X-Ray Scattering
with synchrotron radiation

E. Ercan Alp

Advanced Photon Source

Argonne National Laboratory, Argonne, Illinois 60439

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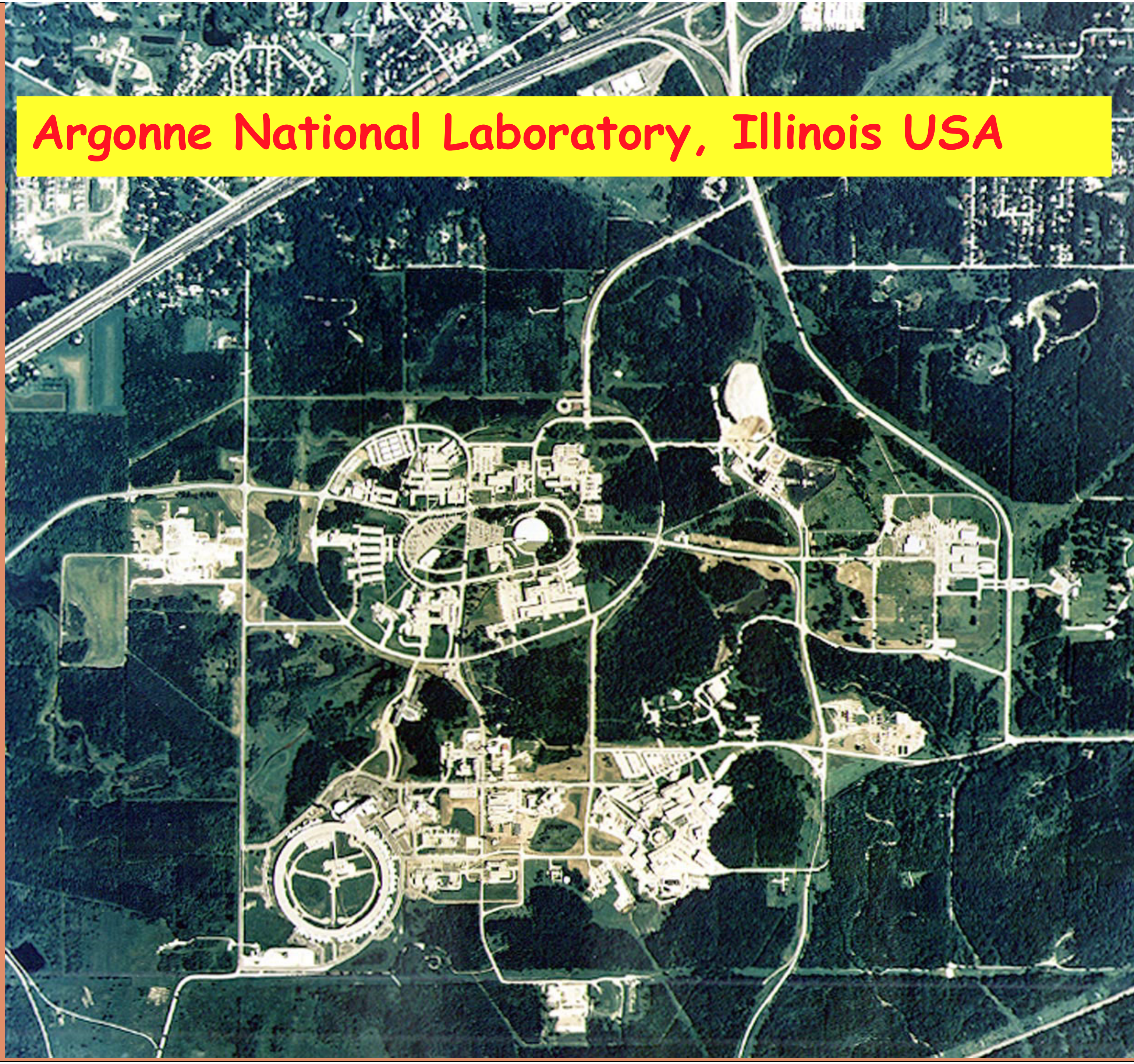
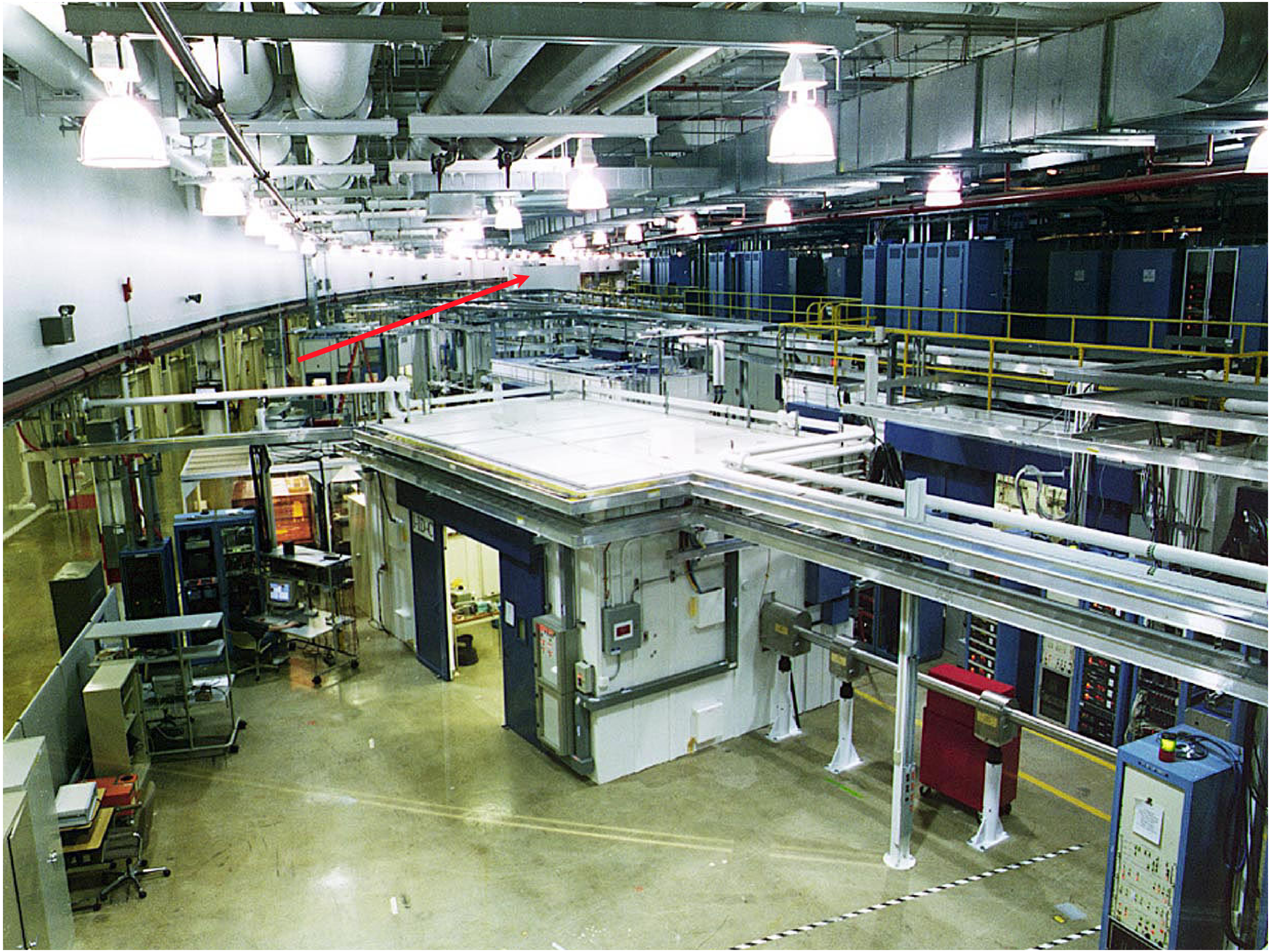
Amman, Jordan

Advanced Photon Source

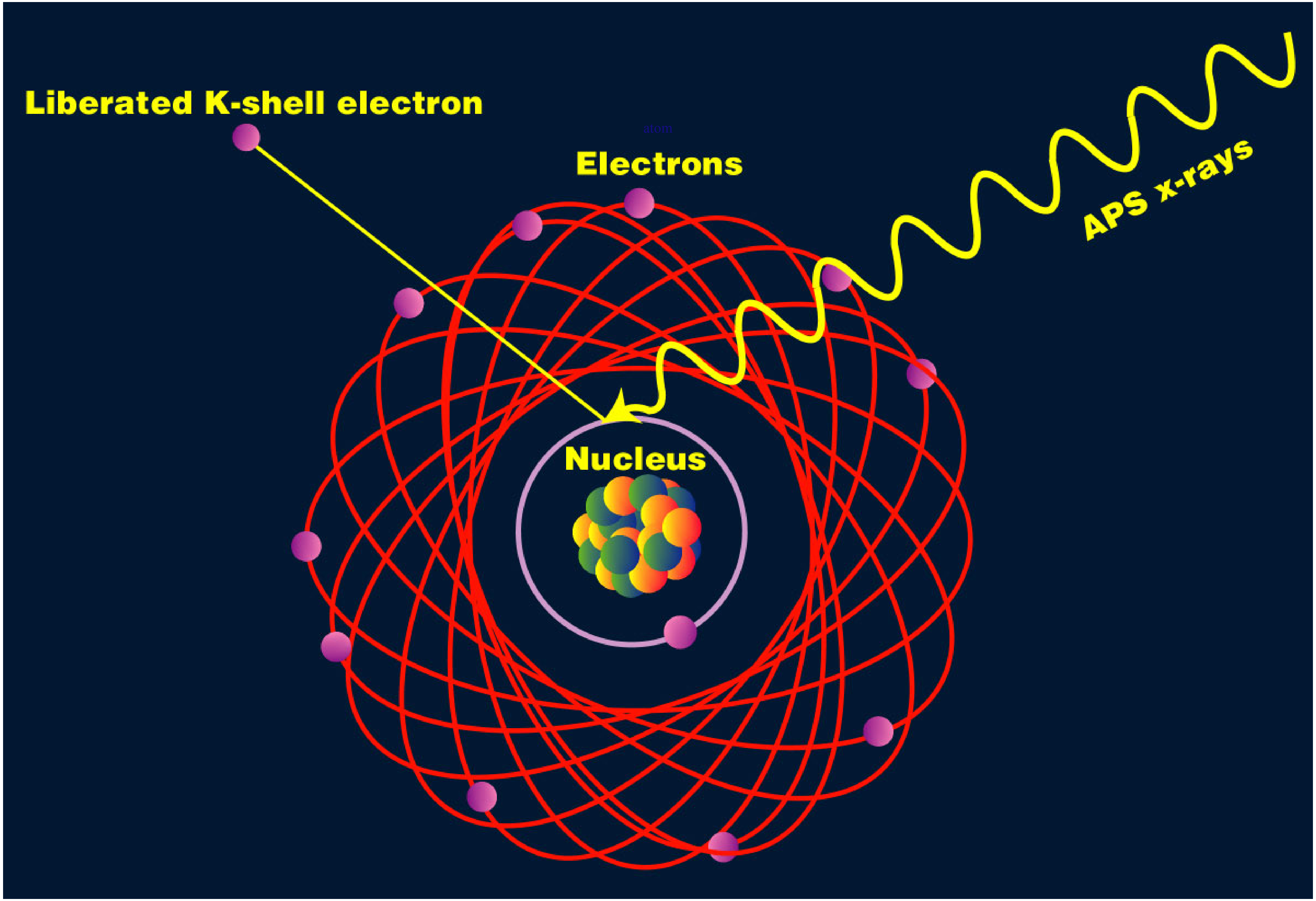
Argonne National Laboratory, Illinois USA





What is x-ray scattering ?

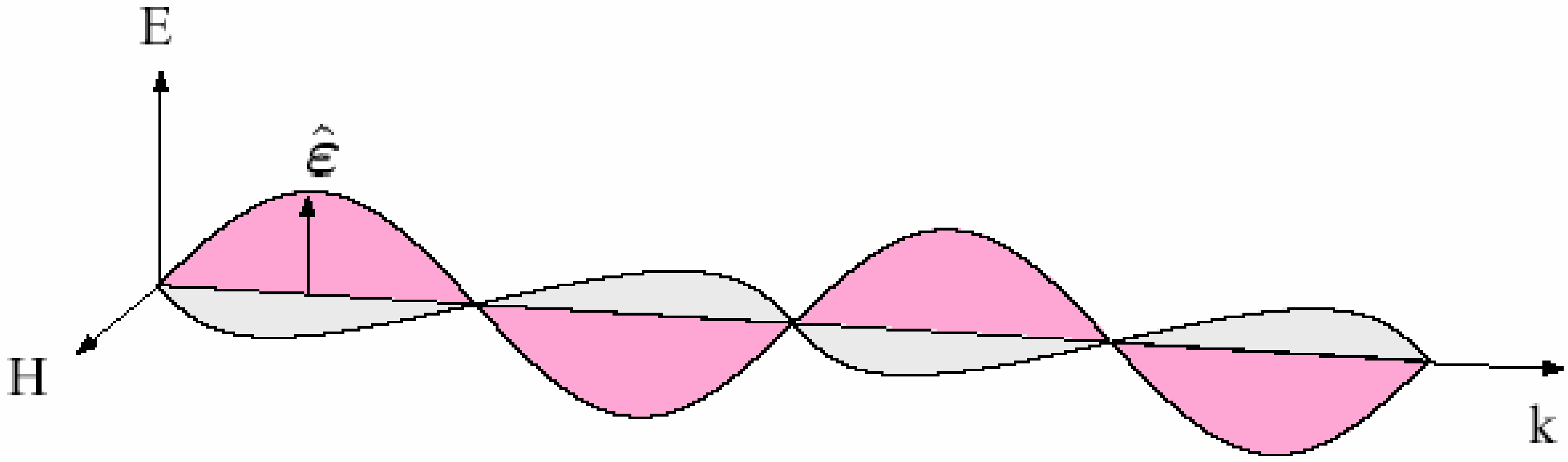
- Scattering
  - Coherent or incoherent
- Diffraction
  - Always coherent
- Spectroscopy
  - Frequency distribution


Liberated K-shell electron
Electrons
APS x-rays
Nucleus

Elements of Modern X-Ray Physics

Jens Als-Nielsen & Des McMorrow

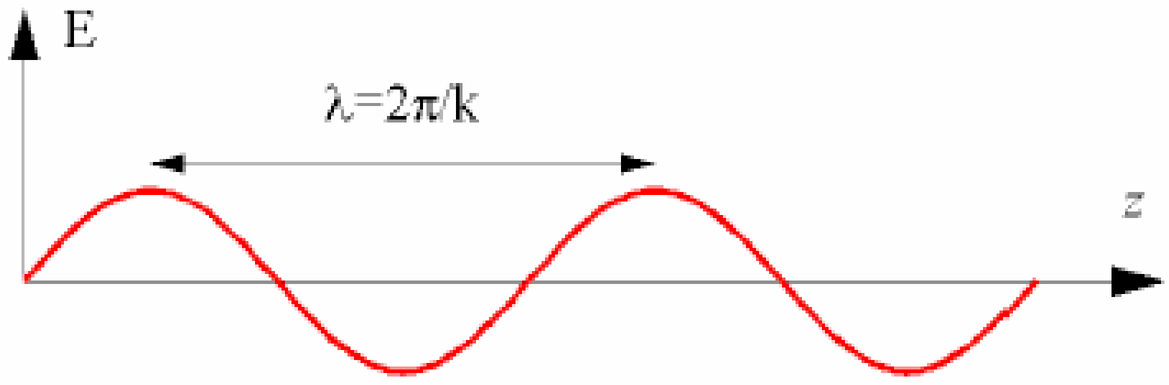
J. Wiley, 2001



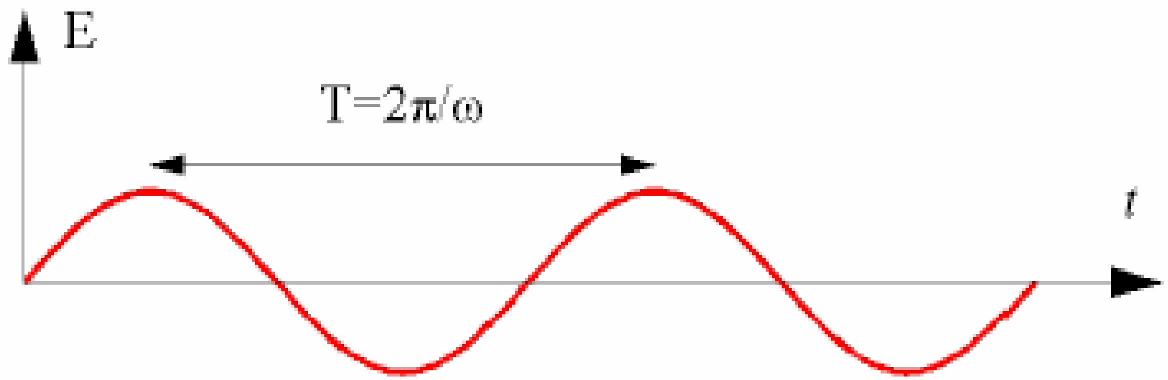
X-rays are transverse electromagnetic waves where electric and magnetic fields are perpendicular to the direction of propagation (Barla, 1904).

Electromagnetic waves

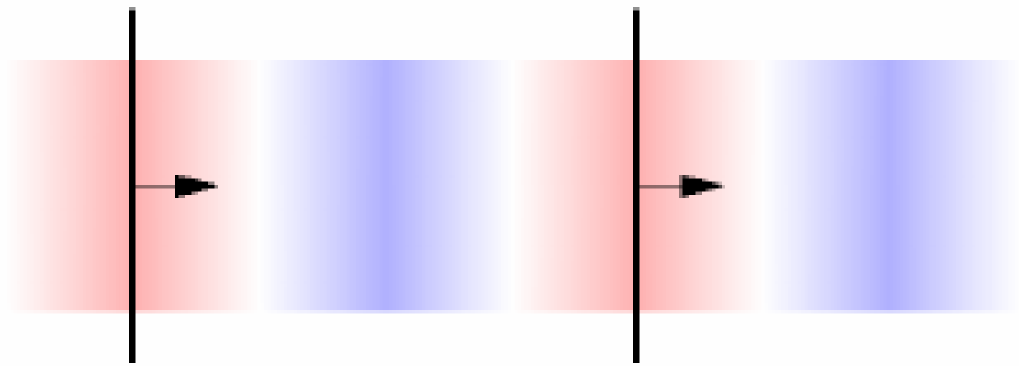
Spatial variation
k= wave number
λ=wavelength



Temporal variation
ω = angular frequency



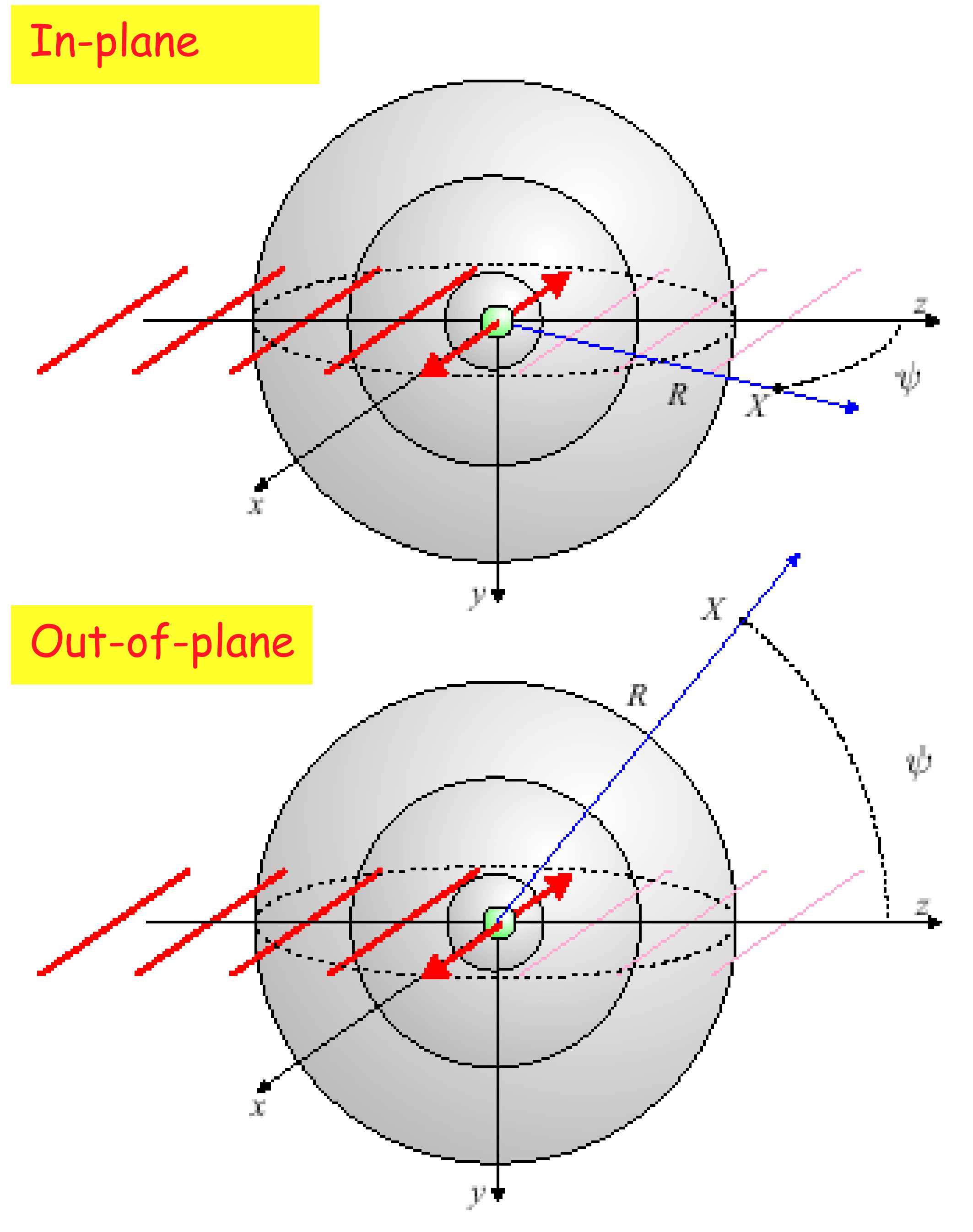
Top view showing high
and low field amplitudes

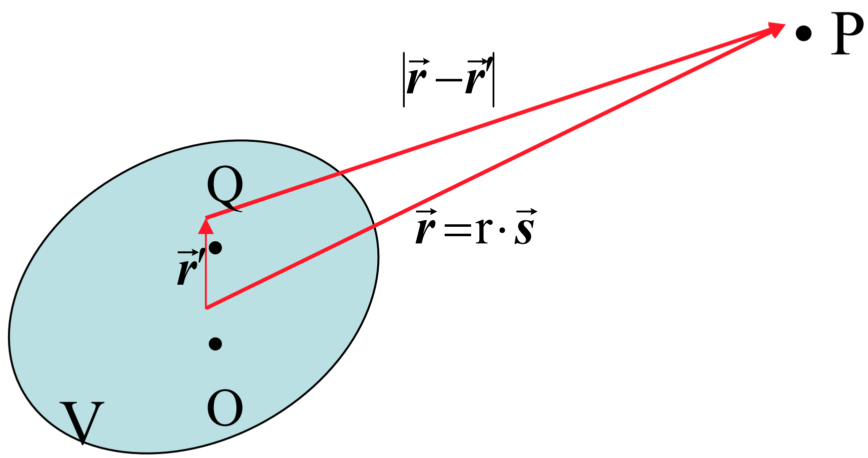


Classical description of scattering of radiation by a charged particle

The incident plane wave incident upon an electron sets the electron in oscillation. The oscillating electron then radiates, experiencing a

phase shift of π.





Principles of Optics

Born & Wolf

Cambridge University Press

7th edition (1999)

Scattering from one electron can be classically viewed as radiation emitted from a dipole.

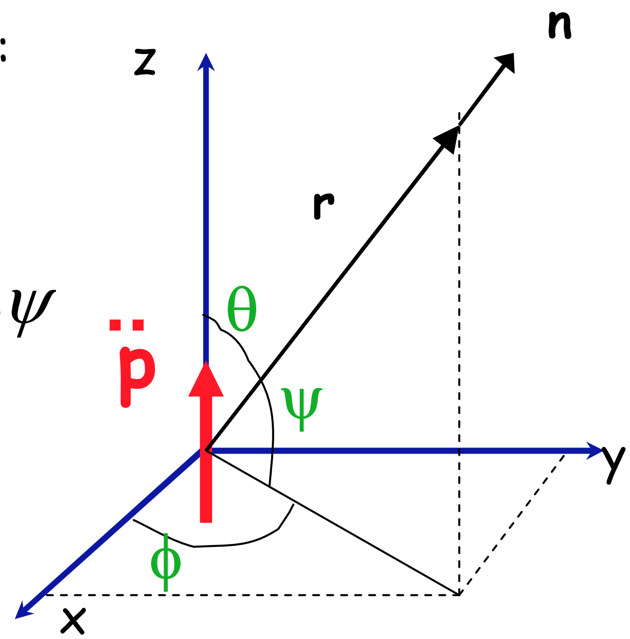
The radiated field at a distance R as a function of time is given by:

$$E_{rad}(R,t)=\frac{-e}{4\pi\varepsilon_0 c^2 R}a_X(t'),\quad t'=t-R/c$$

Classical electron radius

Acceleration = force/mass

Acceleration seen by the observer at $\psi = \pi/2$ is zero:



$$a_X(t') = \frac{-e}{m} E_{x0} e^{-i\omega t'} \cos\psi = \frac{-e}{m} E_{in} e^{-i\omega R/c} \cos\psi$$

$$E_{rad}(R,t) = -\frac{-e}{4\pi\varepsilon_0 c^2 R} \frac{-e}{m} E_{in} e^{-i\omega R/c} \cos\psi$$

$$\frac{E_{rad}(R,t)}{E_{in}} = -\frac{-e}{4\pi\varepsilon_0 c^2 R} \frac{-e}{m} \frac{e^{ikR}}{R} \cos\psi$$

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82 \cdot 10^{-13} m$$

Classical electron radius
Thomson scattering length

Differential Scattering cross-section

$$\frac{I_{scattered}}{I_{incident}} = \left(\frac{d\sigma}{d\Omega}\right) = \frac{|E_{rad}|^2 R^2 \Delta\Omega}{|E_{inc}|^2 A_0} = r_0^2 \cos^2\psi$$

when all angles are included

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{8\pi}{3}\right) r_0^2 = 0.655 \text{ barn, } 1 \text{ barn} = 10^{-24} \text{ cm}^2$$

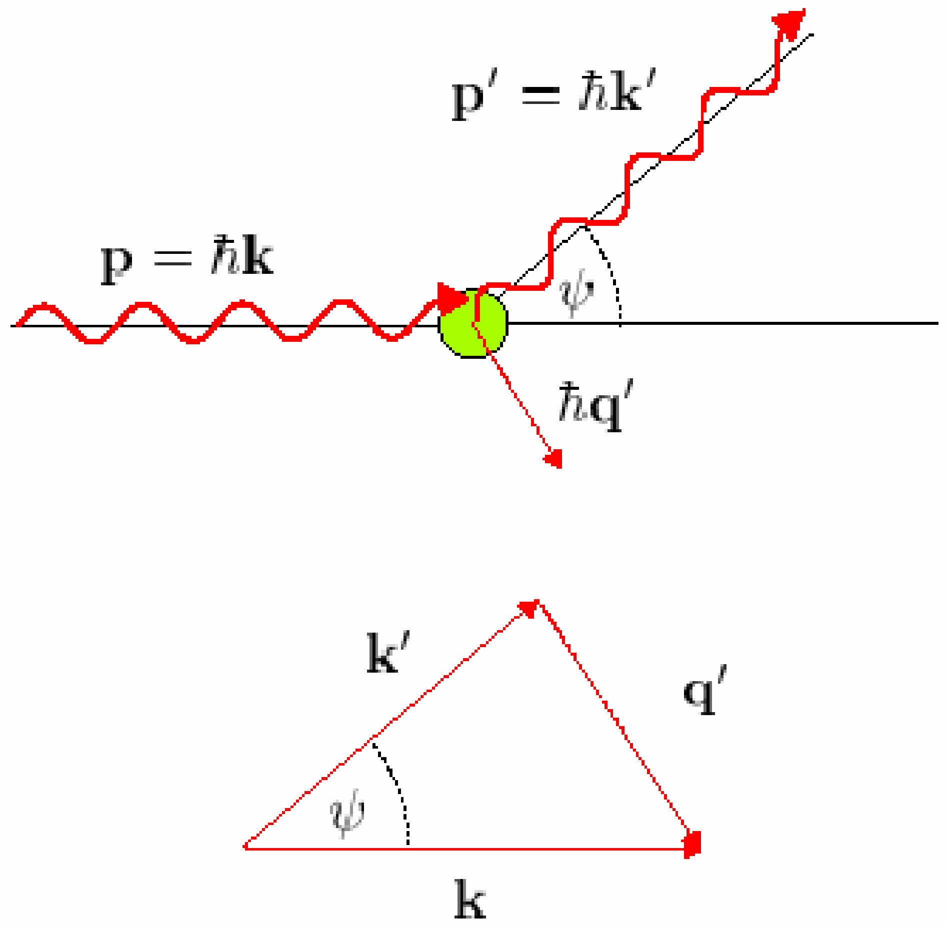
The interesting aspect of this result is that the classical scattering Cross-section from an electron is INDEPENDENT of energy

Scattering cross-section (cont'd)

$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 P$$

$$P = \begin{cases} 1 & \text{synchrotron radiation, vertical scattering plane} \\ \cos^2\varphi & \text{synchrotron radiation, horizontal scattering plane} \\ \frac{1}{2}\left(1+\cos^2\varphi\right) & \text{unpolarized source like x-ray tube} \end{cases}$$

Momentum and energy transfer in a scattering process



Scattering of electromagnetic waves from charged particles

Born Approximation

Consider a monochromatic electromagnetic field scattering from a isotropic, static medium with :

$$\nabla^2 E(r,\omega) + k^2 n^2(r,\omega) E(r,\omega) = 0$$

This equation has already some simplifications like dielectric constant

has a slow variation with position, $\varepsilon(r,\omega) = n^2(r,\omega)$

where n is the index-of-refraction, or refraction index of the medium.

Born & Wolf, ***Principles of Optics***, 7th edition, pp 695-700 (1999)

If we take a single Cartesian component of ***E (r,ω)*** as ***U (r,ω),*** we can write the following scalar equation ***:***

$$\nabla^2 U(r,\omega) + k^2 n^2(r,\omega) U(r,\omega) = 0$$

$$\nabla^2 U(r,\omega) + k^2 U(r,\omega) = -4\pi F(r,\omega) U(r,\omega)$$

$$F(r,\omega) = \frac{1}{4\pi}\left[n^2(r,\omega) - 1\right] \text{ : scattering potential}$$

If the field $U(r,\omega)$ is considered to be sum of incident and scattered fields

$$U(r,\omega) = U^i(r,\omega) + U^s(r,\omega)$$

One can approximate the incident field to be a plane wave, which propogate according to Helmholtz equation:

$$(\nabla^2 + k^2) U^i(r,\omega) = 0$$

and the scattered field

$$(\nabla^2 + k^2) U^s(r,\omega) = -4\pi F(r,\omega) U(r,\omega)$$

An inhomogeneous differential equation can be solved using Green's function approach:

$$\left(\nabla^2 + \mathrm{k}^2\right)\boldsymbol{G}(\vec{r} - \vec{r}', \omega) = -4\pi\delta(\vec{r} - \vec{r}')$$

and choose $\boldsymbol{G}(\vec{r} - \vec{r}', \omega) = \dfrac{e^{i\mathrm{k}|\mathbf{r}-\mathbf{r}'|}}{|\vec{r} - \vec{\mathbf{r}}'|}$

When the field propagates in a specific direction in real space, $\vec{s}_0$**,**

the time independent part of $U^{i}(r,w) = e^{\mathrm{ik}\,\vec{s}_0 \cdot \vec{r}}$**, and**

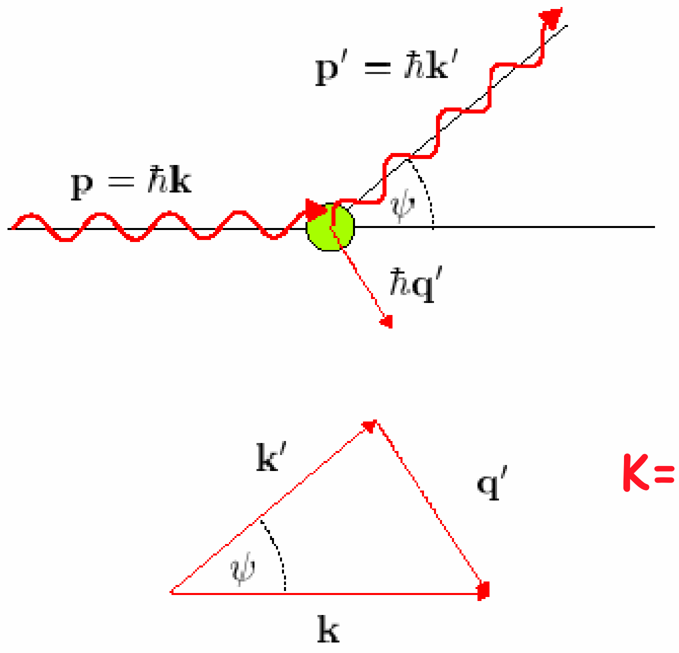
$$U(r,\omega) = e^{\mathrm{ik}\,\vec{s}_0 \cdot \vec{r}} + \int_V F(r',\omega)\, U(r',\omega) \frac{e^{i\mathrm{k}|\mathbf{r}-\mathbf{r}'|}}{|\vec{r} - \vec{\mathbf{r}}'|} \mathrm{d}^3\mathrm{r}'$$

This is an integral equation for the total field ***U(r,ω)*** within the scattering volume V. If the solution inside the volume V (i.e inside the scatterer, for which we have no idea, that's the reason we are doing the experiment) is known, then the solution for the exterior can be obtained.

First order Born approximation

For weakly scattering media, it is possible to obtain solution to the integral equation by a perturbation approach, provided that the scattering medium is weakly interaction with the probe of x-rays.

The first order Born approximation states that amplitude of the scattered wave far away from the scatterer depends entirely on one and only one Fourier component of the scattering potential, namely the one that corresponds to the transferred momentum $K=k(s-s_0)$.



K=k-k'

Conservation of momentum has a correspondence between classical and quantum mechanical treatment:

$$\boldsymbol{p} = \hbar \boldsymbol{k}$$

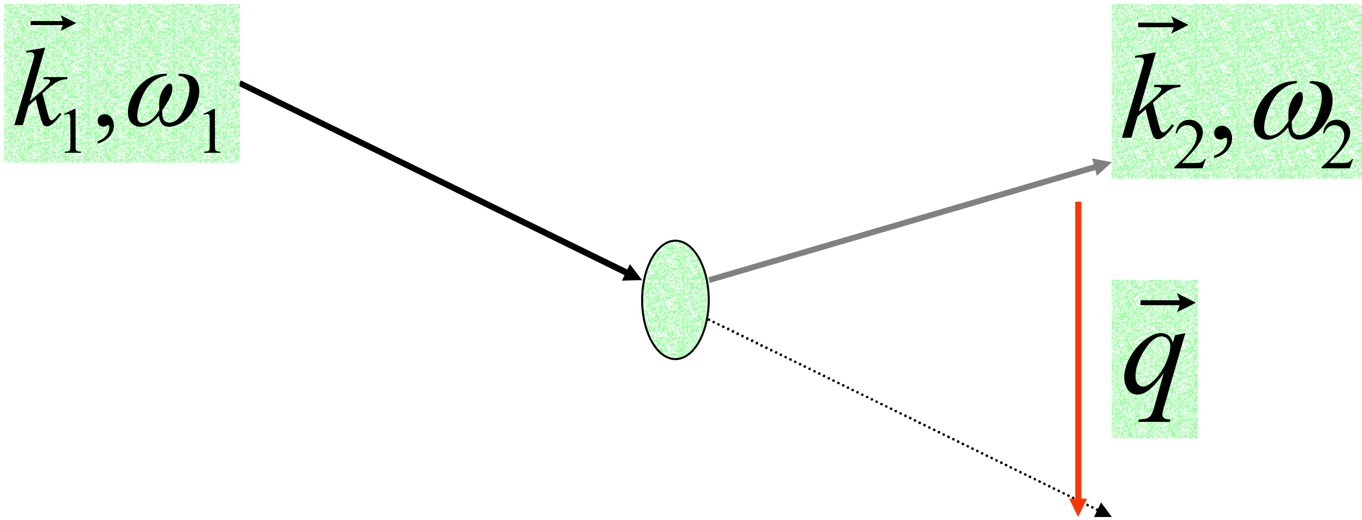
$$\Delta \boldsymbol{p} = \boldsymbol{p} - \boldsymbol{p}' = \hbar \boldsymbol{k}'$$

If a plane wave is incident on the scatterer in the direction of s, the Fourier component of the scattering potential can be determined.

And if one has the ability to vary the amount of momentum transfer at will, then, the scattering potential can be reconstructed.

This is the essence of x-ray scattering experiments.

Scattering geometry and physics



$\omega = \omega_1 - \omega_2$ energy transferred

$\vec{\mathbf{q}} = \vec{k}_1 - \vec{k}_2$ momentum transferred

What is really measured ?

The goal of the experiments is to measure the scattering cross - section

$$\frac{\mathrm{d}^2\sigma}{d\Omega d\omega}(\vec{\mathbf{q}},\hbar\omega)$$

Double differential Scattering cross-section

$$\frac{\mathrm{d}^2\sigma}{d\Omega d\omega}(\vec{q},\hbar\omega) \approx \left(\frac{\mathrm{d}\sigma}{d\Omega}\right)_{Thompson} S(\vec{\mathbf{q}},\omega) + \text{ resonant terms}$$

$$S(\vec{\mathbf{q}},\omega) = \frac{1}{2\pi}\int dt e^{-i\omega t}\left\langle i\left|\sum_{jj'} e^{-i\vec{\mathbf{q}}r_{j'}(t)} e^{i\vec{\mathbf{q}}r_j(0)}\right| f\right\rangle$$

is the Fourier transform of the correlation of the phase of the scattering amplitude at different times

Scattering geometry and physics

The physical origin of the correlations depends on how $1/\vec{\mathbf{q}}$ compares with l_c, the characteristic length, of the system related to the spatial inhomogeneity.

$$\text{when} \quad \vec{\mathbf{q}} \cdot l_c << 1 \qquad \Rightarrow \quad \text{COLLECTIVE BEHAVIOUR}$$

$$\text{when} \quad \vec{\mathbf{q}} \cdot l_c >> 1 \qquad \Rightarrow \quad \text{SINGLE PARTICLE BEHAVIOUR}$$

$$\text{when} \quad \frac{1}{\vec{\mathbf{q}}} \approx d \text{ and } \omega \approx \text{ phonon frequency } \Rightarrow \text{ Collective ion excitation}$$

$$\text{when} \quad \frac{1}{\vec{\mathbf{q}}} \approx r_c \text{ and } \omega \approx \text{ plasma frequency } \Rightarrow \text{ Valence electron excitation}$$

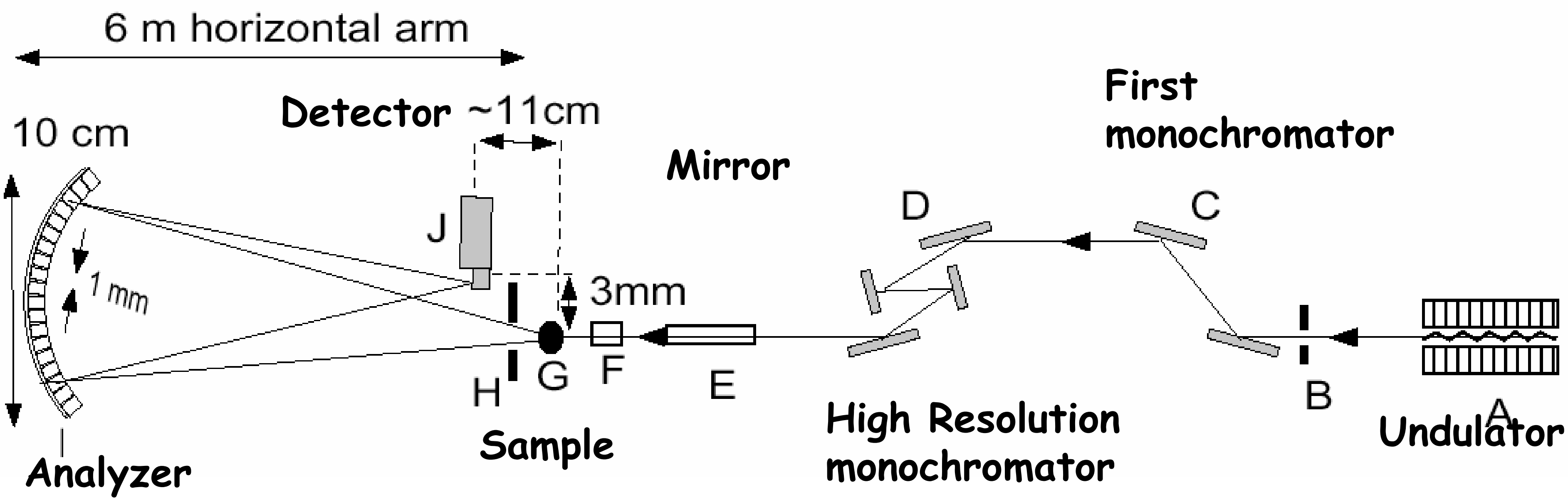
Inelastic X-Ray Scattering

- Study of atomic, electronic and collective excitations
- as a function of energy and spatial extension.
- Energy transfers from neV to keV (10^{12} eV)
- Momentum transfers from 1 to 100 nm^{-1} (10^{2} nm^{-1})
- Bulk probe, non-destructive
- Suitable for wide range of parameter space:
  - Temperature
  - Pressure
  - Magnetic field
  - Chemical doping

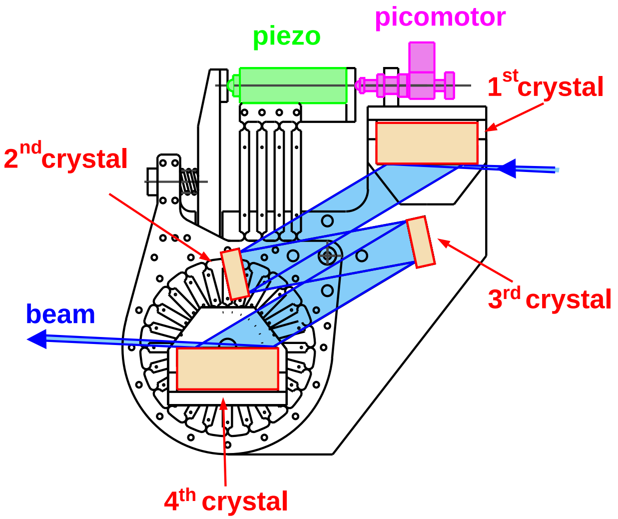
Inelastic X-Ray Scattering (cont'd)

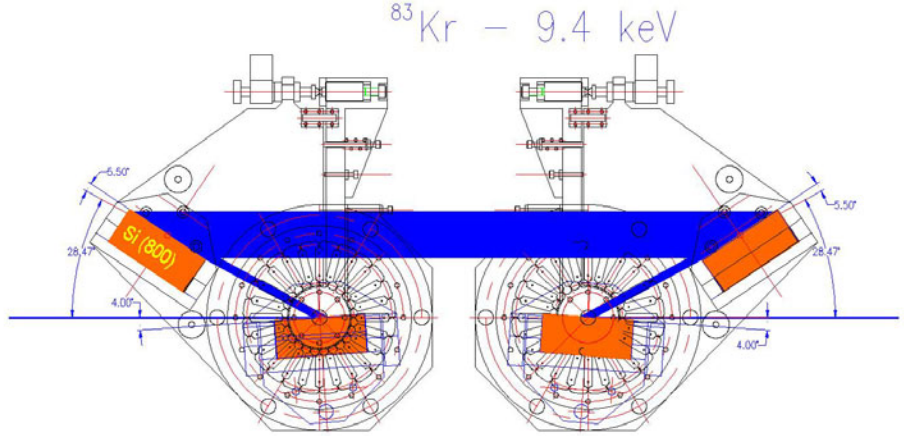
	Energy	Energy Transfer	Science
Nuclear Resonant Inelastic XRay Scattering	6-30 keV	neV-100 meV	Phonons, magnons, thermodynamic and elastic properties
Collective lattice excitations	10-30 keV	1-200 meV	Lattice dynamics, thermal and elastic properties of solids and liquids, phonons
Electronic excitations	0.1-10 keV	1-40 eV	Details of electronic energy levels, symmetry in Correlated electron systems
Compton scattering	10-100 keV	keV	Fermi surface in correlated electron systems, rare-earth compounds, heavy fermions

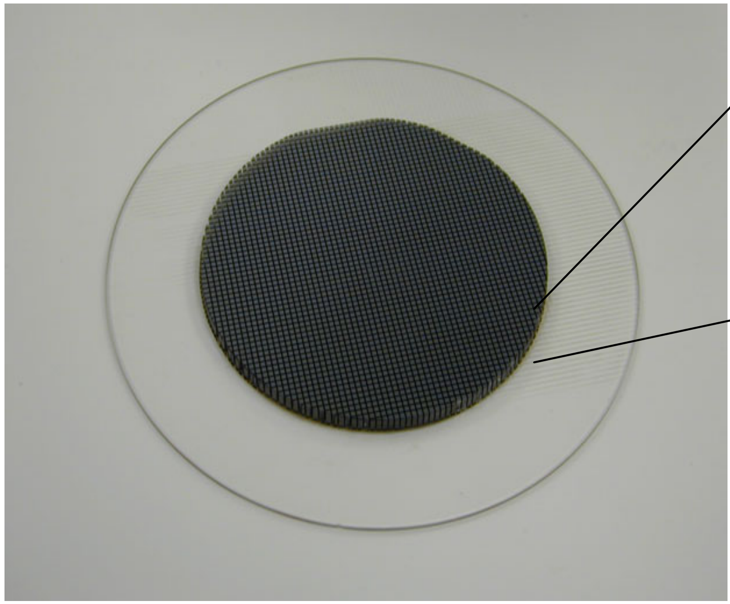
Set-up at 3-ID-C, APS

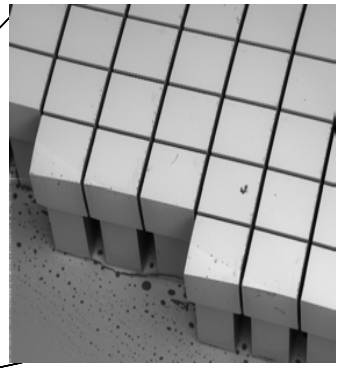


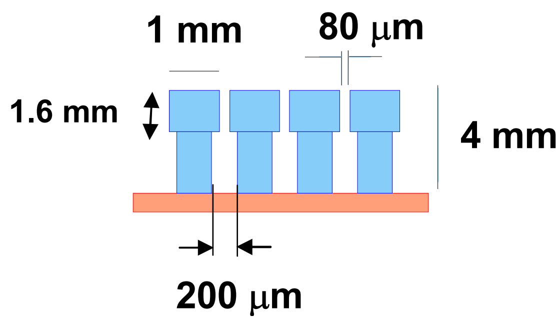
Monochromatization and energy analysis is going to be covered next time





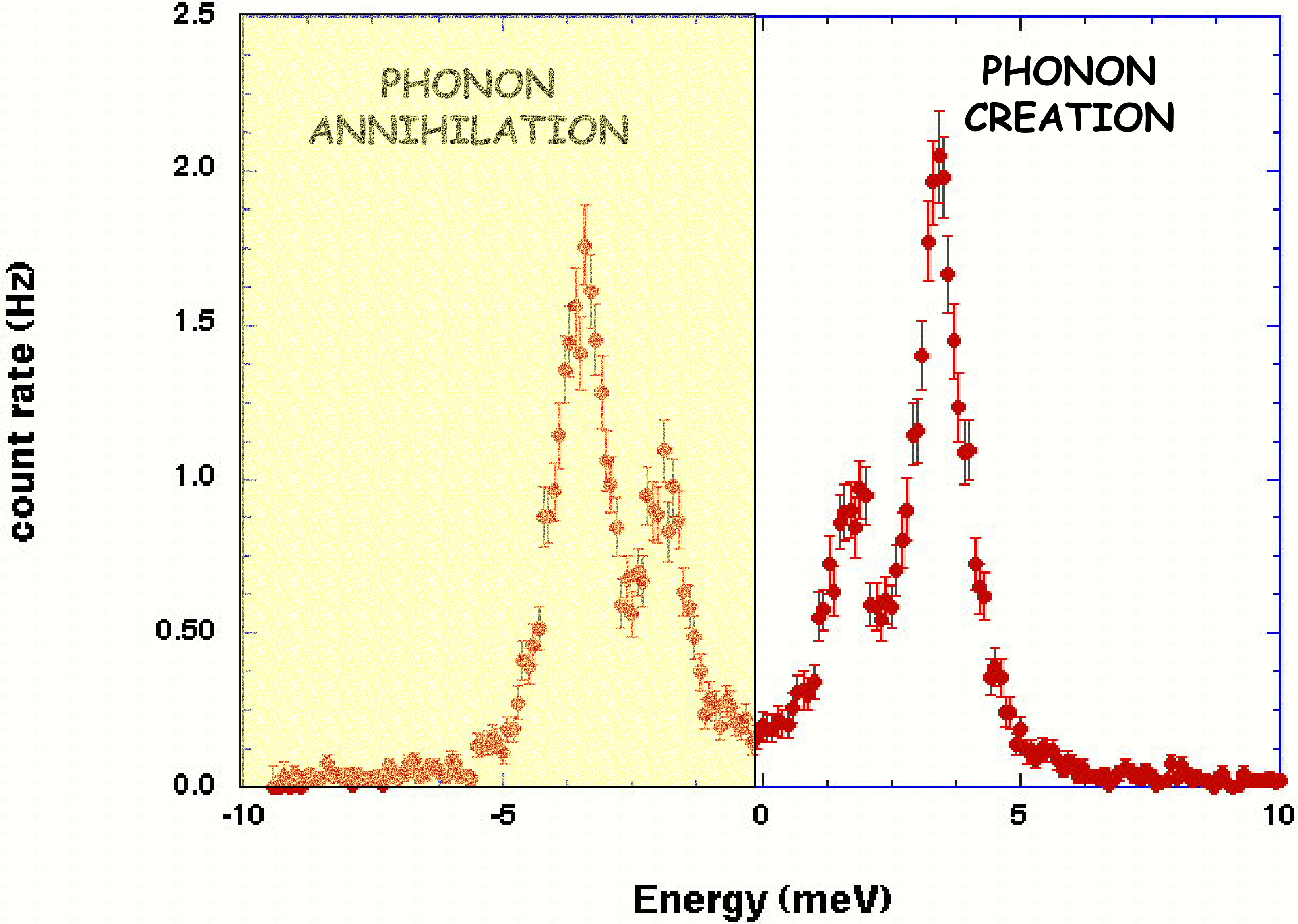




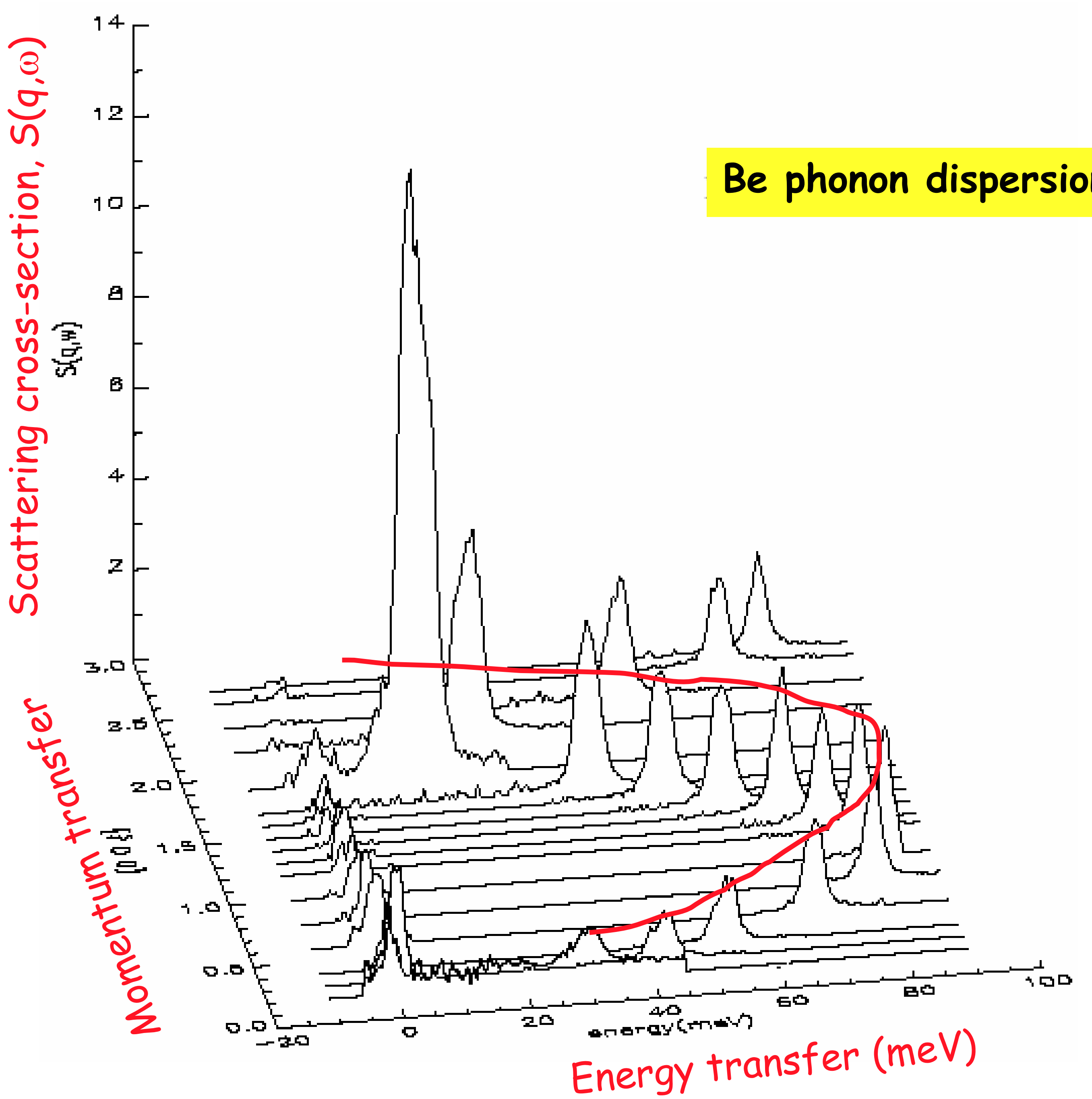


IXS in Al with 1 meV resolution at 25.701 keV

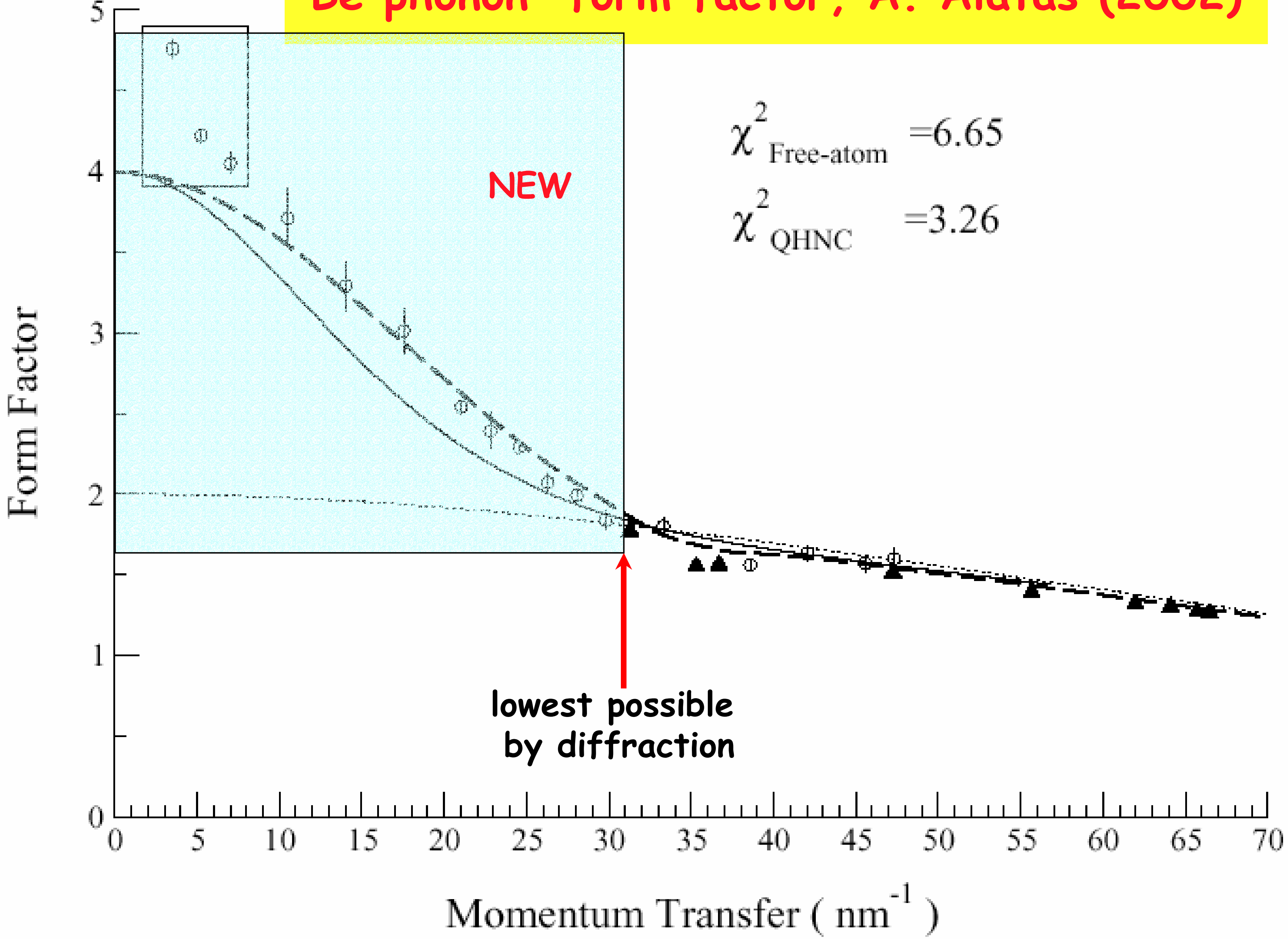
January 30,2002, @ 3-ID of the APS



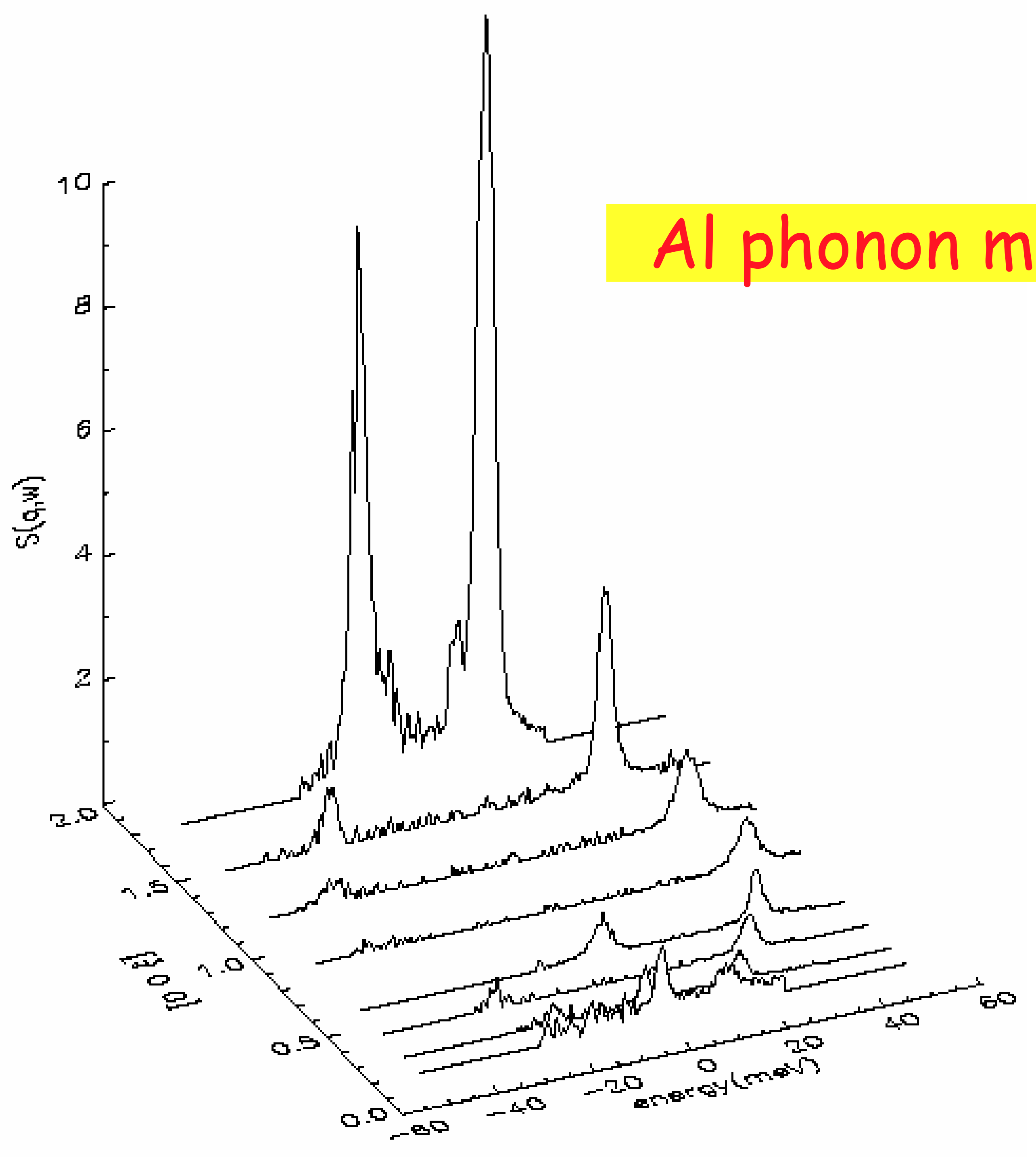
Be phonon dispersion measurements

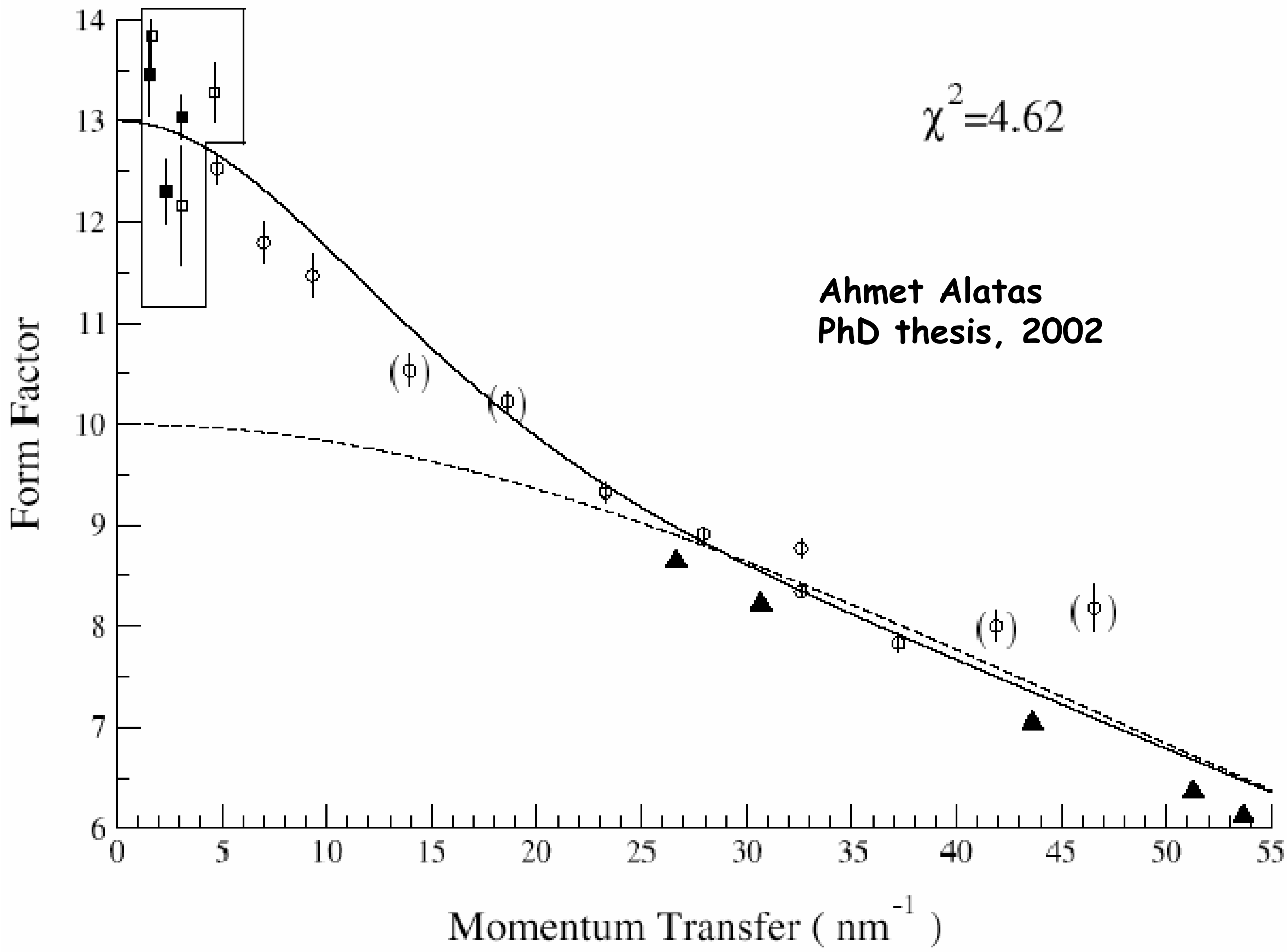


Be phonon form factor, A. Alatas (2002)



Al phonon measurements

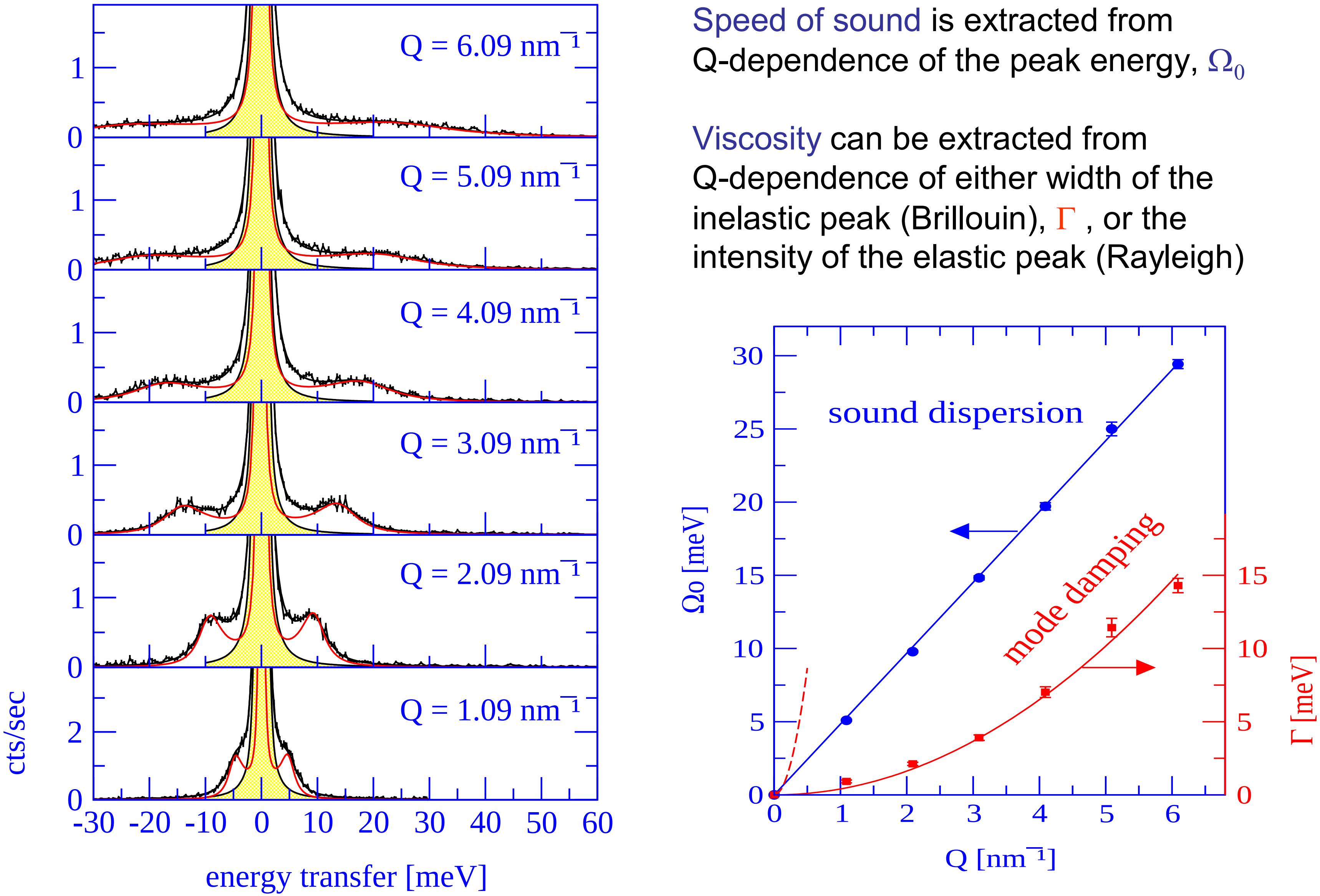



χ^2=4.62
Ahmet Alatas
PhD thesis, 2002
Form Factor
Momentum Transfer (nm^{-1})
14
13
12
11
10
9
8
7
6
0
5
10
15
20
25
30
35
40
45
50
55

Liquid Sapphire @ 2400 K (H. Sinn, D. Price, M. L. Saboungi)

Speed of sound is extracted from Q-dependence of the peak energy, Ω_0

Viscosity can be extracted from Q-dependence of either width of the inelastic peak (Brillouin), Γ , or the intensity of the elastic peak (Rayleigh)



Compton scattering by free electrons

The change in energy of photons as they are scattered by an electron is proportional to Compton scattering length given by

$$\lambdabar_c = \frac{\hbar}{mc}$$

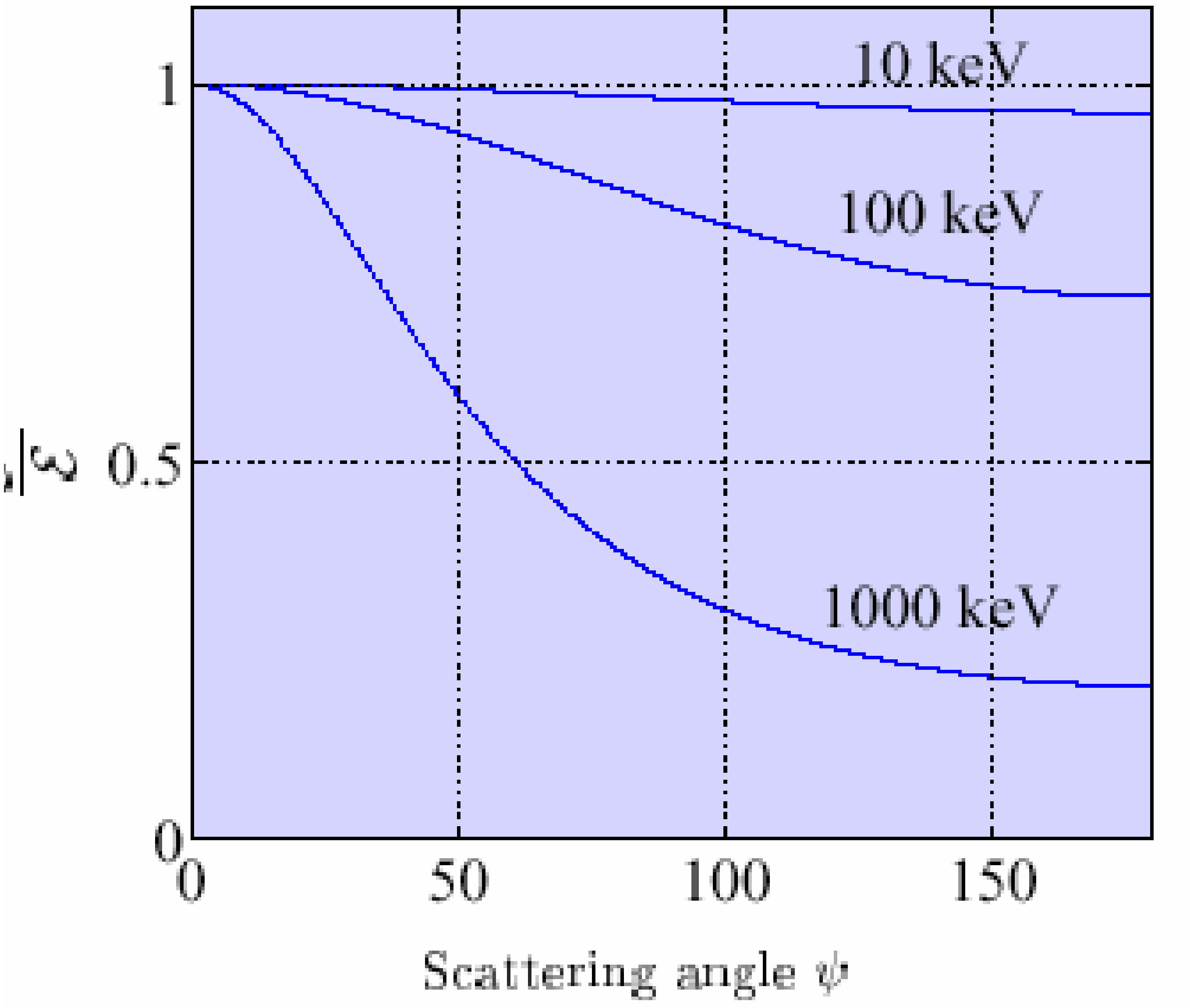
$$\frac{k}{k'} = \frac{\varepsilon}{\varepsilon'} = \frac{\lambda'}{\lambda} = 1 + \lambda_C k(1 - \cos\psi)$$

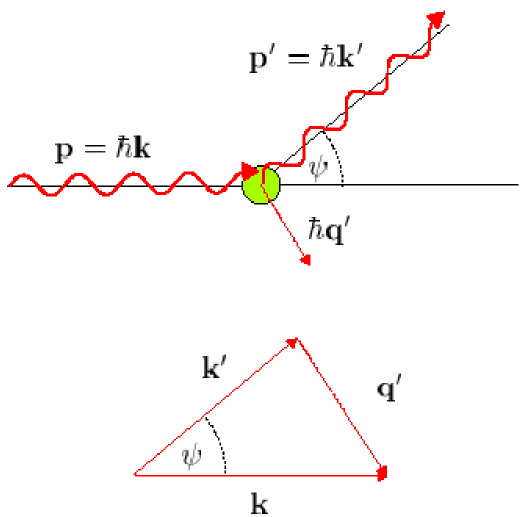
$$\alpha = \frac{r_0}{\lambdabar_c} = \frac{1}{137}$$

It is interesting to note that the ratio between classical electron radius and Compton scattering length is a fundamental constant.

Furthermore, it should be noted that Compton scattering is an extreme example of inelastic x-ray scattering, and it can be used to differentiate between localized (core) electrons and valence (free) electrons.

Energy loss during Compton scattering as a function of angle, and for different incident energies (after Jens Als-Nielsen)





Compton Scattering

3-D reconstruction of electron momentum density in Li

Y. Tanaka, et al
Phys. Rev. B 63 (2001) 045120

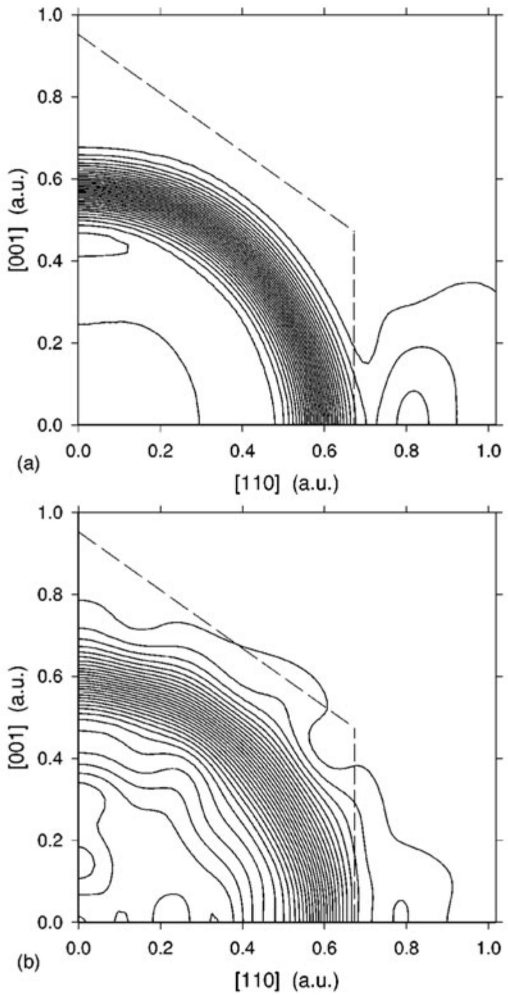


FIG. 4. Contour maps of the theoretical (a) and experimental (b) $\rho(\mathbf{p})$ on the (110) plane reconstructed using the filter function. Resolution broadening is included in the theory. The contour interval is 0.035 electrons/a.u.[3] The dashed lines mark the first Brillouin-zone boundary.

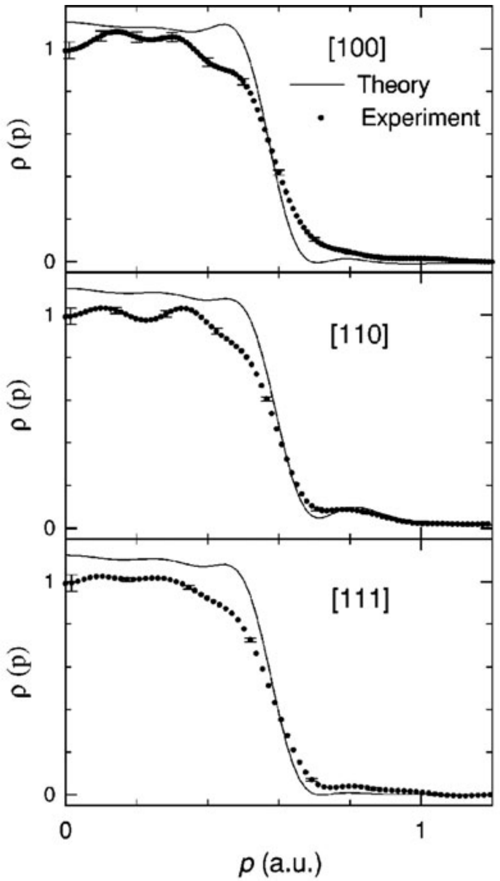


FIG. 6. [100], [110], and [111] sections through the reconstructed theoretical (solid lines) and experimental (dots) momentum densities shown in Fig. 4. Both sets of densities have been normalized such that $B(0)$ equals the number of valence electrons.

$$J(p_z) = \int\int \rho(\mathbf{p})\, dp_x dp_y ,$$

$$\rho(\mathbf{p}) = (2\pi)^{-3} \sum_{\mathbf{k},\nu}^{\text{occ.}} \left| \int \psi_{\mathbf{k},\nu}(\mathbf{r}) \exp(-i\mathbf{p}\cdot\mathbf{r})\, d\mathbf{r} \right|$$

Magnetic Compton Scattering

Measurement of population of (x^2-y^2) and ($3z^2$-r^2) of e_g orbitals in $La_{2-2x}Sr_{1+2x}Mn_2O_7$

(A. Koizumi, et al, Phys. Rev. Lett. 86 (2001) 5589.

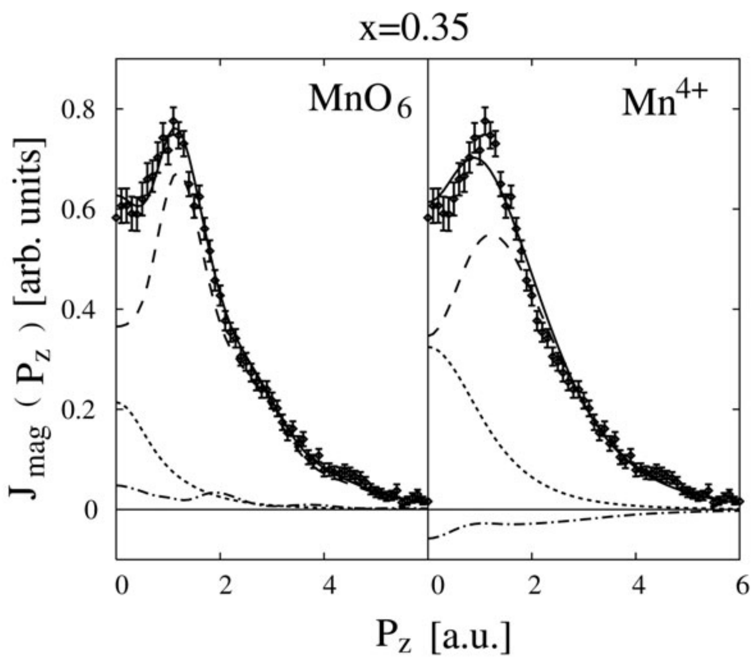


FIG. 1. The magnetic Compton profiles along the [001] direction at $x = 0.35$. Left: Experimental data (diamonds) are shown with fit (solid line) using the MnO_6 cluster orbitals. Error bars indicate experimental statistical errors. Also shown are the t_{2g} orbital contribution (dashed line), the $e_{x^2-y^2}$ orbital contribution (dotted line), and the $e_{3z^2-r^2}$ orbital contribution (dot-dashed line). The spin density per site is 3.65, of which the contribution from t_{2g} is fixed to 3.0. The $e_{x^2-y^2}$ and $e_{3z^2-r^2}$ contributions are 0.46 and 0.19, respectively. Right: The same as the left panel but using the Mn^{4+} orbitals. The $e_{x^2-y^2}$ and $e_{3z^2-r^2}$ contributions are 0.90 and -0.25, respectively.

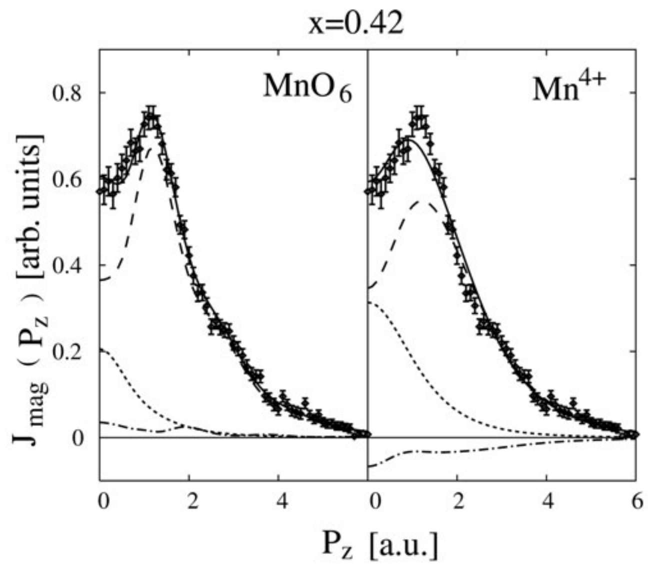


FIG. 2. The same as Fig. 1 but for $x = 0.42$. The spin density per site is 3.58, of which the contribution from t_{2g} is fixed to 3.0. The $e_{x^2-y^2}$ and $e_{3z^2-r^2}$ contributions are 0.44 and 0.14, respectively, for the MnO_6 fit (left), and 0.87 and -0.29, respectively, for the Mn^{4+} fit (right).

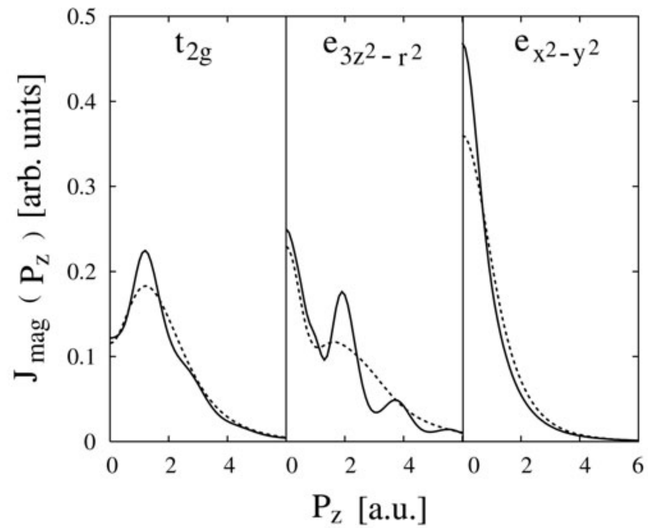
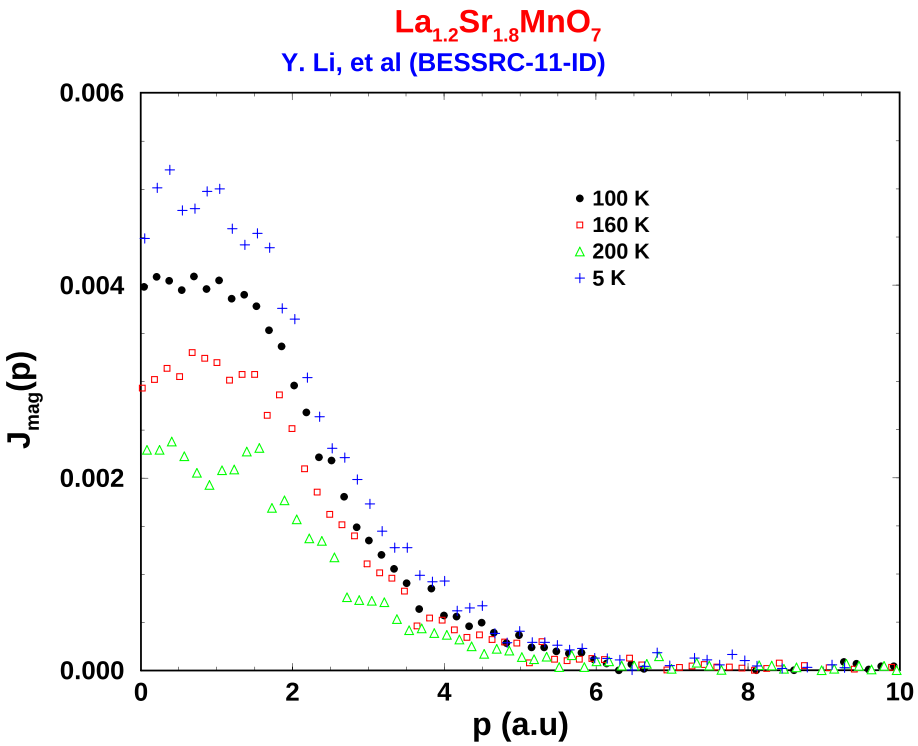
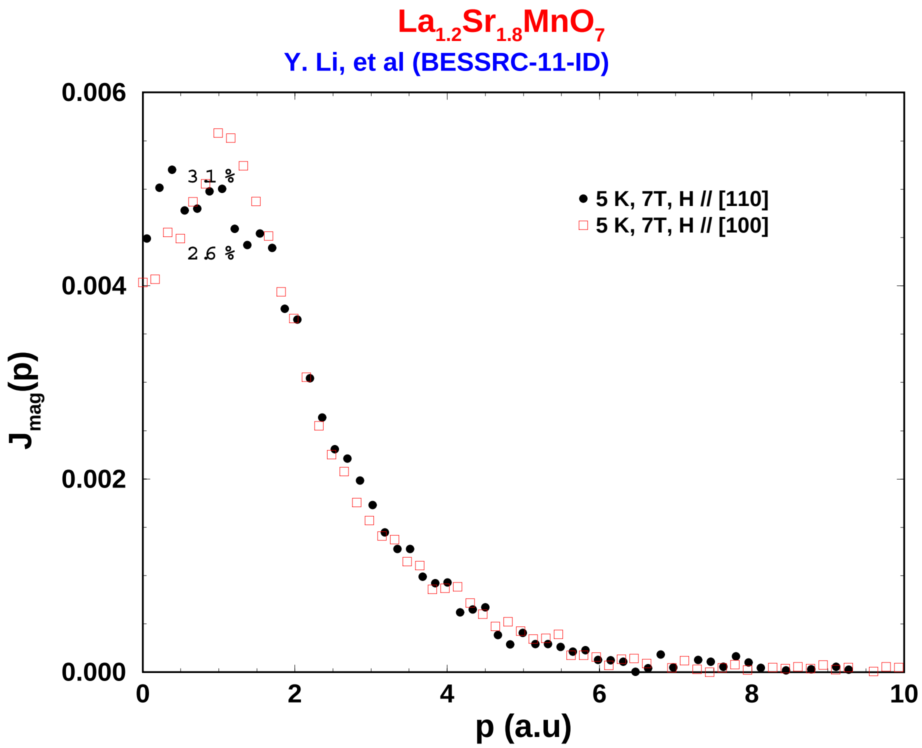


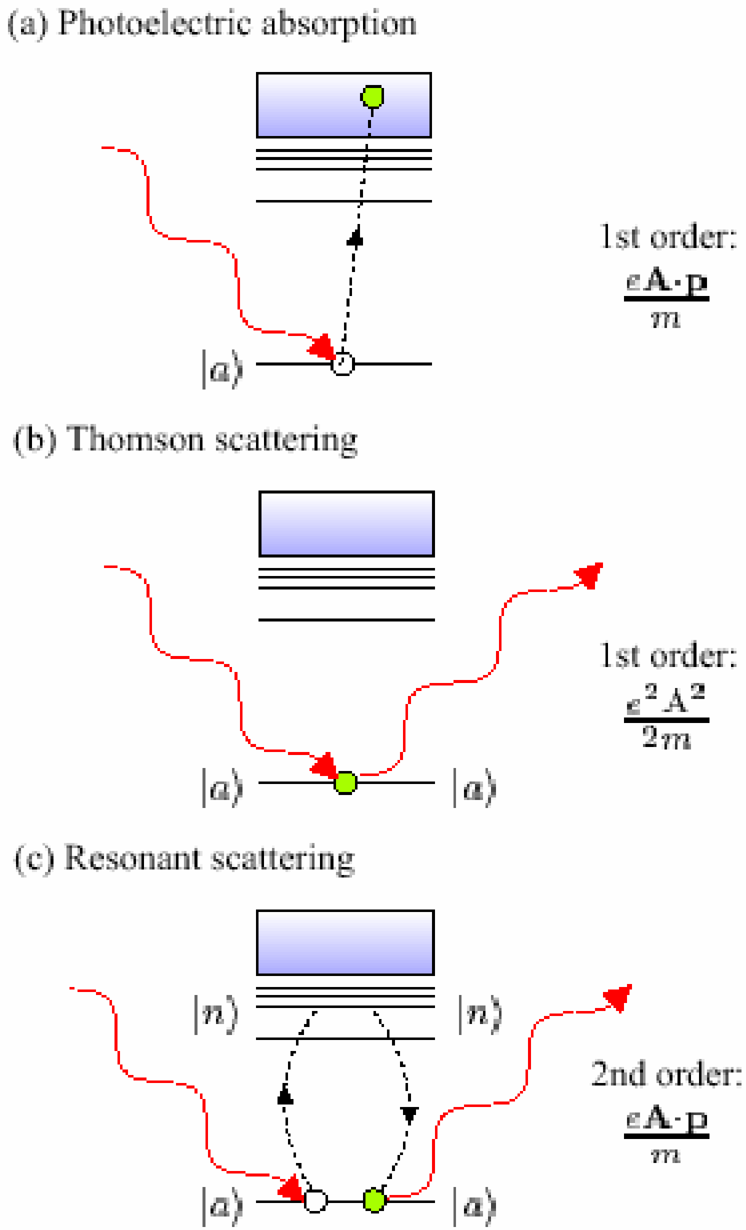
FIG. 3. Calculated magnetic Compton profiles of the t_{2g}, $e_{x^2-y^2}$, and $e_{3z^2-r^2}$ orbitals for the MnO_6 cluster (solid line) and by isolated Mn^{4+} (dashed line).

Magnetic Compton Scattering @ APS

Measurement of the ratio of magnetic electrons to the total electrons



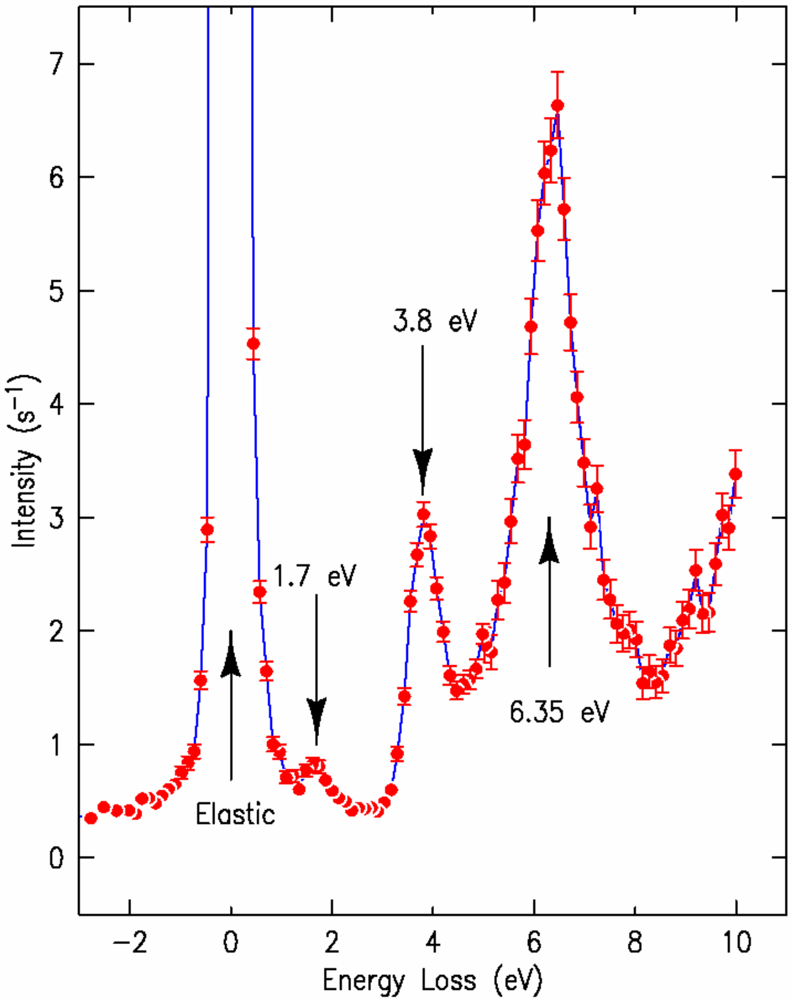



(a) Photoelectric absorption
|a⟩
1st order:
$\frac{e\mathbf{A}\cdot\mathbf{p}}{m}$
(b) Thomson scattering
|a⟩
|a⟩
1st order:
$\frac{e^2 A^2}{2m}$
(c) Resonant scattering
|n⟩
|n⟩
|a⟩
|a⟩
2nd order:
$\frac{e\mathbf{A}\cdot\mathbf{p}}{m}$

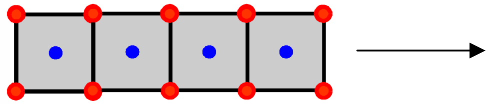
Resonant Inelastic X-ray Scattering

Courtesy to : J. P. Hill, Brookhaven Nat. Lab.

Excitation Spectrum of $CuGeO_3$



Q along c-axis



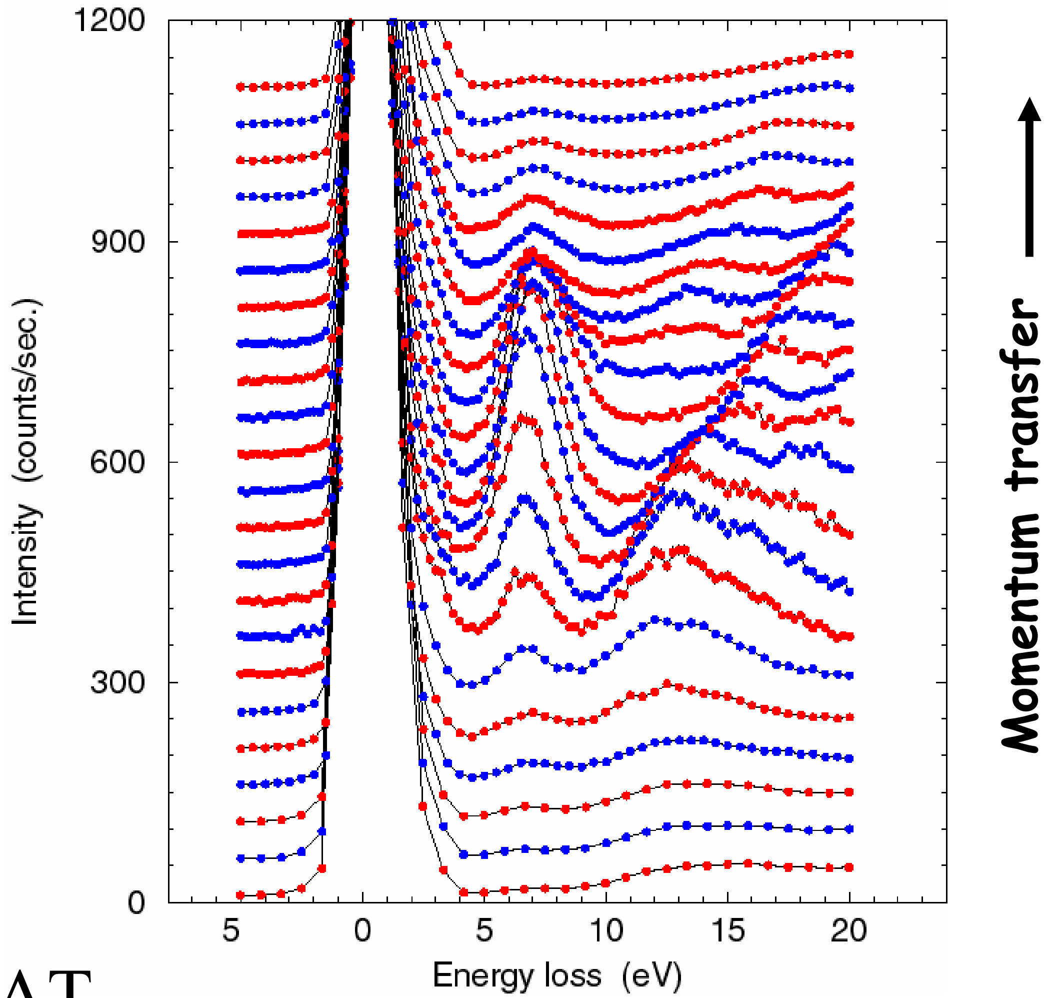
Resolution = 0.3 eV

- 6.35 eV Charge transfer excitation
- 3.8 eV Exciton-like feature.
- 1.7 eV d-d optically forbidden excitation.

CMC-CAT

BROOKHAVEN NATIONAL LABORATORY

For incident photon energies near an absorption edge,
a large resonant enhancement is observed in the inelastic scattering:



$CuGeO_3$

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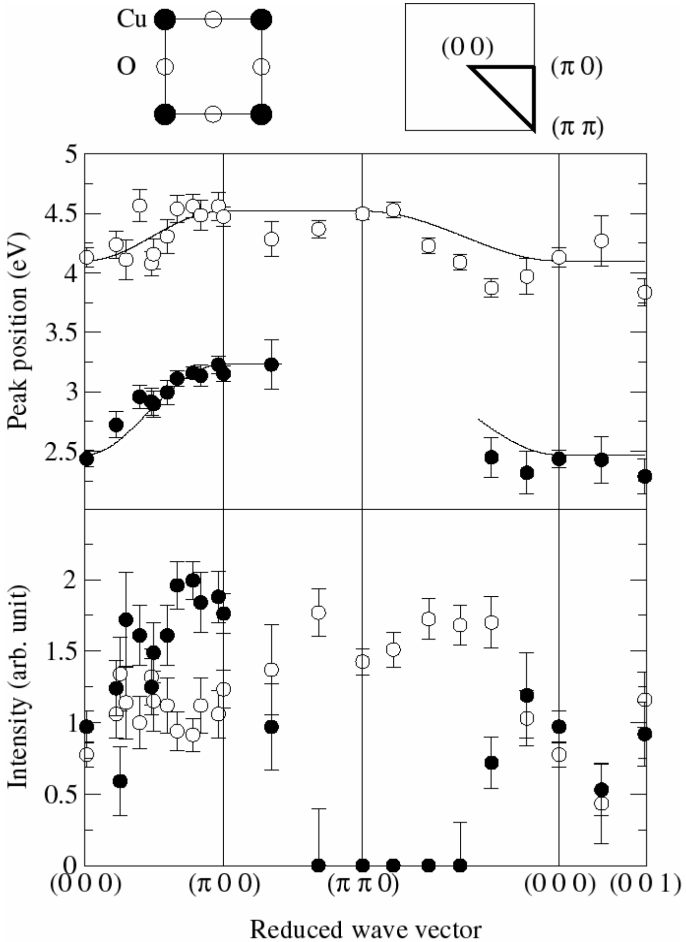
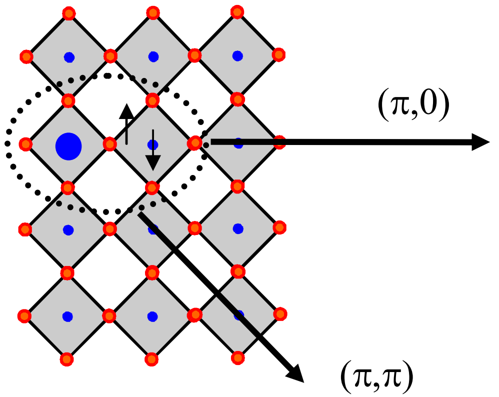
La_2CuO_4

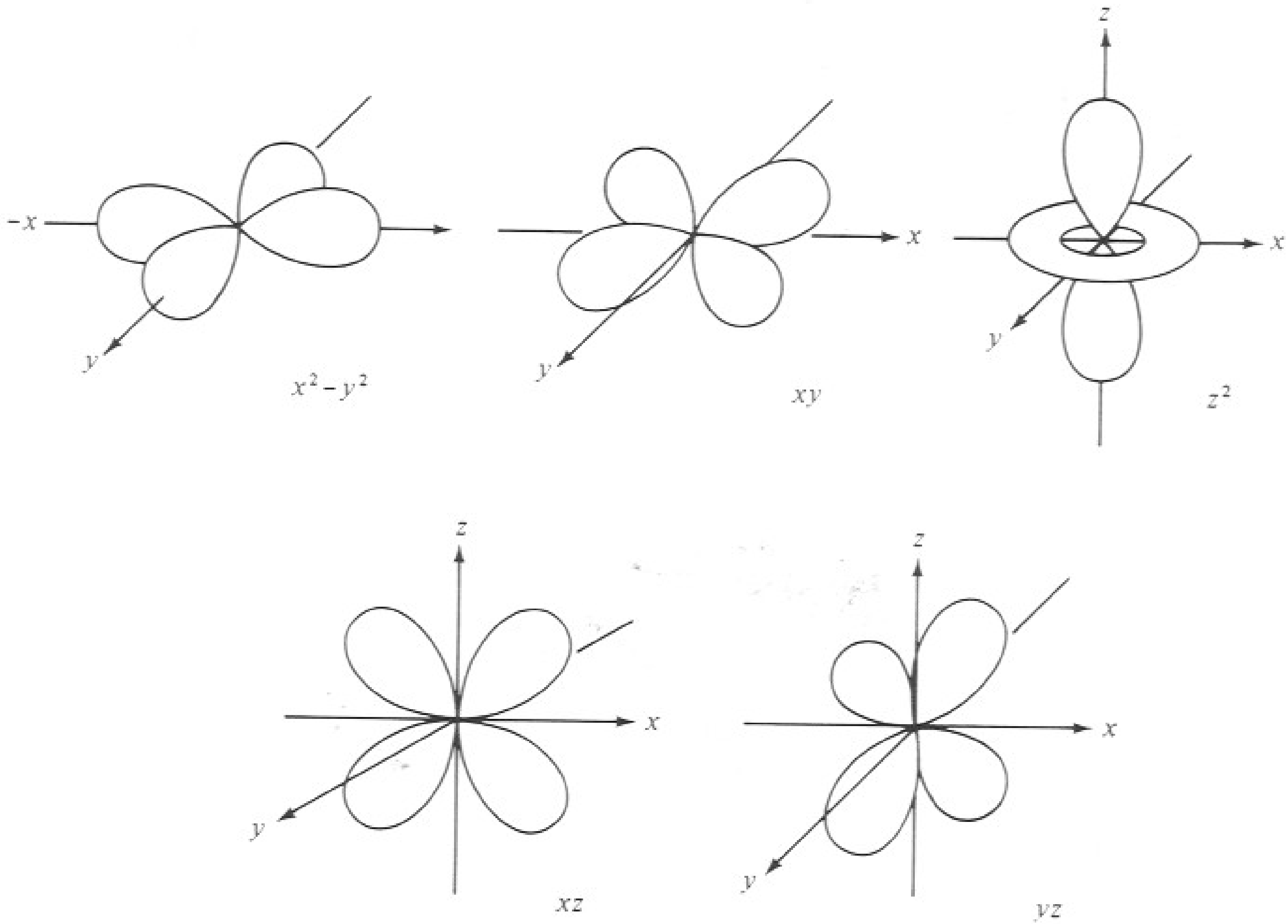




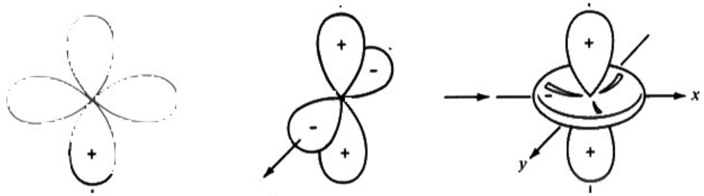
Kim, Hill et al.

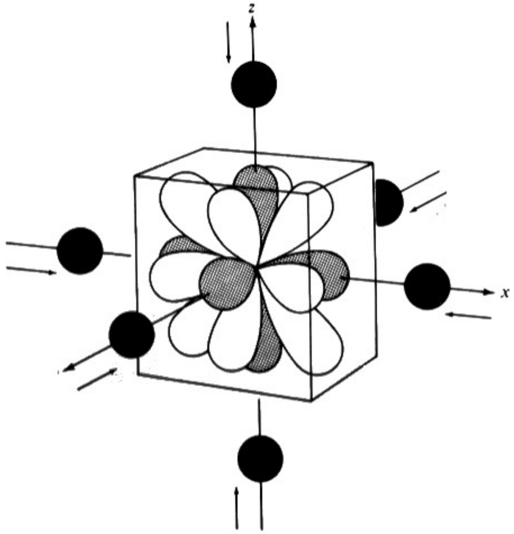
In 1d $CuGeO_3$ no dispersion of exciton. In 2d La_2CuO_4 two excitons seen, with significant dispersion. Provides unique information on UHB and LHB and role of correlations.

Electronic orbitals

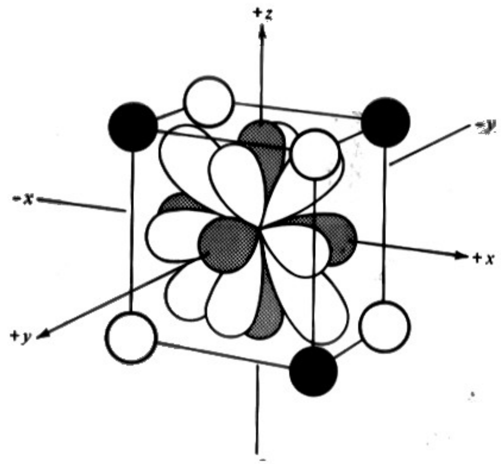


Octahedral and cubic fields

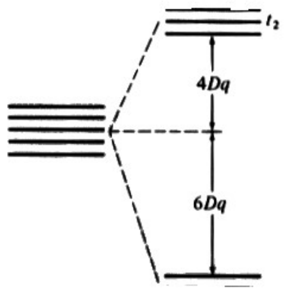




Complete set of d orbitals in an octahedral field. The e_g orbitals are shaded and the t_{2g} orbitals are unshaded. The torus of the d_{z^2} orbital has been omitted for clarity.

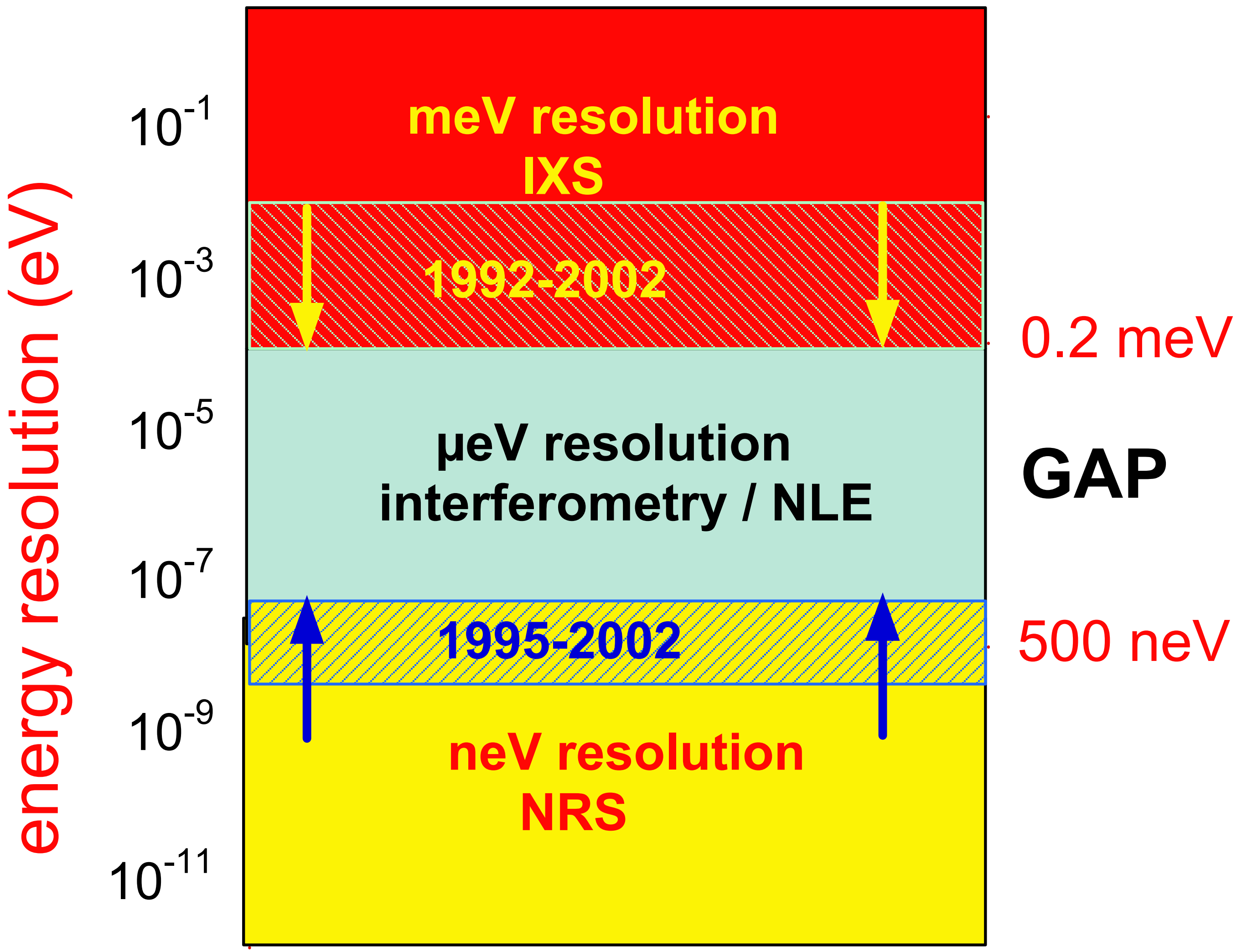


Complete set of d orbitals in a cubic field. All eight ligands produce a field $\frac{8}{9}$ as strong as a corresponding octahedral field (see Fig. 9.8). Either set of four tetrahedral ligands (○ or ●) produces a field $\frac{4}{9}$ as strong as the octahedral field.



Splitting of d orbitals in a tetrahedra field.

High energy resolution x-ray scattering



APS Collaborative Access Teams by Sector & Discipline