Structure Refinement: Part 1

7th X-ray Scattering School

Apurva Mehta

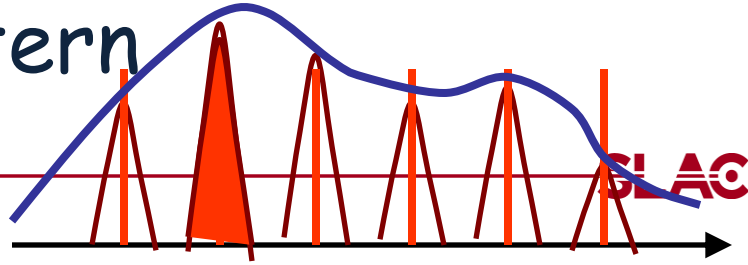
Kevin Stone

U.S. DEPARTMENT OF ENERGY
Office of Science

SSRL

SLAC NATIONAL ACCELERATOR LABORATORY

What does a diffraction pattern tell us?

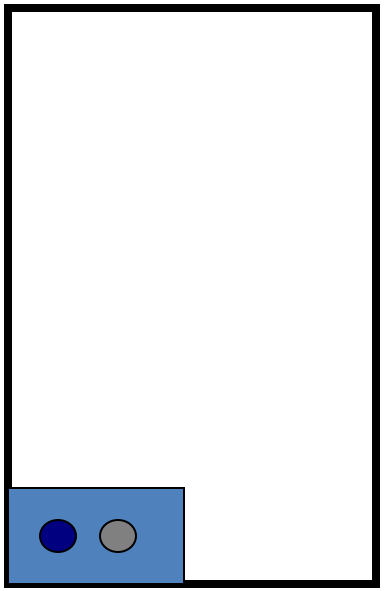


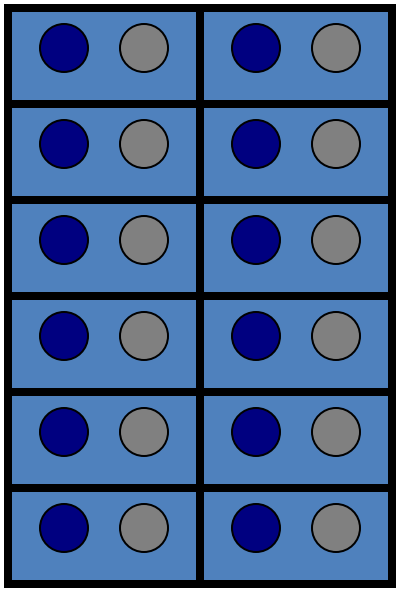
- Peak Shape & Width:
  - Zero order peak

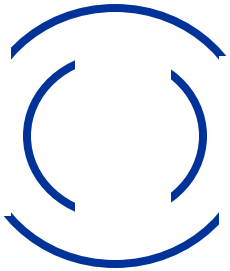
Small Angle Scattering & Reflectivity

  - Higher order peaks
    - crystallite size
    - Strain gradient
- Peak Positions:
    - Phase identification
    - Lattice symmetry
    - Lattice strain
- Peak Intensity:
    - Structure solution
    - Crystallite orientation

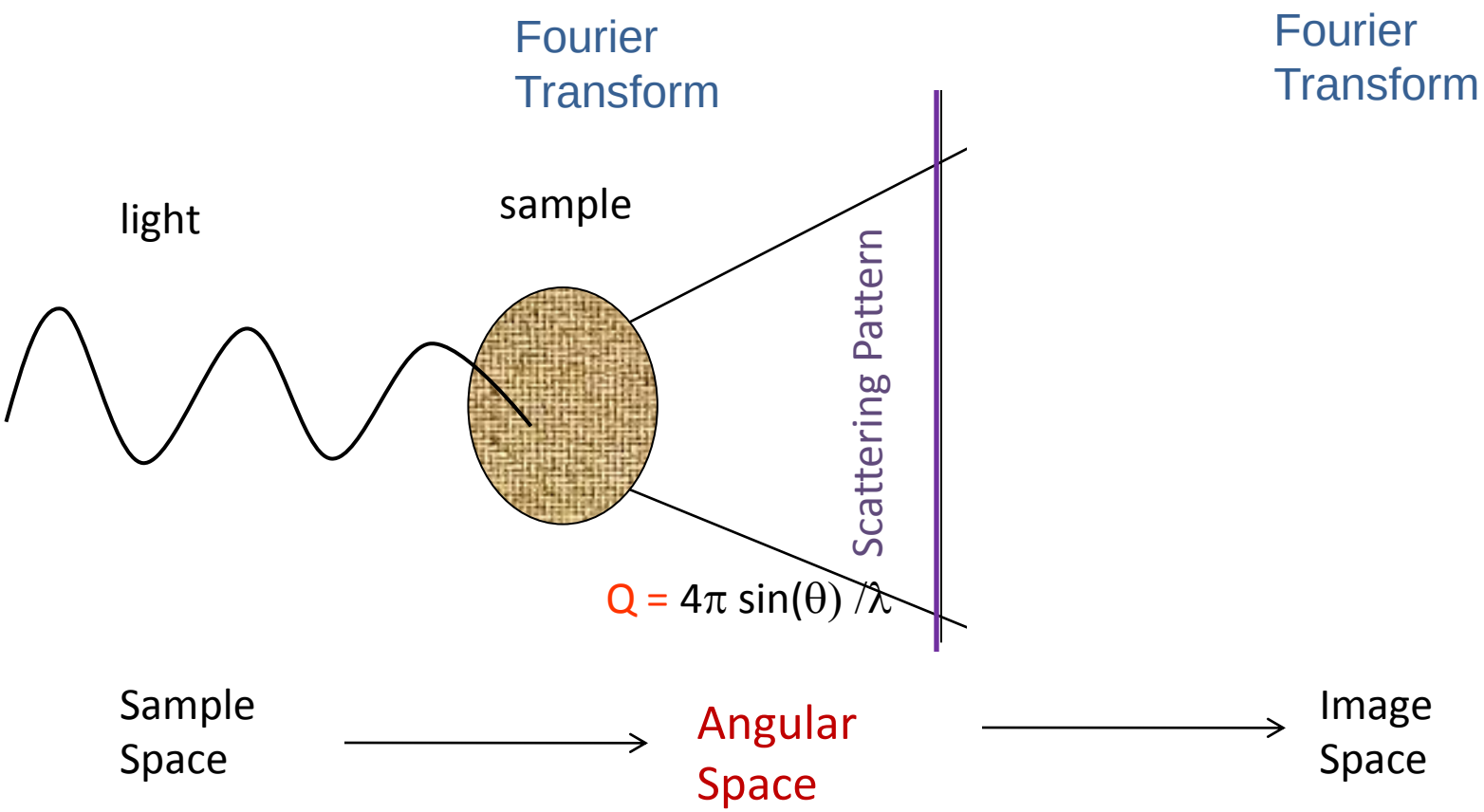
Wide Angle Scattering



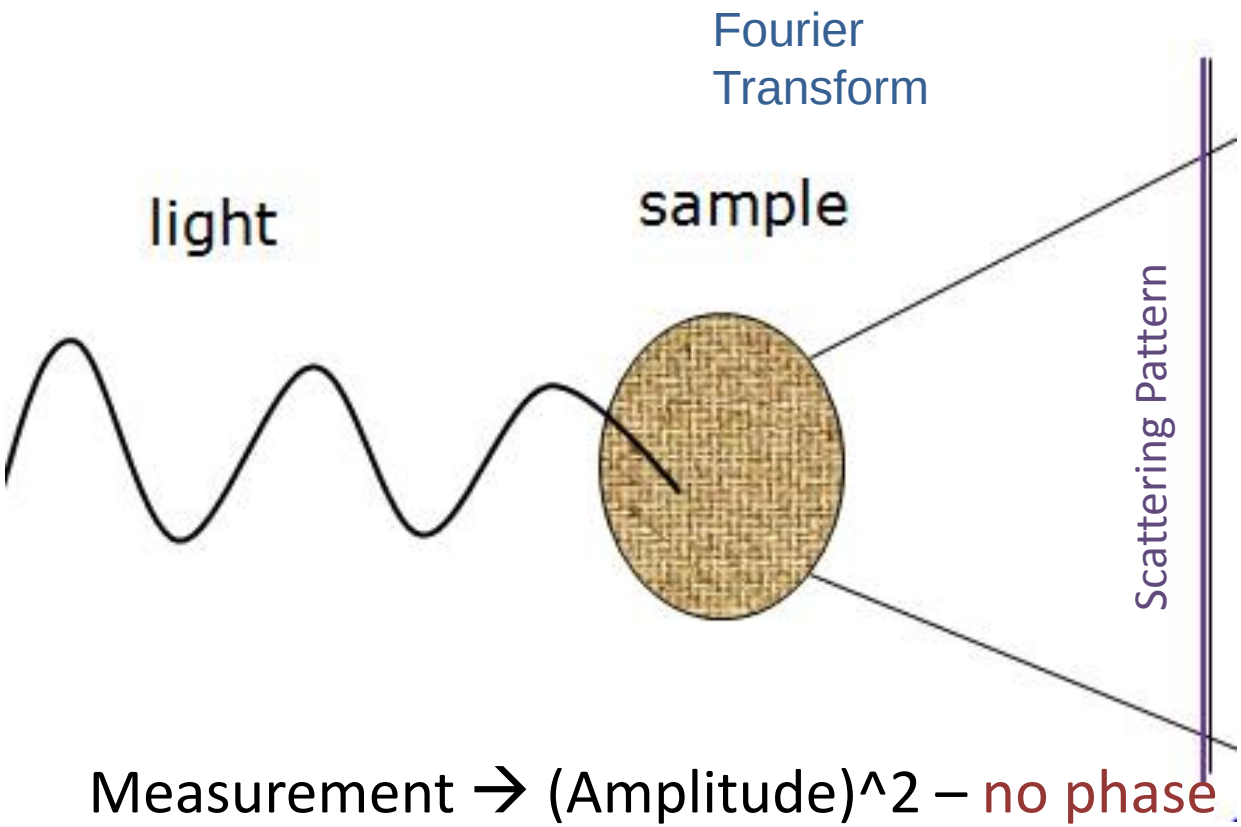




Lensless Imaging



Phase Problem

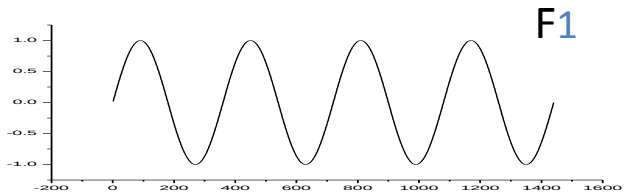


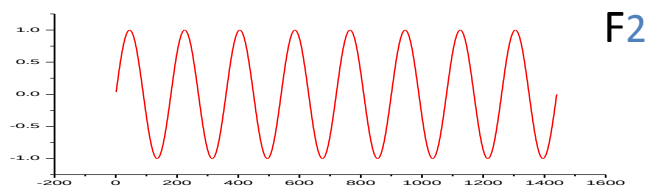
Amplitude*exp(I Phase)

Measurement → (Amplitude)^2 – no phase

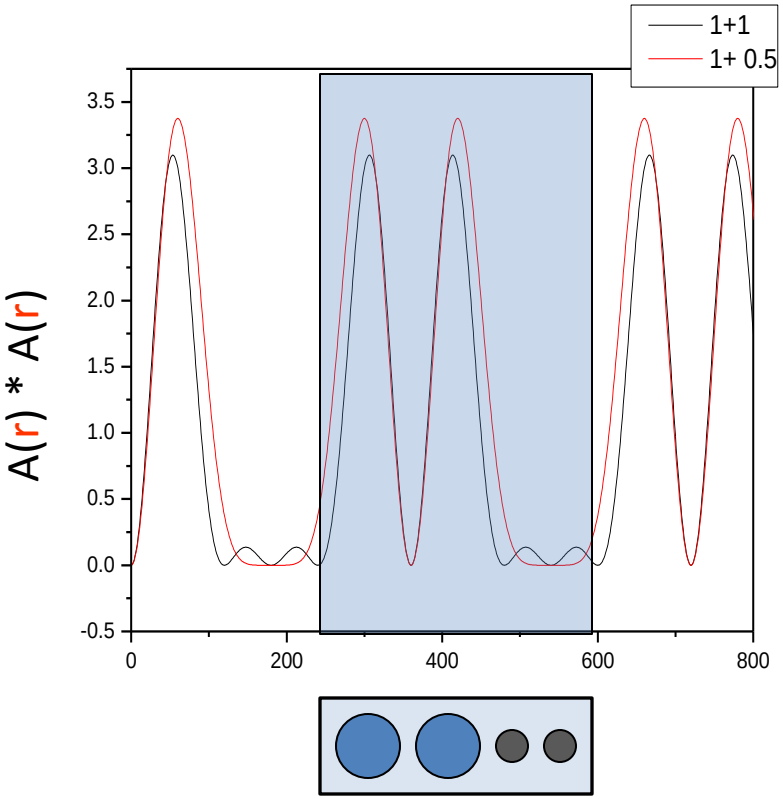
Phase Problem

$$A(r) = FT\{ F1 + aF2\, e^{i(ph)} \}$$

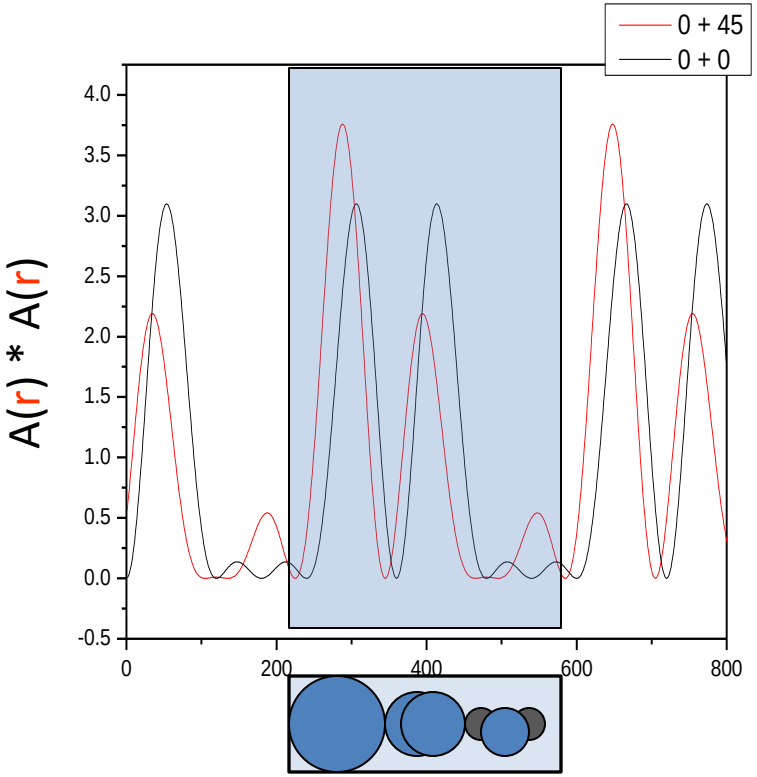




Amplitude unknown

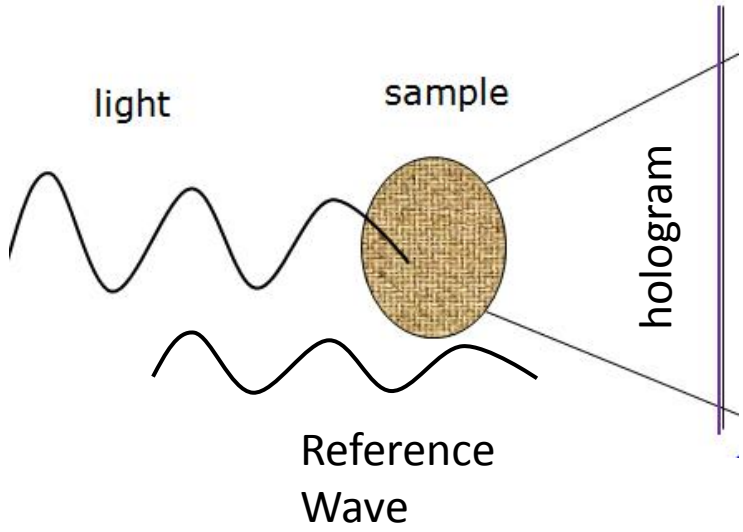


Phase Unknown



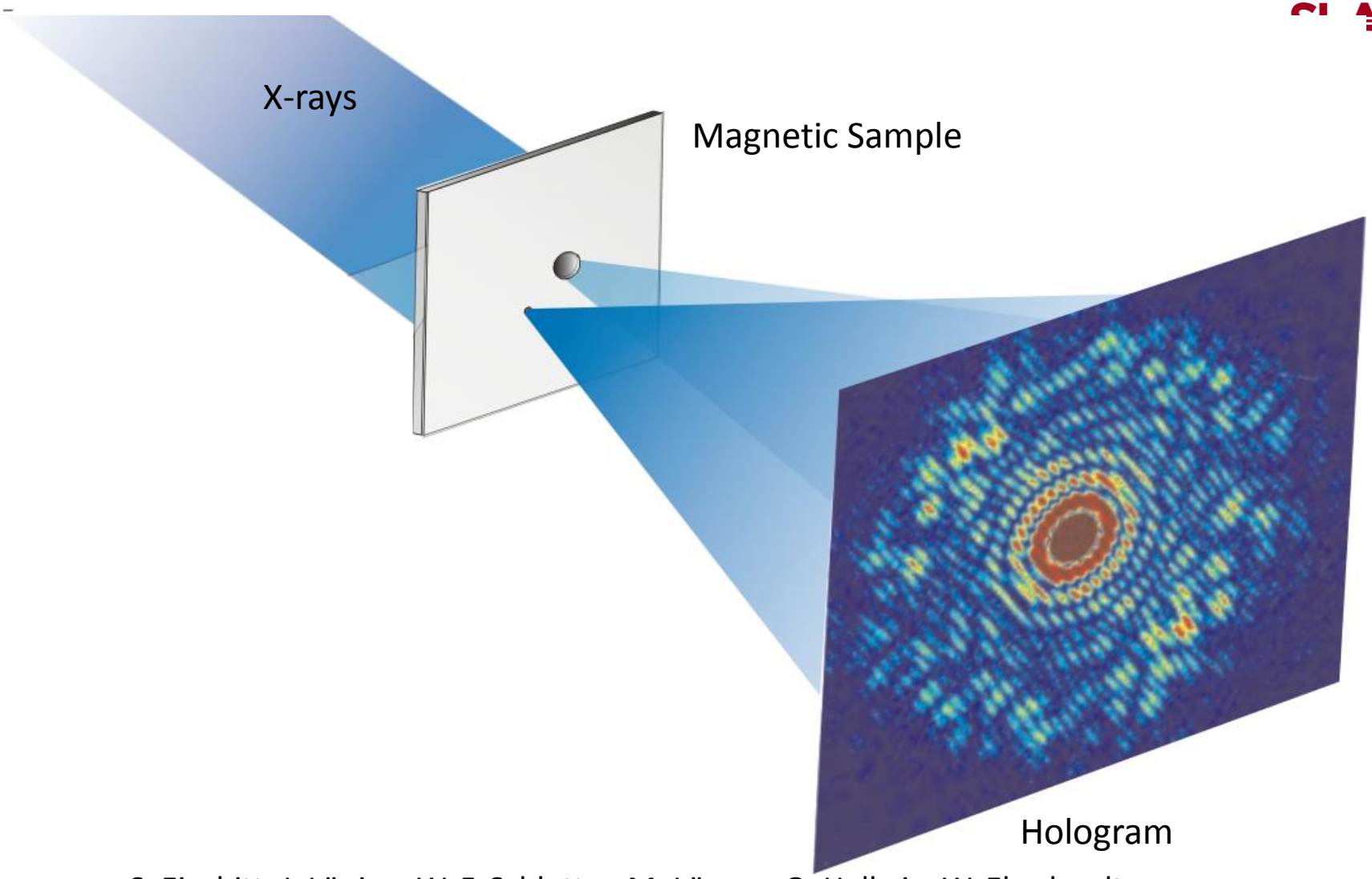
Solving the Phase Problem

- Holographic
- Guess/ Trial+Error



If sufficient coherence

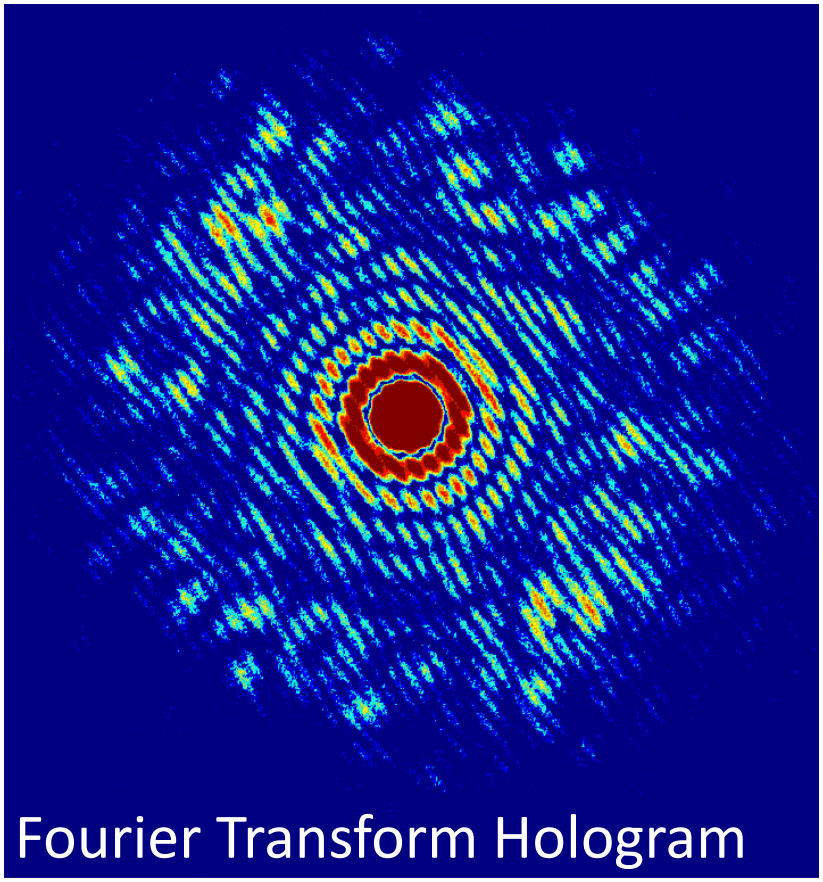
Magnetic x-ray holography



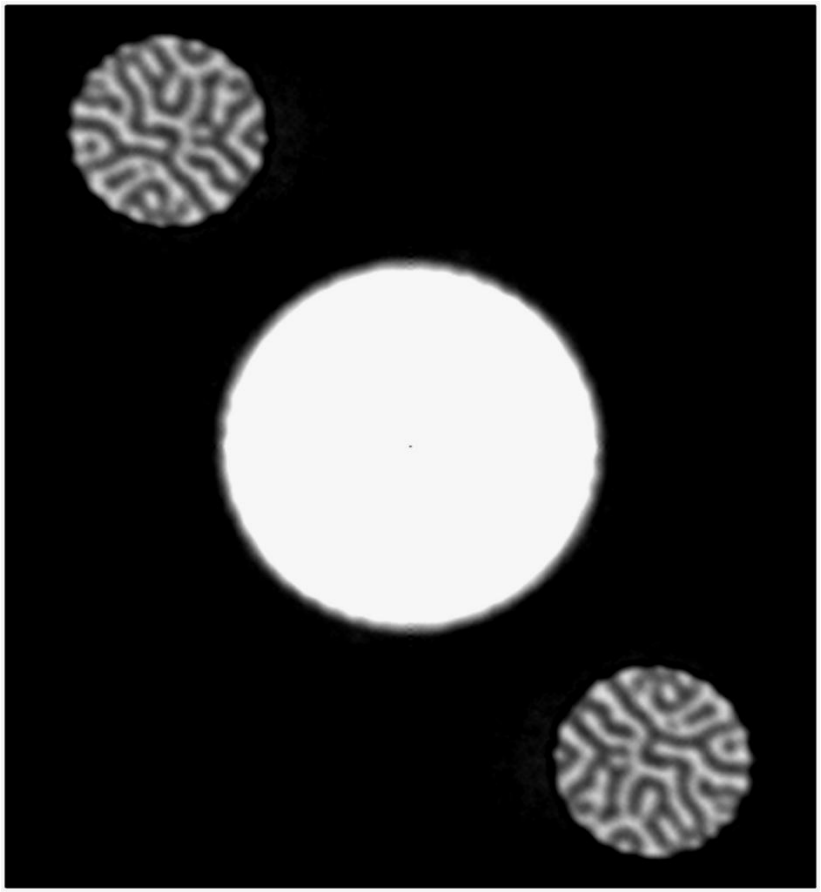
S. Eisebitt, J. Lüning, W. F. Schlotter, M. Lörgen, O. Hellwig, W. Eberhardt, and J. Stöhr. Nature, 432 p885, 2004.

A lensless image

Intensity

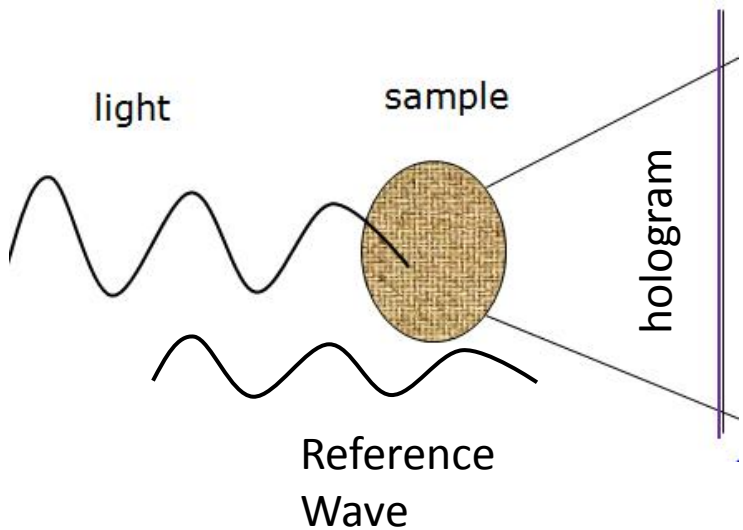


2D Fourier Transform



Solving the Phase Problem

- Holographic



If sufficient coherence

- Guess/ Trial+Error
- X-ray Crystallographic Methods
  - Heavy Atom substitution
  - Patterson Method
  - Multi-wavelength Anomalous Diffraction
  - Reitveld Method
  - Fourier Difference Method
- Iterative Phase Retrival

Solution to Phase Problem

- Phase/Structure must be guessed
  - And then refined.

- How to guess?
  - Heavy atom substitution, SAD or MAD
  - Structure with one stronge scatterer - e.g. U in Phosphates matrix -
  - Similarity to homologous compounds, e.g. NaCl → KCl

  - Patterson function or pair distribution analysis.
    B. Shyam

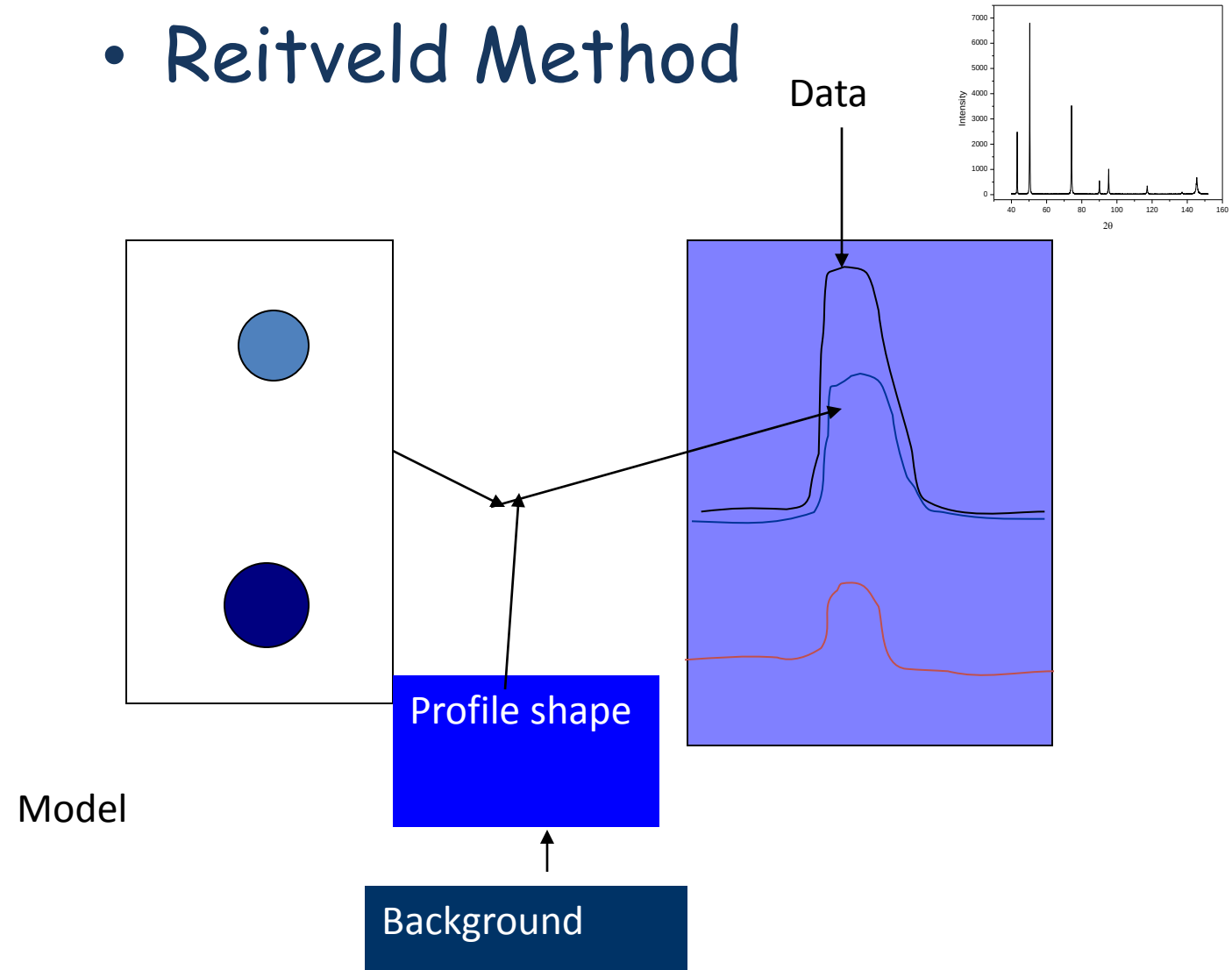
Structure Solution

- 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 materials can not be readily prepared in single-crystal form: their structures obtained via synchrotron powder diffraction
  - Peak overlap a problem – high resolution setup helps
  - Much lower intensity – loss on super lattice peaks from small symmetry breaks. (Fourier difference helps)

Inverse Modeling Method 1

- Reitveld Method

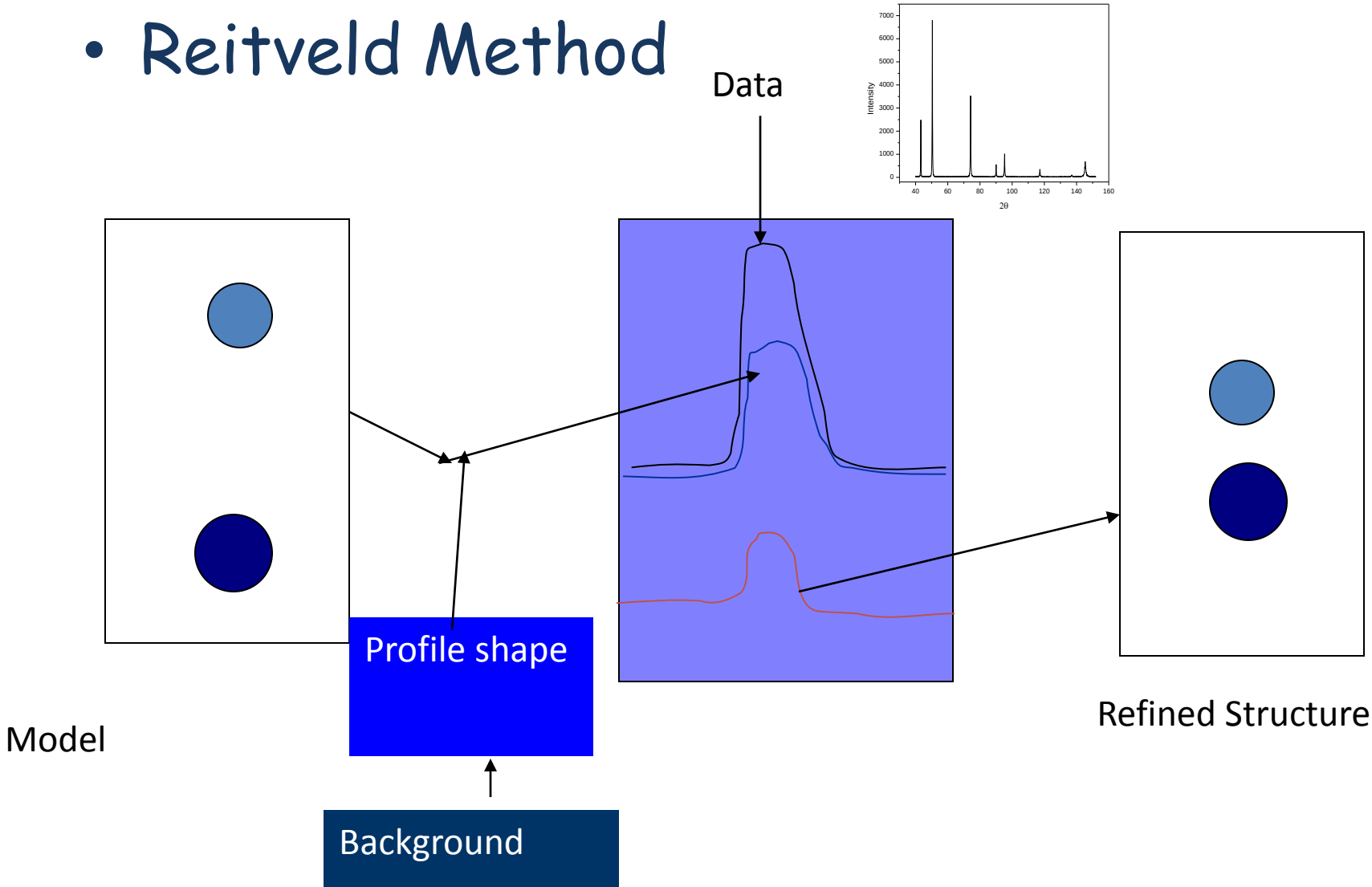


Profile Shape function

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

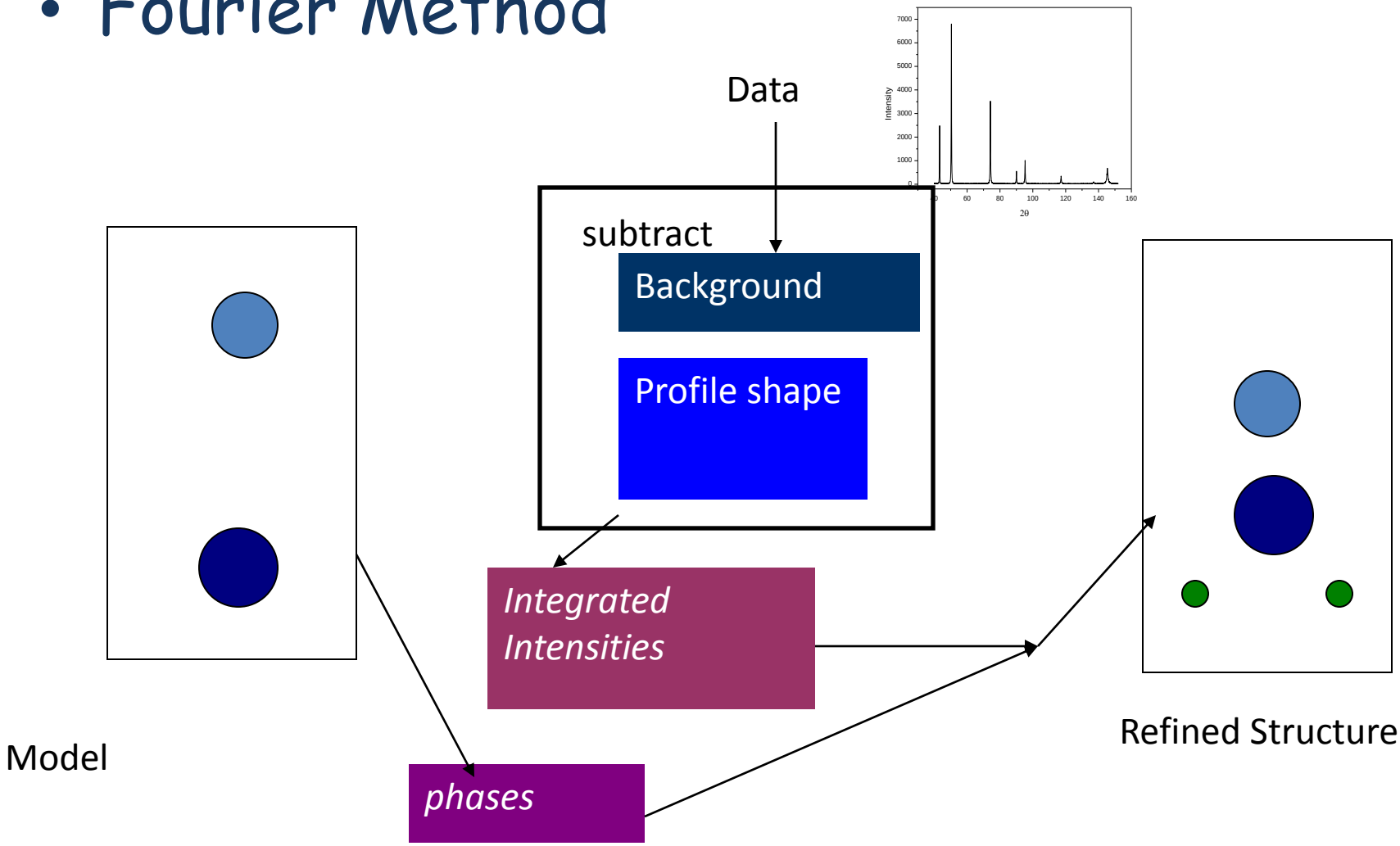
Inverse Modeling Method 1

- Reitveld Method



Inverse Modeling Method 2

- Fourier Method



Inverse Modeling Methods

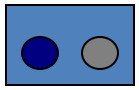
Linda Lim will say much more….

- 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.

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



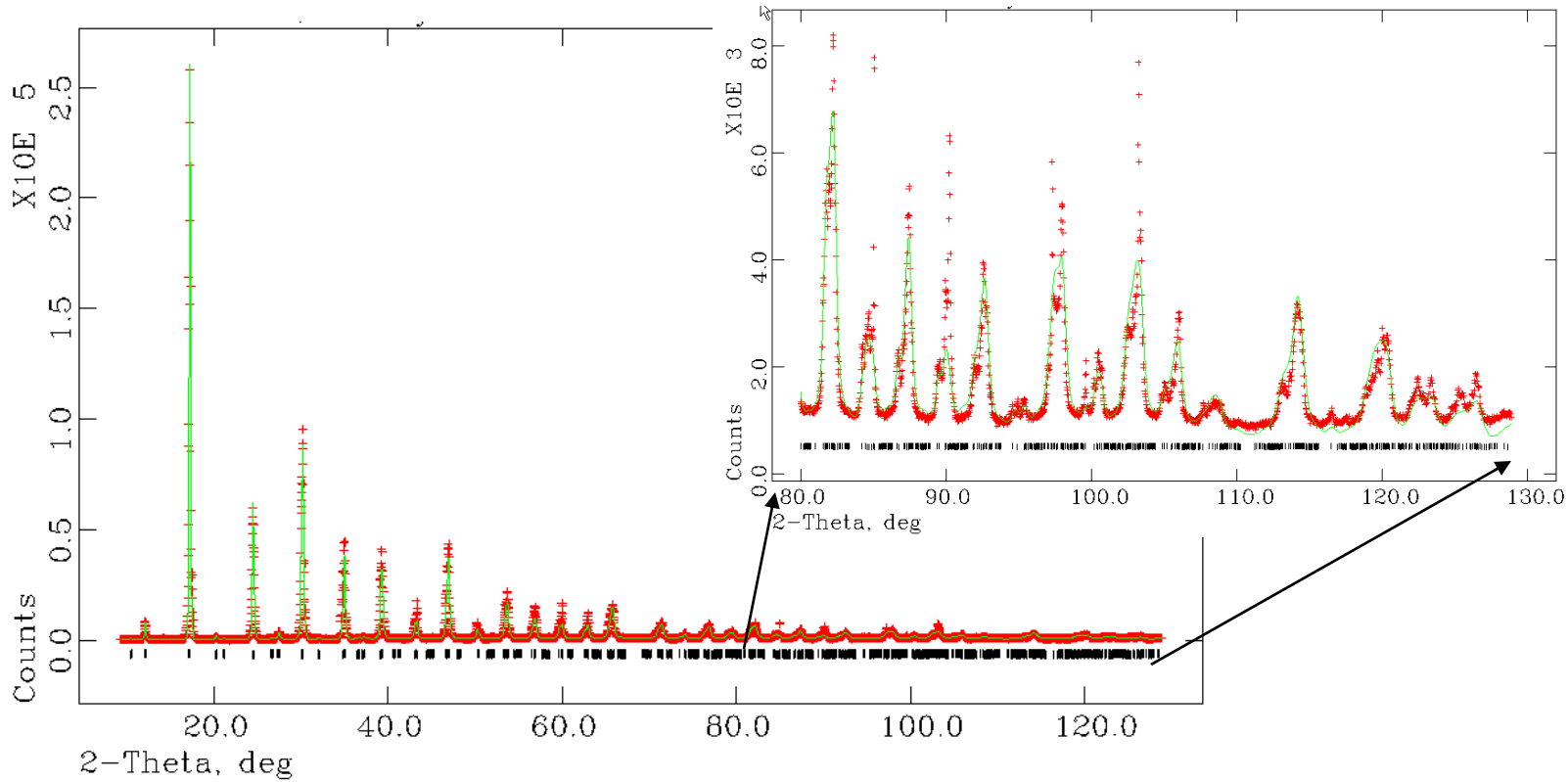
- Guess the motif and its placement
  - Phases for each hkl
- Measure the peak widths
  - Use an appropriate profile shape function
- Construct a full diff. pattern and compare with measurements

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

Need for High Q

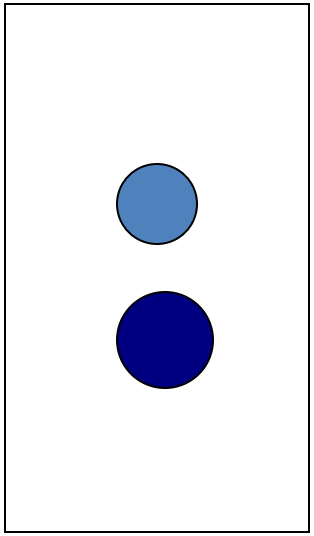


Many more reflections at higher Q.

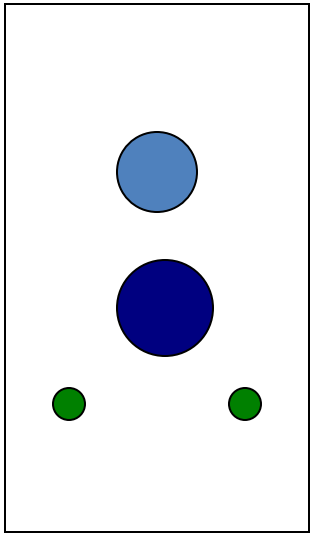
Therefore, most of the structural information is at higher Q

Structure Refinement Method

Reitveld Method



Fourier Difference Method



Questions?