Lesson 1
XRD and Rietveld Refinement

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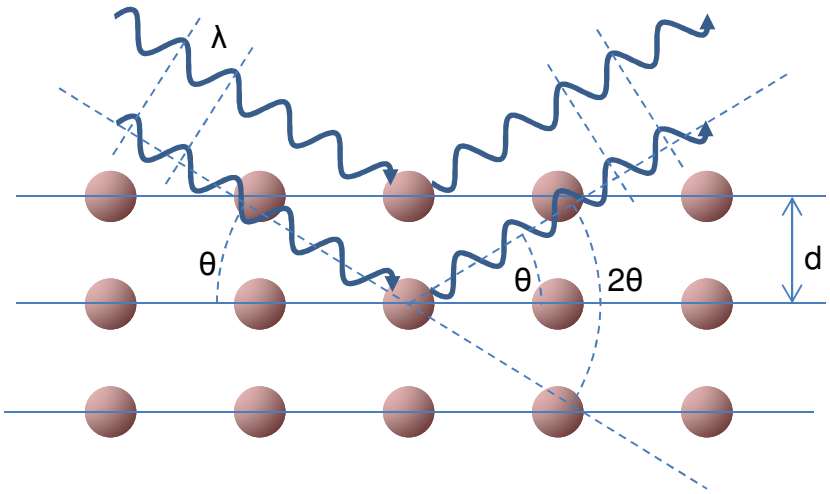
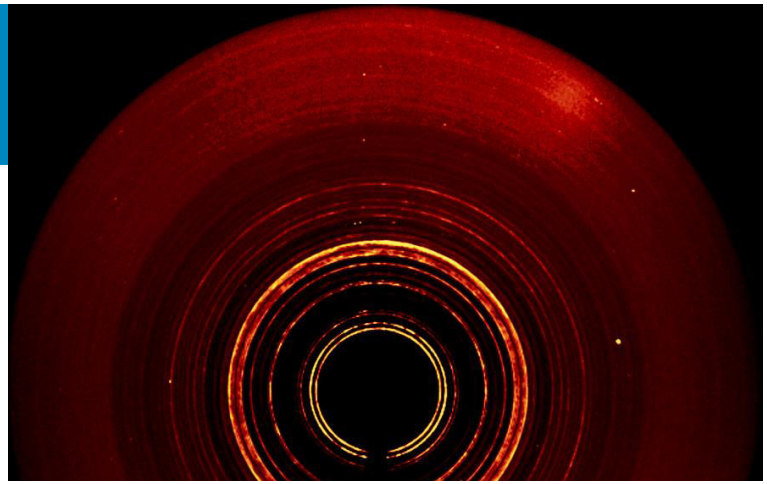
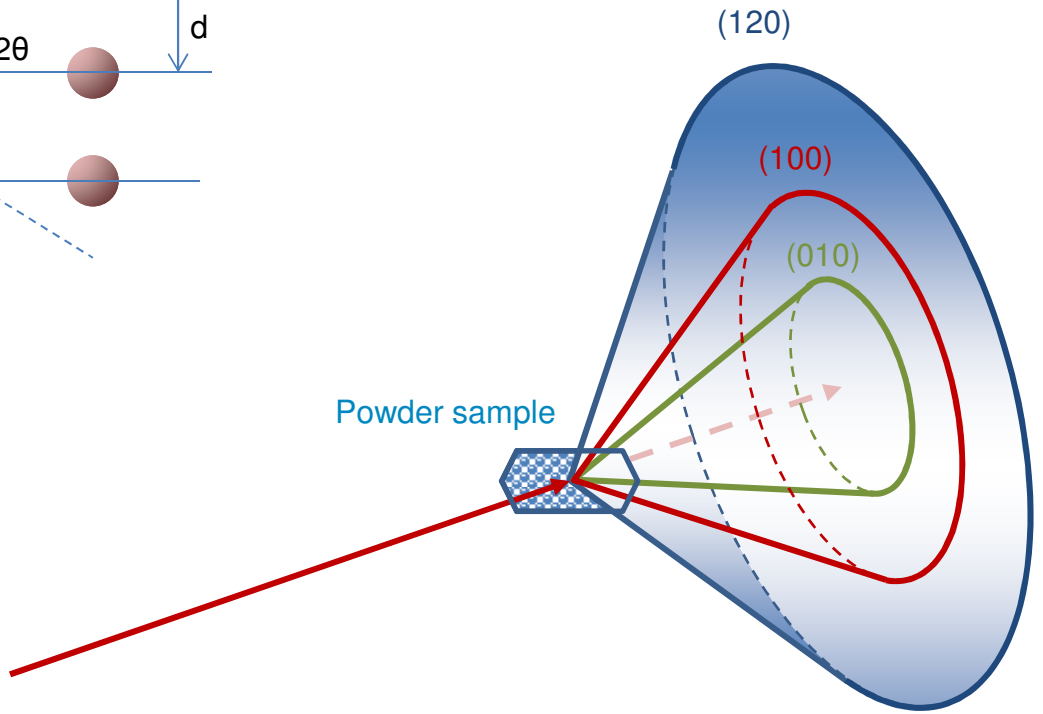
Powder Diffraction

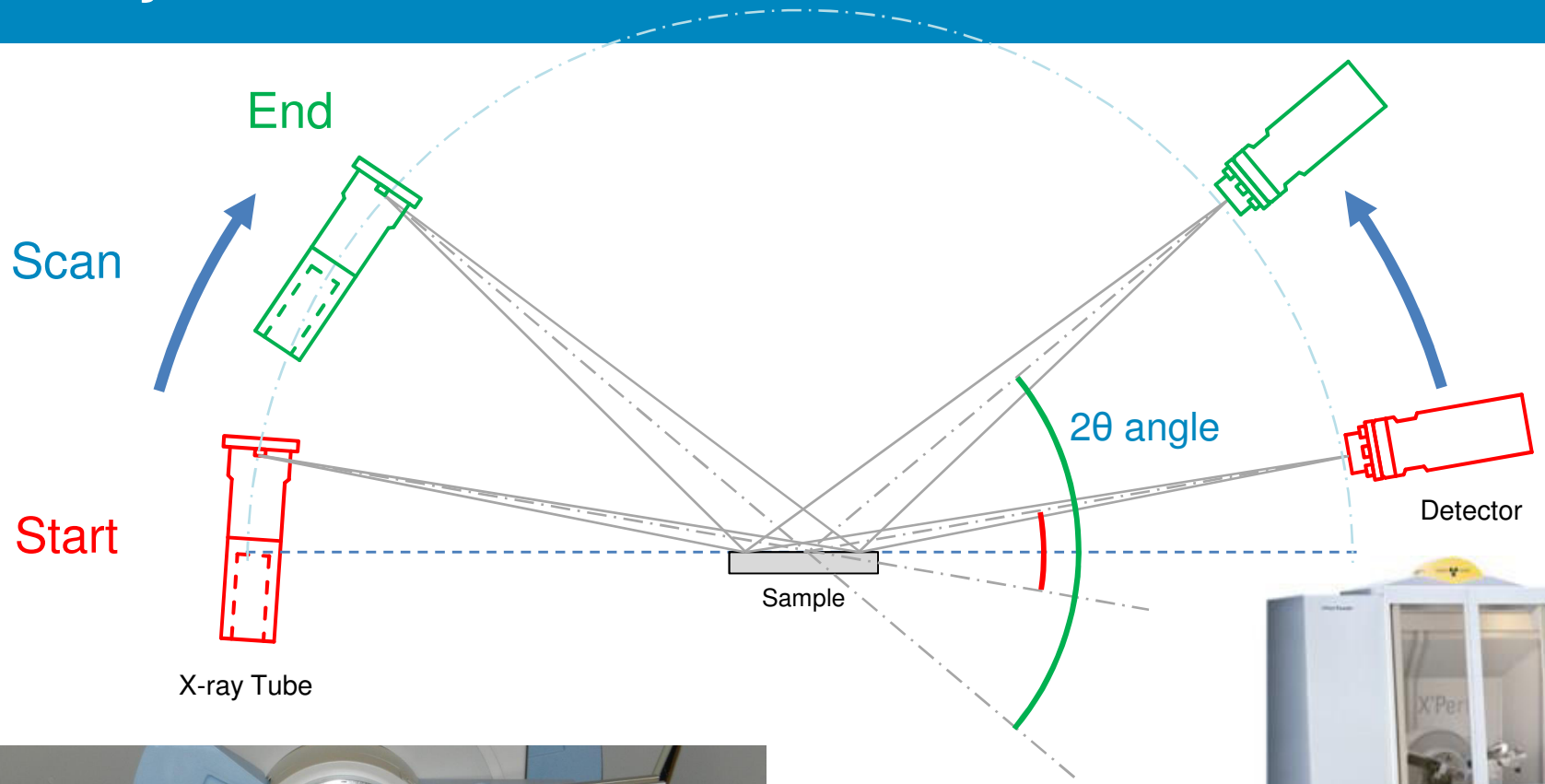
$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$

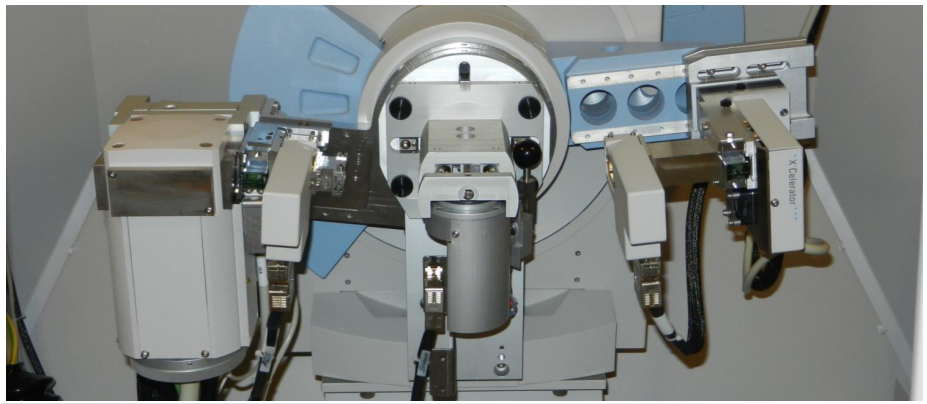






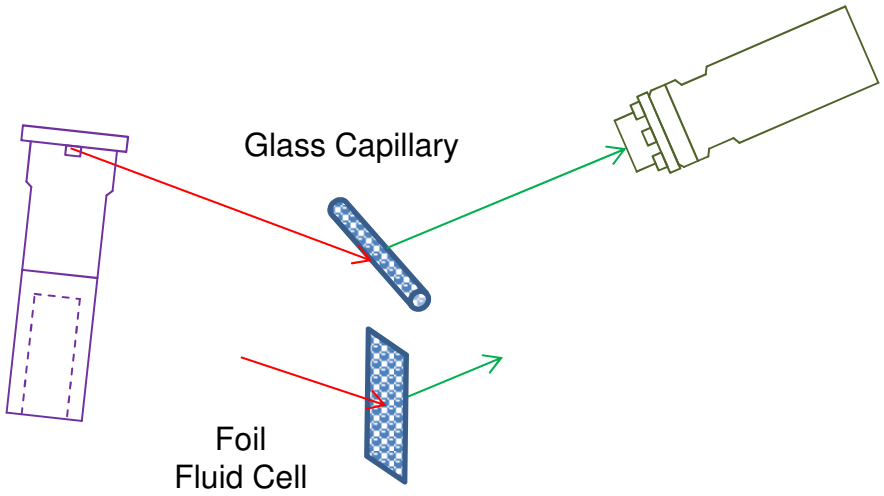
X-ray Diffractometer





Digital Diffractometers

Transmission Geometry

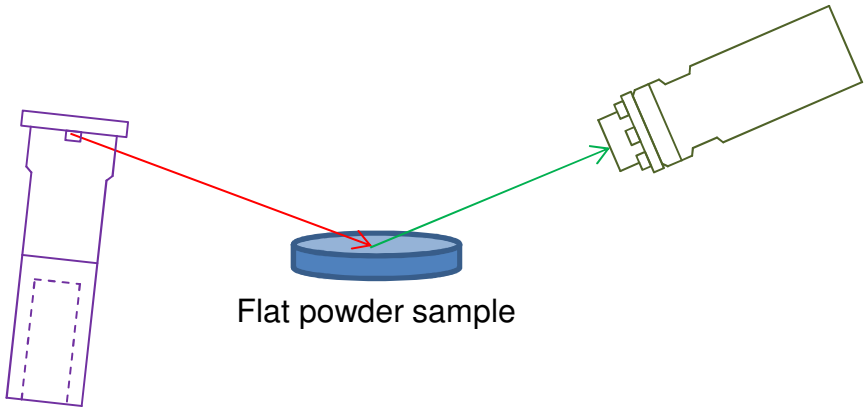


Capillaries are ideal for:

- Light atoms (Polymers, Pharmaceuticals)
- Small amounts
- Hazardous materials
- Air-sensitive materials

Use characteristic radiation with low absorption coefficient

Reflective Geometry

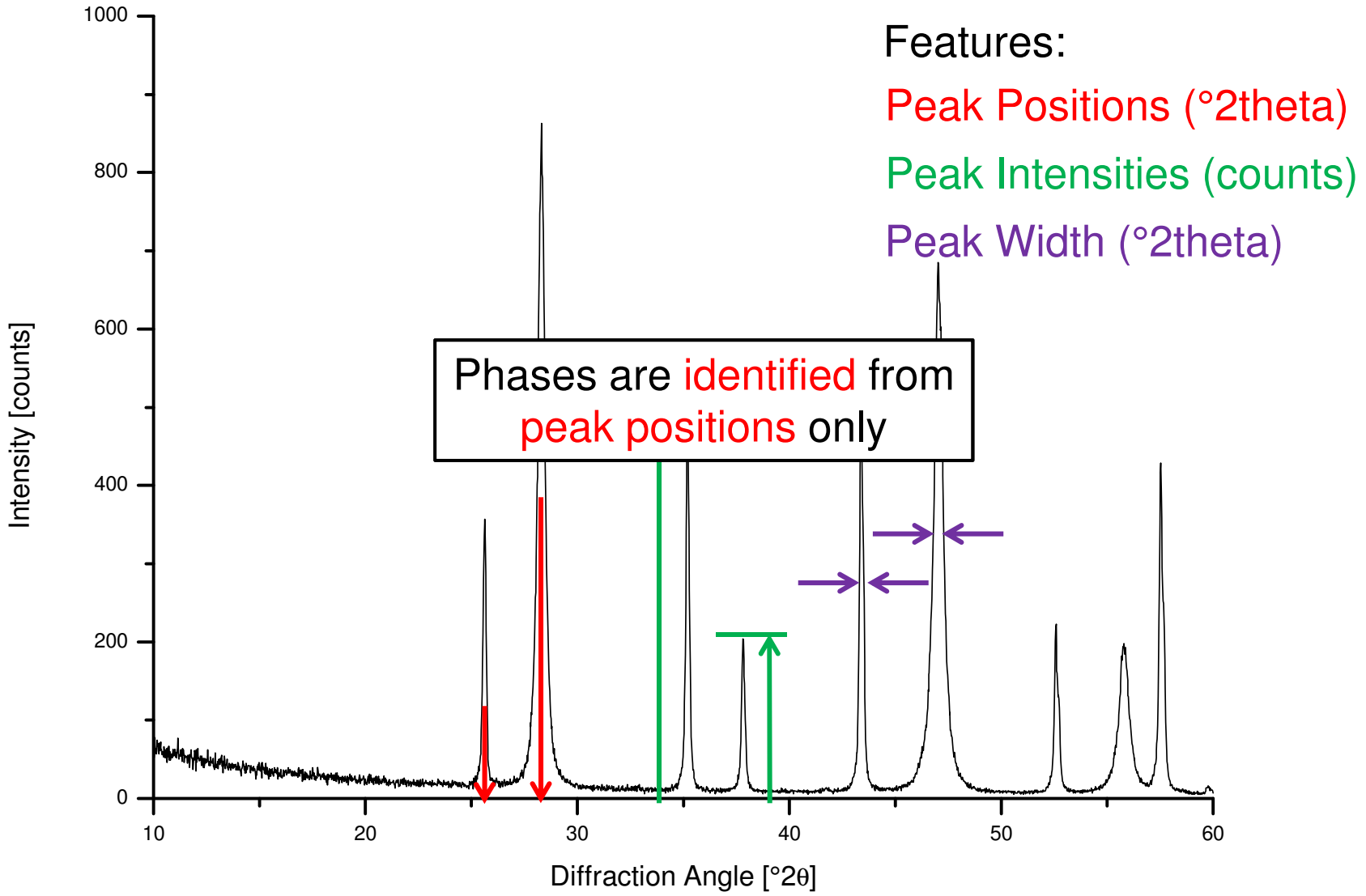


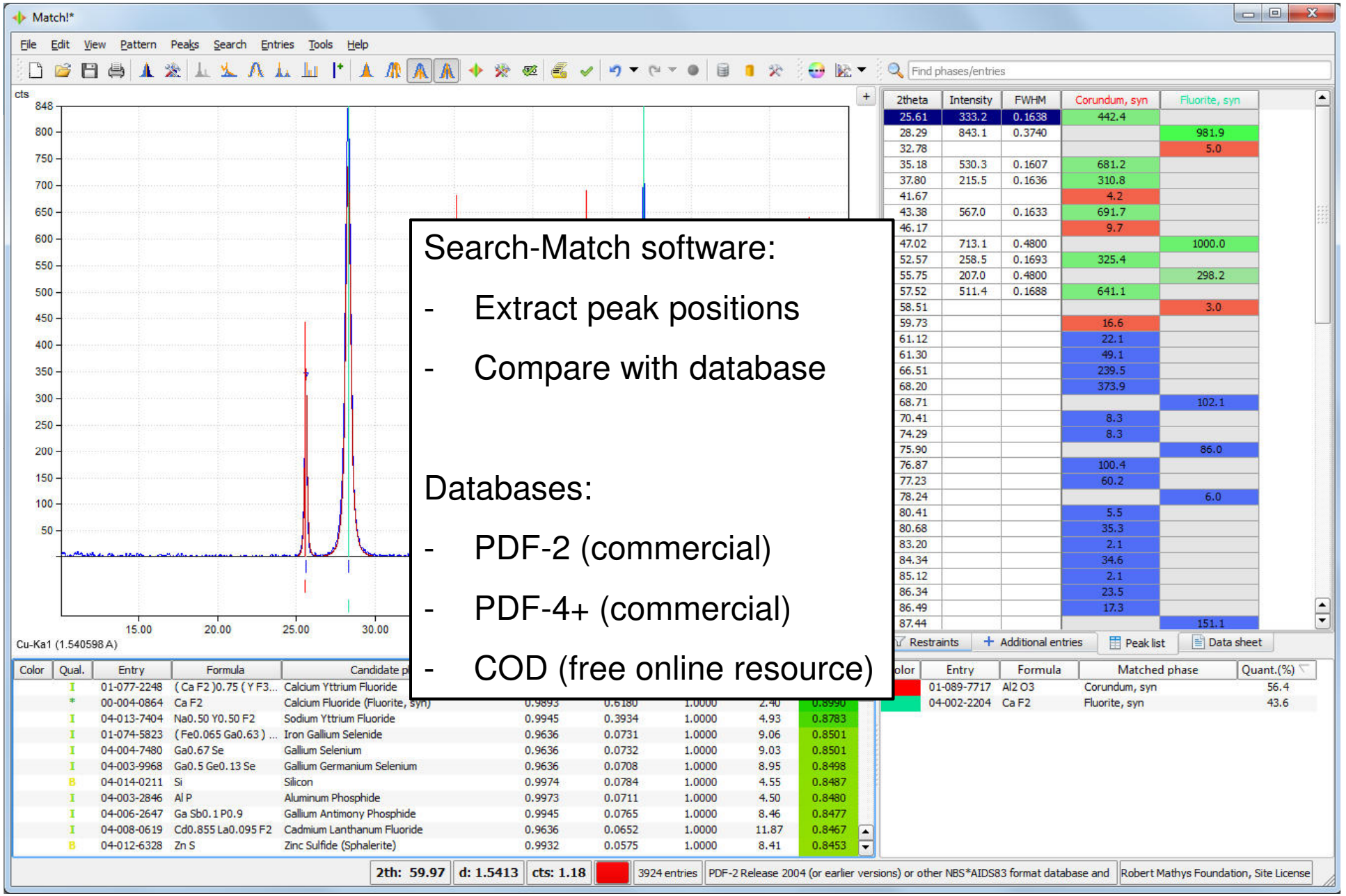
Reflective Geometry is ideal for:

- Absorbing materials (Ceramics, Metals)
- Thin films
- Texture analysis

Use characteristic radiation with high absorption coefficient

Diffraction Pattern





Search-Match software:

- Extract peak positions
- Compare with database

Databases:

- PDF-2 (commercial)
- PDF-4+ (commercial)
- COD (free online resource)

Rietveld Refinement

For more than just identification:

Rietveld refinement

Prof. Hugo Rietveld

Extracts much more information from powder XRD data:

- Unit cell dimensions
- Phase quantities
- Crystallite sizes / shapes
- Atomic coordinates / Bond lengths
- Micro-strain in crystal lattice
- Texture effects
- Substitutions / Vacancies

No phase identification!

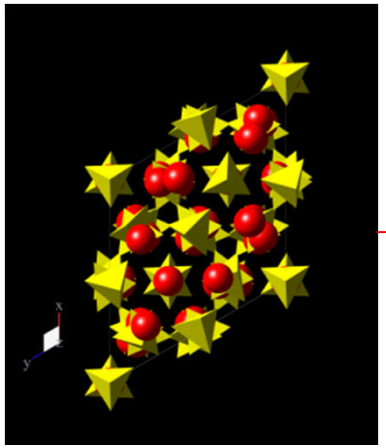
Identify your phases first
(unknown phase → no Rietveld refinement)

No structure solution
(just structure refinement)

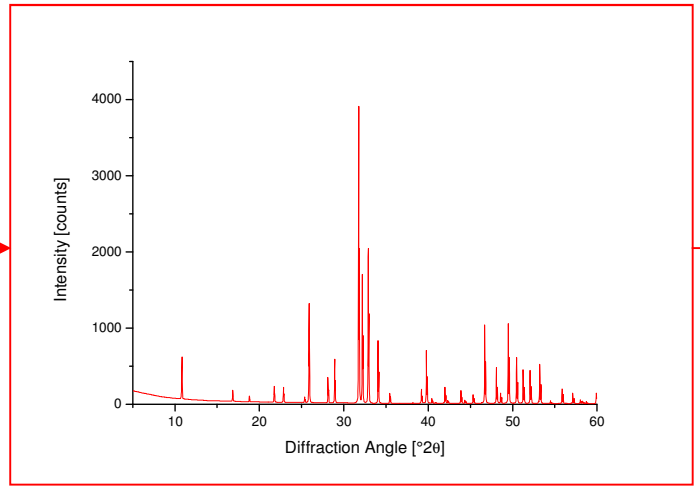
Needs excellent data quality!

Rietveld Refinement

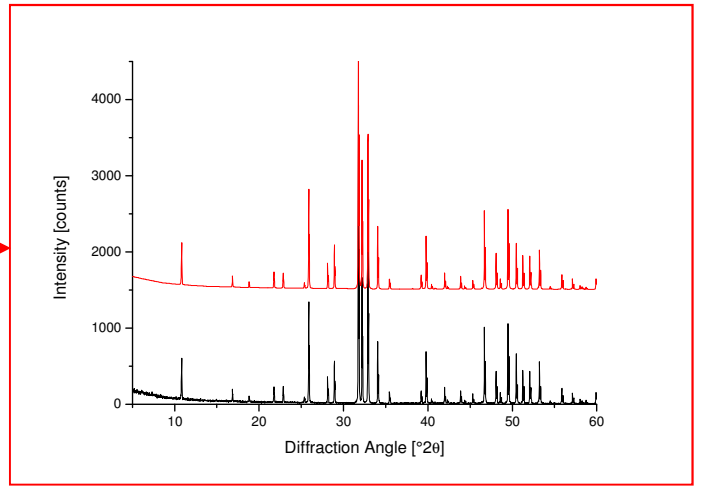
Known structure model



Calculate theoretical diffraction pattern



Compare with measured pattern



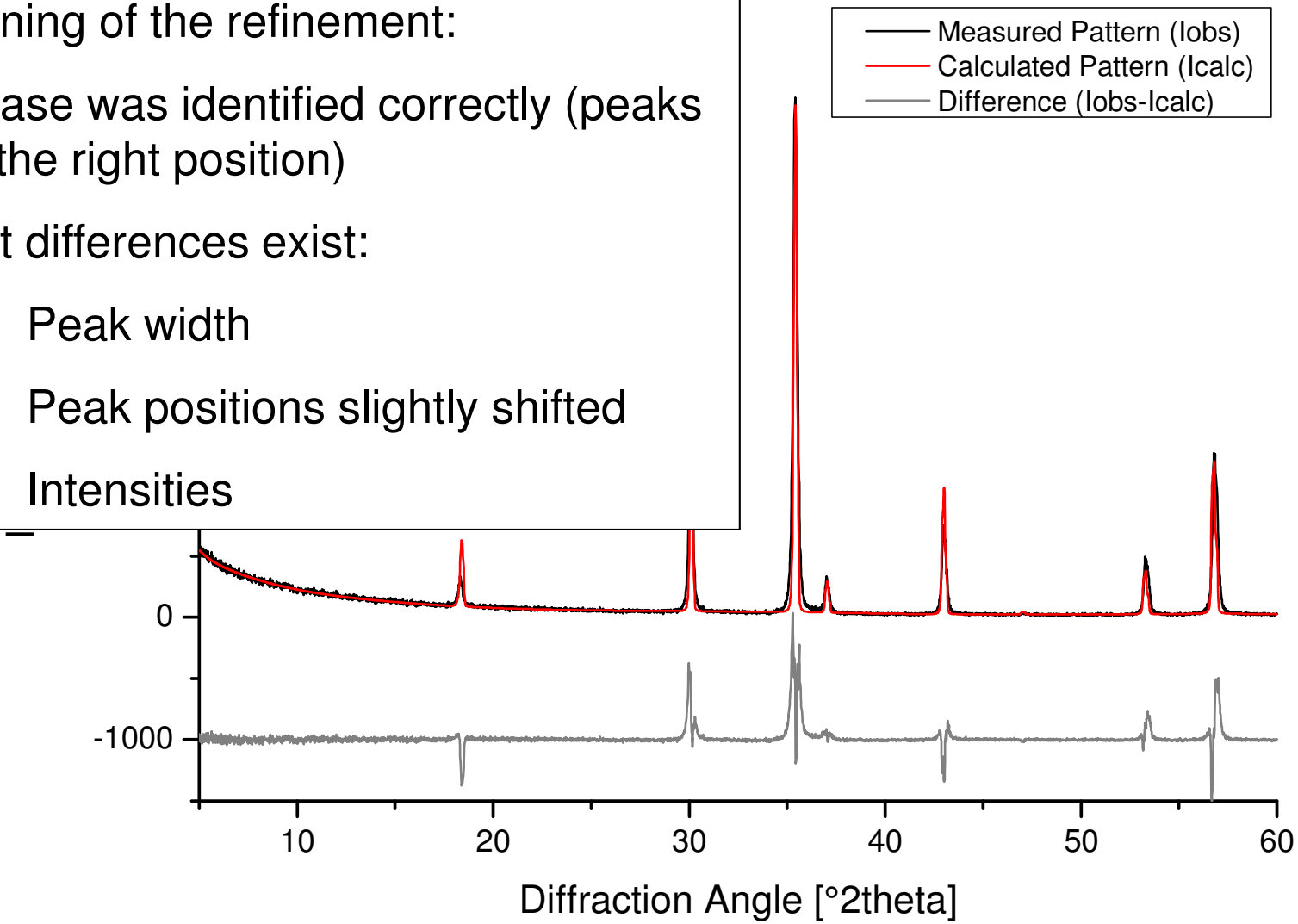
Optimize structure model, repeat calculation

Minimize differences between calculated and observed pattern by least-squares method

Rietveld Refinement

Beginning of the refinement:

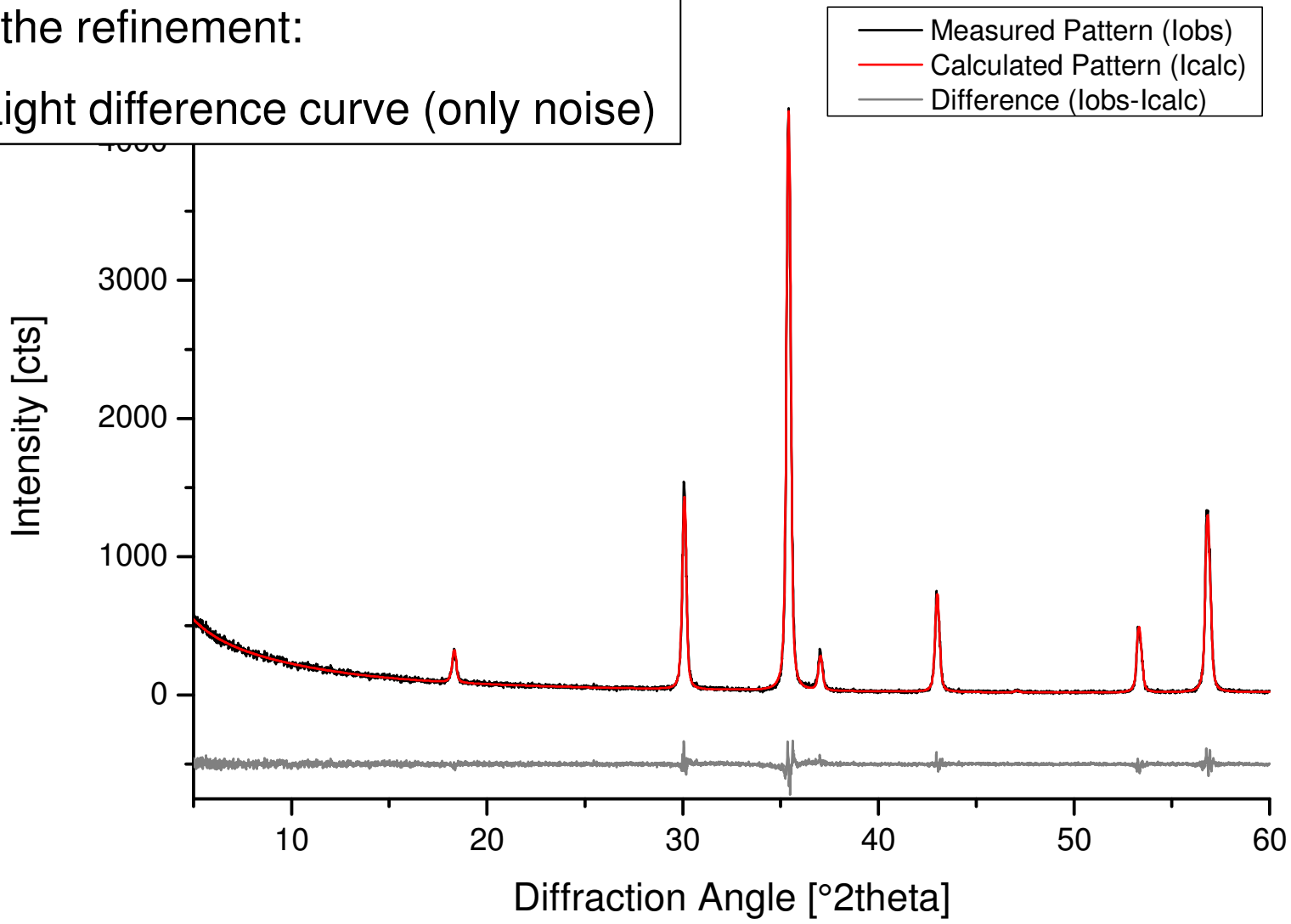
- Phase was identified correctly (peaks at the right position)
- But differences exist:
  - Peak width
  - Peak positions slightly shifted
  - Intensities



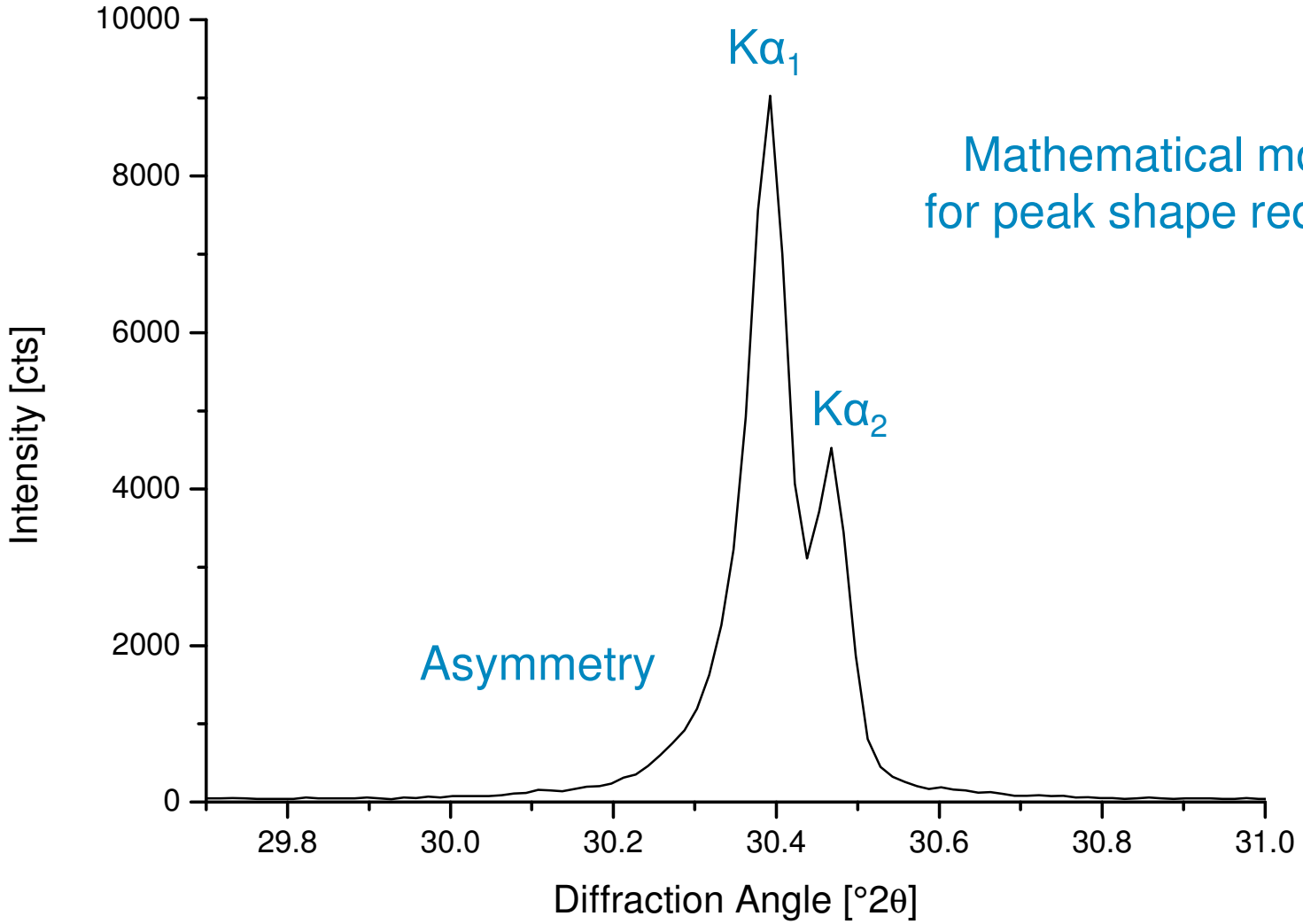
Rietveld Refinement

After the refinement:

- Straight difference curve (only noise)



Modelling the Peak Profile



Modelling the Peak Profile

Traditional («Rietveld») Approach:

Pseudo Voigt curves for $K\alpha_1$, $K\alpha_2$ and $K\beta$

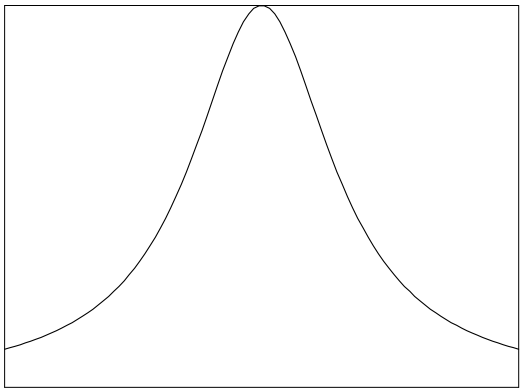
$$V_P(x) = n * L(x) + (1-n) * G(x)$$

Lorentzian curve

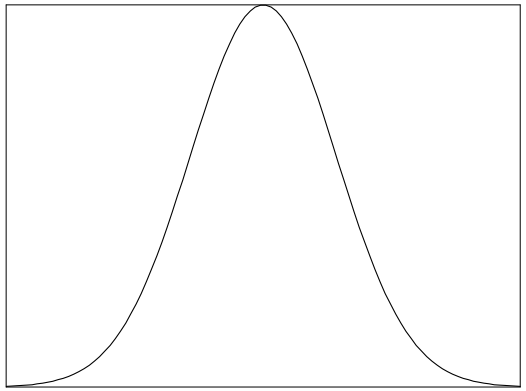
$$L(x) = \frac{1}{1+(\frac{x-x_0}{\omega})^2}$$

Gaussian curve

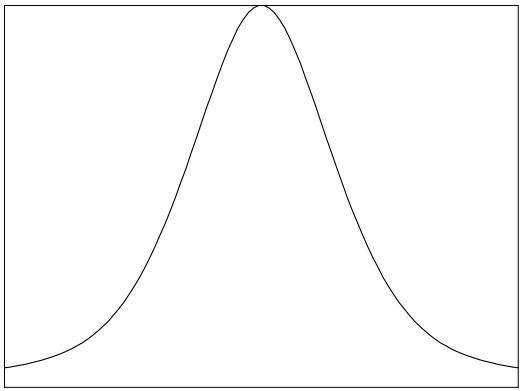
$$G(x) = \exp[-\ln(2)\cdot(\frac{x-x_0}{\omega})^2]$$



Lorentzian (ω = 1.0)

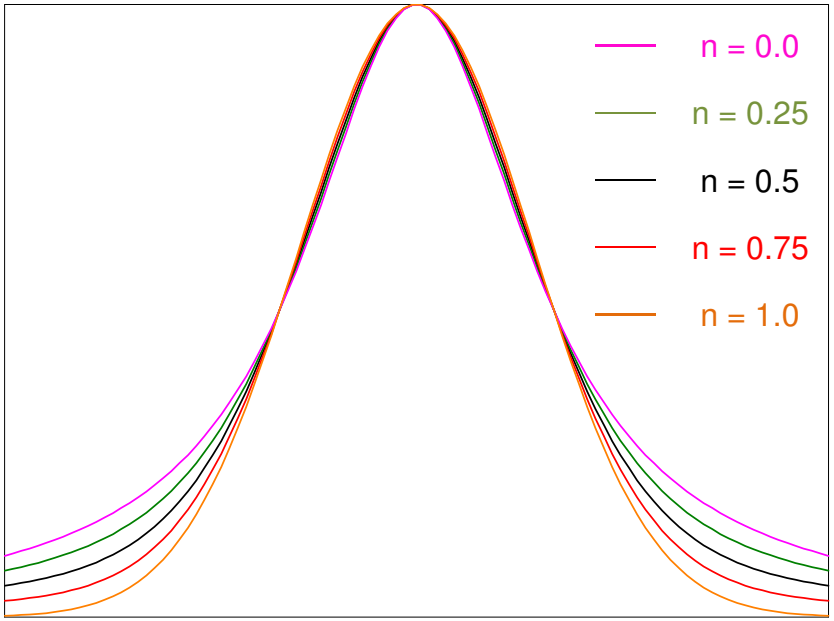


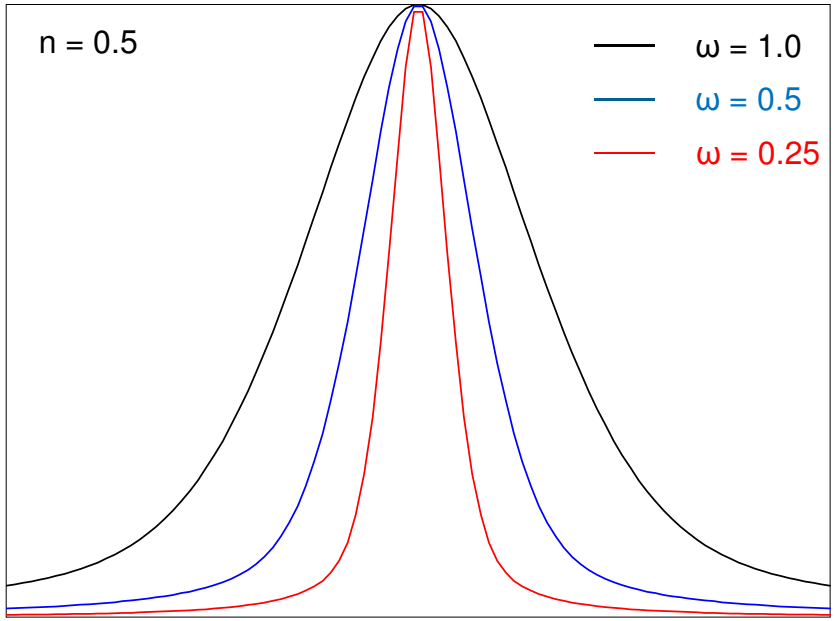
Gaussian (ω = 1.0)



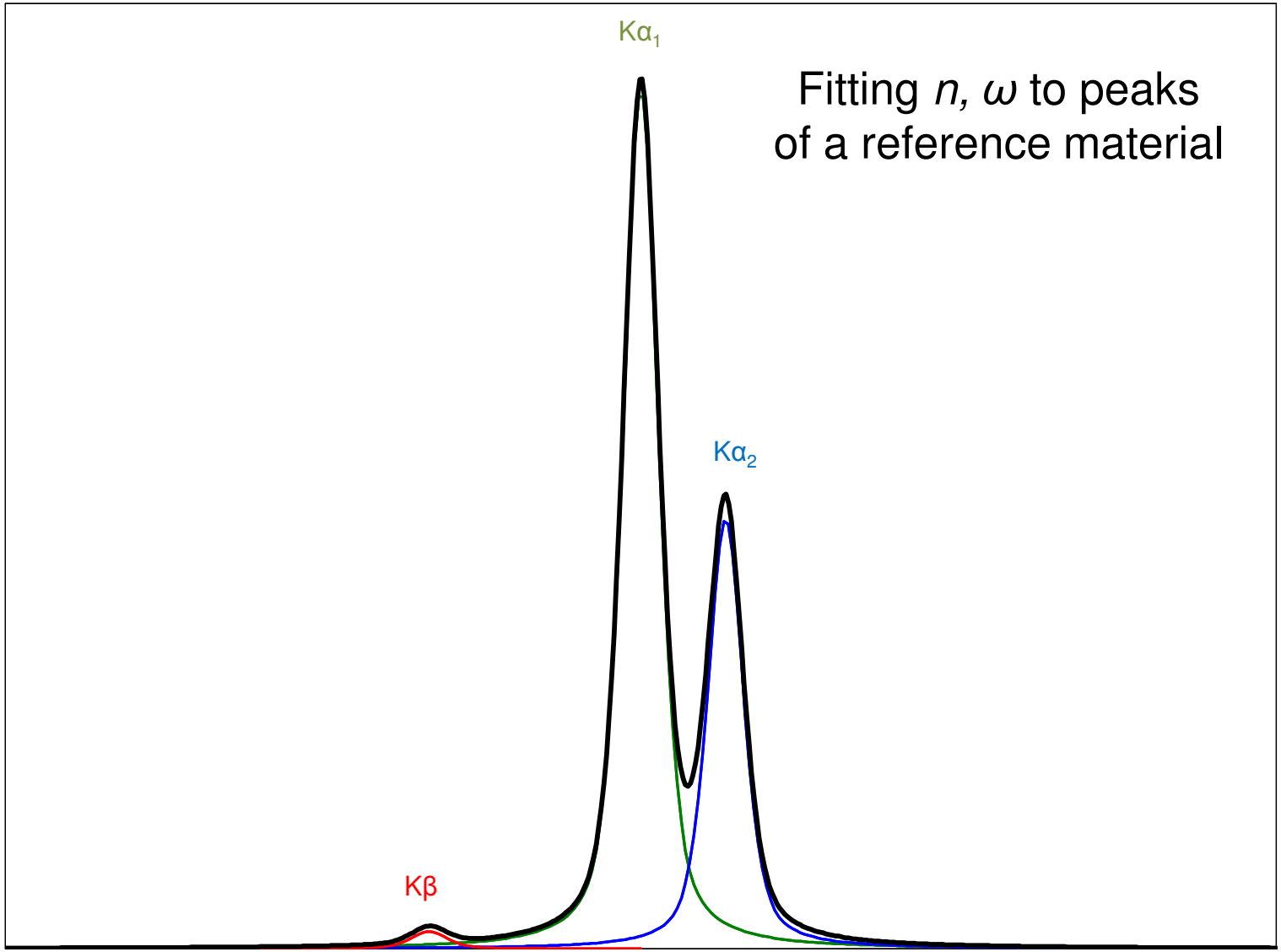
Pseudo-Voigt (n = 0.5)

Pseudo-Voigt Curves

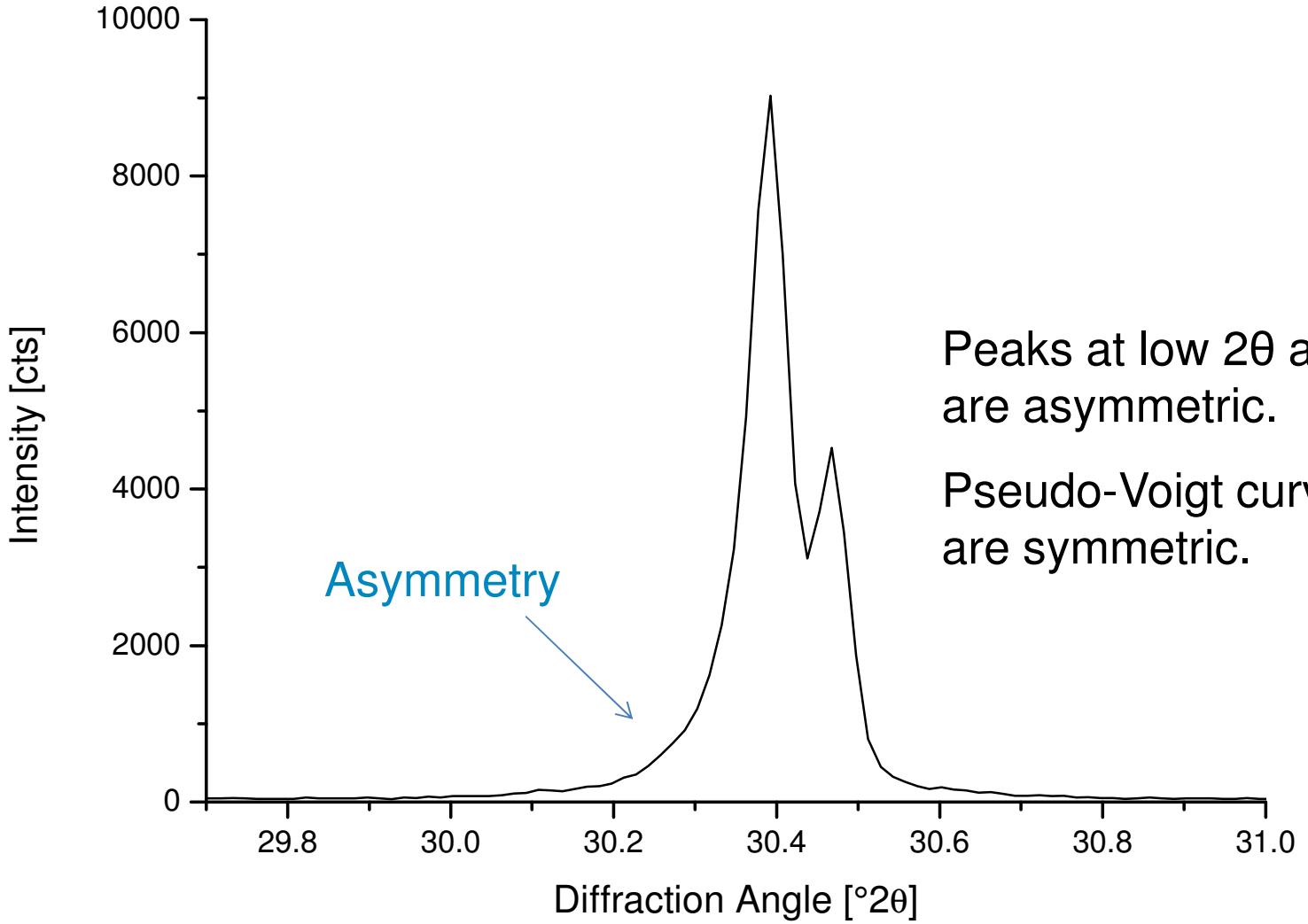




Pseudo-Voigt Curves



Pseudo-Voigt: Problems



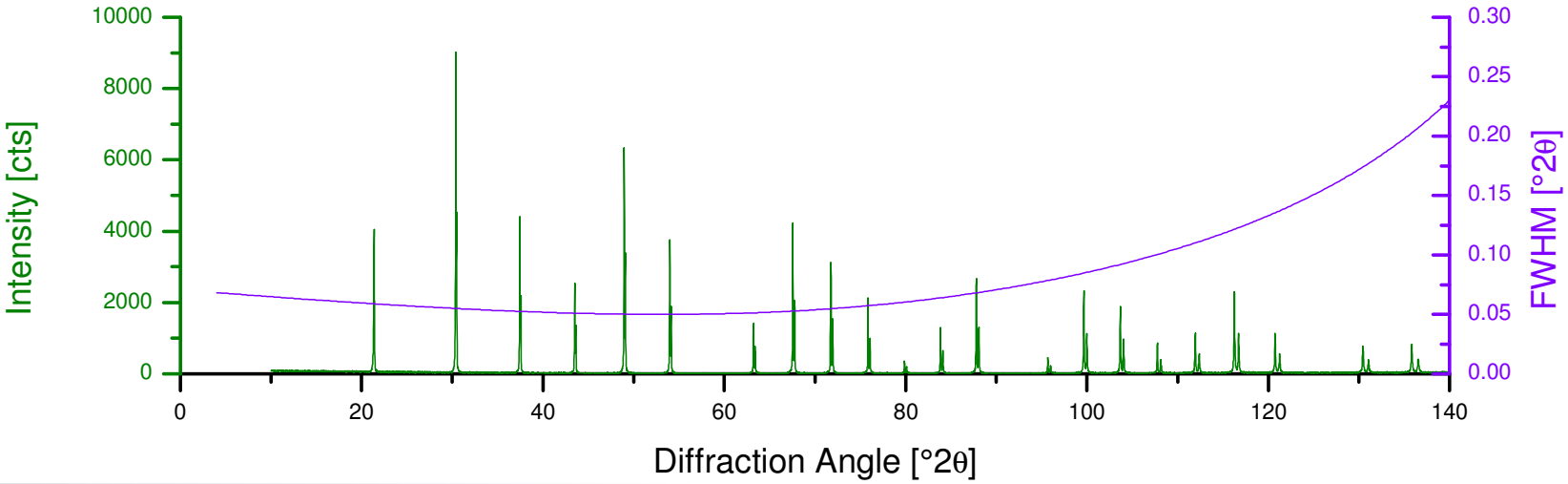
Peaks at low 2θ angles are asymmetric.

Pseudo-Voigt curves are symmetric.

Alternatives to Pseudo-Voigt Function

Alternatives to PV function:

- Pearson VII
- Thompson-Cox-Hastings PV
- Split PV
- PV with axial divergence
  (Finger-Cox-Jephcoat PV)

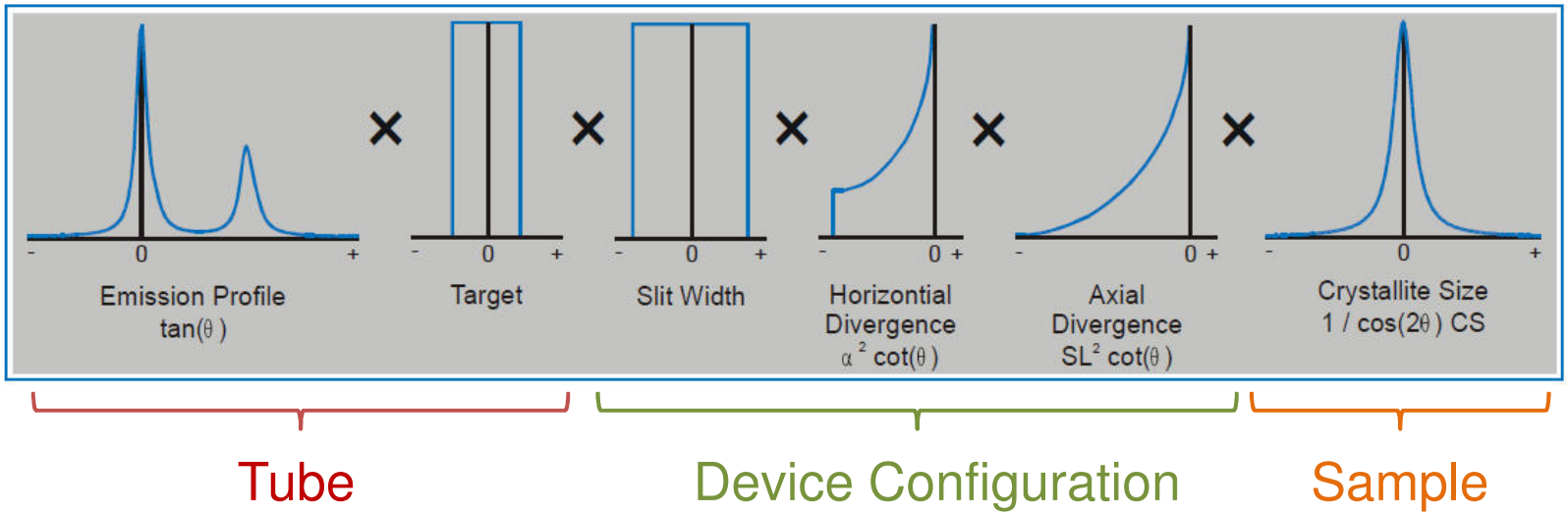


Fundamental Parameters Approach FPA

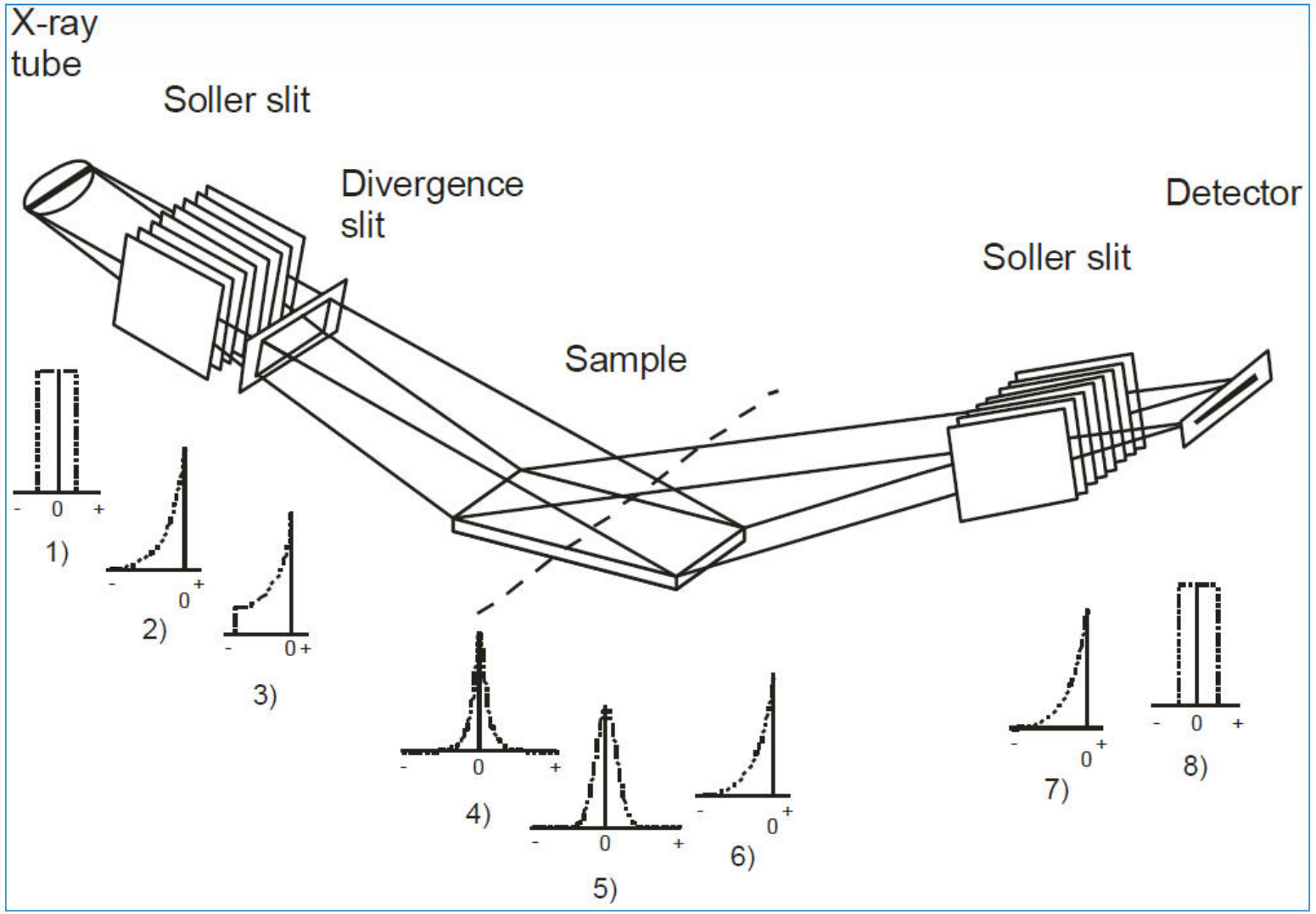
Calculate the peak profile from the device configuration

Take into account the contributions of:

- Source emission profile (X-ray wavelength distribution from Tube)
- Every optical element in the beam path (position, size, etc.)
- Sample contributions (peak broadening due to crystallite size & strain)



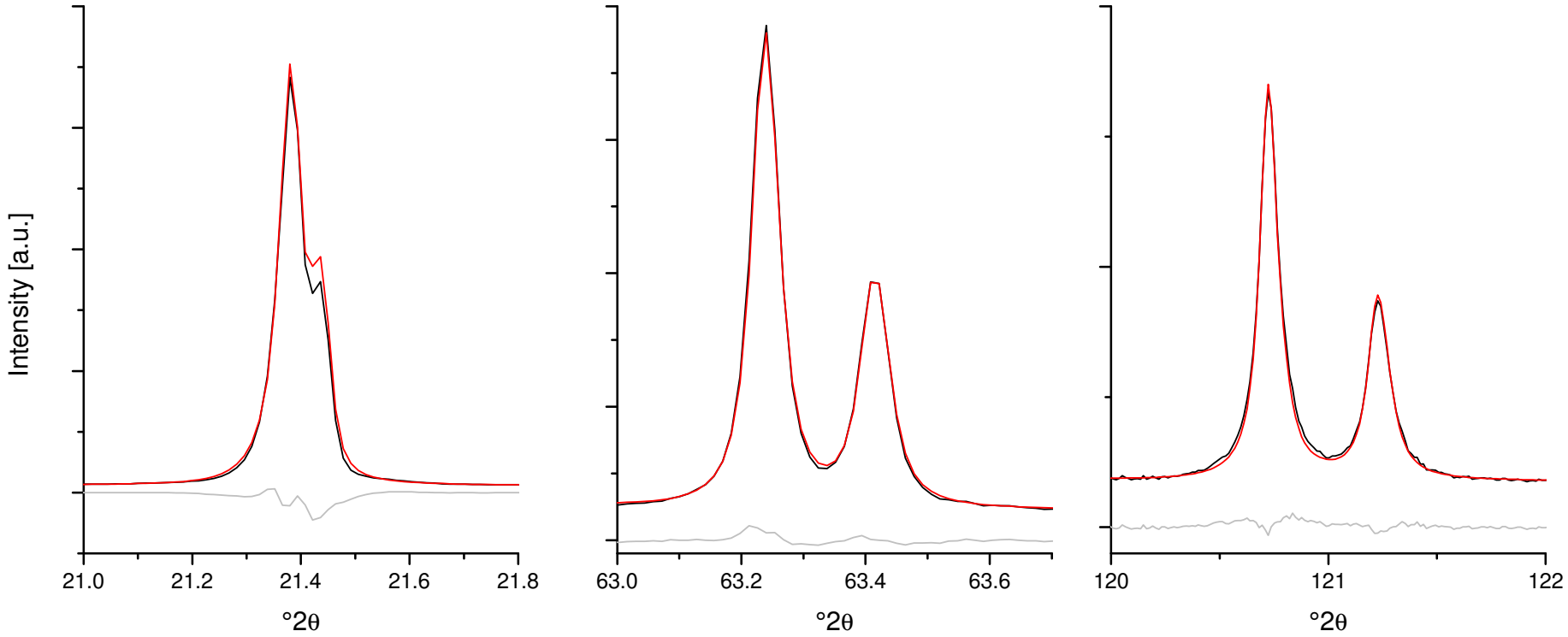
Fundamental Parameters Approach



www.bruker.com

Fundamental Parameters Approach

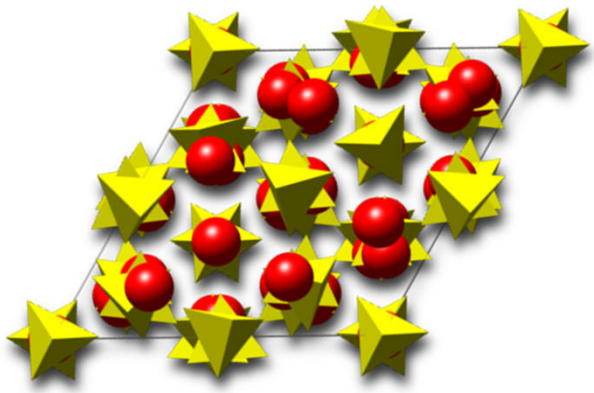
If done properly:



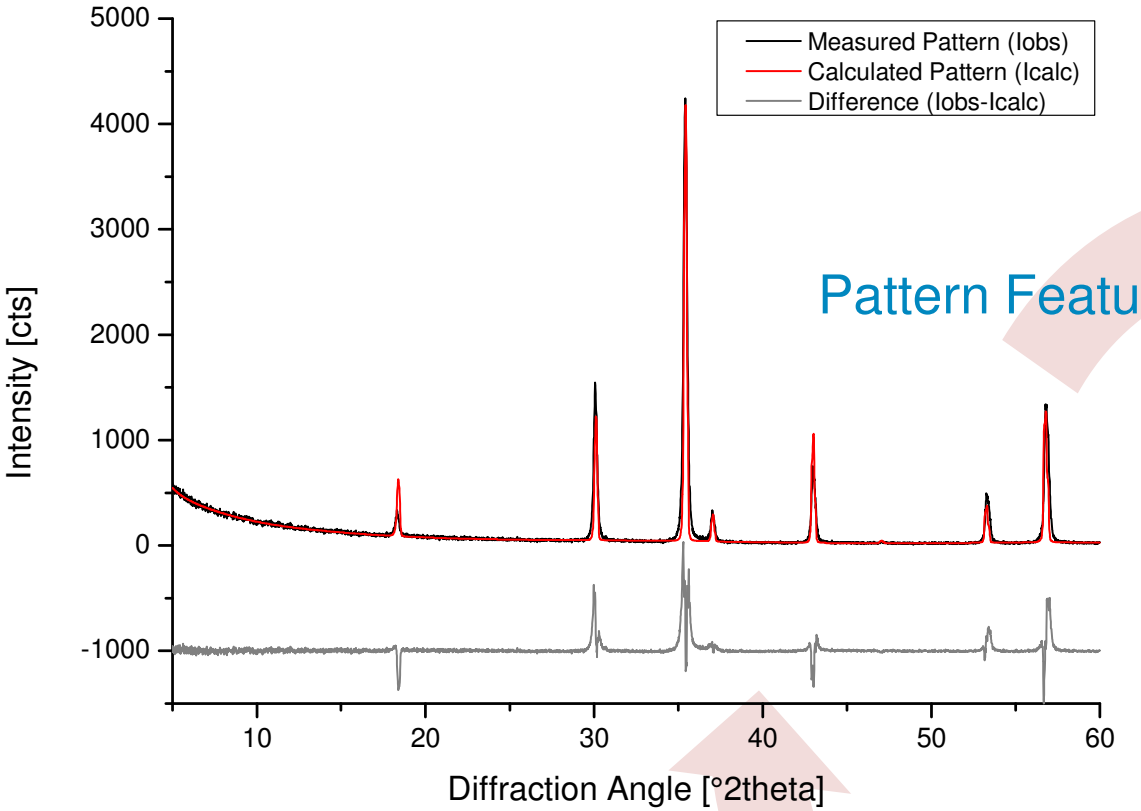
Very good description of the peak profile

Summary: Rietveld Basics

- Calculate XRD pattern from model structure
- Minimize differences between calculated and measured pattern
- Accurate mathematical description of peak profile required:
  - Classical Rietveld approach: Fit a peak shape function (PV or similar) to reference pattern
  - Fundamental Parameters Approach: Calculate peak profile from device configuration

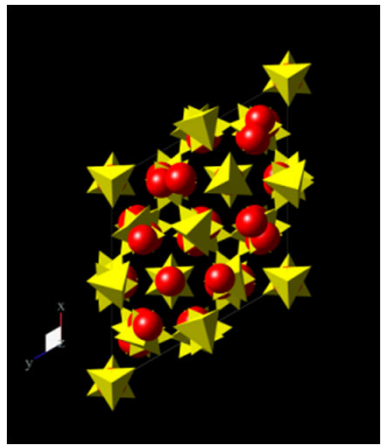


Refinement Strategies

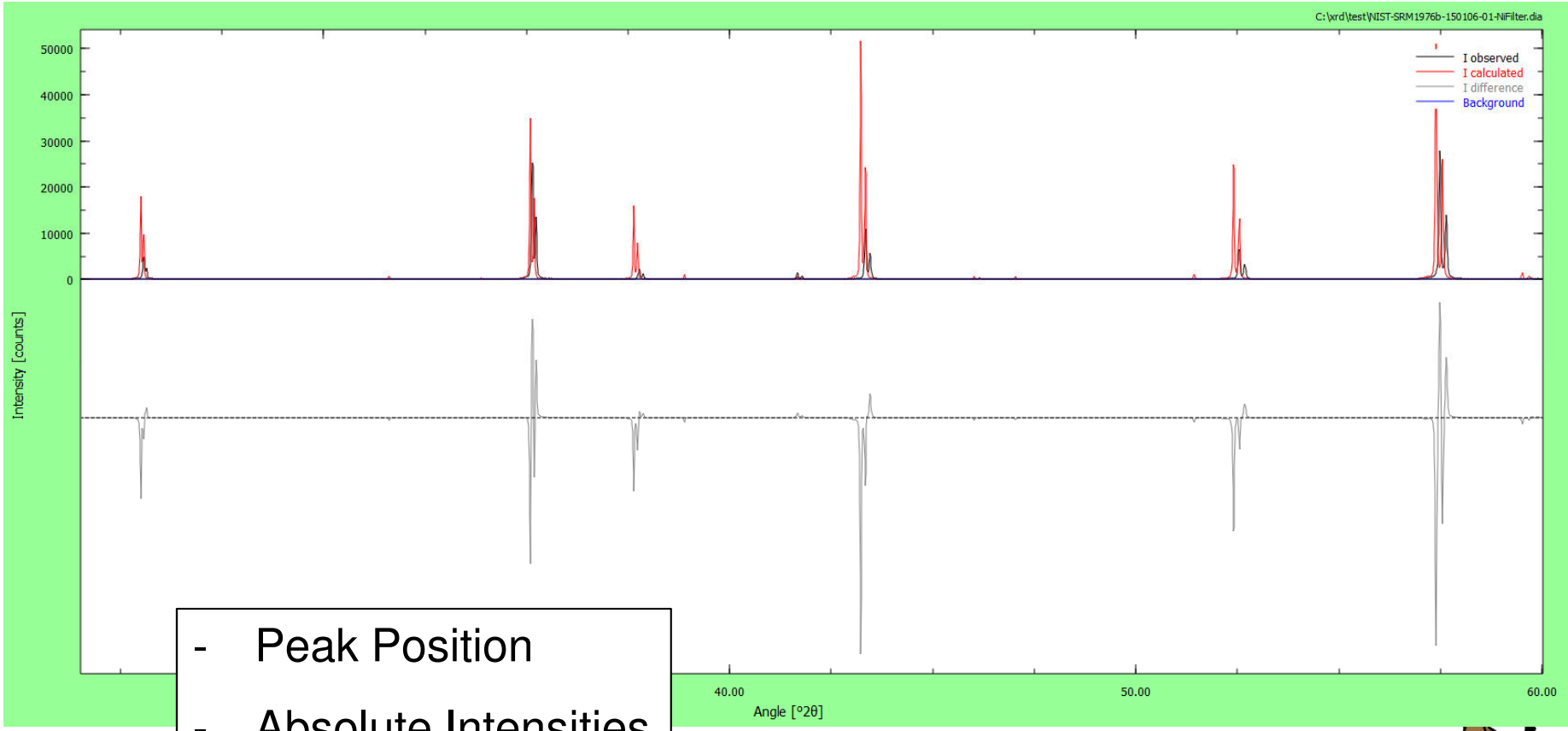


Relation

Pattern Features – Structural Features



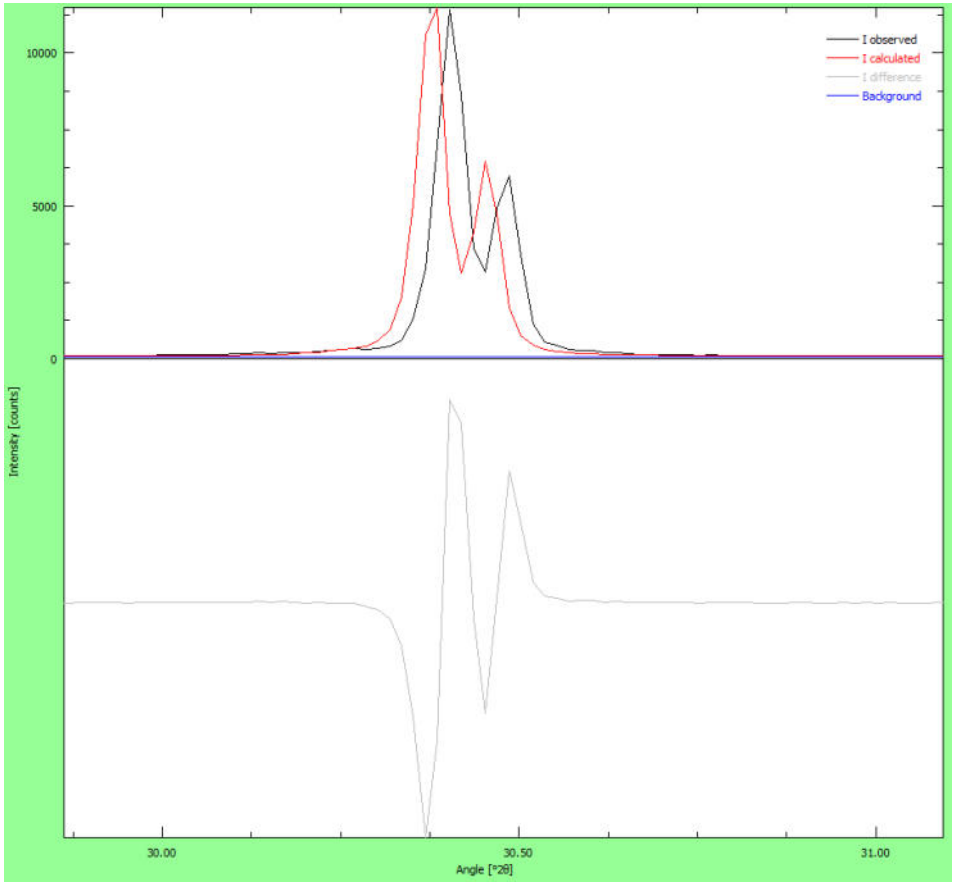
Refinement Strategy: Mismatches



- Peak Position
- Absolute Intensities
- Relative Intensities
- Peak Width

How to fix this?

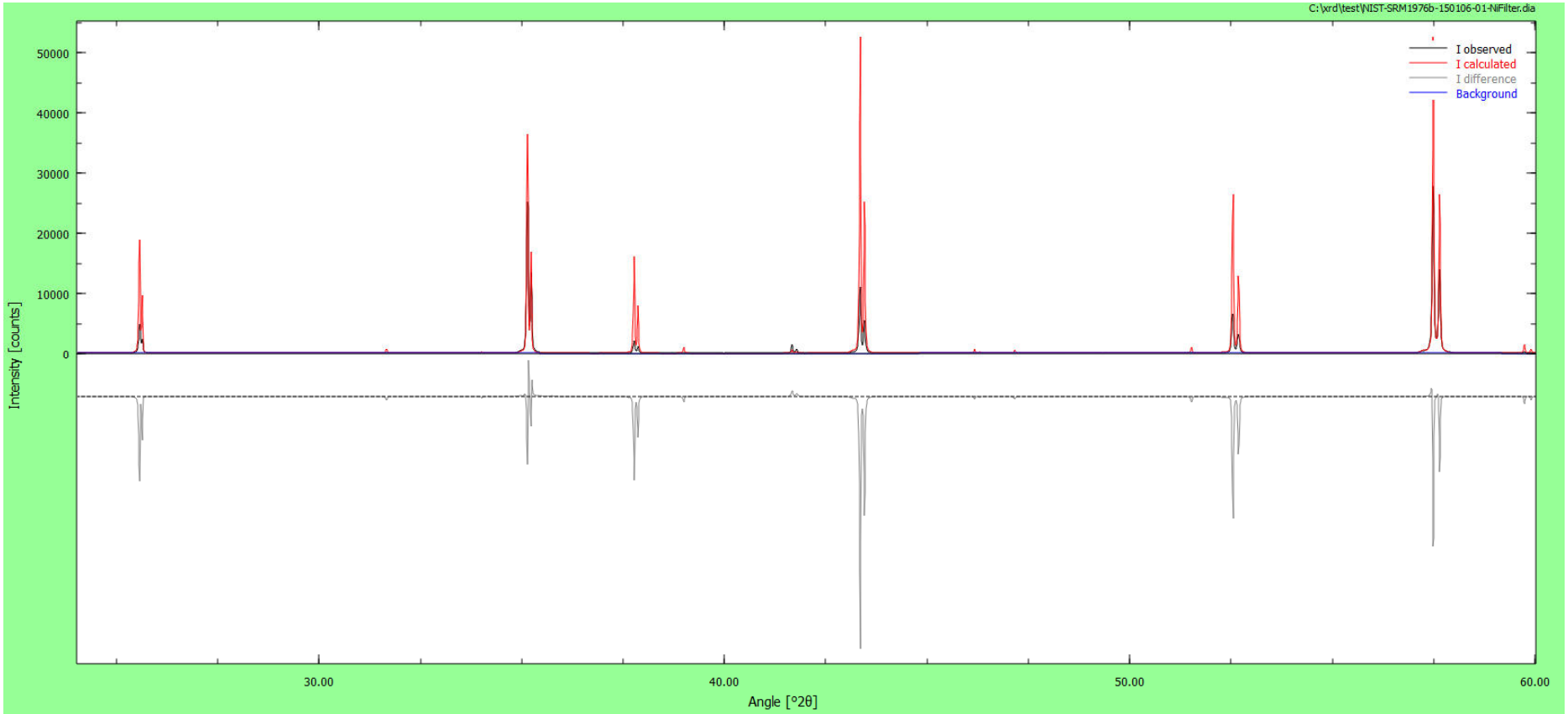
Refinement Strategies



Wrong peak positions:

- Unit cell dimensions
- Sample height displacement
- Zero-shift (instrument misalignment)

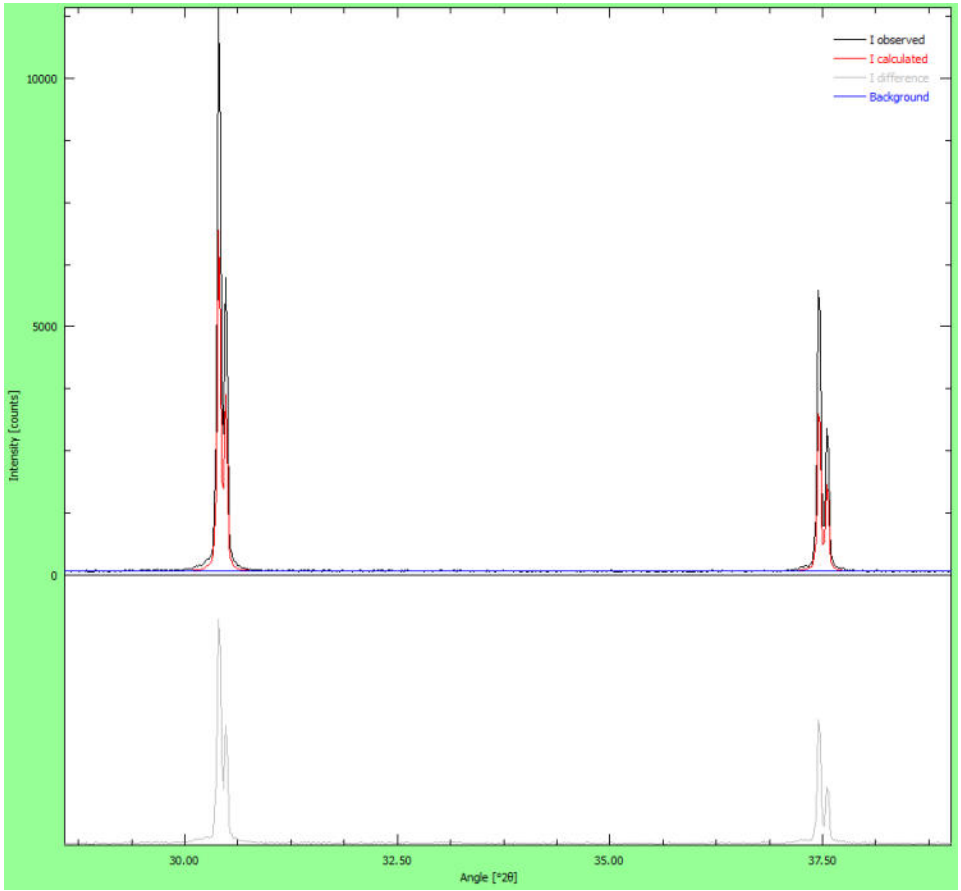
Refinement Strategies



Refined unit cell dimensions:

Peak positions matched!

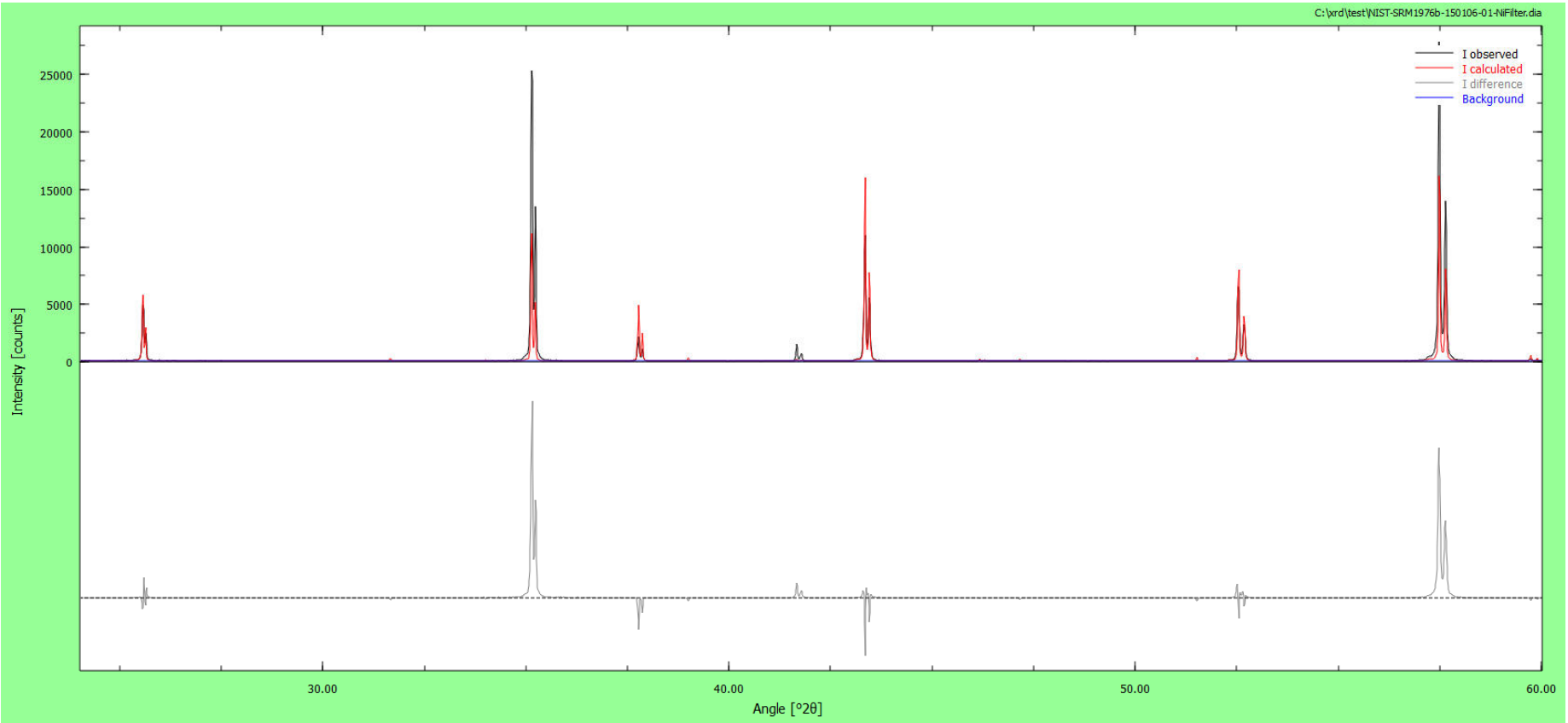
Refinement Strategies



Wrong absolute intensities:

- Weight fraction (scaling)

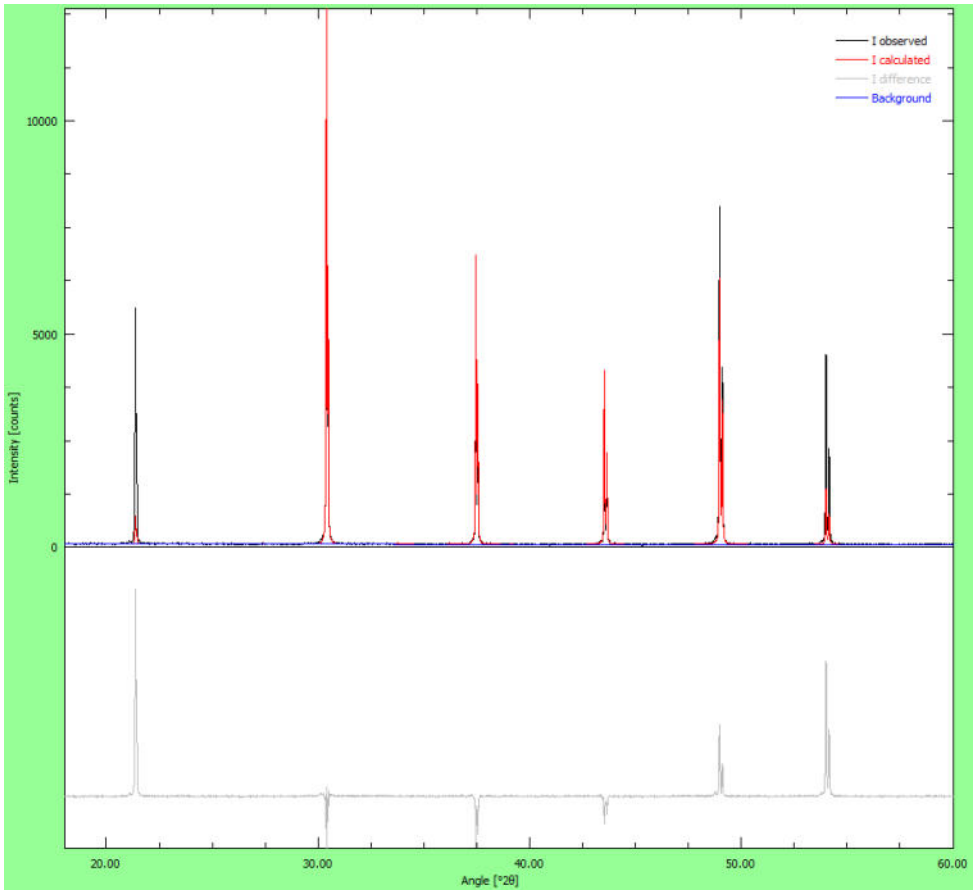
Refinement Strategies



Refined scale factor:

Intensities improved (but not fixed)!

Refinement Strategies

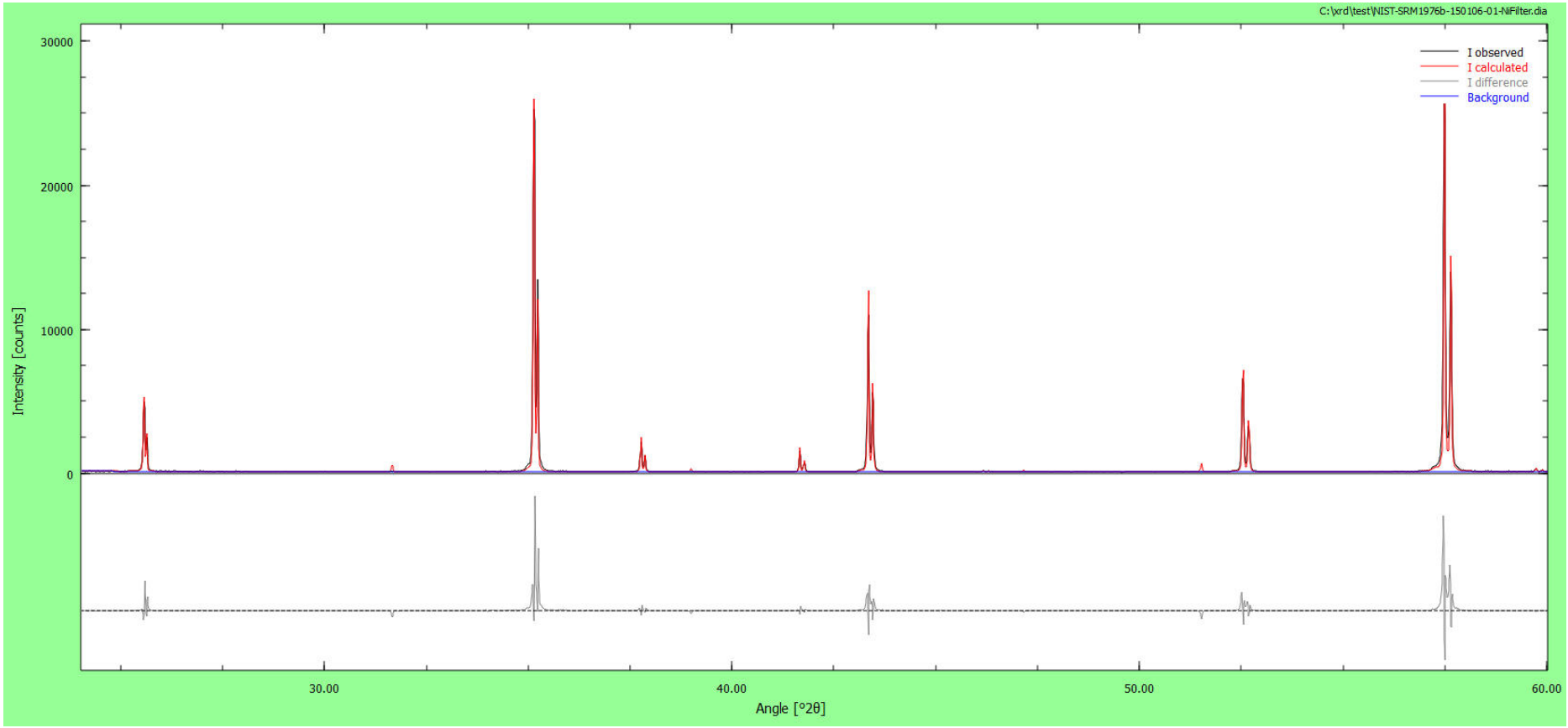


Wrong relative intensities:

Let's try this first

- Preferred orientation
- Graininess
- Atomic species
- Atomic coordinates
- Site occupancies
- Thermal displacement parameters

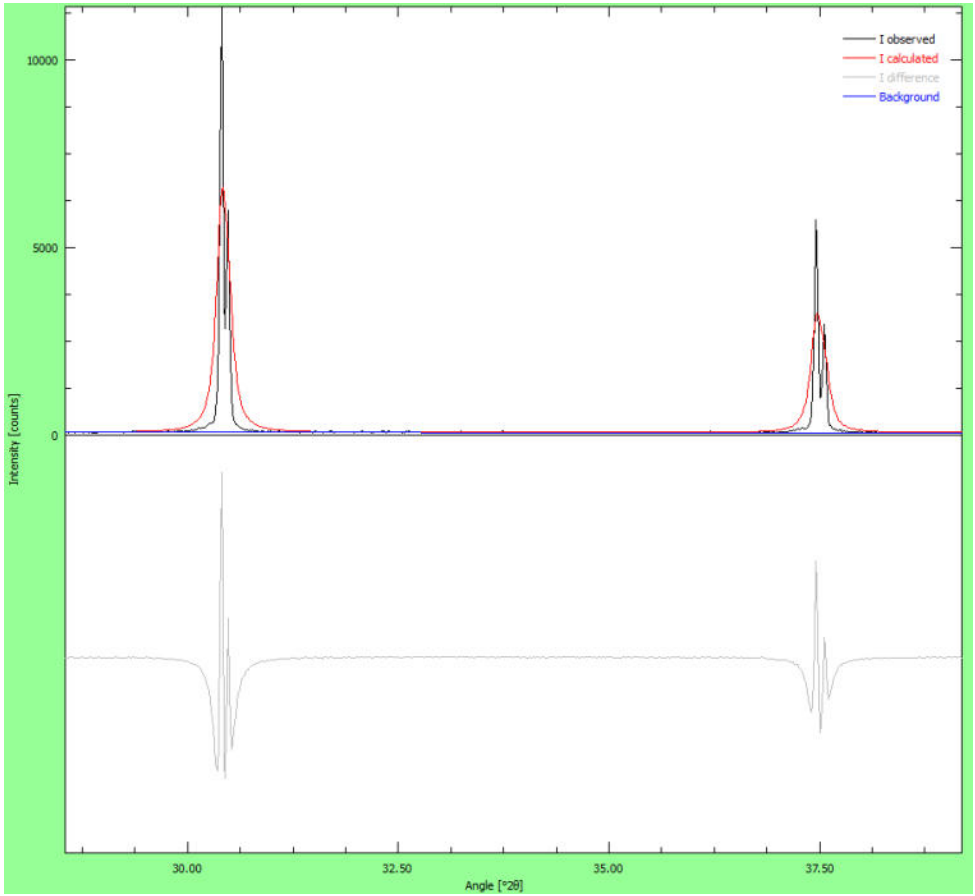
Refinement Strategies



Refined texture:

Intensities fixed!

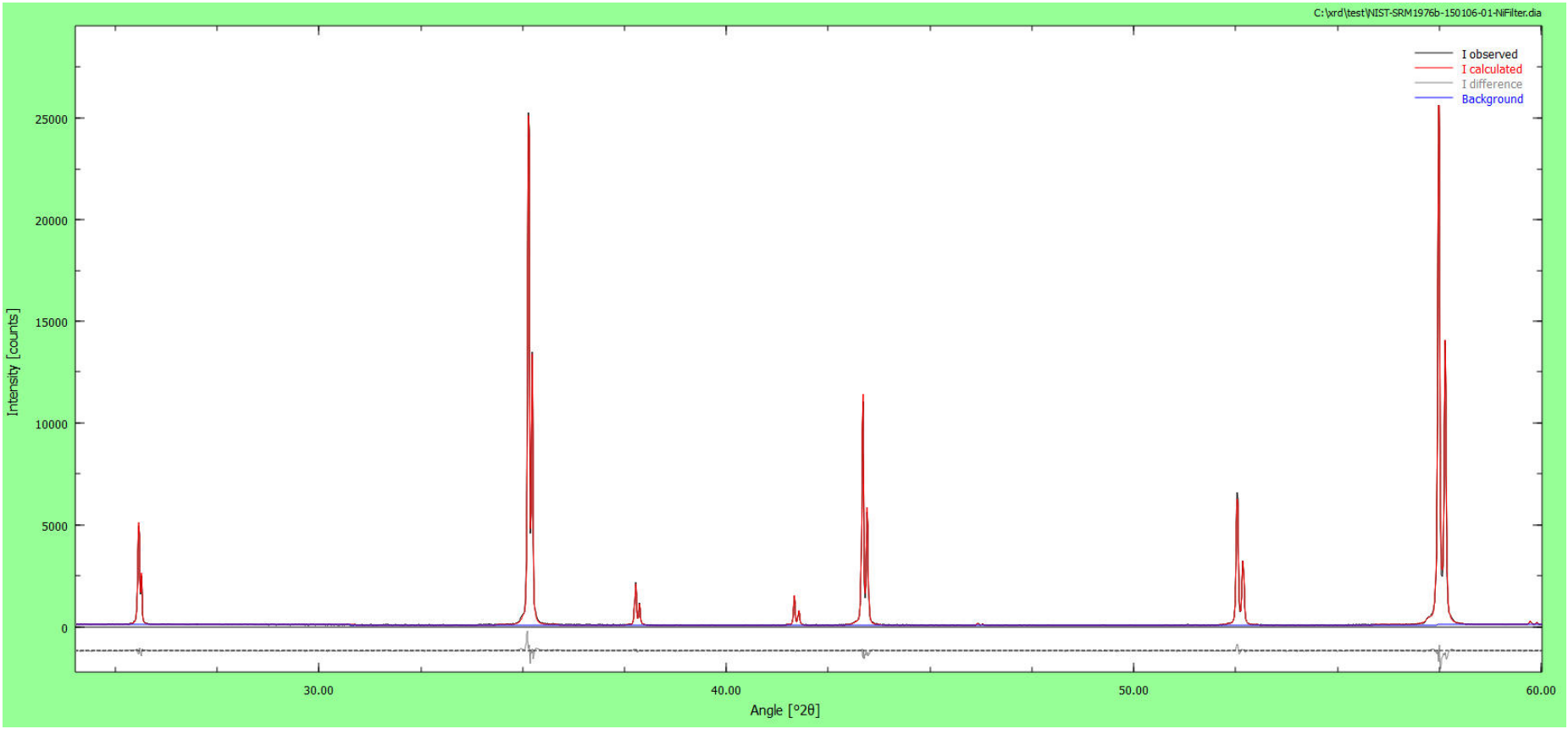
Refinement Strategies



Wrong peak width:

- Crystallite size
- Micro-strain in crystal structure
- Surface roughness

Refinement Strategies



Refined crystallite sizes and micro-strain:

Peak shape fixed!

Refined Crystal Structure

Phase composition: 100% Al_2O_3 Corundum

Starting Model

Parameter	Value
Unit cell *a*	0.4775 nm
Unit cell *c*	1.2993 nm
Crystallite Size	Inf.
Atomic Coordinates Al	0.0 / 0.0 / 0.3522
Atomic Coordinates O	0.3062 / 0.0 / 0.25

Refined

Parameter	Value
Unit cell *a*	0.4760127 +- 0.0000028 nm
Unit cell *c*	1.2995974 +- 0.0000077 nm
Crystallite Size	1267 +- 138 nm
Atomic Coordinates Al	0.0 / 0.0 / 0.3522
Atomic Coordinates O	0.3062 / 0.0 / 0.25

Summary: Refinement Strategy

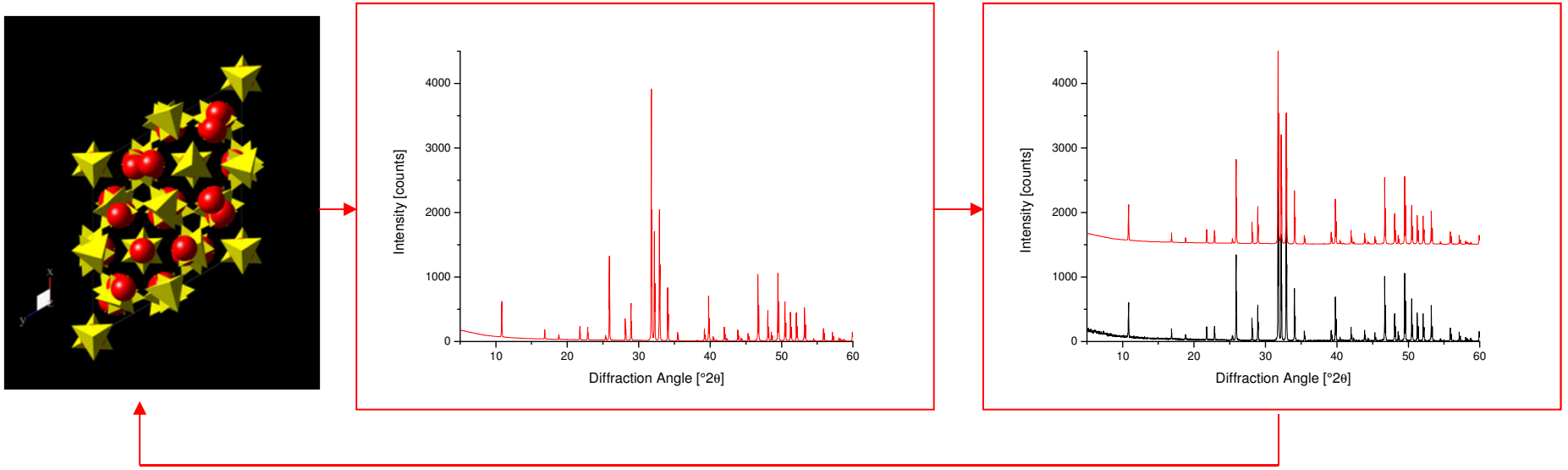
Effect in diffraction pattern	Origin in crystal structure model
Wrong peak positions	Unit cell dimensions Sample height displacement Zero-shift
Wrong absolute intensities	Weight fraction (scaling)
Wrong relative intensities	Preferred orientation Grainy sample Atomic species / Substitutions / Vacancies Atomic coordinates Site occupancies Thermal displacement parameters
Wrong peak width	Crystallite size Micro-strain Surface roughness Transparency

Rietveld Refinement

Known structure model

Calculate theoretical diffraction pattern

Compare with measured pattern



Optimize structure model, repeat calculation

Minimize differences between calculated and observed pattern by least-squares method

Rietveld Software Packages

Academic Software:

- Fullprof
- GSAS
- BGMN
- Maud
- Brass
- … many more[1)]

FPA

Commercial Software:

- HighScore+ (PANalytical)
- Topas (Bruker)
- Autoquan (GE)
- PDXL (Rigaku)
- Jade (MDI)
- WinX^{POW} (Stoe)

Commercial UI for BGMN

Lesson 2: BGMN and Profex

1) http://www.ccp14.ac.uk/solution/rietveld_software/index.html