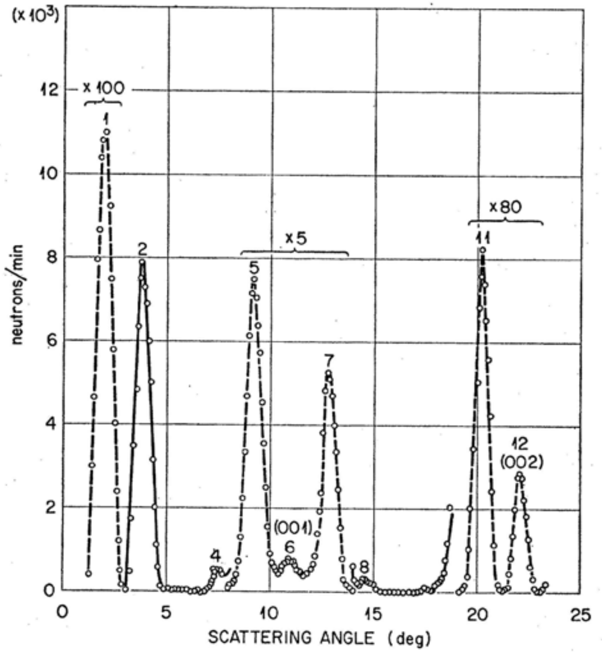
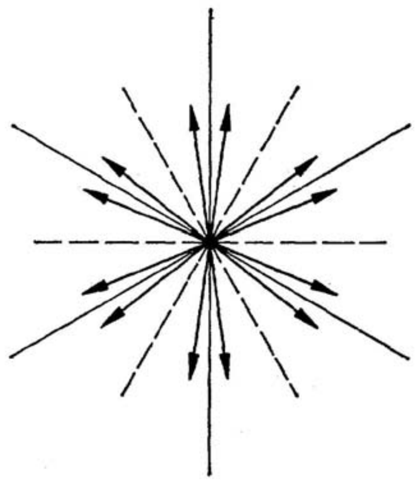
Neutron Scattering



Crystal-field produces a Bunched Spiral



•Higher order reflections (i.e. higher order Fourier components) observed

•Modulation is not sinusoidal => spins form a bunched spiral

X-ray Magnetic Scattering

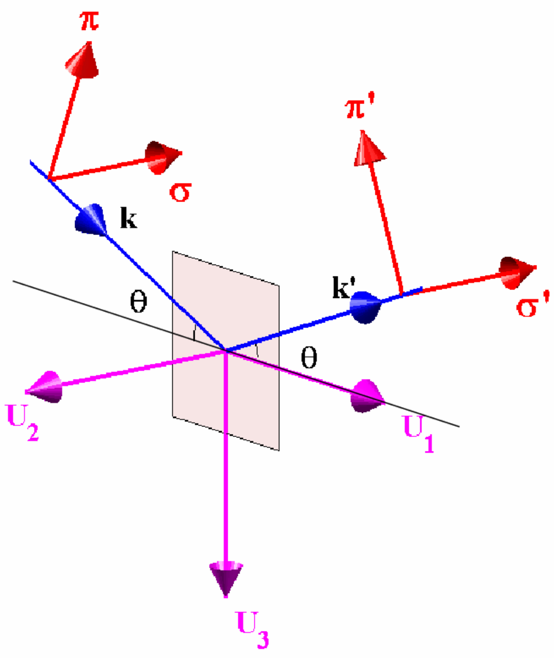
Magnetic scattering length

$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right)\left[\frac{1}{2}\boldsymbol{L}(\boldsymbol{Q})\cdot A'' + \boldsymbol{S}(\boldsymbol{Q})\cdot B\right]$$

$\boldsymbol{L}(\boldsymbol{Q})$ and $\boldsymbol{S}(\boldsymbol{Q})$ are Fourier transforms

of the atomic and spin magnetization densities

A'' and B contain the dependence on $\boldsymbol{k}, \boldsymbol{k}', \hat{\varepsilon}$ and $\hat{\varepsilon}'$



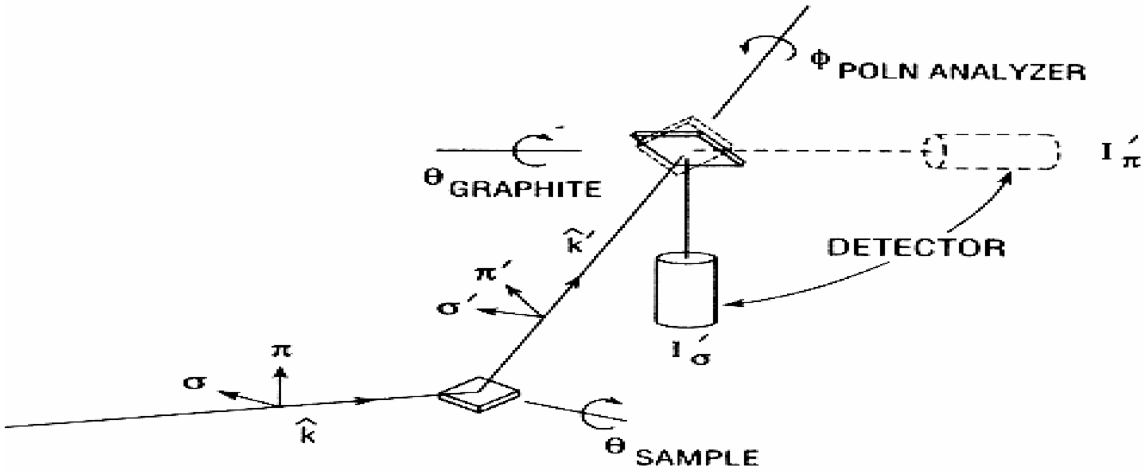
$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right) \times$$

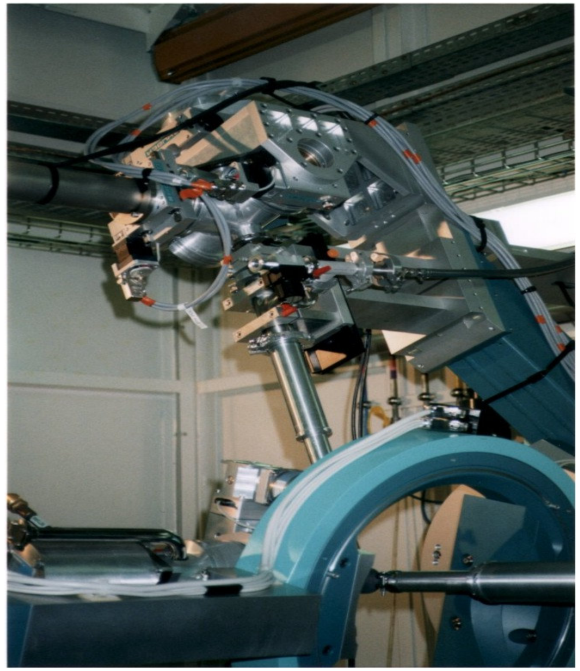
	$\hat{\varepsilon}_{\perp} \equiv \sigma$	$\hat{\varepsilon}_{\parallel} \equiv \pi$
$\hat{\varepsilon}'_{\perp}$	$\sin 2\theta S_2$	$-2\sin^2\theta\left[\left(L_1 + S_1\right)\cos\theta - S_3\sin\theta\right]$
$\hat{\varepsilon}'_{\parallel}$	$2\sin^2\theta\left[\left(L_1 + S_1\right)\cos\theta - S_3\sin\theta\right]$	$\sin 2\theta\left[2\sin^2\theta L_2 + S_2\right]$

Blume and Gibbs, PRB 1988

X-ray Magnetic Scattering: Experimental Considerations

- Versatile diffractomter required
- Tunable photon energy, 1-15 keV
- Well defined incident polarization
- Polarization analysis
- Azimuthal degree of freedom



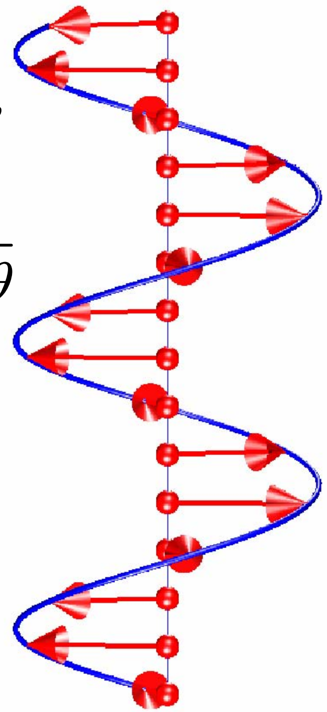


X-ray Magnetic Scattering
Example: scattering from a magnetic spiral

Assume for clarity that

$$\langle \boldsymbol{L} \rangle = 0 \text{ and } \boldsymbol{S} = S(\cos(qa\ell), \sin(qa\ell))$$

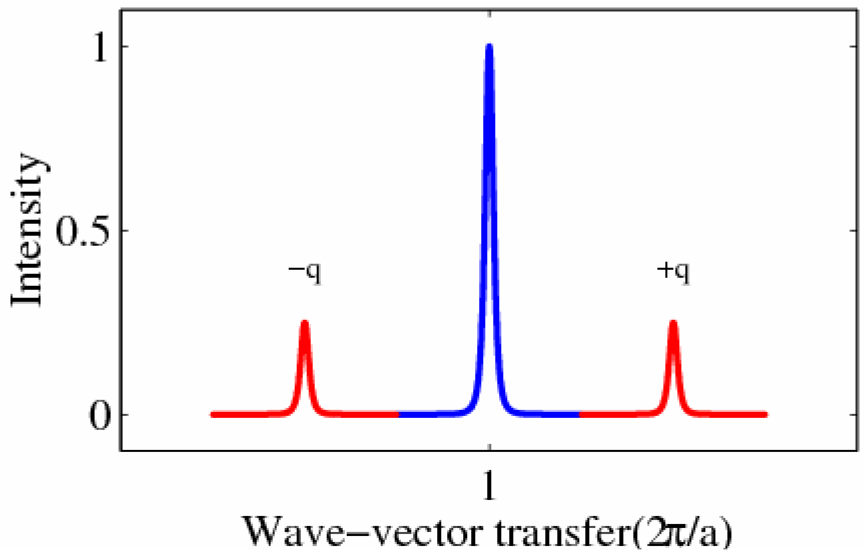
and that experiment is done with σ polarized light and no analyser



$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right) S \sum_{\ell} e^{i(Q\pm q)a\ell} \times$$

	$\hat{\varepsilon}_{\perp} \equiv \sigma$	$\hat{\varepsilon}_{\parallel} \equiv \pi$
$\hat{\varepsilon}'_{\perp}$	$\pm i \sin 2\theta$	$-2\sin^2\theta\cos\theta$
$\hat{\varepsilon}'_{\parallel}$	$2\sin^2\theta\cos\theta$	$\pm i \sin 2\theta$

$$\left(\frac{d\sigma}{d\Omega}\right)^{Magnetic} = r_0^2 \left(\frac{\hbar\omega}{mc^2}\right)^2 S^2 \sin^2 2\theta (1+\sin^2\theta)\delta(Q-G\pm q)$$

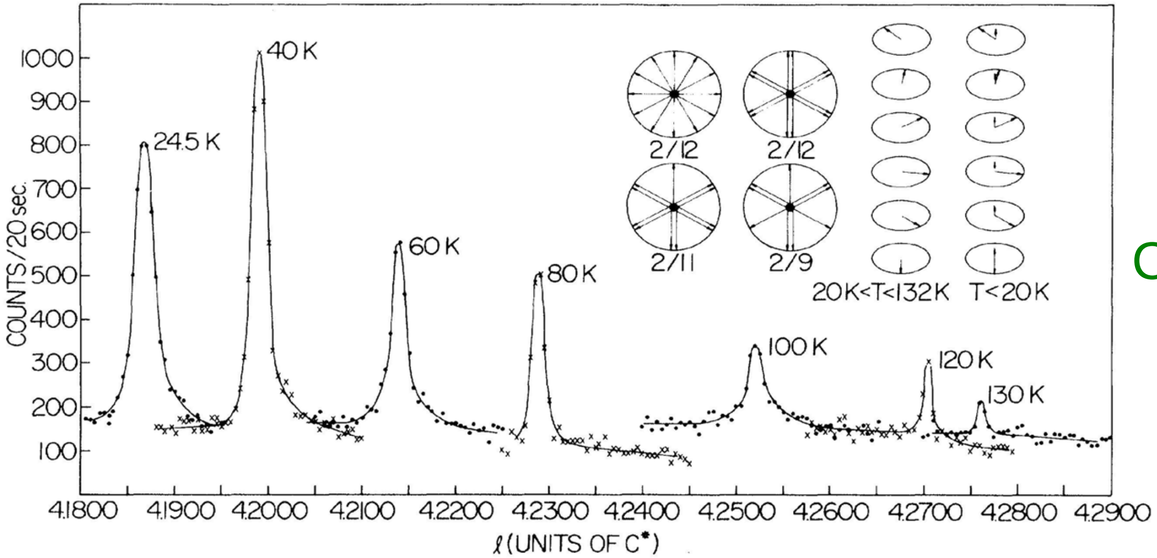


VOLUME 55, NUMBER 2 PHYSICAL REVIEW LETTERS 8 JULY 1985

Magnetic X-Ray Scattering Studies of Holmium Using Synchrotron Radiation

Doon Gibbs, D. E. Moncton, K. L. D'Amico, J. Bohr,[a] and B. H. Grier[b]
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
(Received 26 March 1985)

(1985) First Synchrotron Radiation Studies of Magnetism



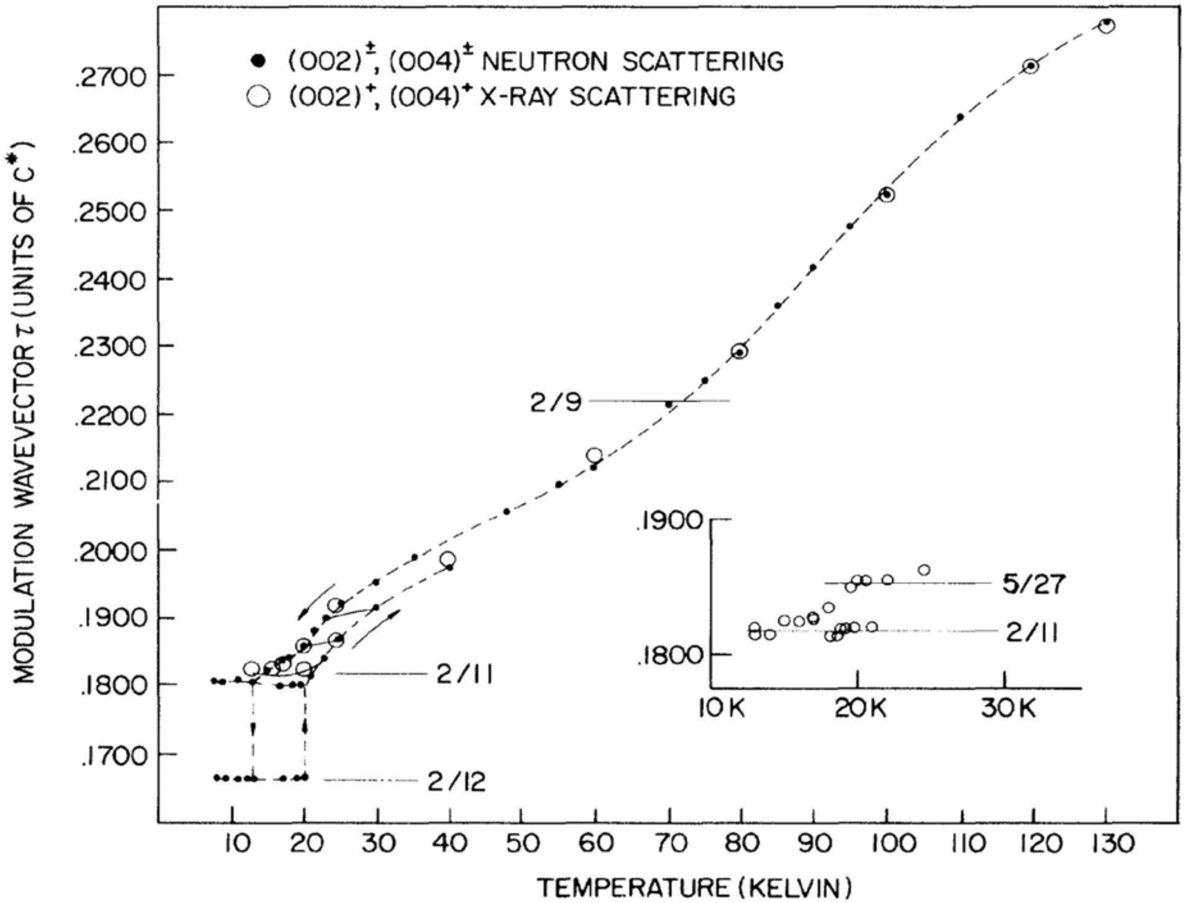
Synchrotron Source: Counts per 20s

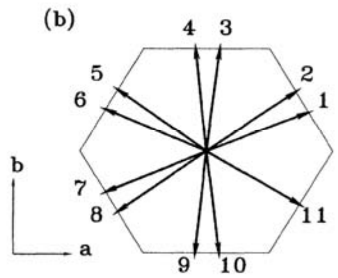
Advantages of Non-resonant X-ray Magnetic Scattering

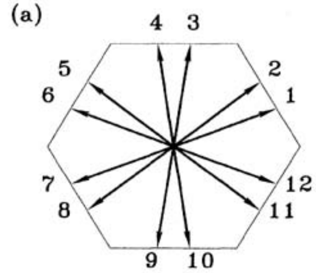
- High-resolution technique (Phase transitions)
- Separation of orbital and spin magnetization densities
- Highly focussed beams (Small samples)

Spin-slip structures in Holmiun

Fundamental revision of understanding of rare earths







High resolution of X-ray technique reveals existence of “magic” commensurate values of the helical wavevector

PHYSICAL REVIEW B VOLUME 51, NUMBER 22 1 JUNE 1995-II

Trigonal interactions in holmium

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R.A. Cowley and D.A. Jehan
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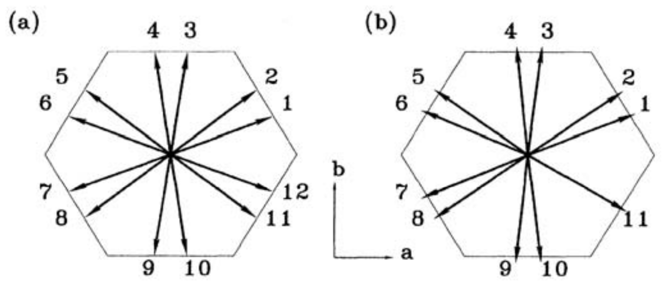
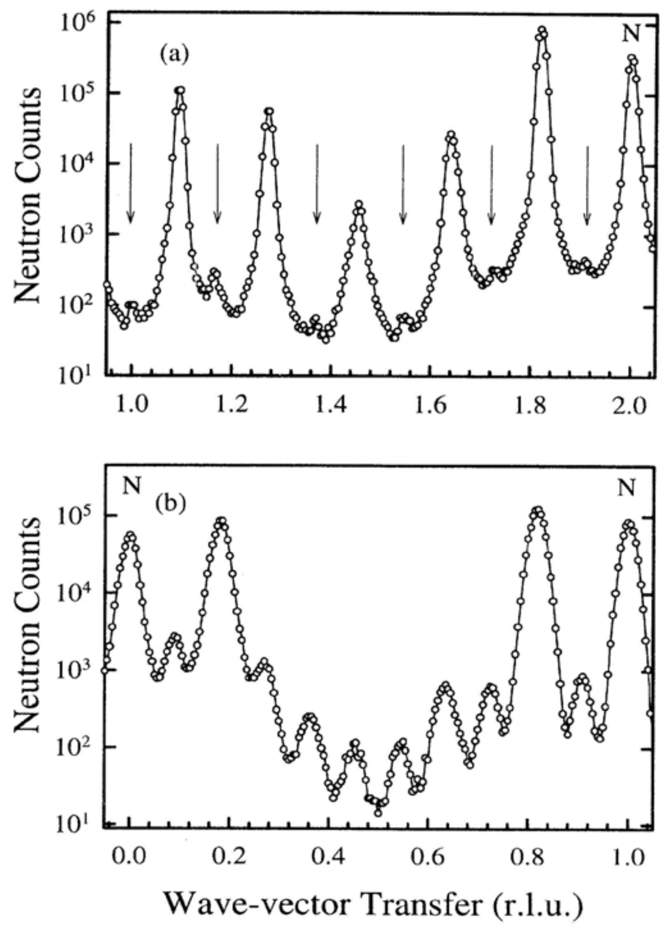
(Received 25 October 1994)



Neutron Scattering

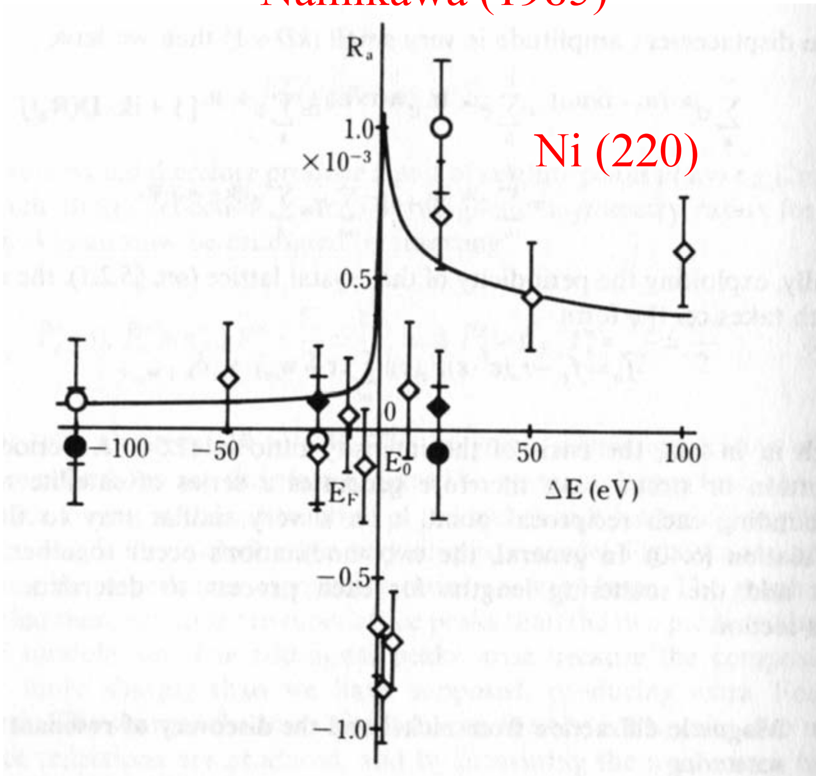


- Neutron scattering allowed a full understanding of the magnetic structures in Holmium
- Revealed importance of Trigonal interactions
- Development of self-consistent mean-field model

”Interesting magnetic effects might occur near an absorption edge”Blume (1985)

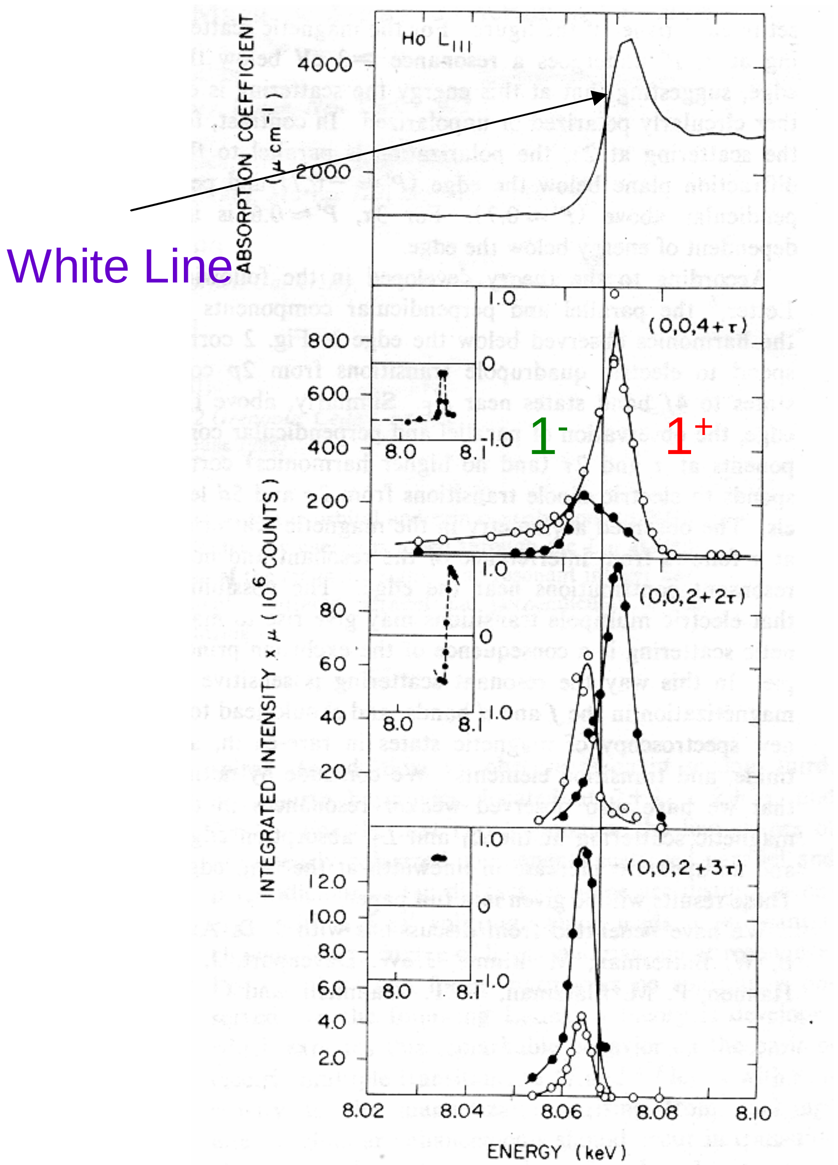
(1985) First Resonant Scattering from a Ferromagnet

X-ray Resonant Magnetic Scattering from Nickel
Namikawa (1985)



Resonant Scattering at the L edges of Holmium

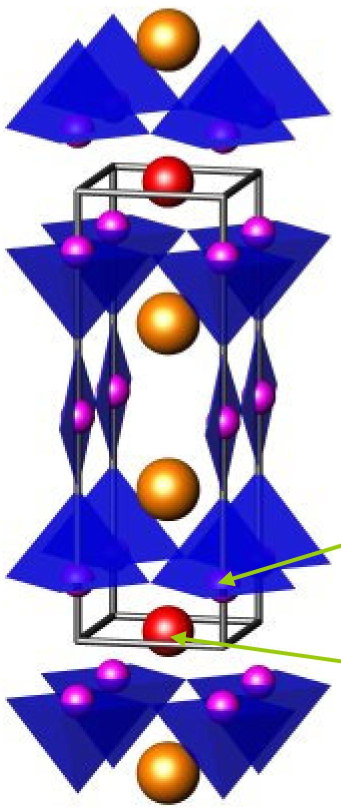
Gibbs, Harshman, Isaacs, McWhan, Mills and Vettier (1988)



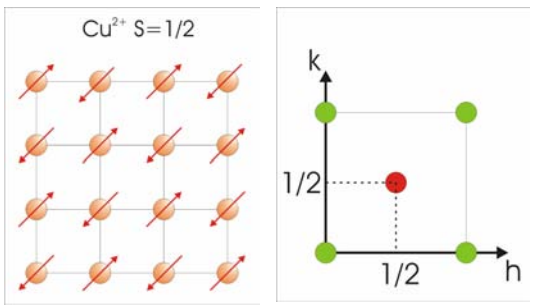
- •100 fold increase when tuned to the L_3 edge
- •Two distinct types of transition are observed: one above and one below the edge
- •Higher order satellites observed up to 4th order
- •Polarization state changes with satellite index, eg,
  - 1^+: rotated $\sigma \rightarrow \pi$
  - 1^- : unrotated $\sigma \rightarrow \sigma$
- •Signal disappears at T_N
- •Can associate peaks with transitions to bound states
  - 1^+: $2p \rightarrow 5d$ Dipole
  - 1^-: $2p \rightarrow 4f$ Quadrupole
- **•XRMS is Born: A New Element and Electron Shell Sensitive Probe!**

Magnetism and absence superconductivity in $PrBa_2Cu_3O_{6+x}$

- Insulator at all x
- Non Superconducting
- Magnetism is anomalous



Neutron Scattering:
(½,½,0) type order



Cu^{2+} *3d* moments at ~300 K

Pr^{3+} *4f* moments at ~20 K
(cf. 0-2 K other rare-earths)

Open Questions:

- Which moments are actually ordered?

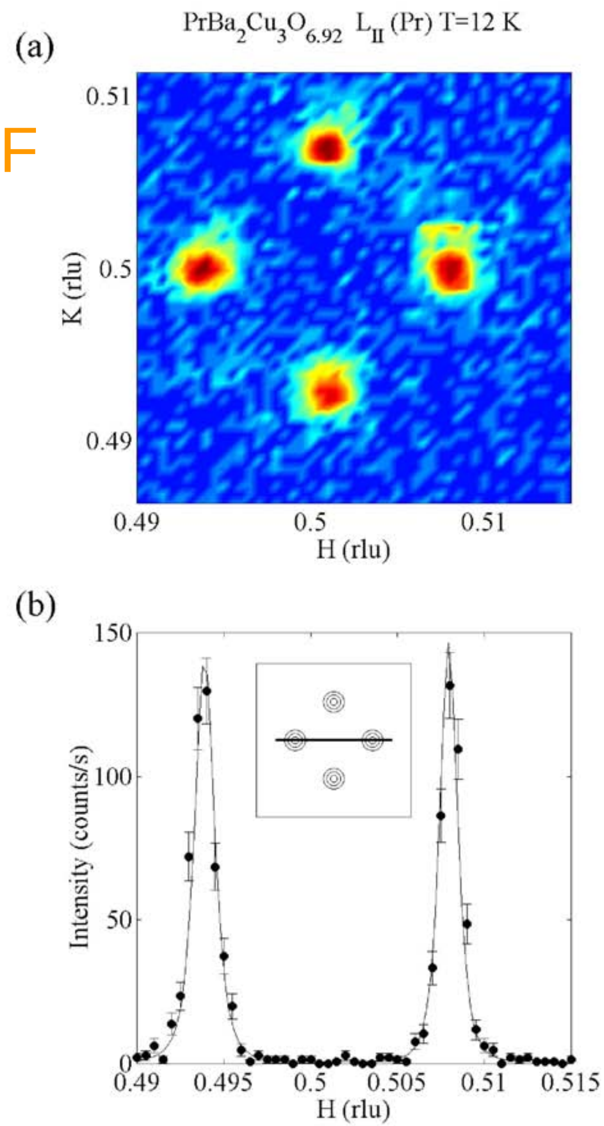
(NMR: vanishingly small Pr moments)?

- What is the magnetic structure?

- Why is it not a superconductor?

Incommensurate Magnetic Order in $PrBa_2Cu_3O_{6.92}$
Exploitation of high-Q resolution

ID20, ESRF

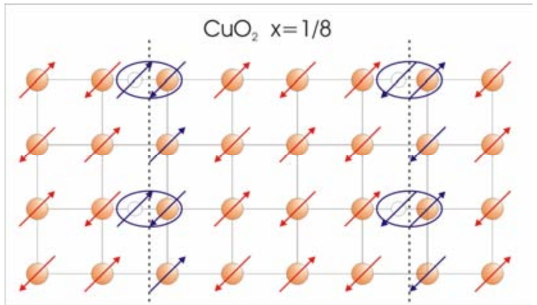


Pr L_{II} edge

2p -> 5d

2p -> 4f

Evidence for Static Stripes?

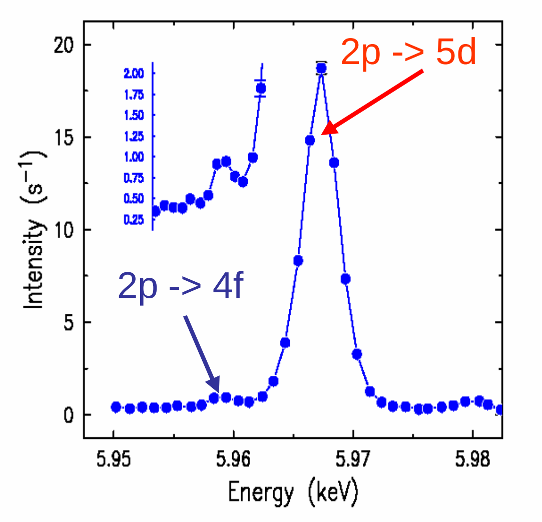


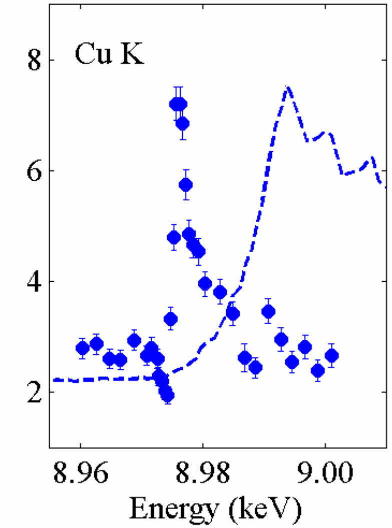
Static stripes destroy Superconductivity

Element and Shell Specificity

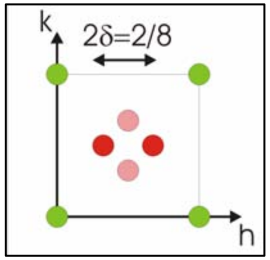
Pr L edges:
Dipole: 2p -> 5d;
quadrupole 2p->4f

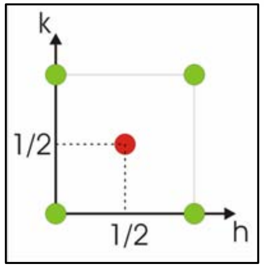
Cu K edge:
Quadrupole: 1s-> 3d





Pr orders
Incommensurately
(½+δ,½,0) for $T<T_{Pr}$





Cu orders
Commensurately
(½,½,0) for $T>T_{Pr}$

Magnetism and the Absence of Superconductivity in $PrBa_2Cu_3O_{6.92}$

Higher resolution reveals new physics

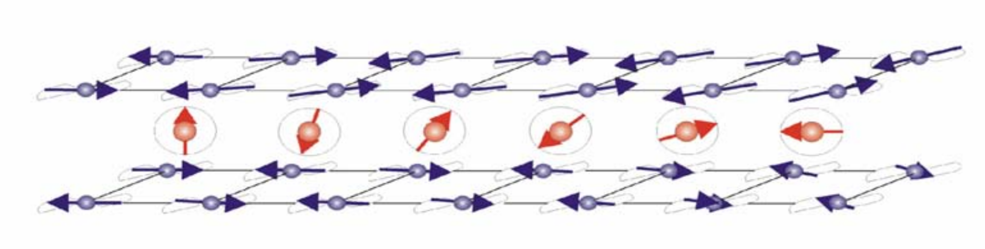
Pr *4f* : incommensurate for $T < T_N$ (Pr)

Element and shell specificity

Cu *3d*: commensurate for T_N (Pr) $< T < T_N$ (Cu)

This rules out formation of spin stripes as a mechanism for the suppression of superconductivity

Resonances enable element specific magnetic crystallography

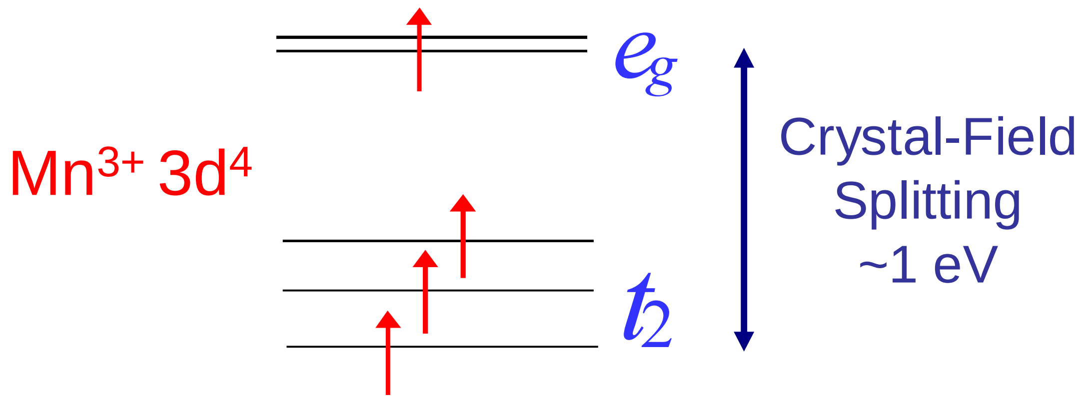


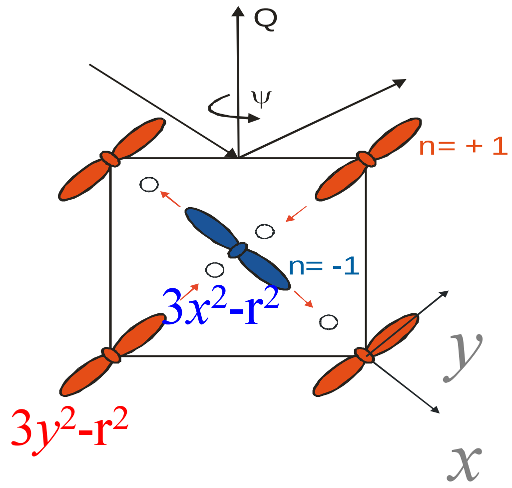
Strong coupling between Cu and Pr - consistent with strong Pr 4f-O 2p hybridization (Fehrenbacher and Rice)

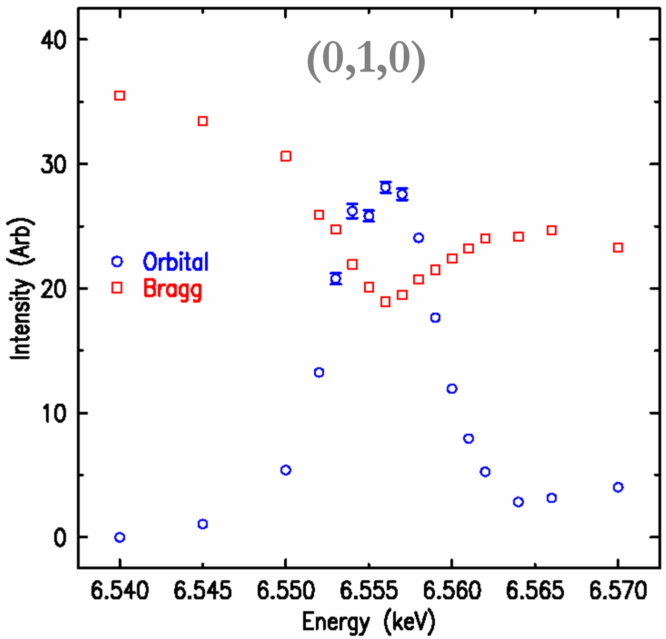
Multipolar Order

Resonant X-ray Scattering from $LaMnO_3$

Murakami, Hill, Gibbs, Blume *et al.*, PRL (1998)





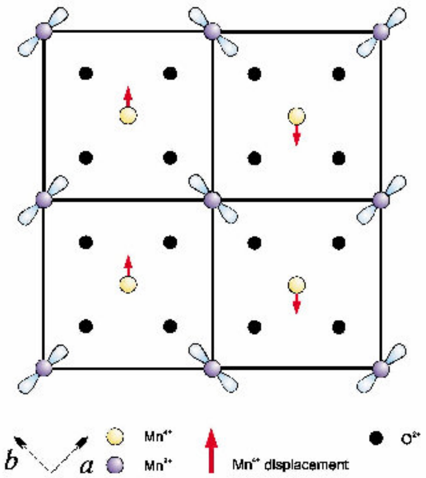


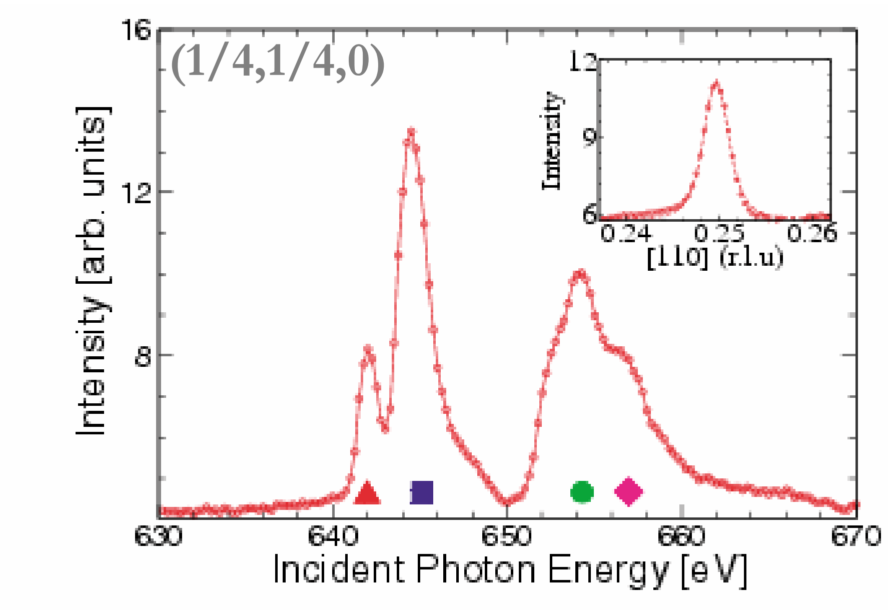
Mn K edge
Dipole E1-E1 channel
1s -> 4p

Orbital Order

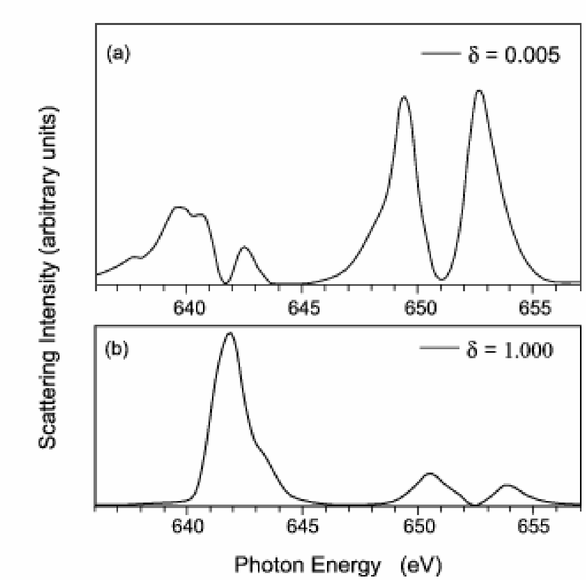
Direct Observation of Orbital Ordering in $La_{0.5}Sr_{1.5}MnO_4$
Wilkins et al., PRL (2003)

Mn L edge
Dipole E1-E1 channel
2p -> 3d





Caslteton and Alterelli PRB (2000)

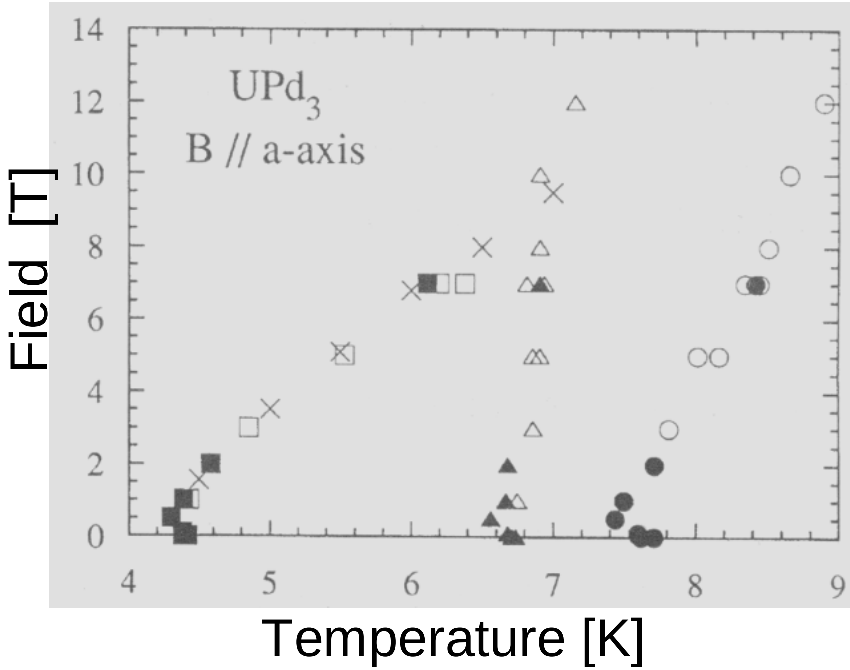


UPd_3

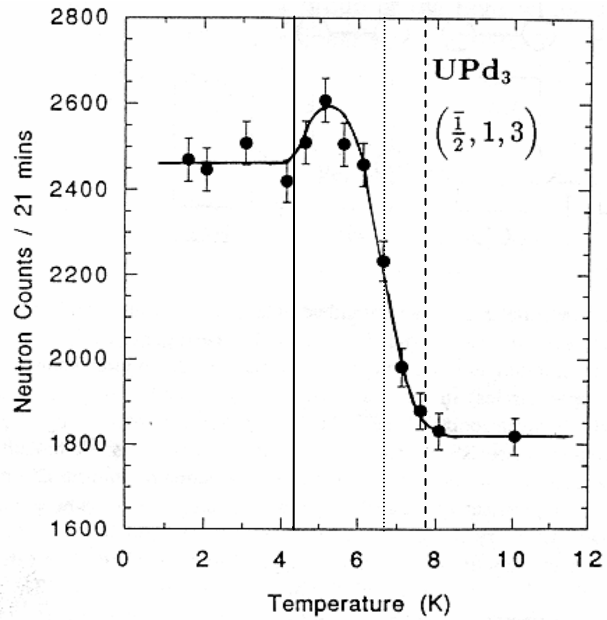
Structure: ***dhcp*, 2 U sites, hex. and quasi-cubic**

Electronic configuration: **Localised U^{4+}, $5f^2$**
Neutrons and CEF analysis
Singlet ground states at both sites
$\chi_{cubic} \gg \chi_{hex}$

Phase transitions:



Neutron diffraction:
Lattice distortions in UPd_3
McEwen et al.

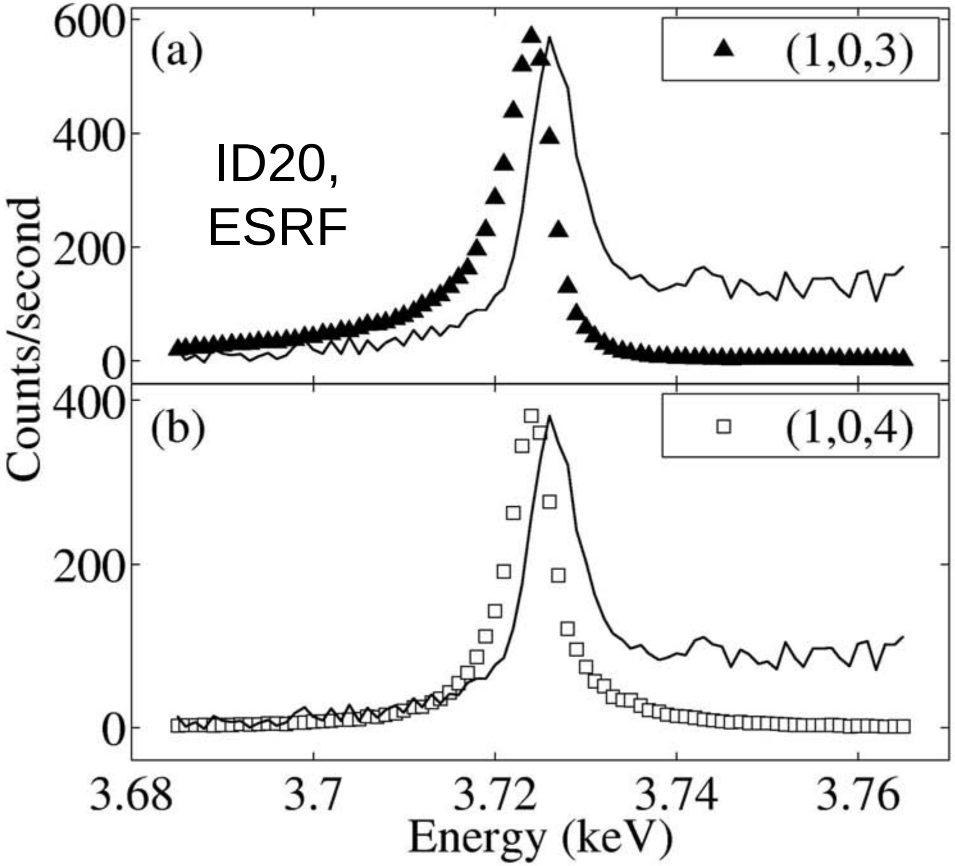


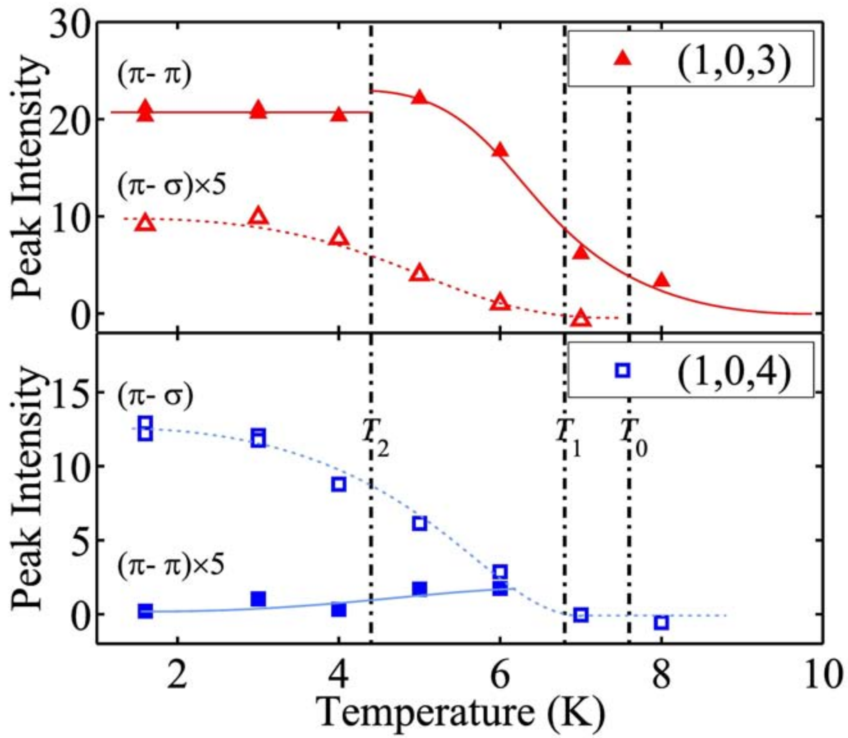
Direct evidence for antiferroquadrupolar order in UPd_3

D.F. McMorrow, K.A. McEwen, U. Steigenberger et al. PRL (2001)

Resonant Scattering at the U M_{IV} edge

Low-temperature response, T=1.5 K



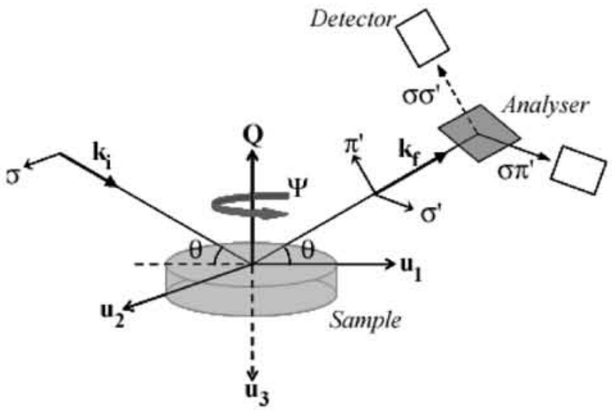


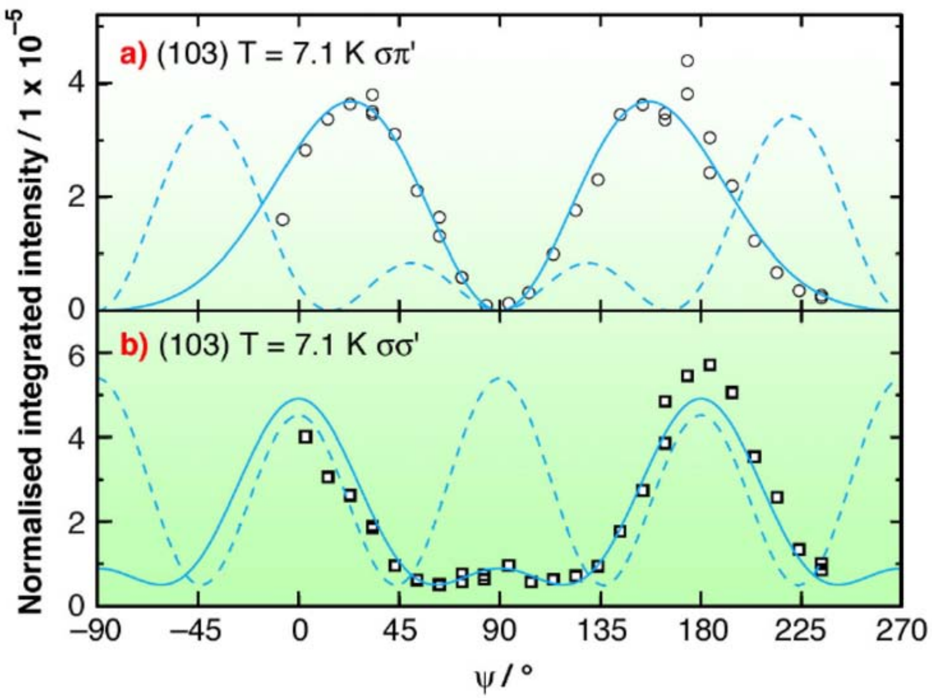
Resonance: 3d -> 5f

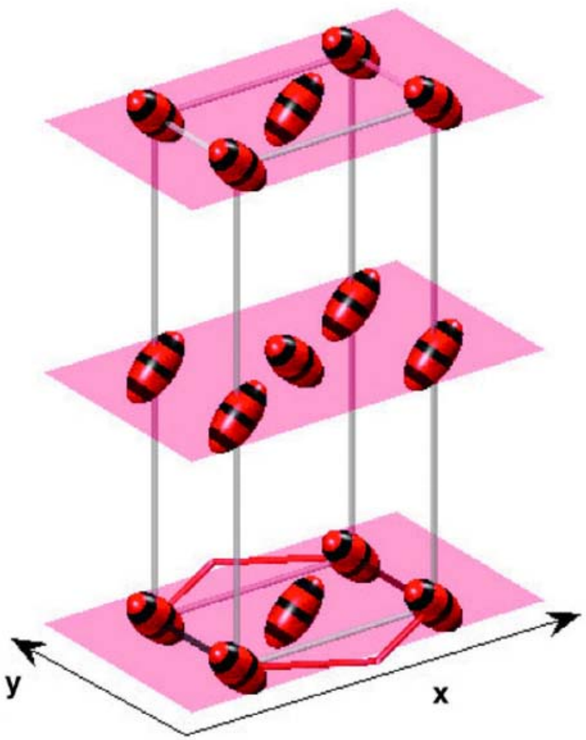
Long-range order of the 5*f* U electrons

Determination of the antiferroquadrupolar order parameters in UPd_3

H. C. Walker, K.A. McEwen, D.F. McMorrow et al. PRL (2006)







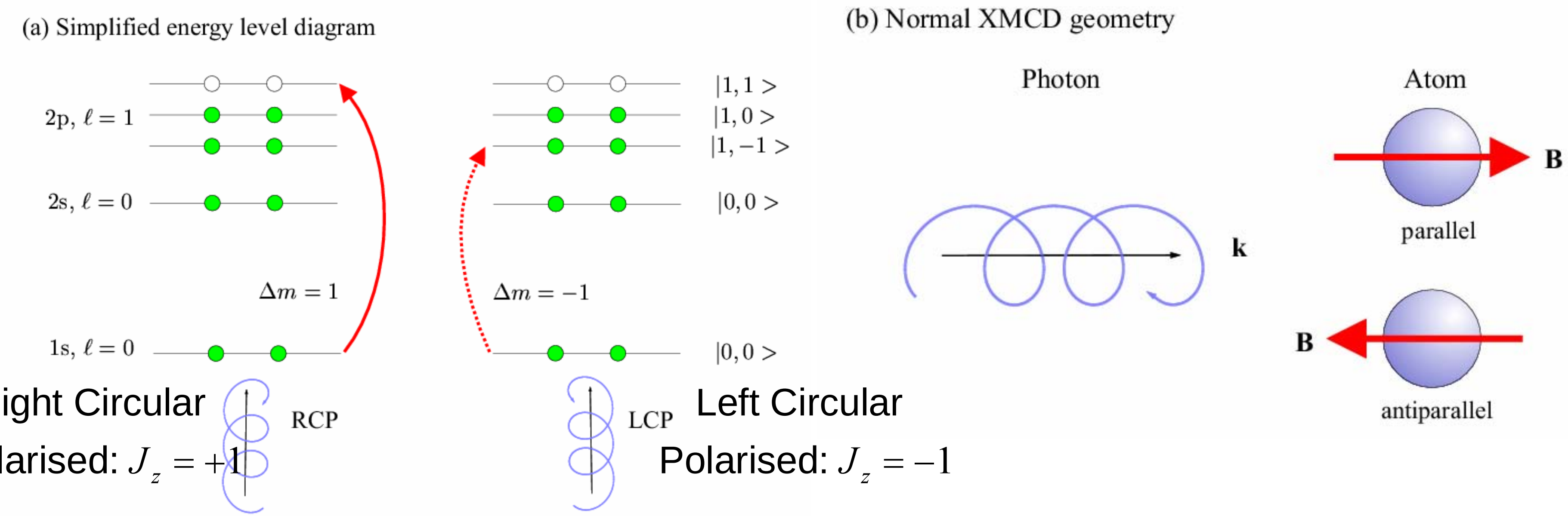
Order parameter is Q_{zx}

Not Q_{x2-y2}

Absorption and Dichroism

Dichroism: Preferential absorption of one of two orthogonal photon polarization states.

Assume Circularly polarized lights and Dipole Selction rules: $\Delta\ell = \pm 1$



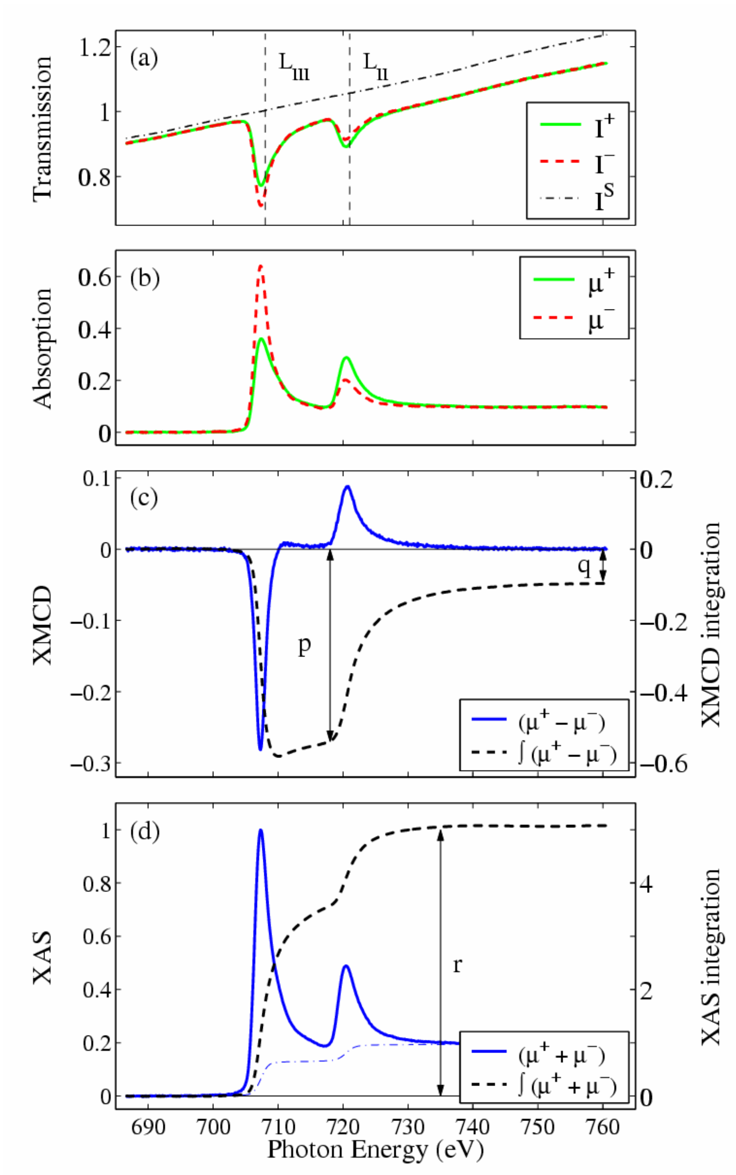
Right Circular Polarised: $J_z = +1$

Left Circular Polarised: $J_z = -1$

X-ray Magnetic Circular Dichroism: Erskine and Stern (1975), Thole et al. (1985), van der Laan et al. (1986), Schutz et al. (1987)

X-ray Magnetic Circular Dichroism

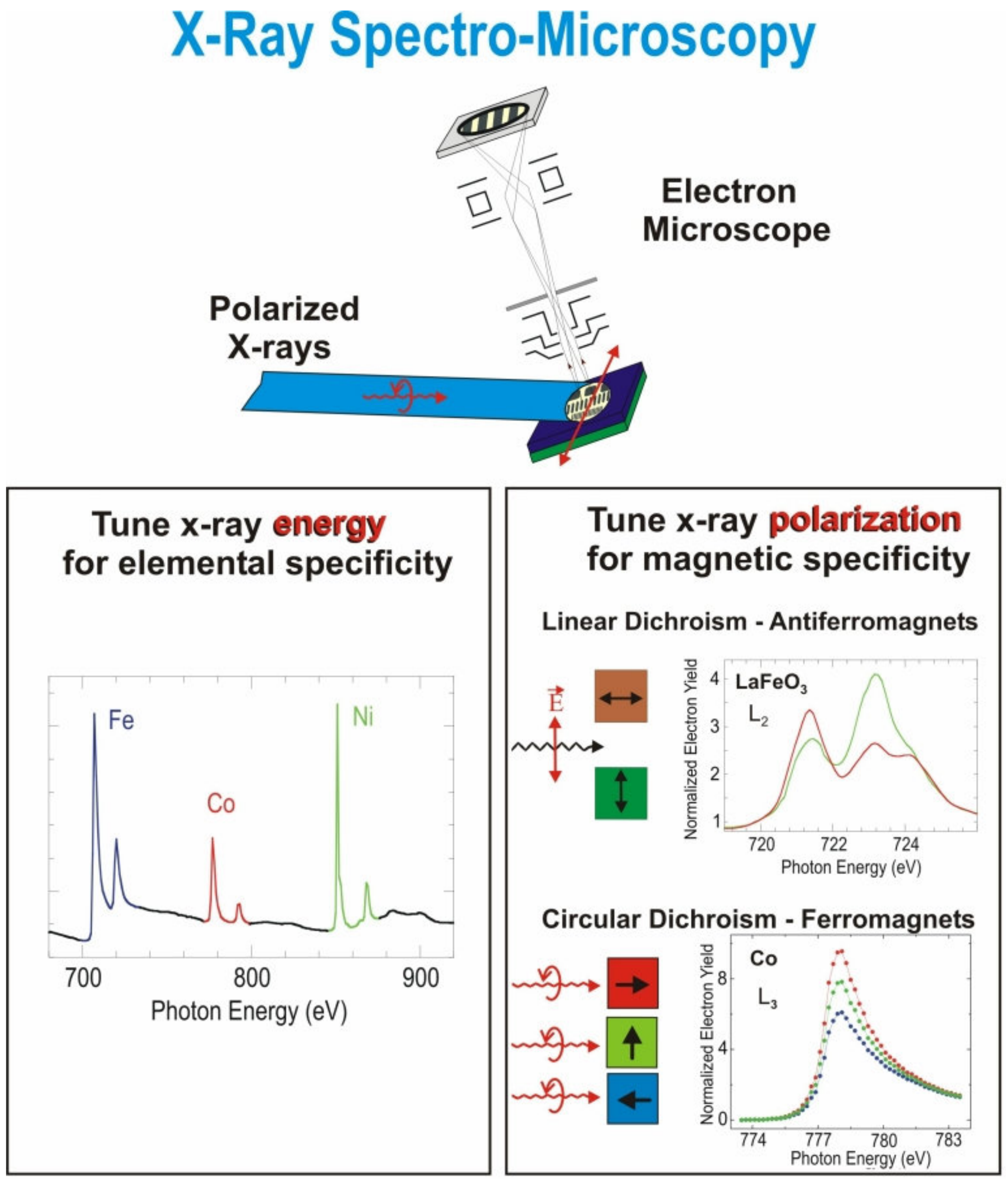
Iron thin films, Chen et al. PRL (1995)



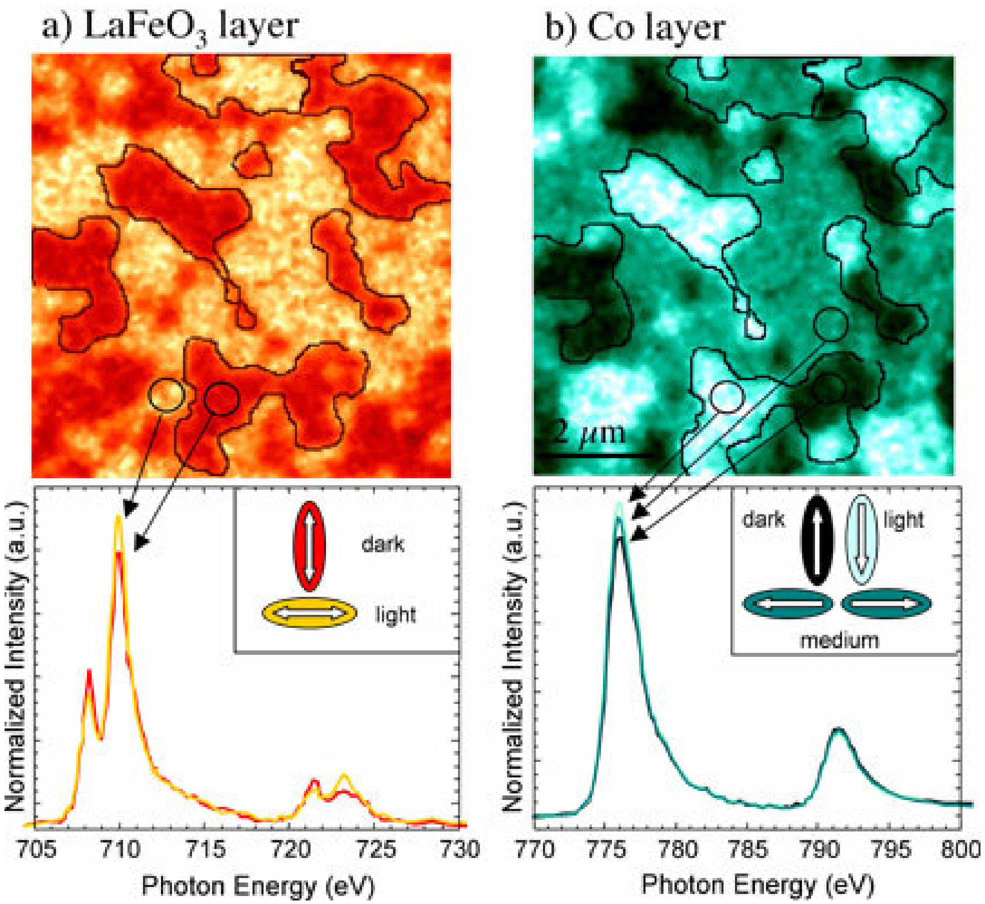
XMCD Sum Rules: Obtain the orbital and spin moments from integrals of the dichroic signal over the appropriate edges. (Thole et al. (1992), Carra et al. (1993))

$$m_{orb}[\mu_B / atom] = -\frac{4q(10 - n_{3d})}{r}$$

$$m_{spin}[\mu_B / atom] \approx -\frac{(6p - 4q)(10 - n_{3d})}{r}$$

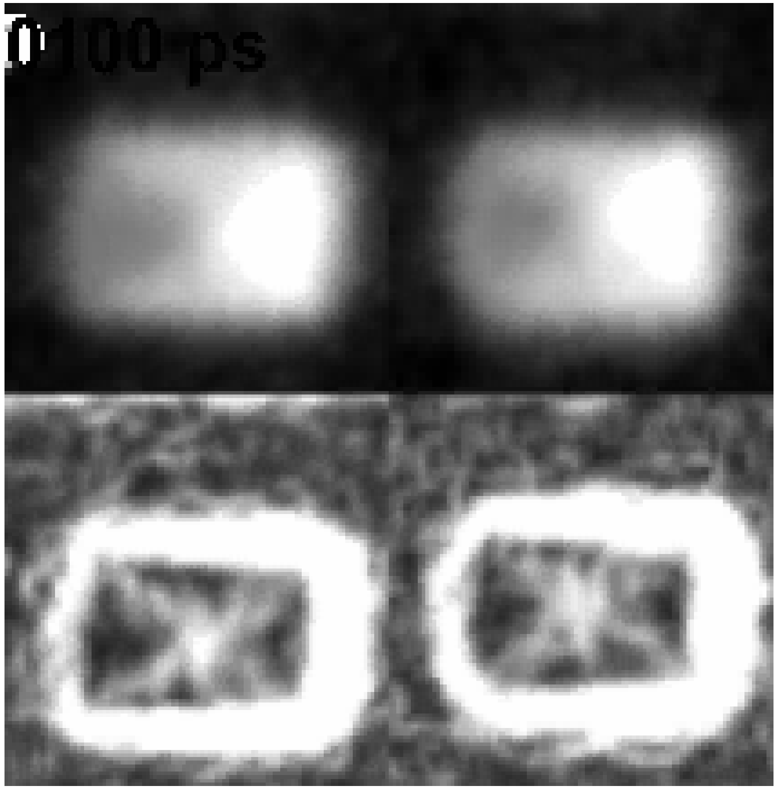

X-Ray Spectro-Microscopy
Electron Microscope
Polarized X-rays
Tune x-ray energy for elemental specificity
Fe
Co
Ni
700
800
900
Photon Energy (eV)
Tune x-ray polarization for magnetic specificity
Linear Dichroism - Antiferromagnets
E
LaFeO3
L2
Normalized Electron Yield
1
2
3
4
720
722
724
Photon Energy (eV)
Circular Dichroism - Ferromagnets
Co
L3
Normalized Electron Yield
0
4
8
774
777
780
783
Photon Energy (eV)

PEEM Reveals Spin Alignment in Magnetic Layers



http://www-ssrl.slac.stanford.edu/stohr/

PICOSECOND MAGNETIZATION DYNAMICS



http://www-ssrl.slac.stanford.edu/stohr/

Magnetism: Neutrons and X-rays

Neutrons:

- Interaction is "simple" and understood
- Interaction with magnetism as strongly as with "structure"
- Polarized techniques
- Inelastic Scattering (magnons, crystal-field levels)
- Information on electron structure is very indirect
- Large samples
- L and S inseperable

X-rays:

- Interaction is "complex"
- Interaction is "complex"!!!
- Interaction with magnetism is weak except for some resonant processes
- Polarized techniques
- Jury is still out on inelastic processes – likely not to be useful
- Element and electron shell specific at resonance
- Small samples
- L and S separable (non-resonant)