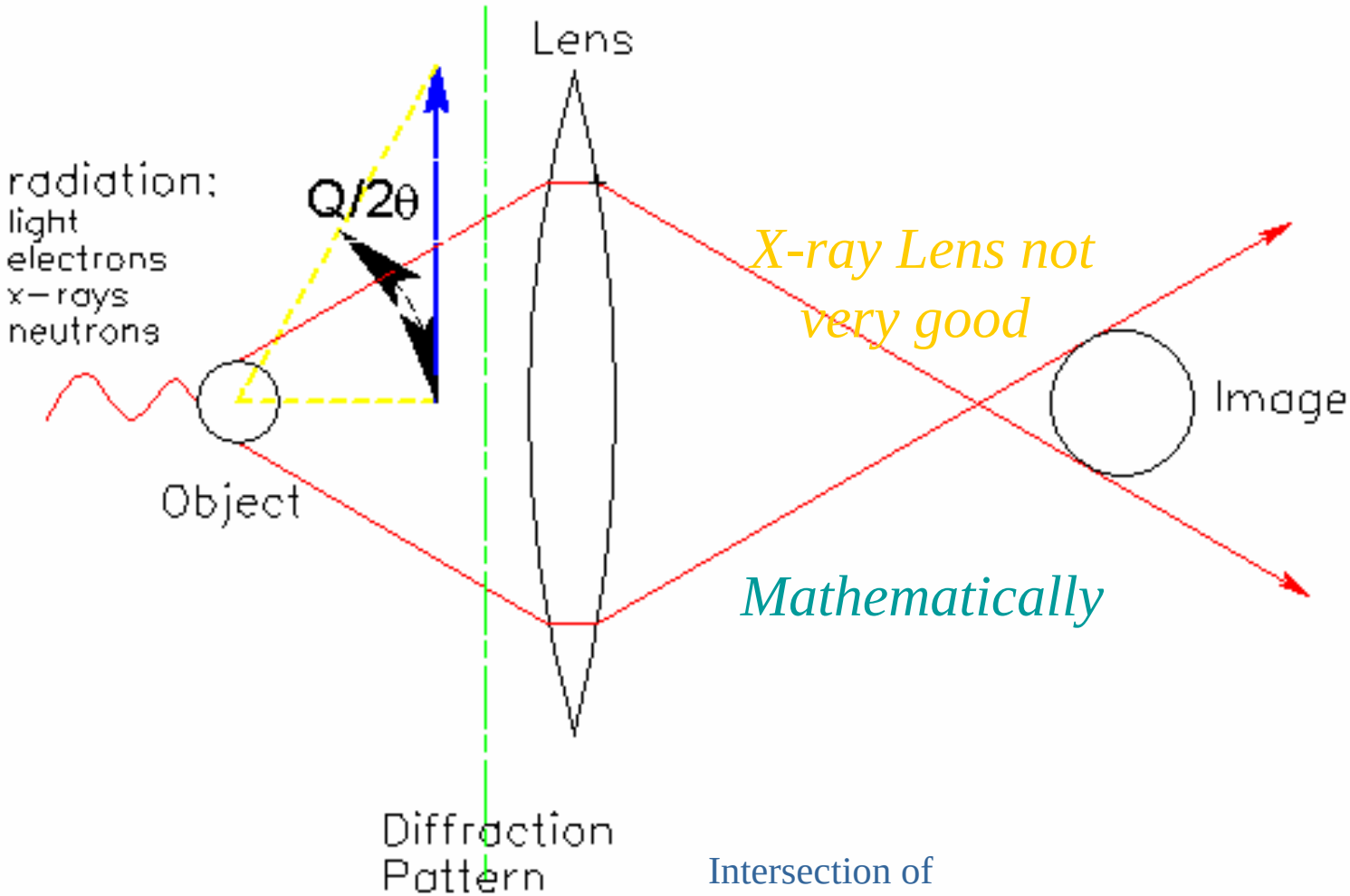
Structural Analysis

Apurva Mehta

Physics of Diffraction



Intersection of

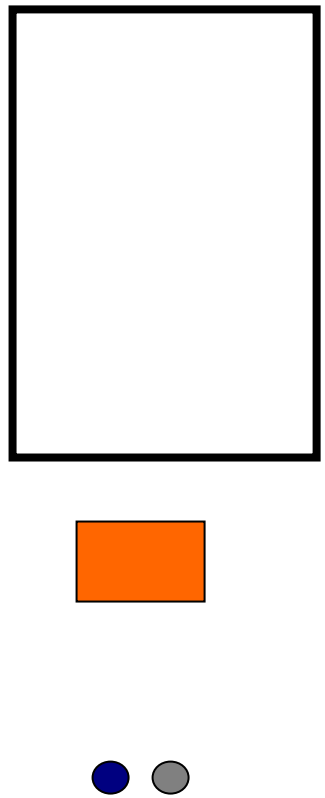
Ewald sphere with Reci Lattice

outline

- Information in a Diffraction pattern
- Structure Solution
- Refinement Methods
- Pointers for Refinement quality data

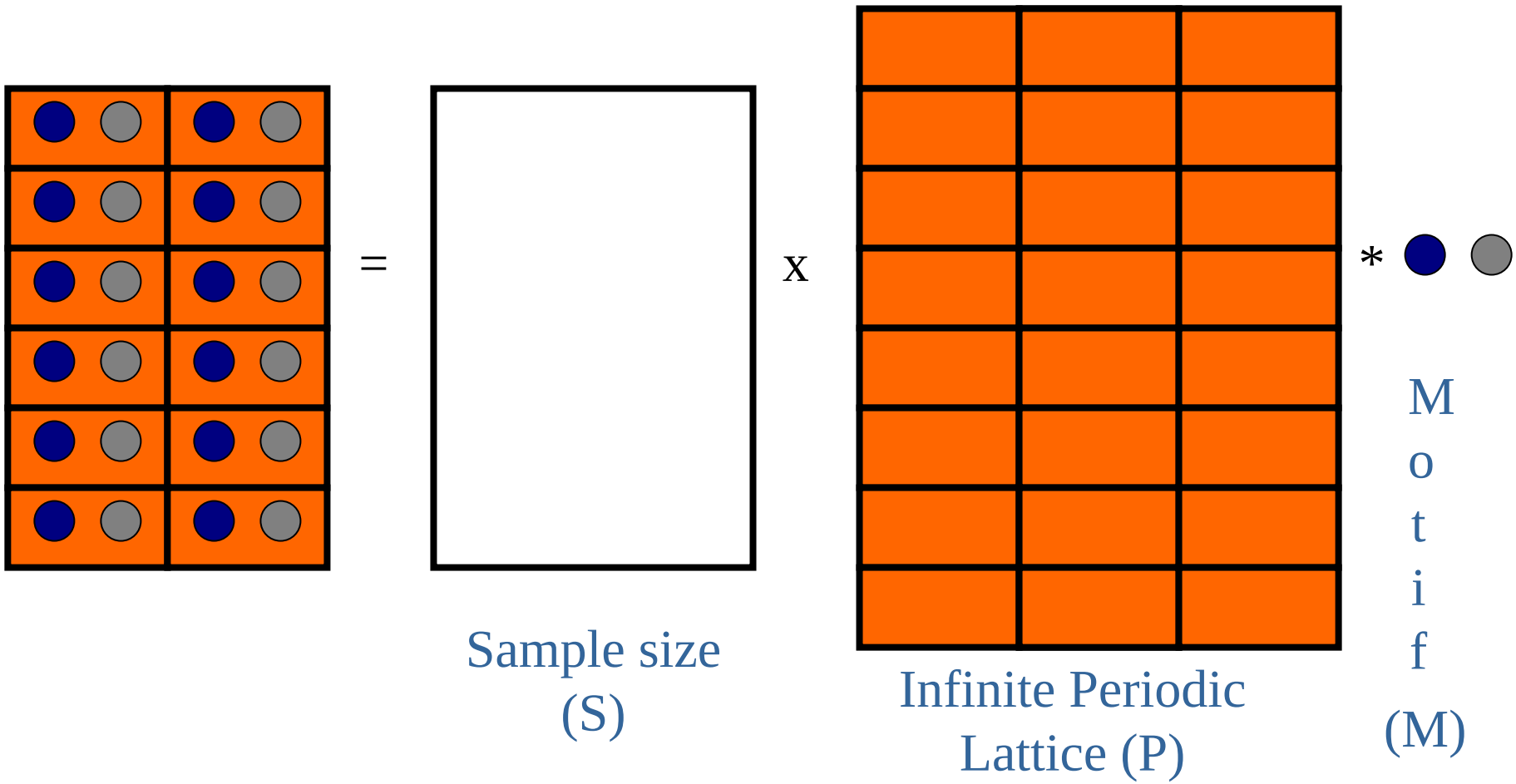
What does a diffraction pattern tell us?

- Peak Shape & Width:
  - crystallite size
  - Strain gradient
- Peak Positions:
  - Phase identification
  - Lattice symmetry
  - Lattice expansion
- Peak Intensity:
  - Structure solution
  - Crystallite orientation



Sample ←→ Diffraction

Diffraction Pattern ~ {FT(sample) } {FT(sample) }



Sample ←→ Diffraction

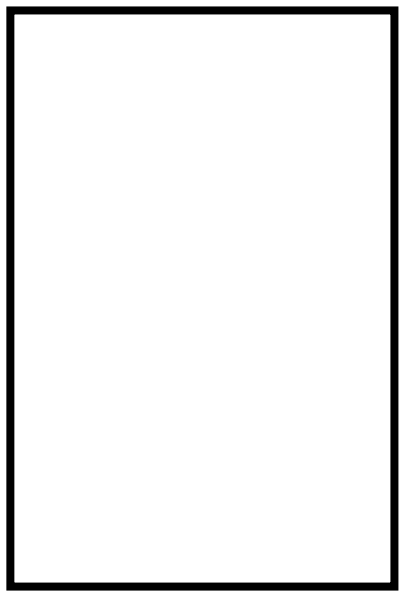
$$FT(Sample) = FT((S \times P)*M)$$

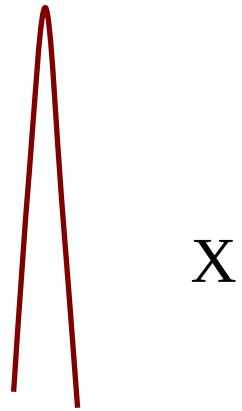
Convolution theorem

$$FT(Sample) = FT(S \times P) \times FT(M)$$

$$FT(Sample) = (FT(S) * FT(P)) \times FT(M)$$

FT(S)

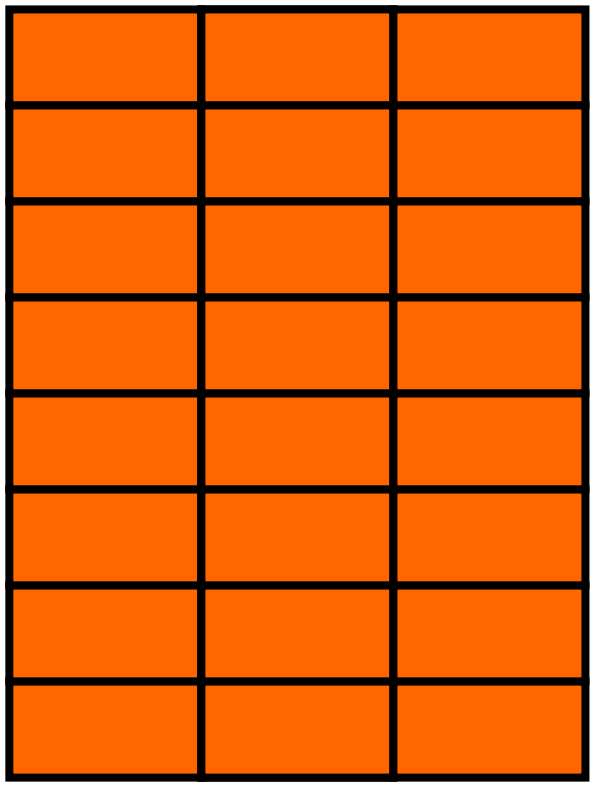




X

Y

FT(P)



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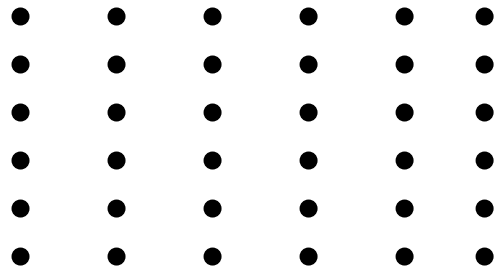
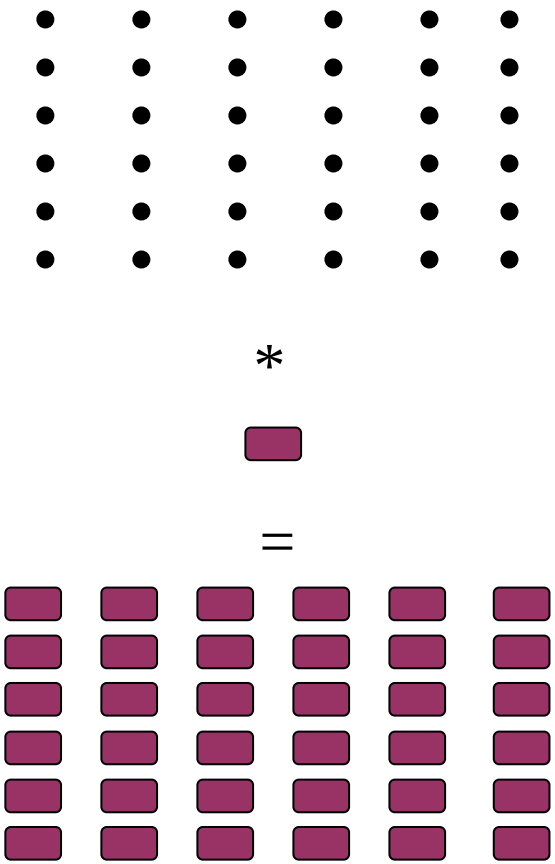
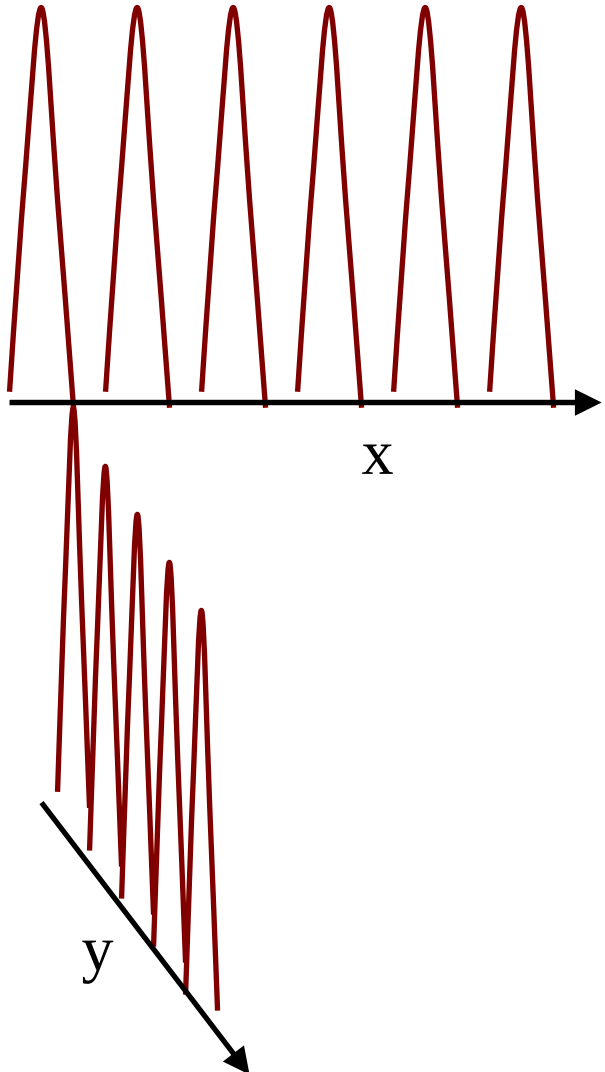
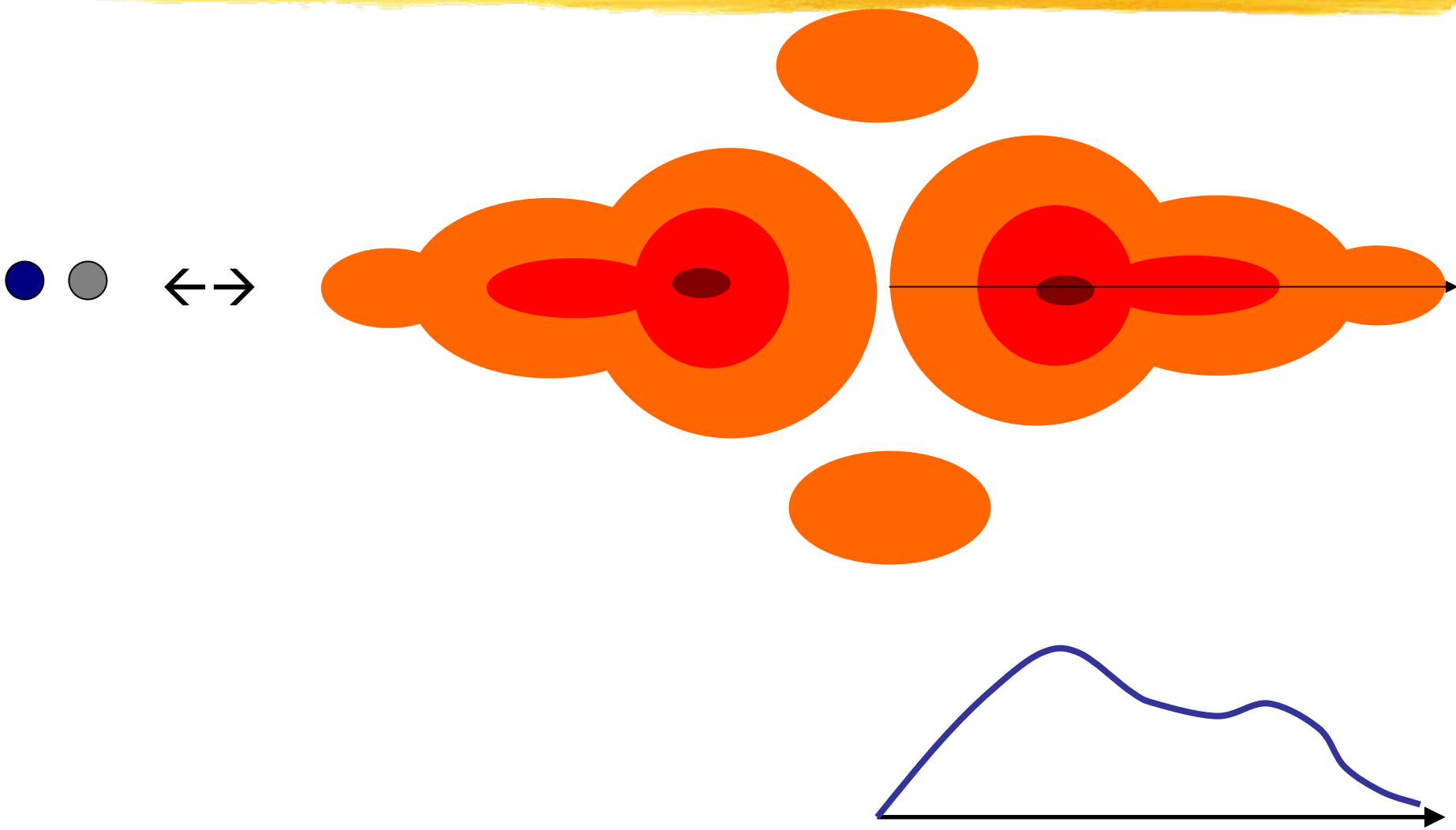


FT (S x P) = FT(S) * FT(P)



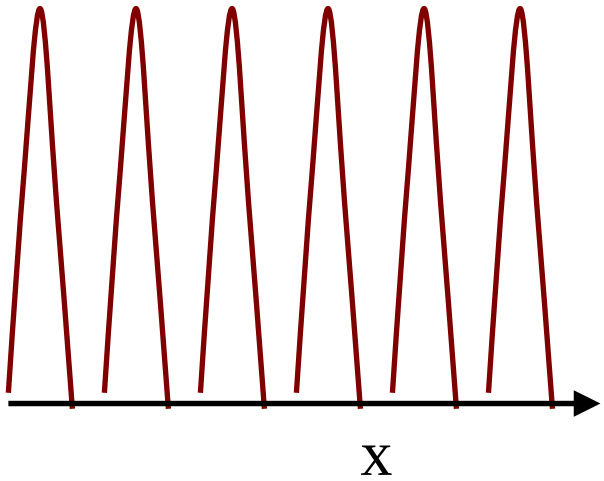


FT(M)

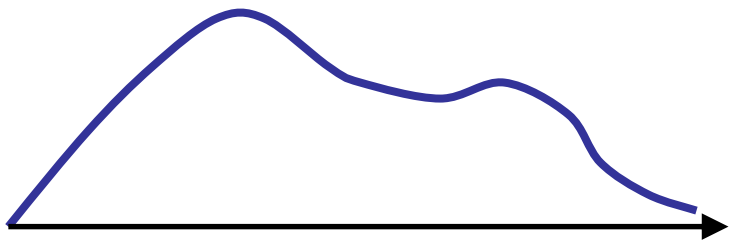


FT(sample) = FT(S x P) x FT(M)

Along X direction



X



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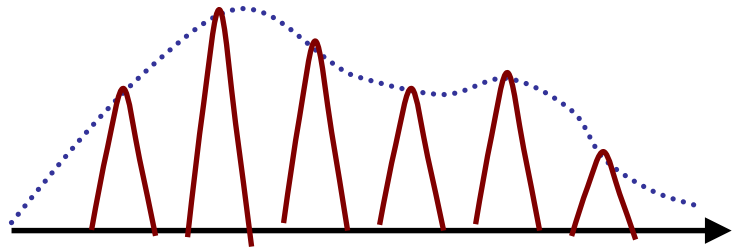

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- Peak Positions:
  - Phase identification
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- Peak Intensity:
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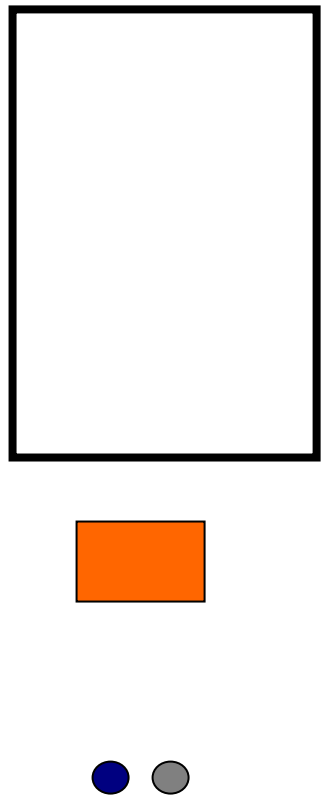
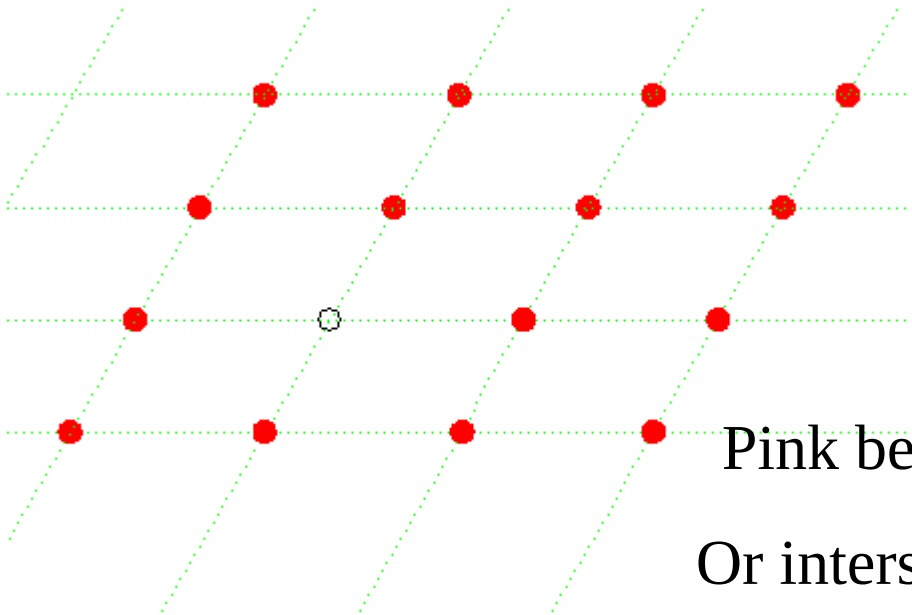


Structure Solution

- Single Crystal
  - Protein Structure
  - Sample with heavy Z problems Due to
    - Absorption/extinction effects
  - Mostly used in Resonance mode
    - Site specific valence
    - Orbital ordering.
- Powder
  - Due to small crystallite size kinematic equations valid
  - Many small molecule structures obtained via synchrotron diffraction
  - Peak overlap a problem – high resolution setup helps
  - Much lower intensity – loss on super lattice peaks from small symmetry breaks. (Fourier difference helps)

Diffraction from Crystalline Solid

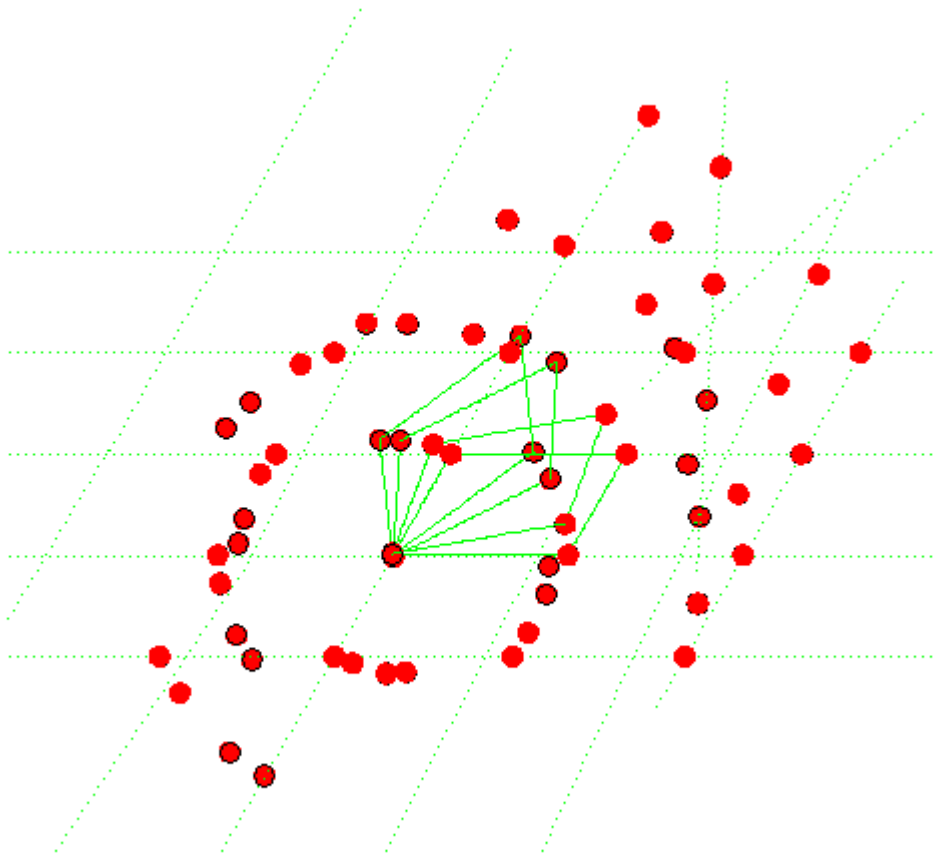
- Long range order ----> diffraction pattern periodic
- crystal rotates ----> diffraction pattern rotates



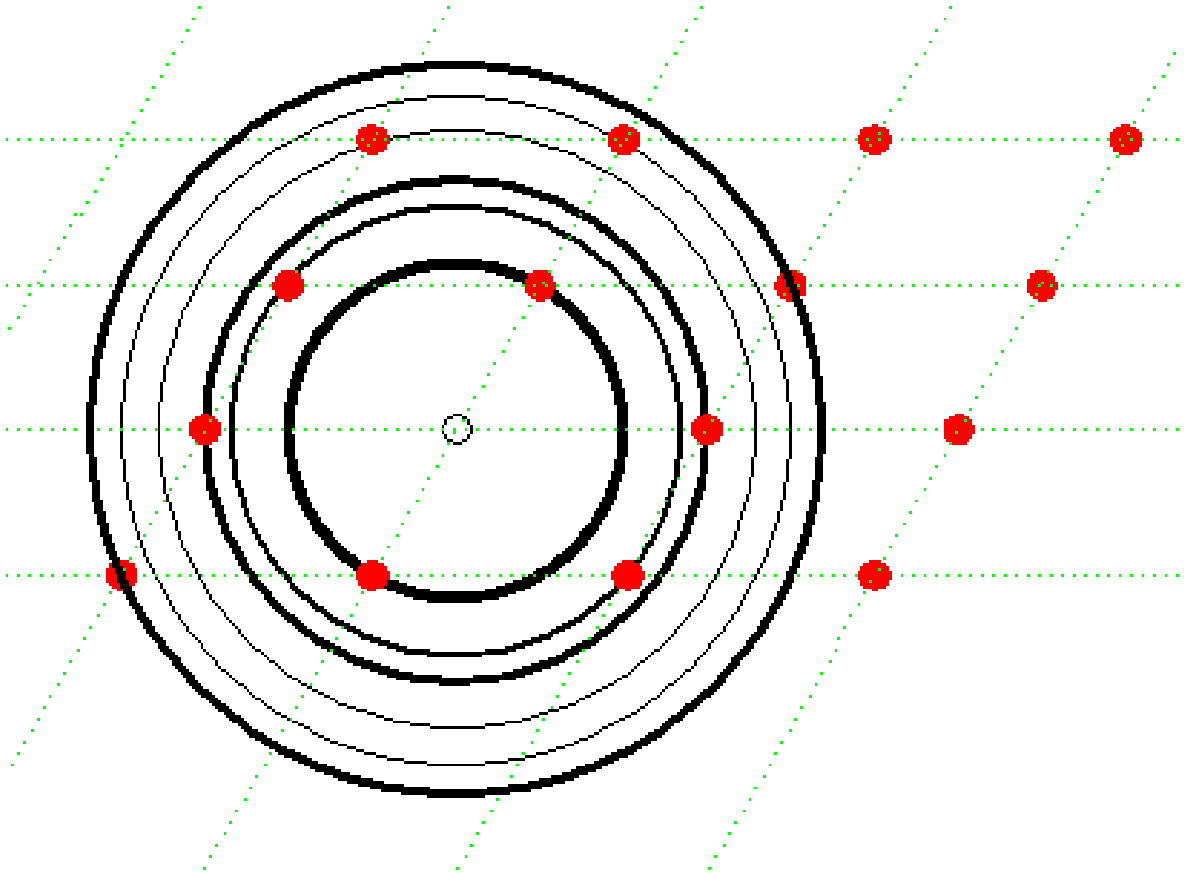
Pink beam laue pattern

Or intersection of a large Ewald Sphere with RL

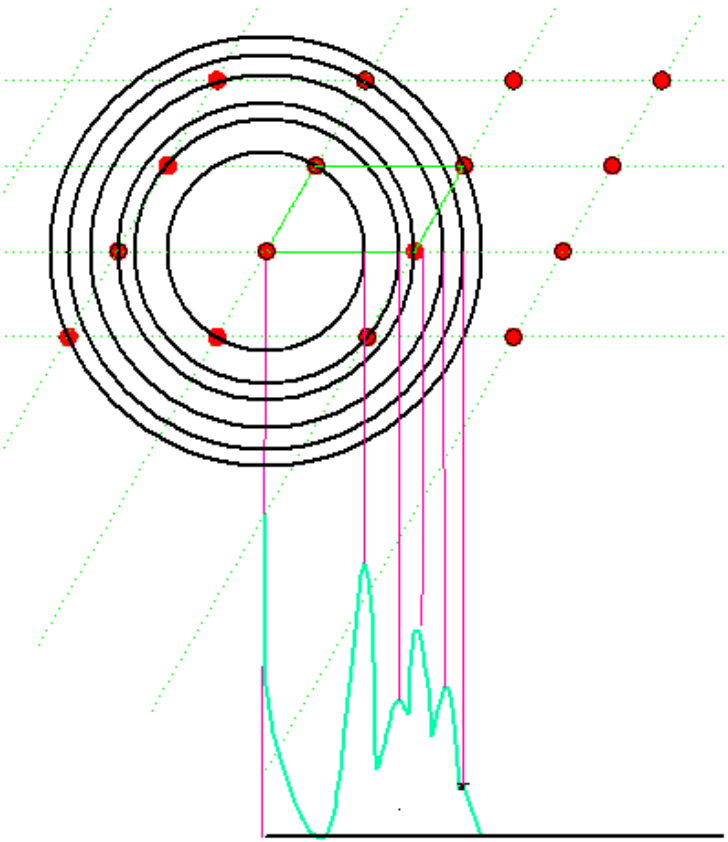
From 4 crystallites



From Powder



Powder Pattern

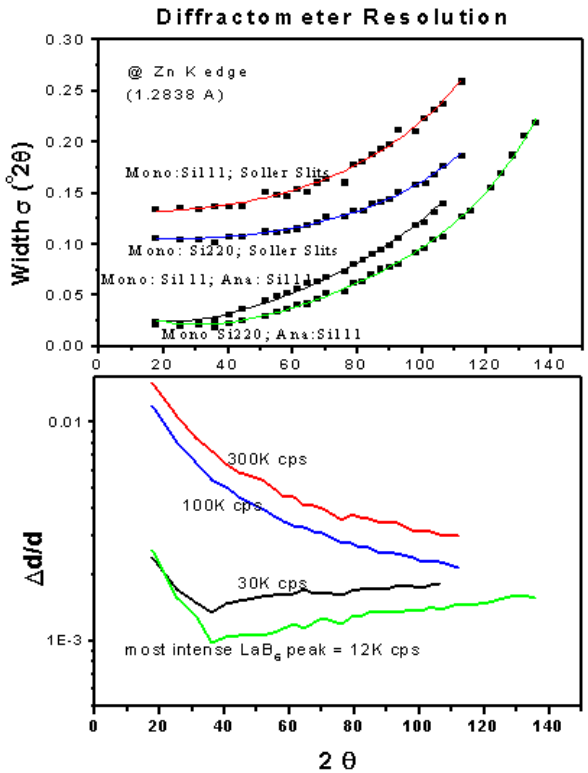


- Loss of angular information
  - Not a problem as peak position = fn(a, b & α)
- Peak Overlap :: A problem
  - But can be useful for precise lattice parameter measurements

Peak Broadening

- ~ (invers.) “size” of the sample
  - Crystallite size
  - Domain size
  - Strain & strain gradient
- Diffractometer resolution should be better than Peak broadening But not much better.

Diffractometer Resolution



$$W_d^2 = M^2 \times \phi_b^2 + \phi_s^2$$

$$M = (2 \tan\theta / \tan\theta_m - \tan\theta_a / \tan\theta_m - 1)$$

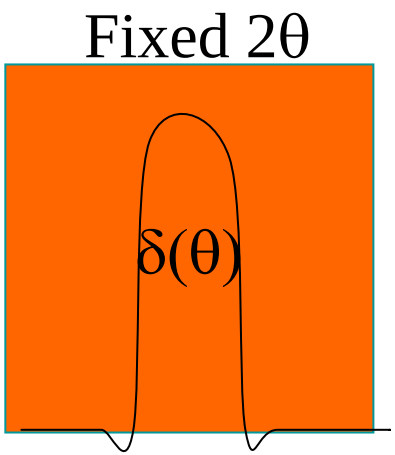
Where

ϕ_b = divergence of the incident beam,

ϕ_s = cumulative divergences due to slits and apertures

θ, θ_a and θ_m = Bragg angle for the sample, analyzer and the monochromator

Powder Average



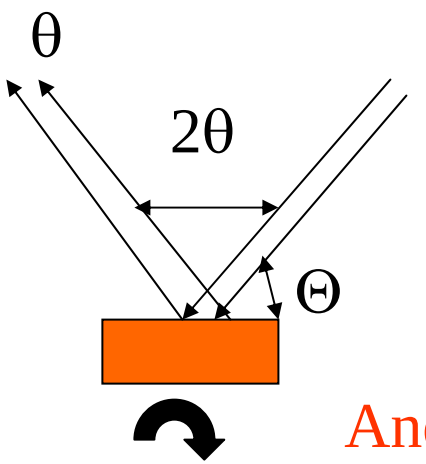
Single crystal – no intensity
Even if Bragg angle right,
But the incident angle wrong

$$\Theta +/- \delta(\Theta) = \theta +/- \delta(\theta)$$

$\delta(\theta)$ = Mosaic width ~ 0.001 – 0.01 deg

$\delta(\Theta)$ = beam dvg ~ >0.1 deg for sealed tubes

~ 0.01 deg for synchrotron

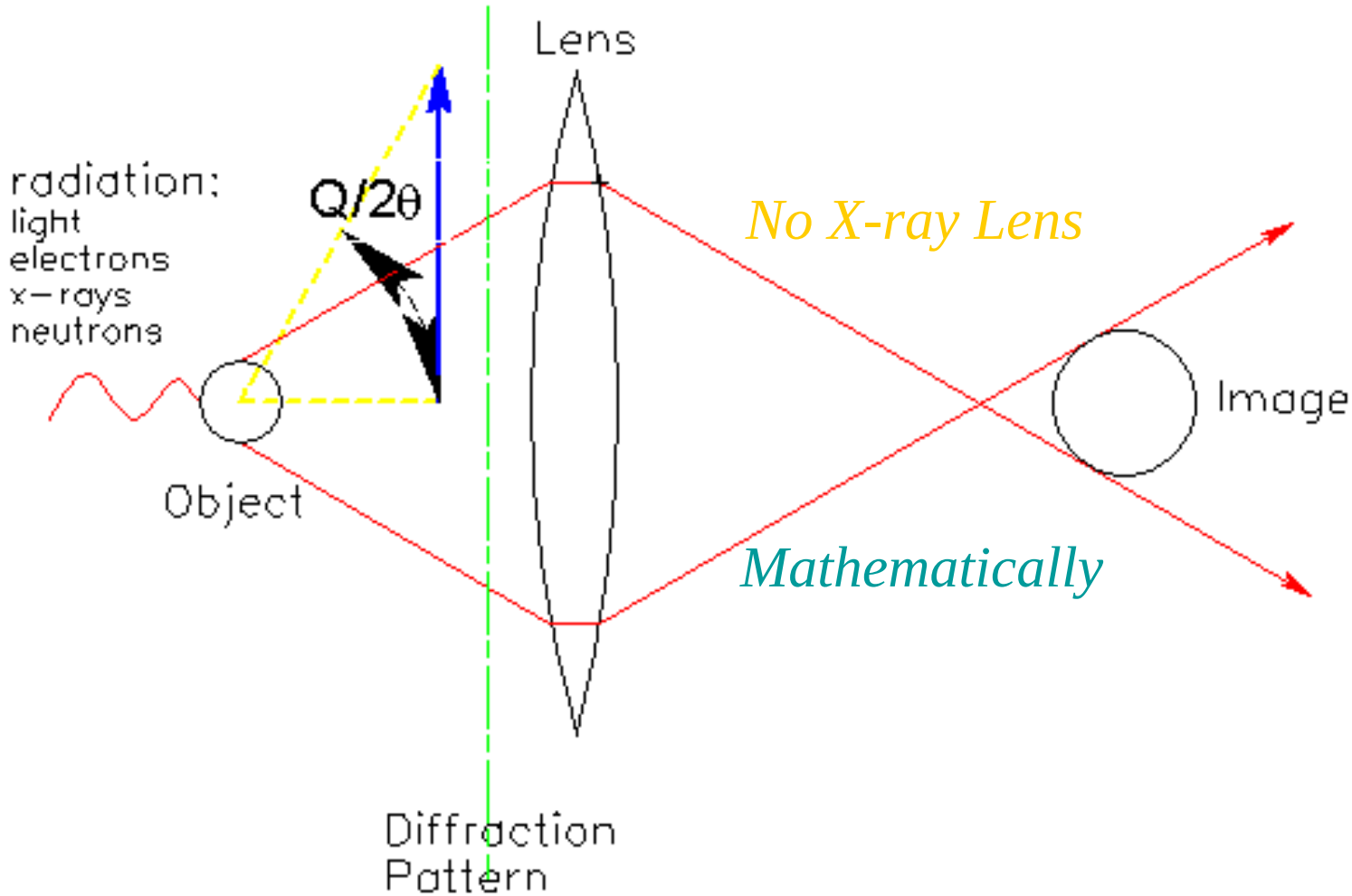


For Powder Avg

Need <3600 rnd crystallites – sealed tube
Need ~ 30000 rnd crystallites - synchrotron

Powder samples must be prepared carefully
And data must be collected while rocking the sample

Physics of Diffraction



Phase Problem

- $\rho_{xyz} = \Sigma_{hkl} F_{hkl} \exp(-2\pi i\{hx + ky + lz\})$
  - F_{hkl} is a Complex quantity
  - $F_{hkl}(f_i, r_i)$: $(F_{hkl})^2 = I_{hkl}/(K*Lp*Abs)$
- $\rho_{xyz} = \Sigma_{hkl} C\sqrt{I_{hkl}} \exp(-(\phi + \Delta\phi))$
  - $\Delta\phi$ = phase *unknown*
    - Hence Inverse Modeling

Solution to Phase Problem

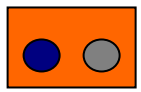
- Must be guessed
  - And then refined.

- How to guess?
  - Heavy atom substitution, SAD or MAD
  - Similarity to homologous compounds

  - Patterson function or pair distribution analysis.

Procedure for Refinement/Inverse Modeling

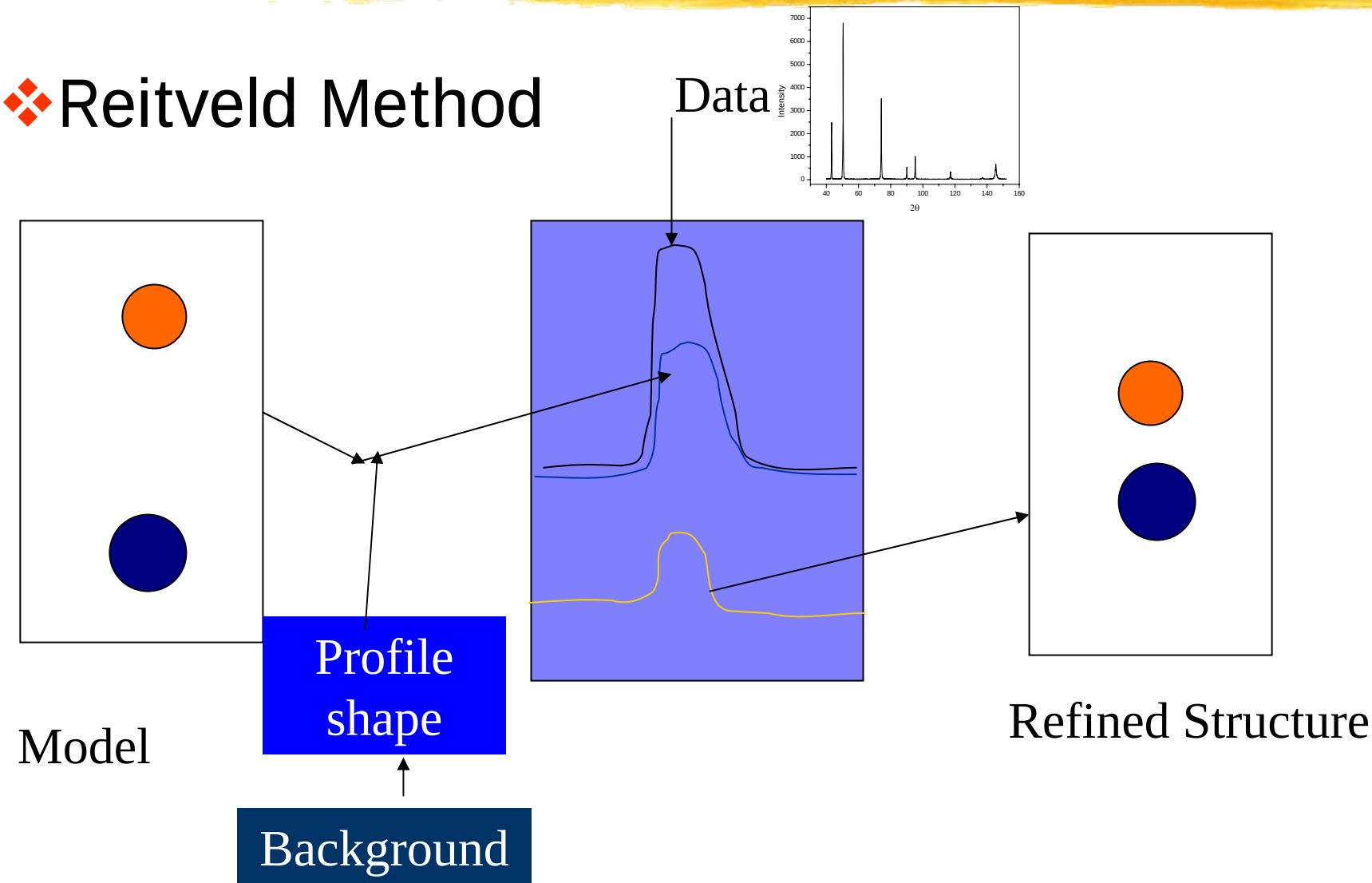
- Measure peak positions:
  - Obtain lattice symmetry and point group
    - Guess the space group.
      - Use all and compare via F-factor analysis



- Guess the motif and its placement
  - Phases for each hkl
- Measure the peak widths
  - Use an appropriate profile shape function
- Construct a full diff. pattern and compare with measurements

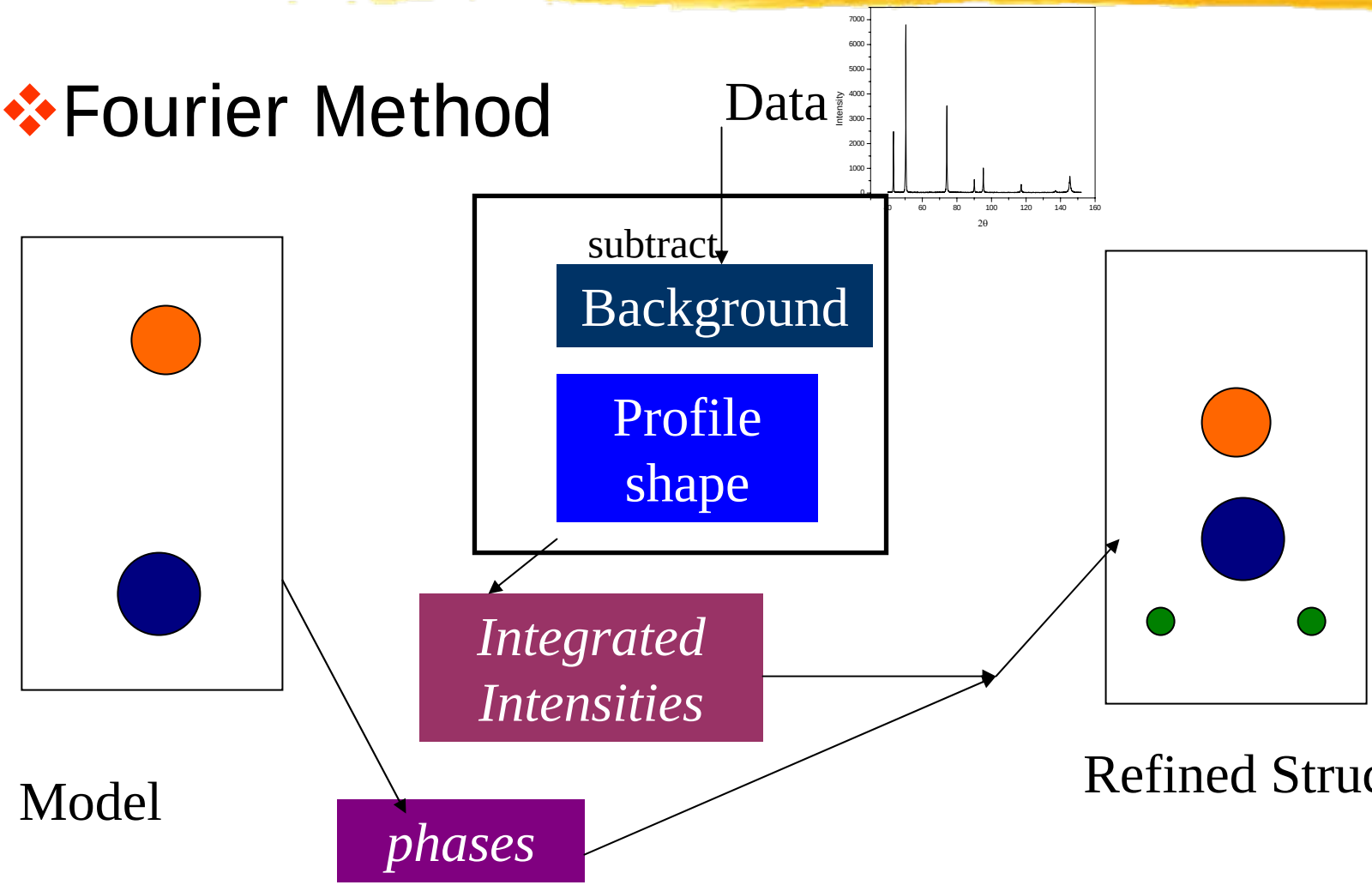
Inverse Modeling Method 1

- Reitveld Method



Inverse Modeling Method 2

- Fourier Method

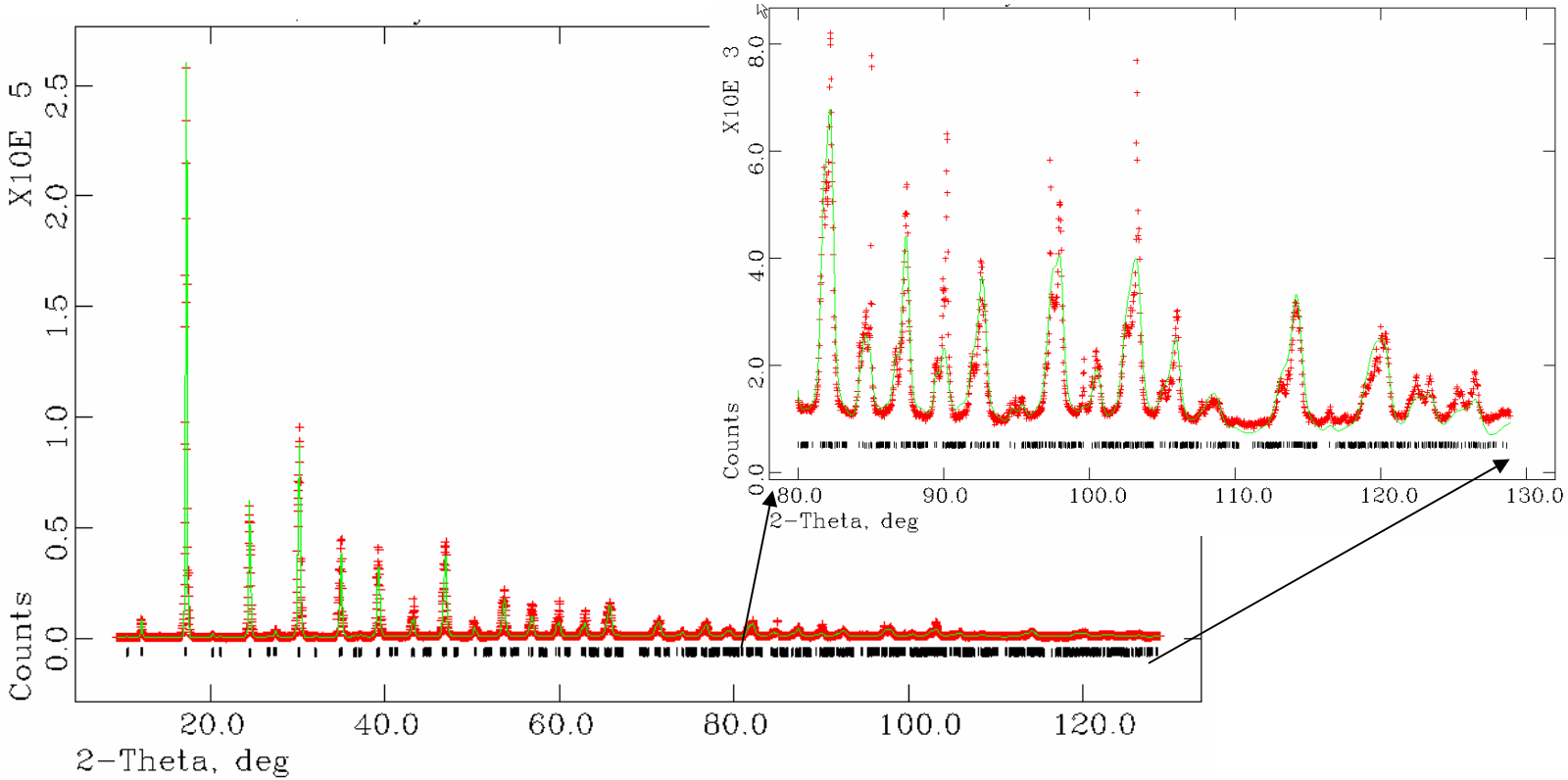


Inverse Modeling Methods

- Rietveld Method
  - More precise
  - Yields Statistically reliable uncertainties
- Fourier Method
  - Picture of the real space
  - Shows “missing” atoms, broken symmetry, positional disorder

- Should iterate between Rietveld and Fourier.
  - Be skeptical about the Fourier picture if Rietveld refinement does not significantly improve the fit with the “new” model.

Need for High Q



Many more reflections at higher Q.

Therefore, most of the structural information is at higher Q

Profile Shape function

- Empirical
  - Voigt function modified for axial divergence (Finger, Jephcoat, Cox)
    - Refinable parameters – for crystallite size, strain gradient, etc...
- From Fundamental Principles

Collect data on Calibrant under the same conditions

- Obtain accurate wavelength and diffractometer misalignment parameters
- Obtain the initial values for the profile function (instrumental only parameters)
- Refine polarization factor

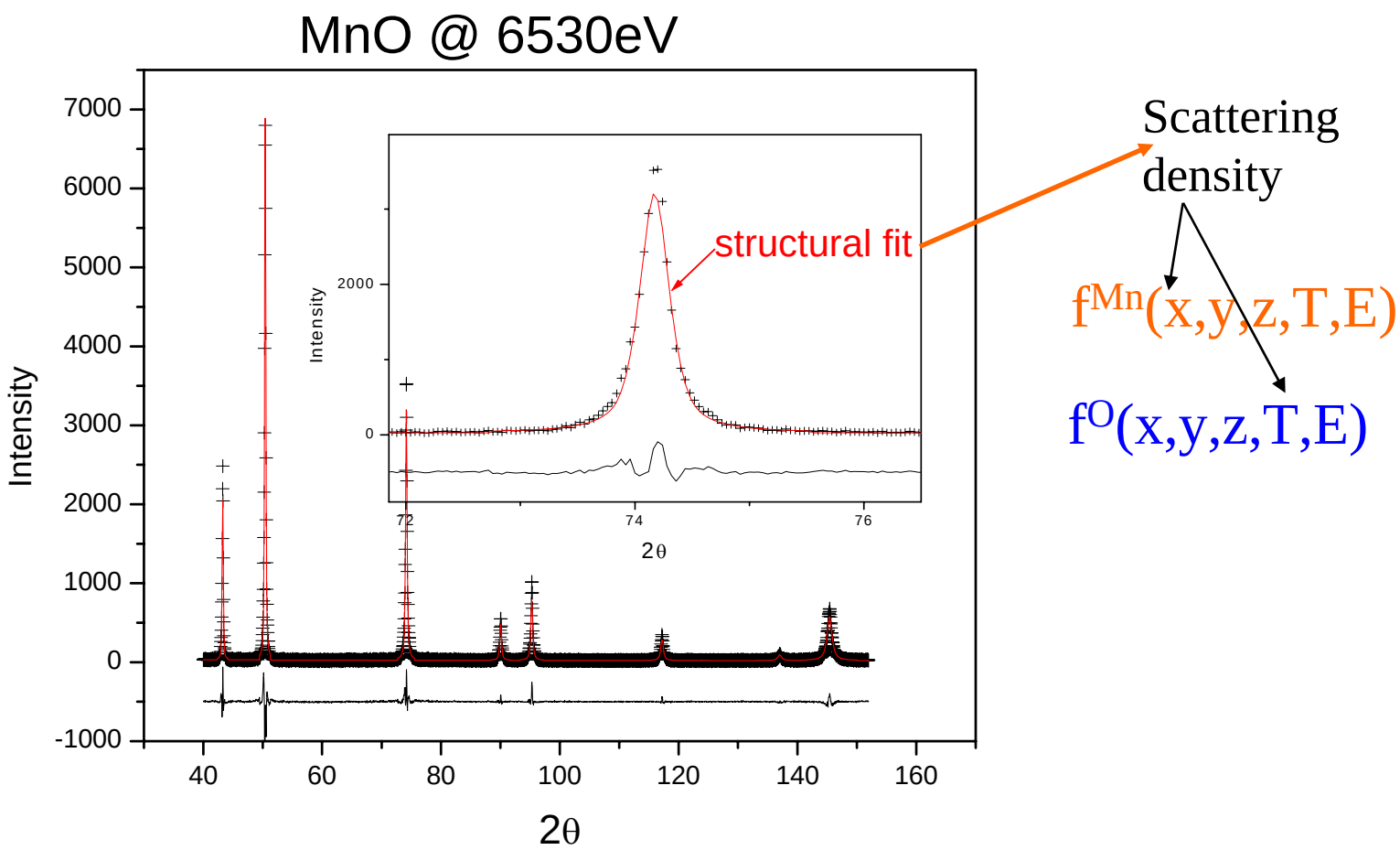
- Tells of other misalignment and problems

Selected list of Programs

- CCP14 for a more complete list
  http://www.ccp14.ac.uk/mirror/want_to_do.html
  - GSAS
  - Fullprof
  - DBW
  - MAUD

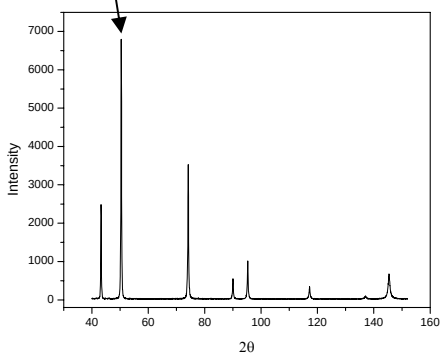
  - Topaz – not free - Bruker – fundamental approach

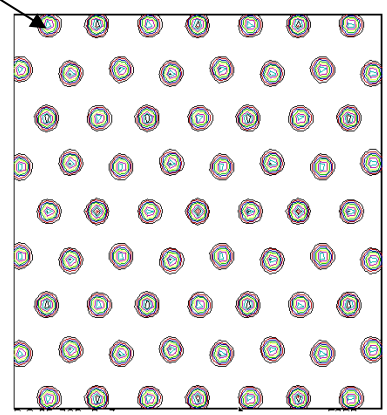
Structure of MnO



Resonance Scattering

$$F_{hkl} = \Sigma_{xyz}\ f_{xyz}\ \exp(2\pi i\{hx + ky + lz\})$$





f_{xyz} = scattering density

Away from absorption edge

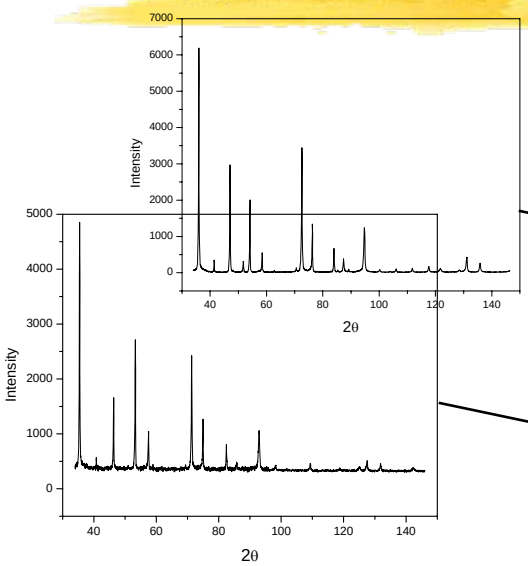
α electron density

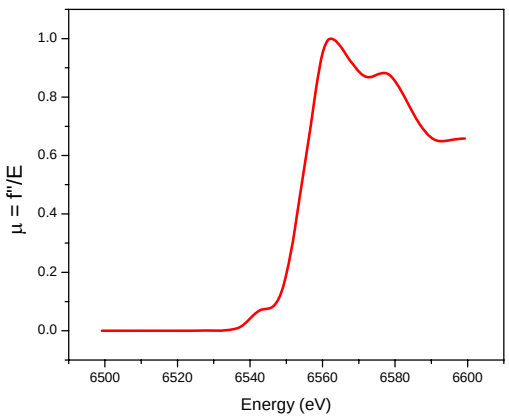
Anomalous Scattering Factors

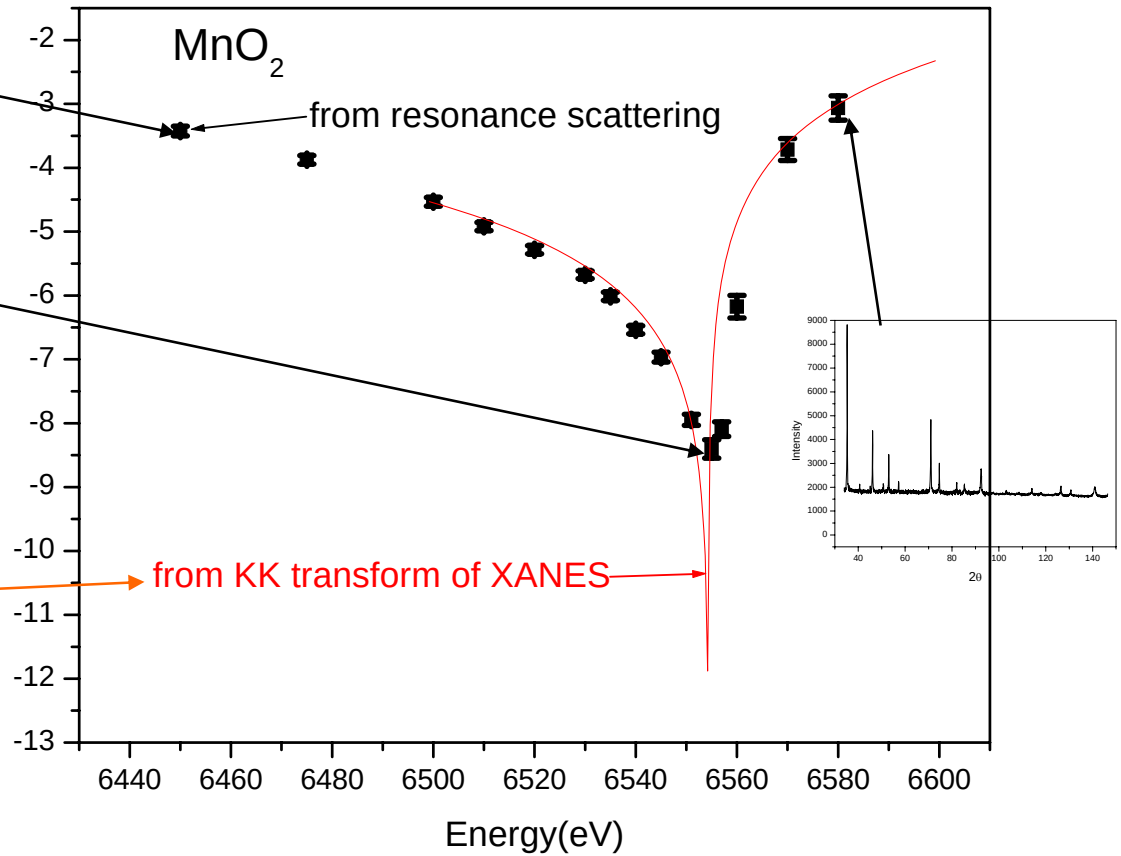
- $f_{xyz} = f_e\{f_i \varepsilon_{xyzT}\}$ f_e = Thomson scattering for an electron
- **$f_i = f_i^0(q) + f_i'(E) + i\, f_i''(E)$**
- **$\mu(E) = E * f_i''(E)$**
- **Kramers -Kronig :: $f_i'(E)$ <-> $f_i''(E)$**

$$f'(E_0) = \frac{2}{\pi} \int_0^\infty f''(E) \frac{E}{E^2 - E_0^2} dE$$

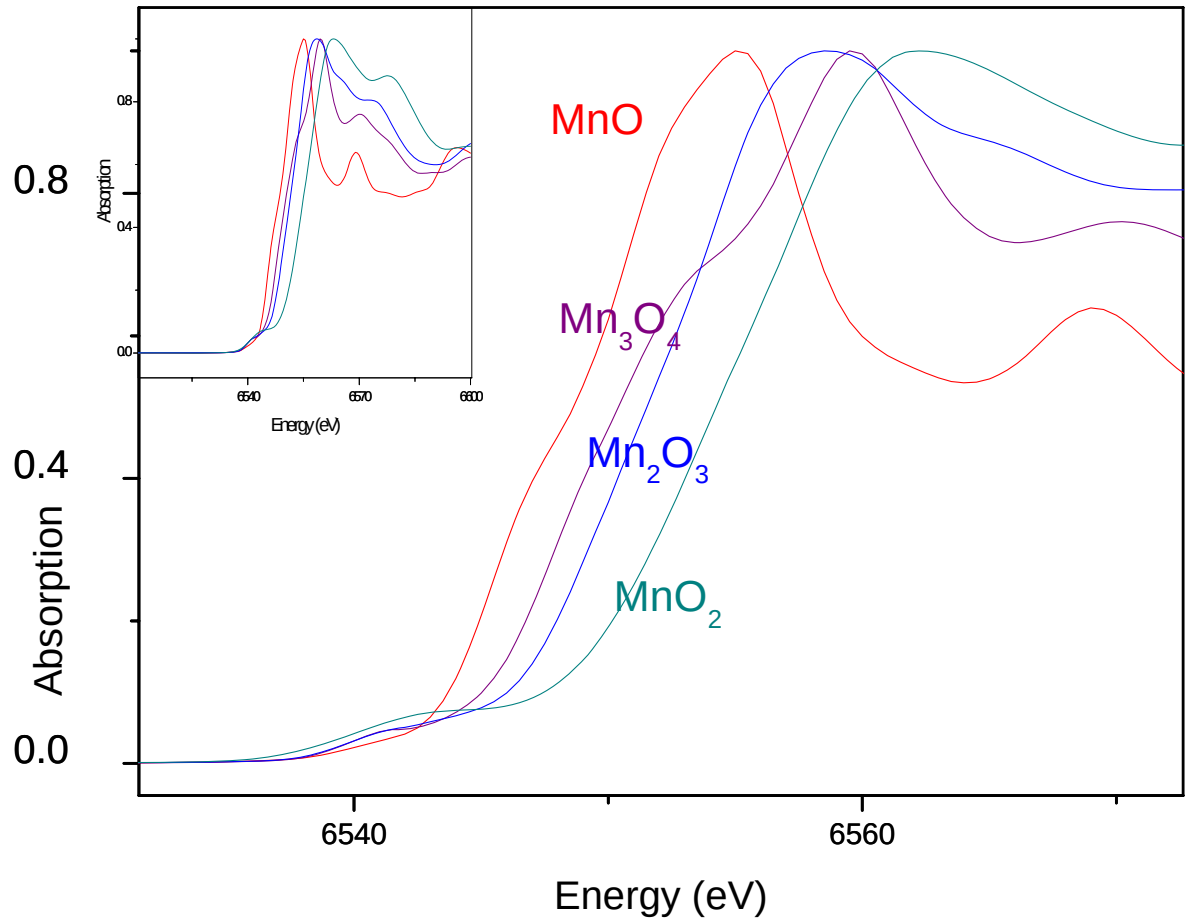
Resonance Scattering vs Xanes







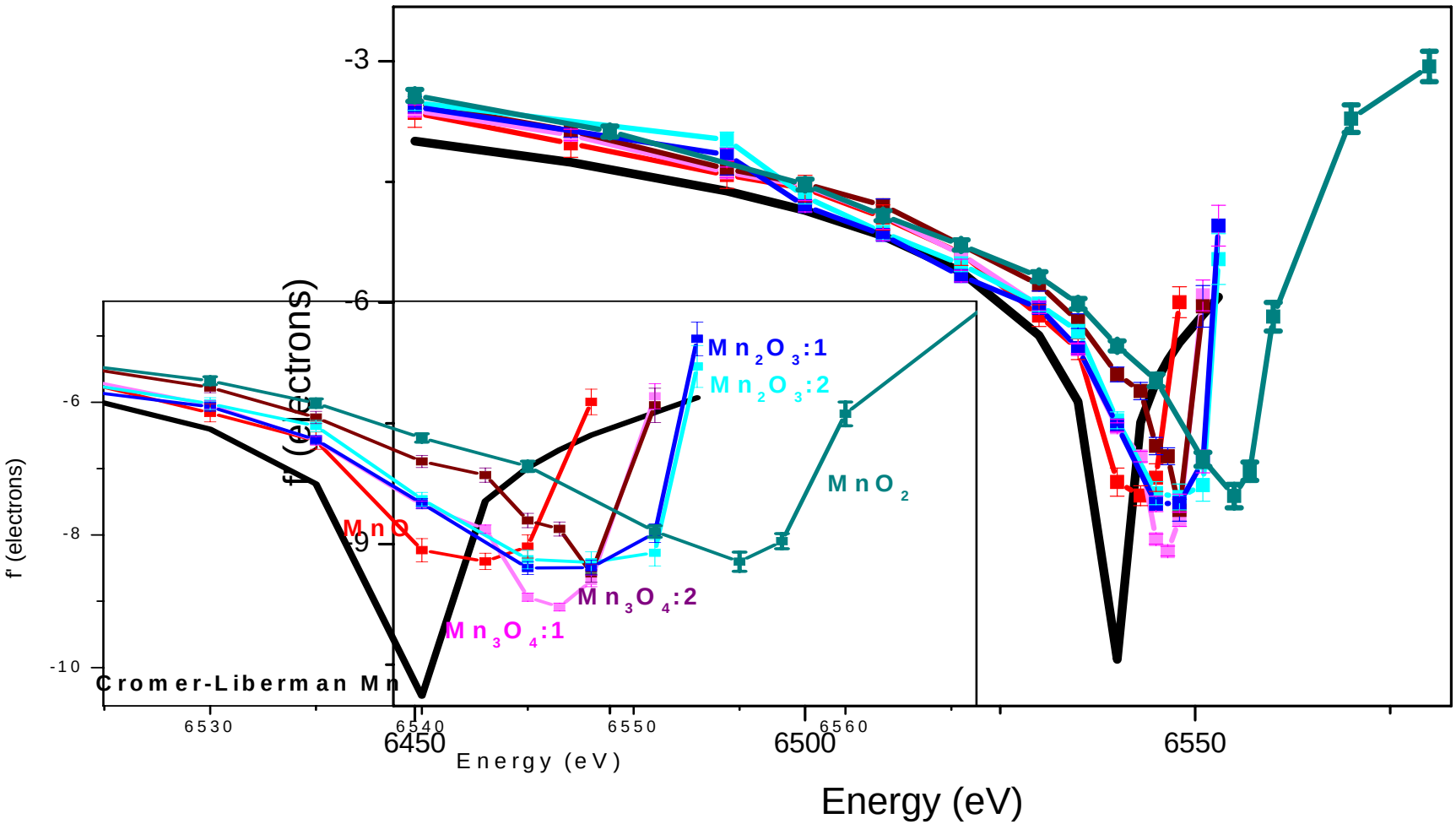
XANE Spectra of Mn Oxides



Mn Valence

Avg.	Actual
MnO_2	Mn
Mn_2O_3	Mn(II)?
Mn_3O_4	Mn(II)?
	Mn(I)?
MnO	Mn(I)?
	Mn

F' for Mn Oxides



Why Resonance Scattering?

- Sensitive to a specific crystallographic phase. (e.g., can investigate FeO layer growing on metallic Fe.)
- Sensitive to a specific crystallographic site in a phase. (e.g., can investigate the tetrahedral and the octahedral site of Mn_3O_4)

Mn valences in Mn Oxides

- Mn valence of the two sites in Mn_2O_3 very similar
- Valence of the two Mn sites in Mn_3O_4 different but not as different as expected.