Isolating the TEM instrumental function for electron PDF (ePDF)

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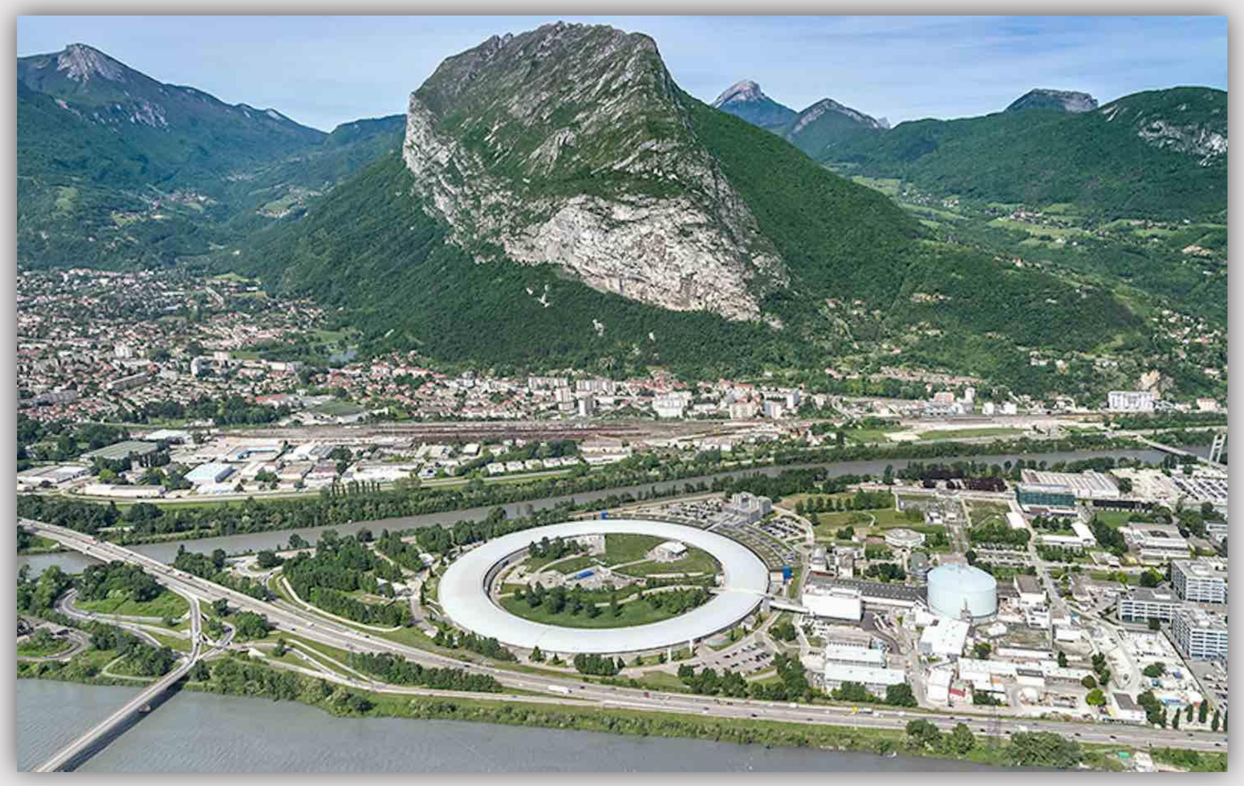
Motivation



X-ray and Neutron PDF: Reliable, quantitative and well-developed.

Electron PDF: Emergent

Advantages: Spatial resolution, elemental contrast, sample amount.

Challenges: Electron form factors, dynamic scattering, instrument function unknown.

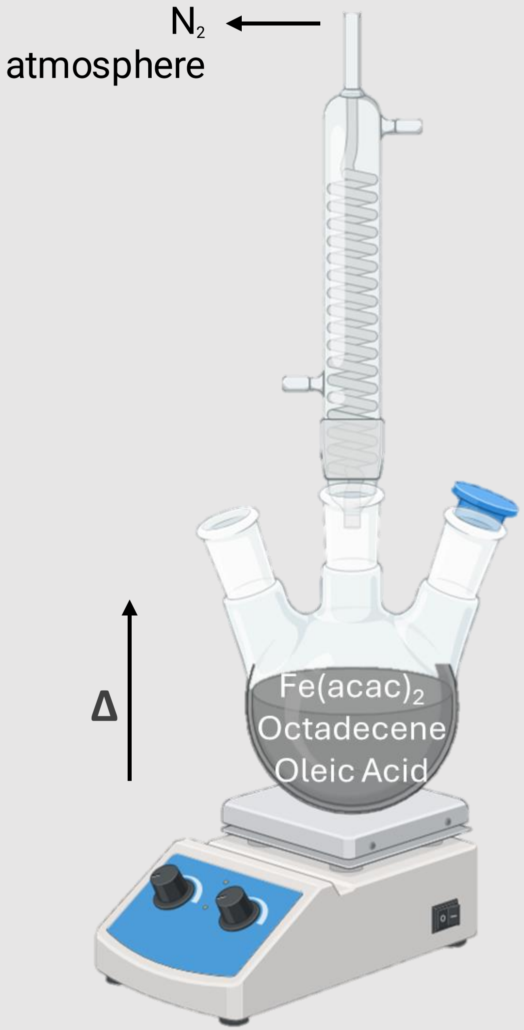
Outline

Transmission electron microscope instrument contribution to electron diffraction modelled by a pseudo-Voigt convolution to a Debye Scattering calculation for monodisperse particles.

- Synthesis and grid preparation
- TEM illumination and setup
- Data processing
- Modelling and Refinement

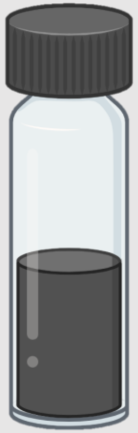
Synthesis of Fe_3O_4 particles

1 Synthesis

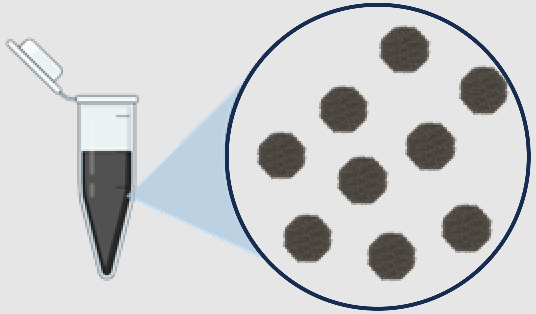


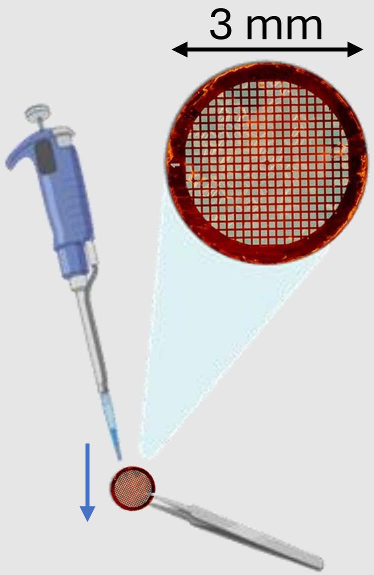
2 Centrifuging

3 Redispersion



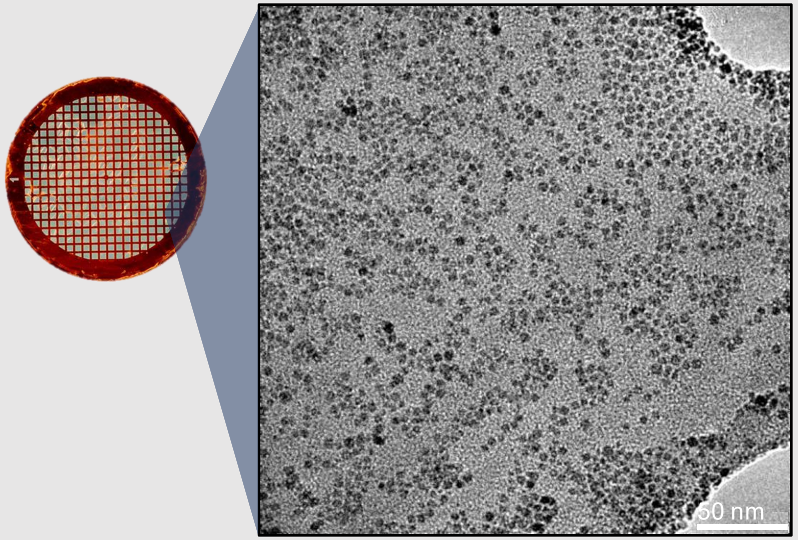
4 Vertical drop casting

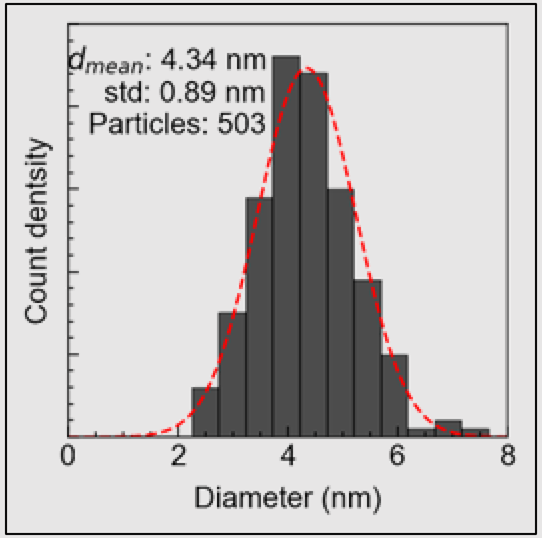


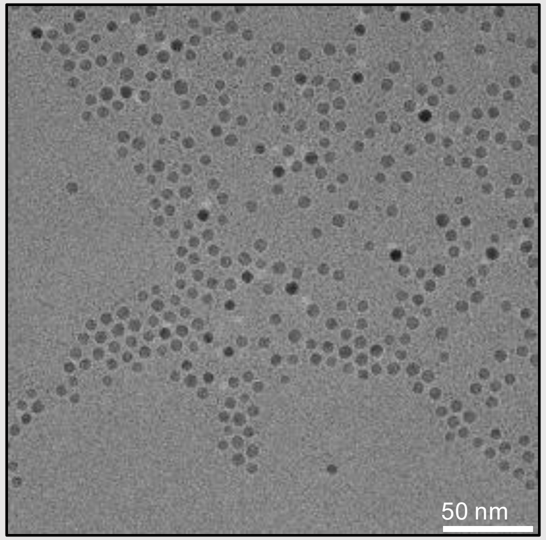


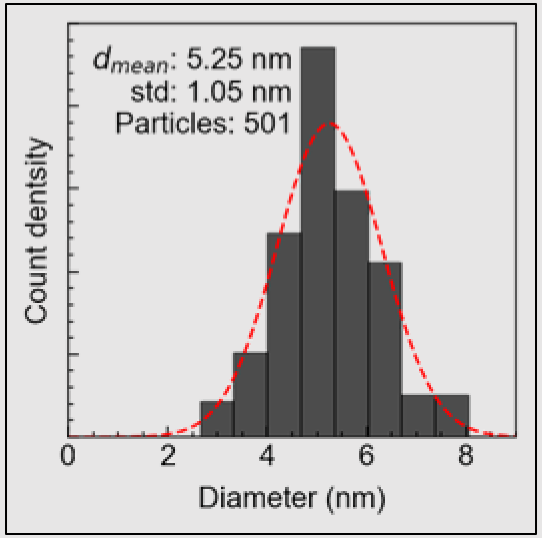
Monophasic Fe_3O_4 Nanoparticles

Narrow Distribution

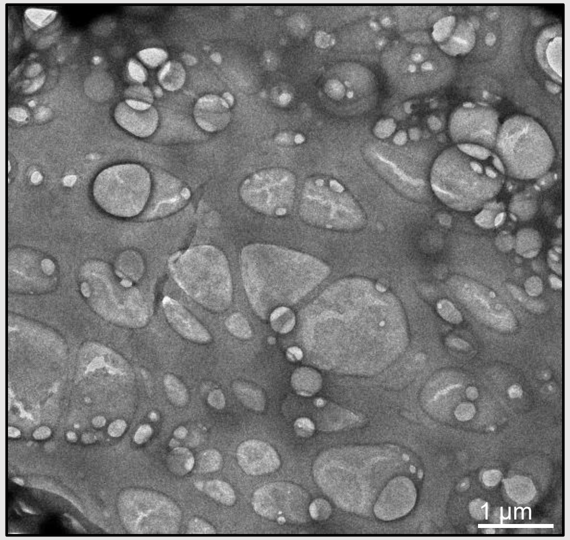


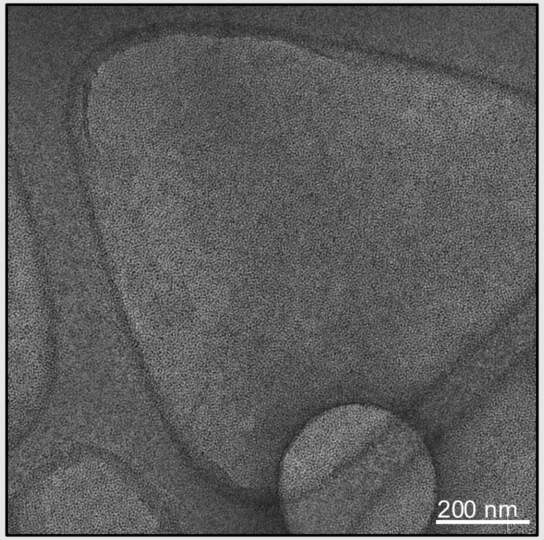


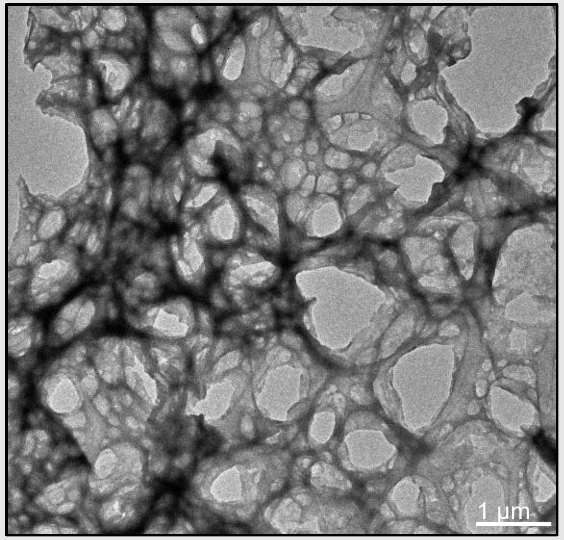


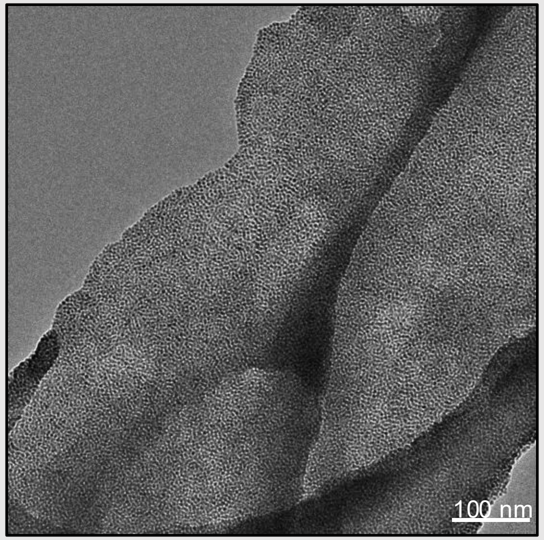


Thin Film Formation

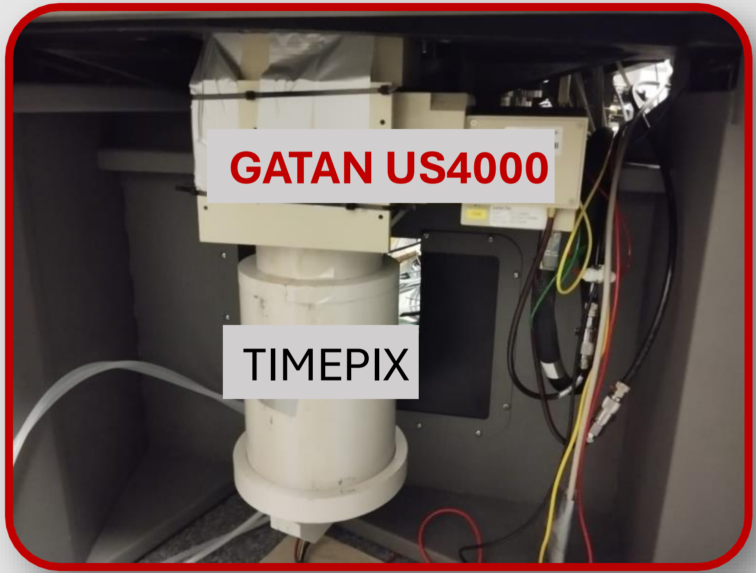






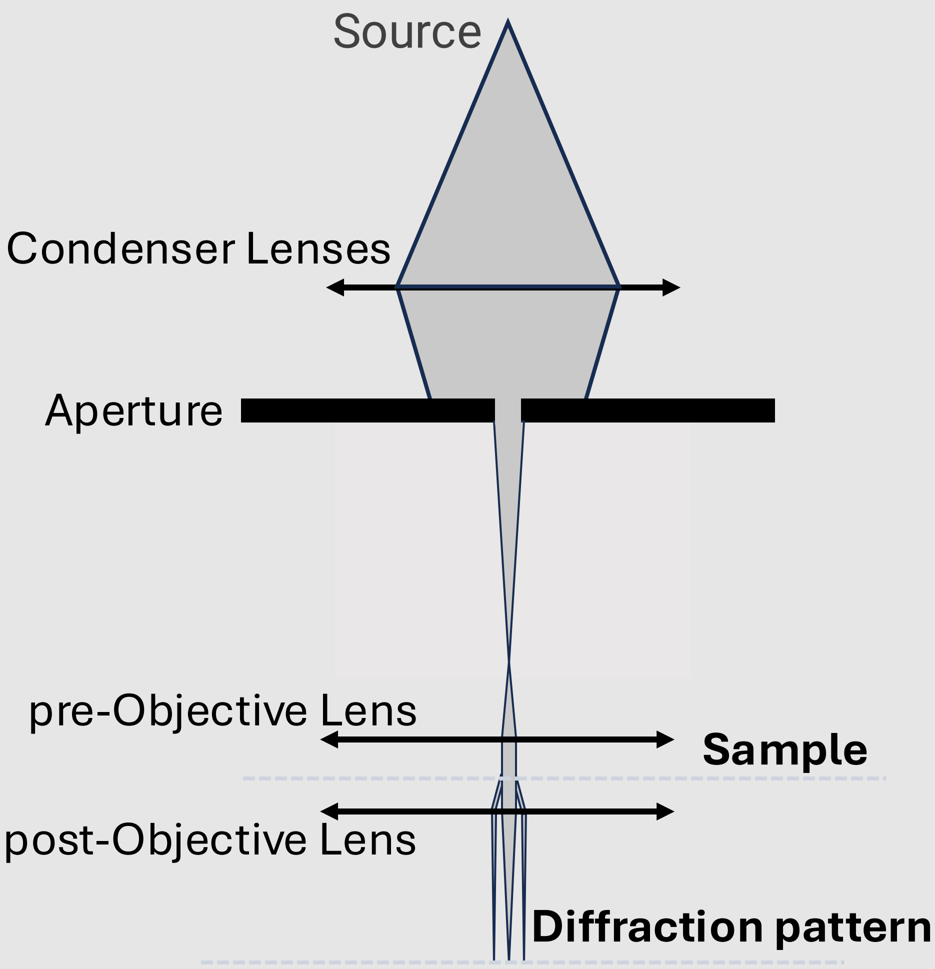


TEMs & Detectors

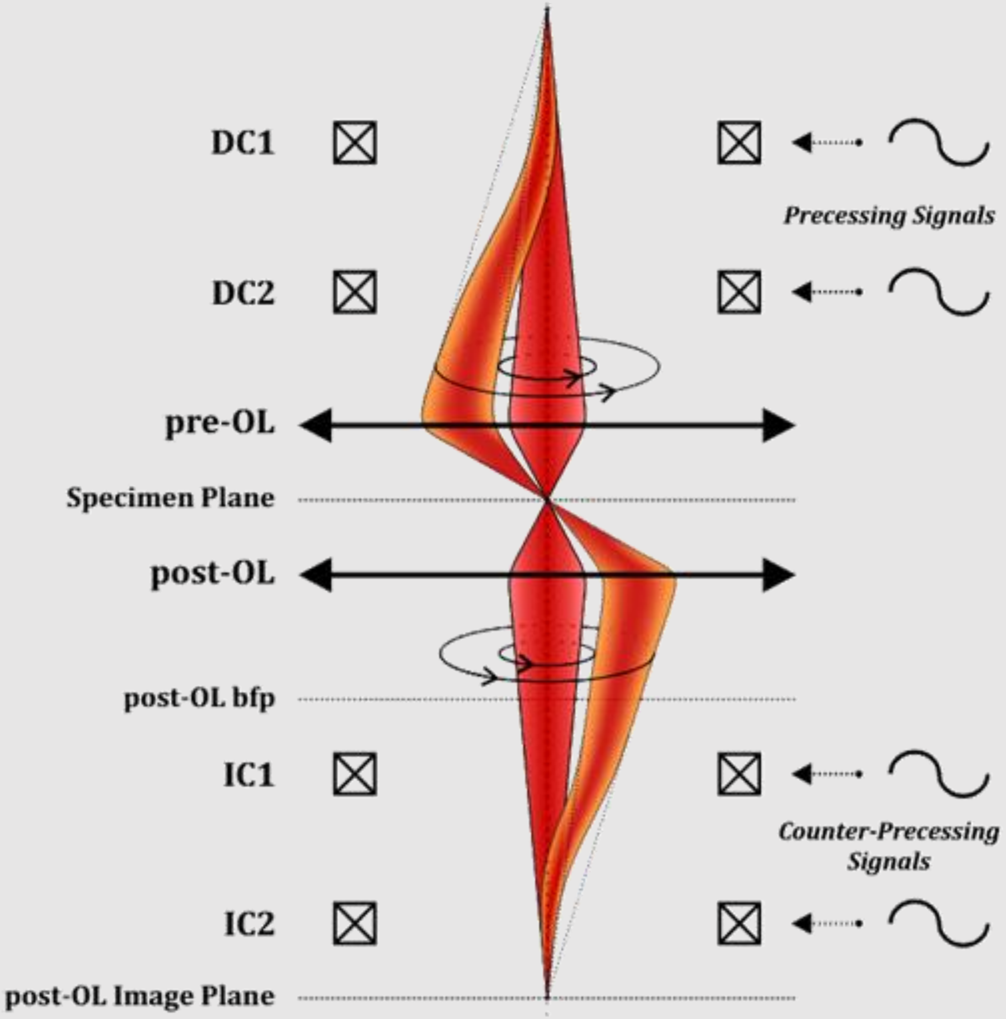


TEM Configuration

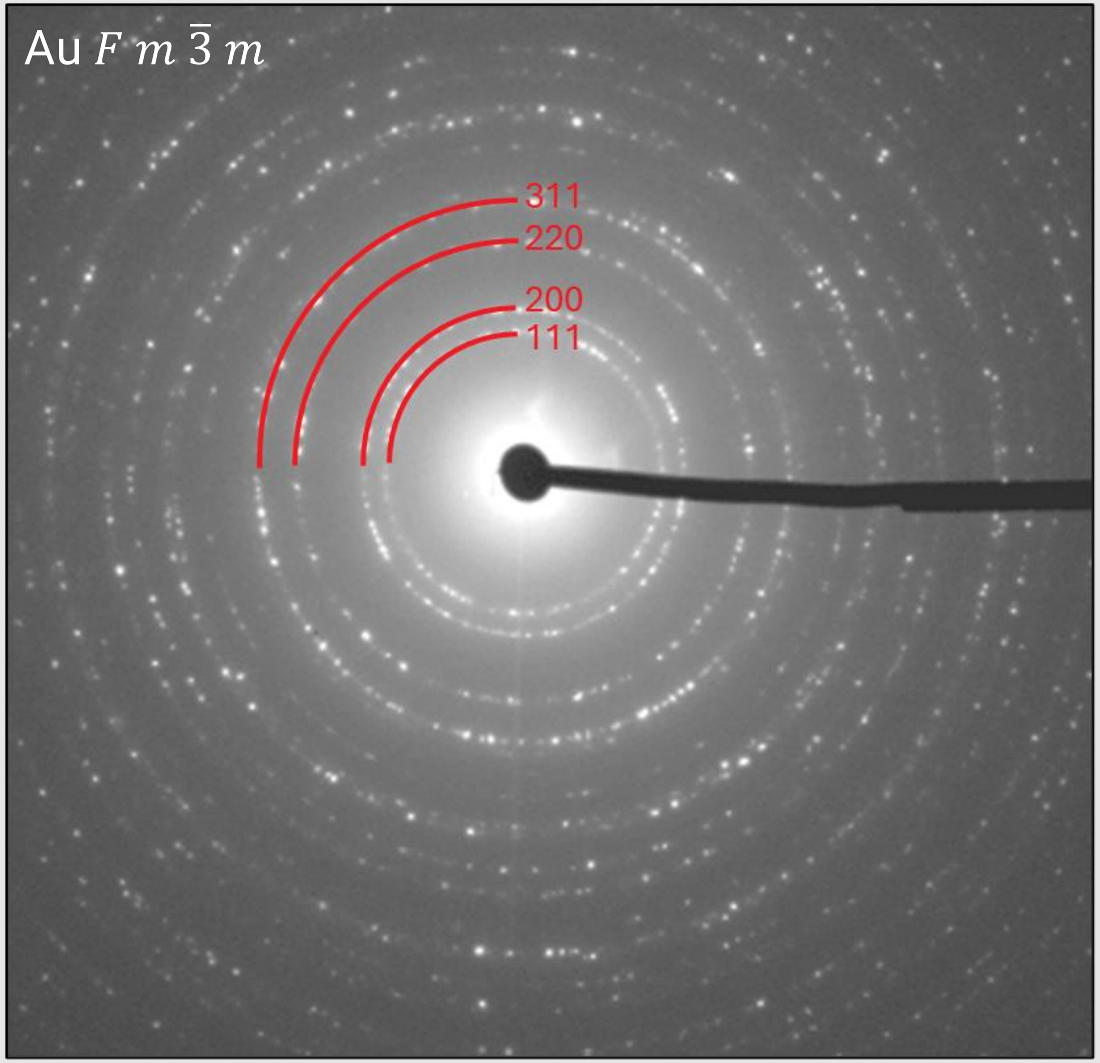
Aperture and Lenses

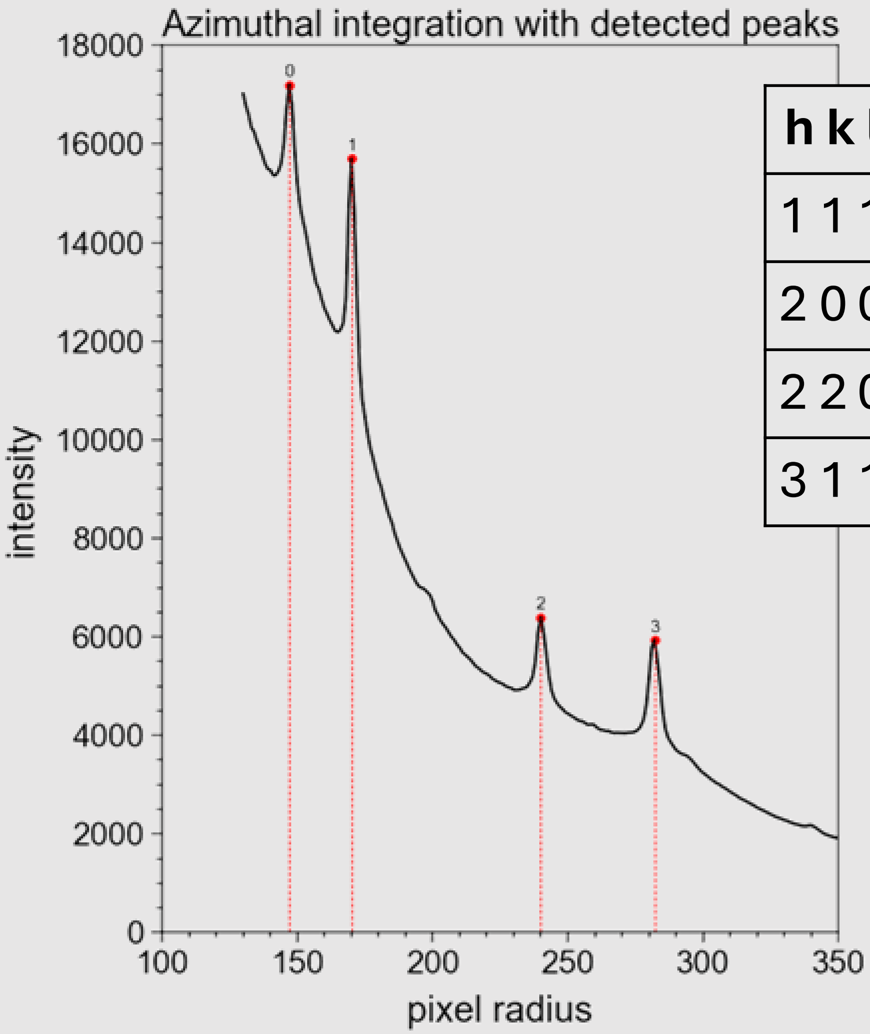


Precession Module



Reciprocal Space Calibration





h k l	d_{ref}	d_a	$d_a - d_{ref}$
1 1 1	2.355	2.368	0.01
2 0 0	2.039	2.041	0.002
2 2 0	1.442	1.448	0.006
3 1 1	1.230	1.235	0.005

Data Acquisition

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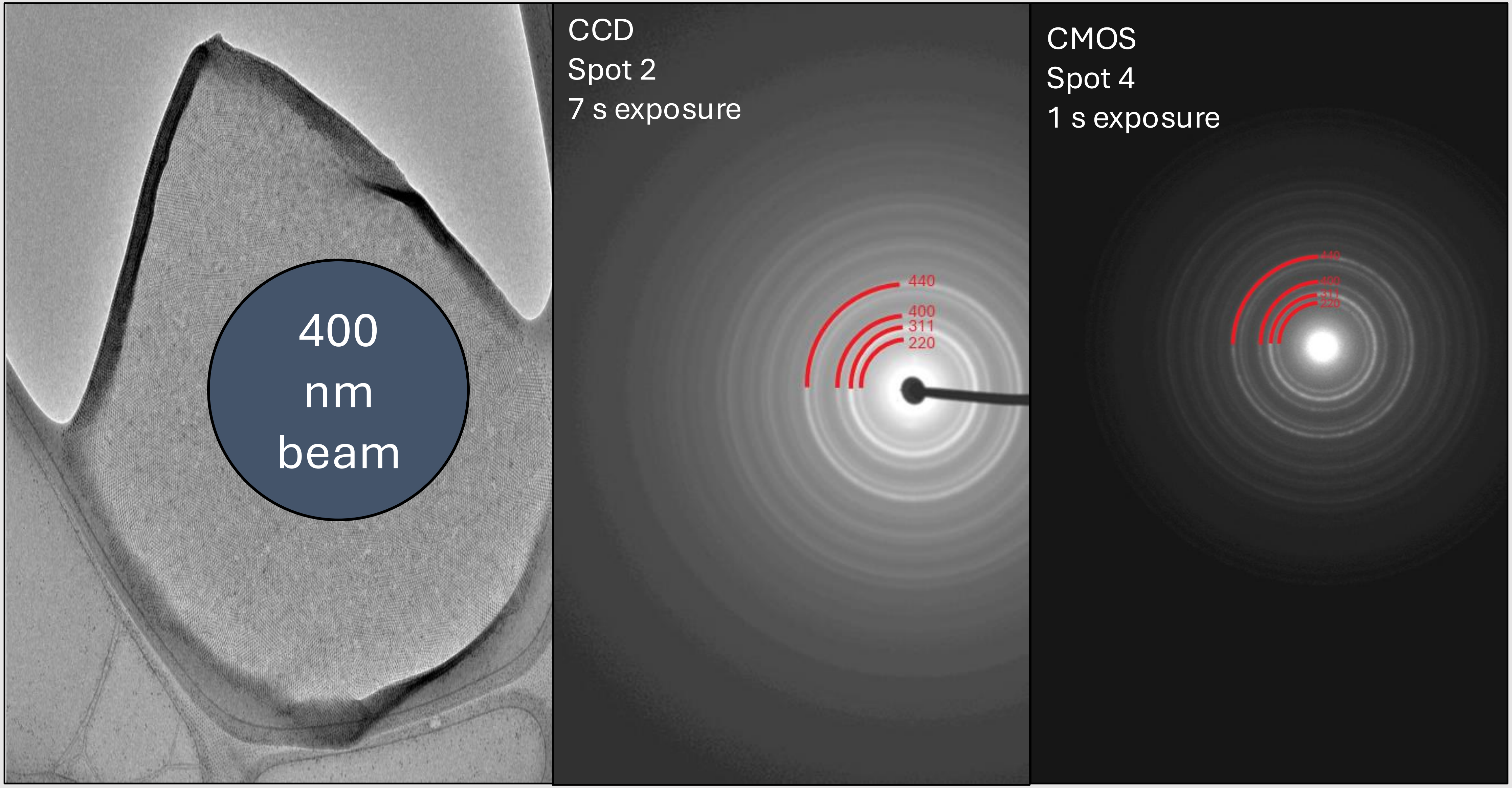

Data Processing

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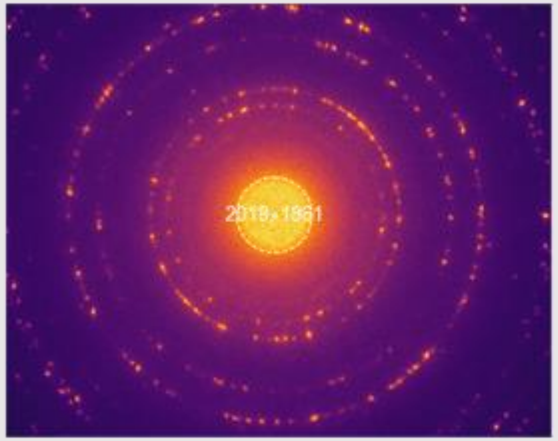
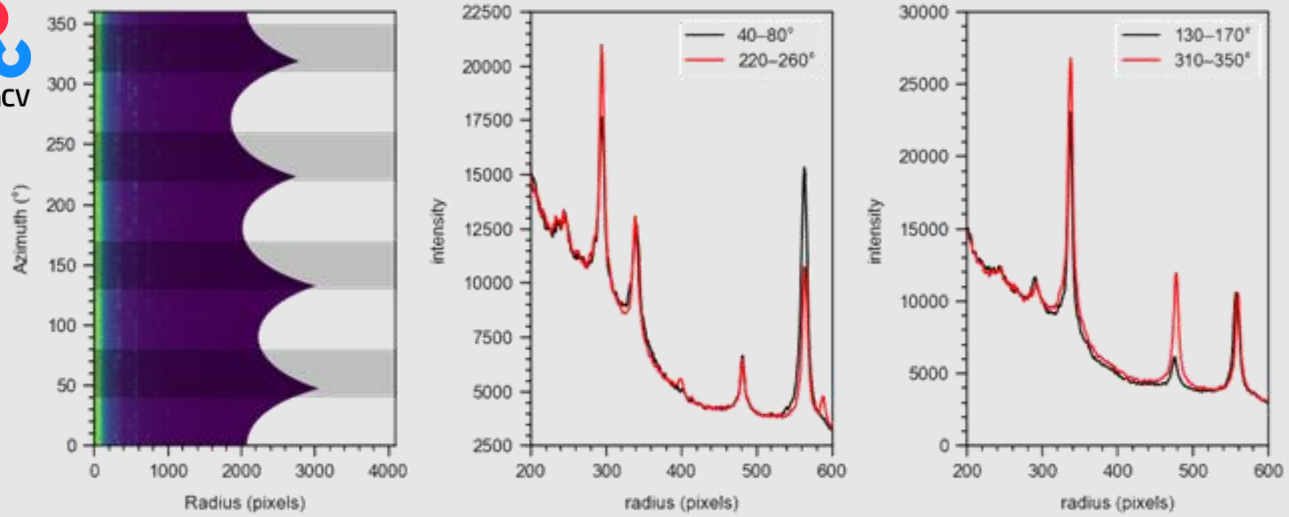
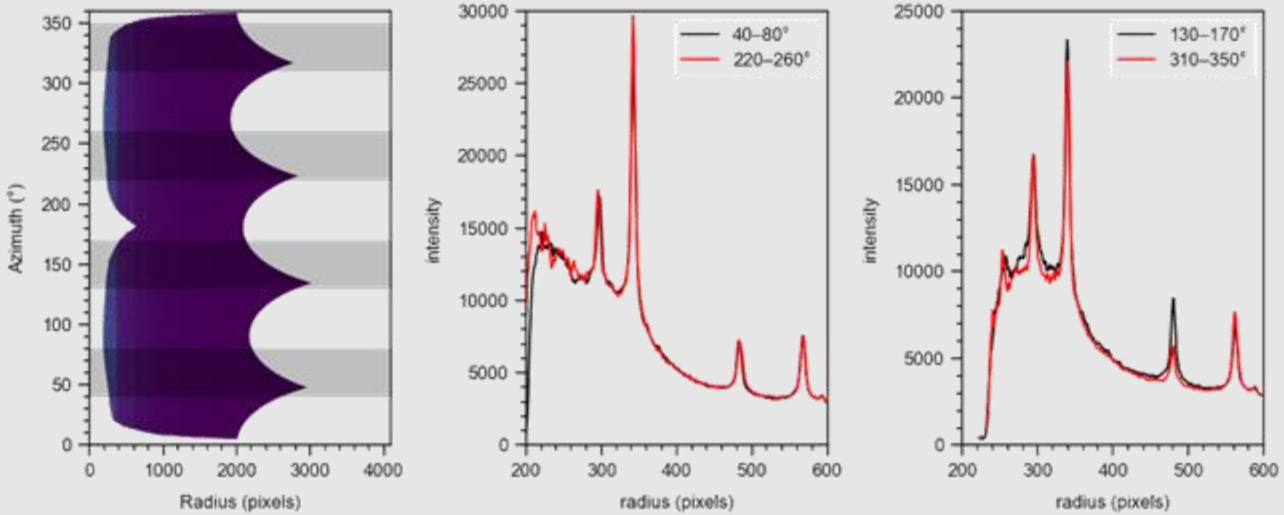


Center Finding

OpenCV

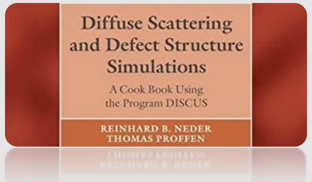


Beamstopper Removal



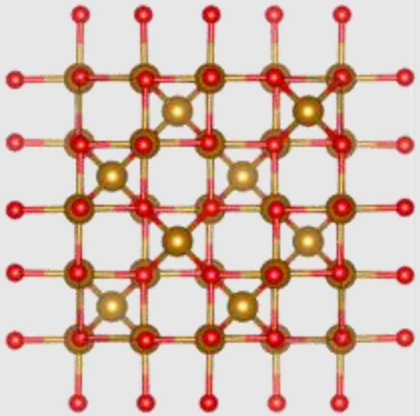
Self-developed routine in Python

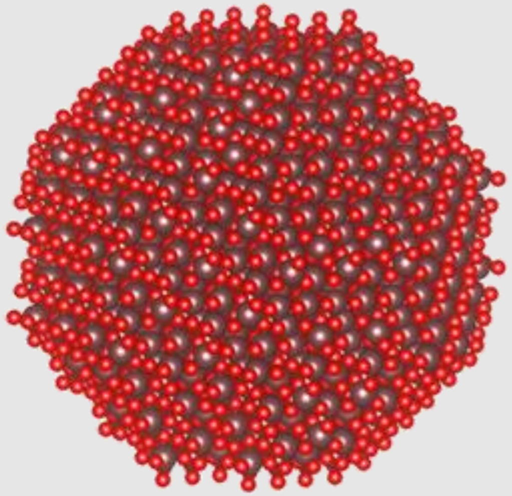
Diffraction Pattern Modelling

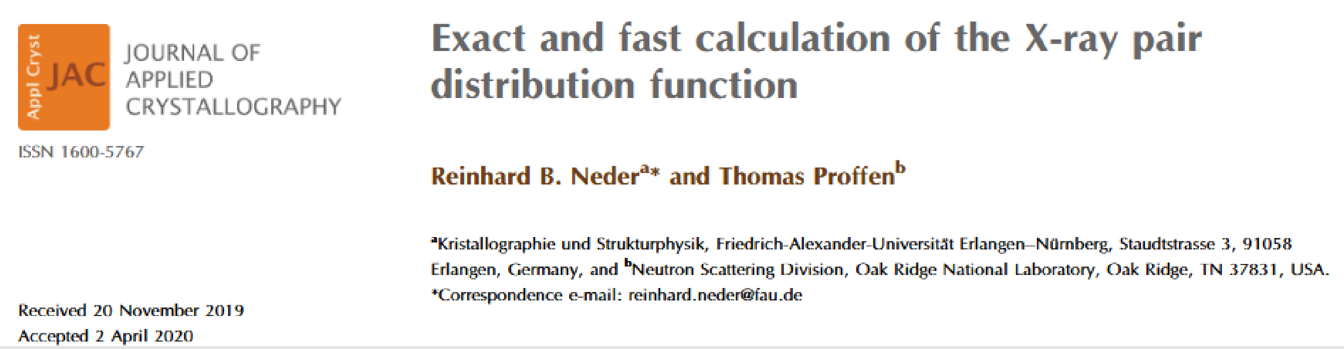


Spherical Particle model

Space Group : F d -3 m (Cubic Inverse Spinel)
a = 8.934 Å







JAC JOURNAL OF APPLIED CRYSTALLOGRAPHY
Appl Cryst
ISSN 1600-5767
Received 20 November 2019
Accepted 2 April 2020

Exact and fast calculation of the X-ray pair distribution function

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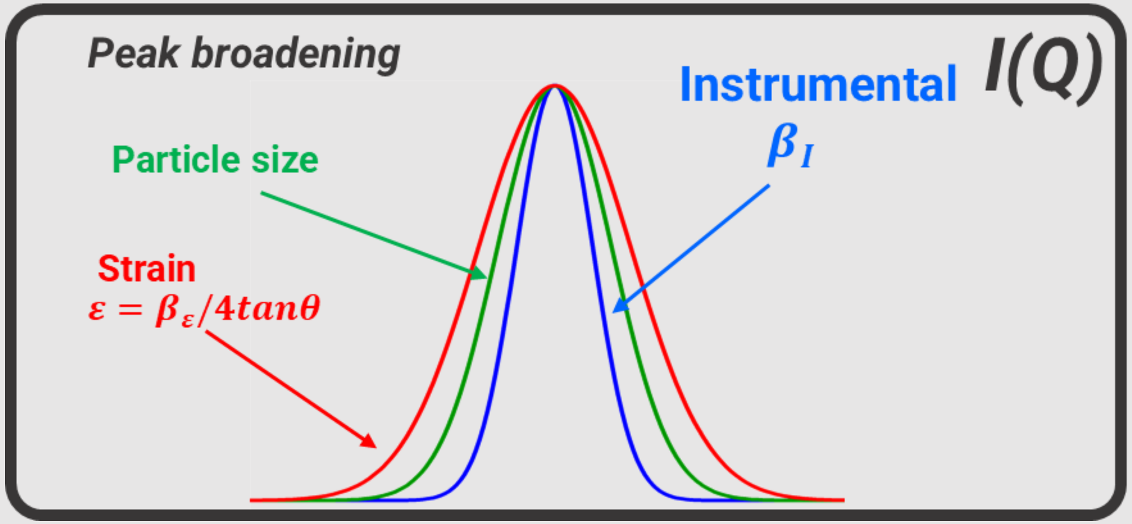
Debye Scattering Equation

$$\text{Debye}(Q) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j \frac{sin(Qr_{ij})}{Qr_{ij}}$$

Refined Parameters

Sample Contribution



Instrumental Convolution

$$\mathrm{PV}(\mathrm{Q}) = (1 - \eta)\mathrm{L} + \eta\mathrm{G}$$

$$\mathrm{I}(\mathrm{Q}) = \mathrm{Debye}(\mathrm{Q}) \otimes \mathrm{PV}(\mathrm{Q})$$

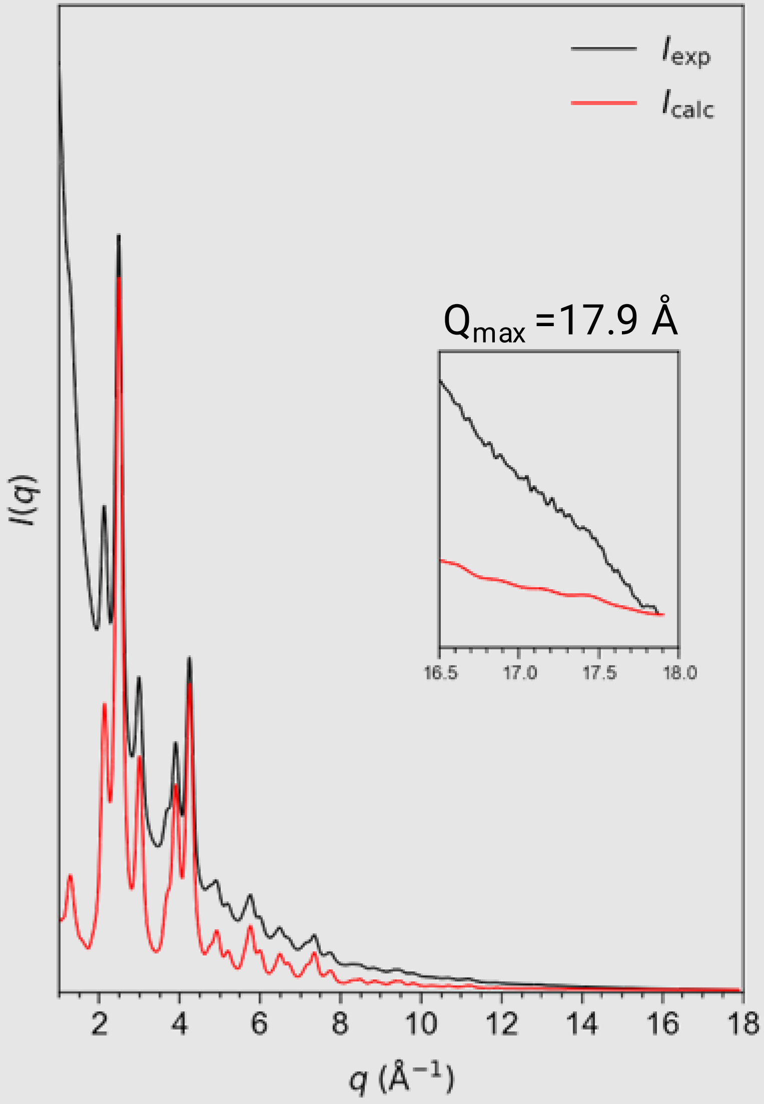
$$\mathrm{FWHM}_{\mathrm{Q}}^2 = \mathrm{u} \cdot \mathrm{Q}^2 + \mathrm{v} \cdot \mathrm{Q} + \mathrm{w}$$

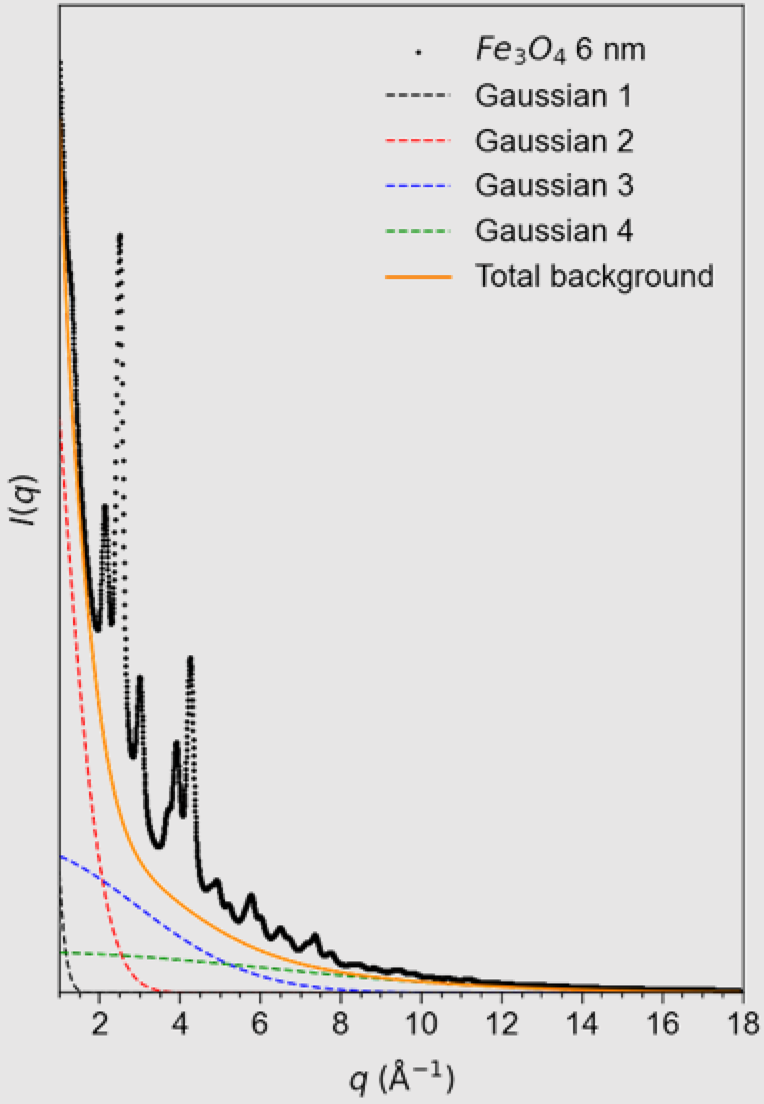
Fixed: Unit Cell Length (a), Particle Size

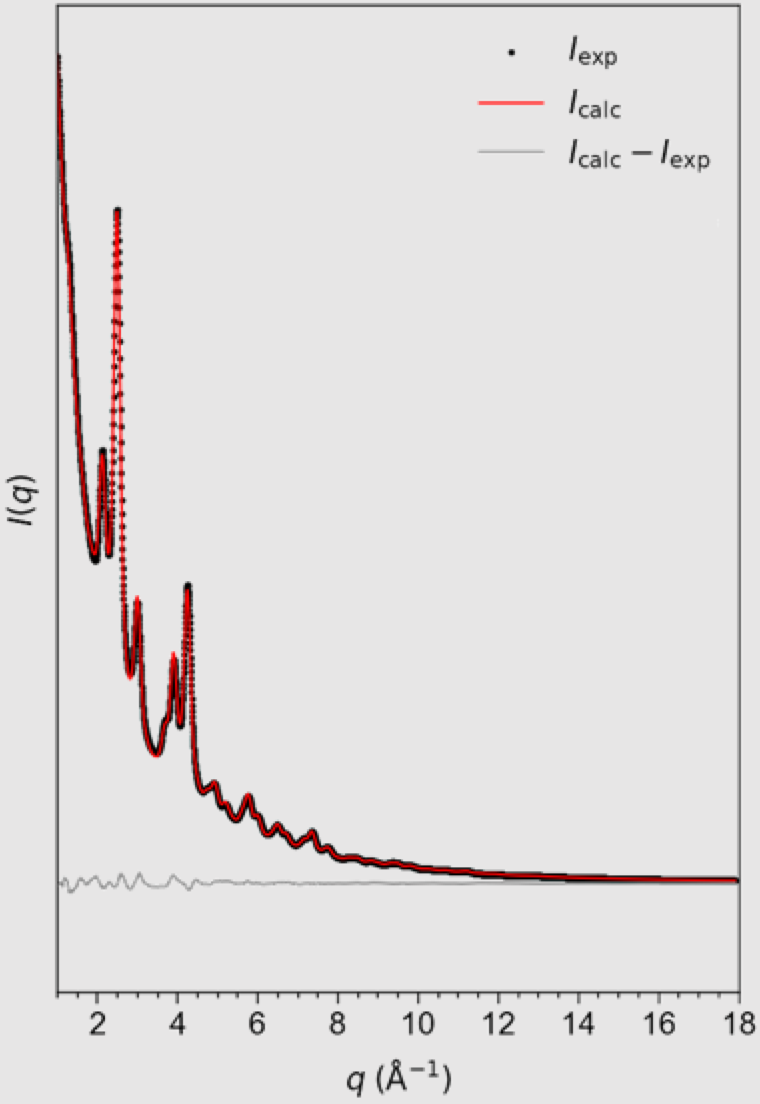
Refined: Instrument contribution (w), Thermal parameters (B), Background, Scale

Unaccounted: Strain

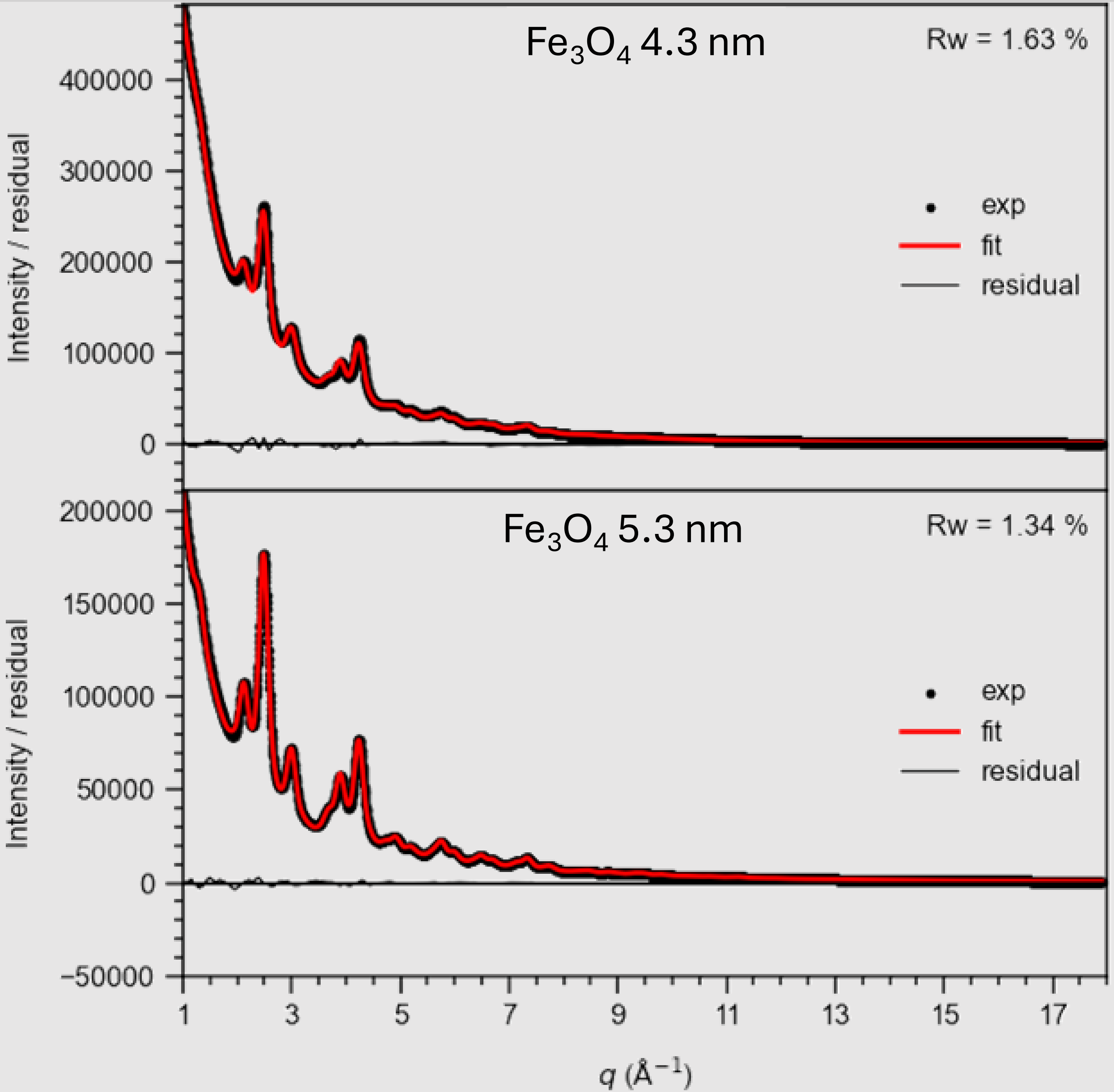
Background Modelling







Debye Refinement



3 regions of interest (ROIs)

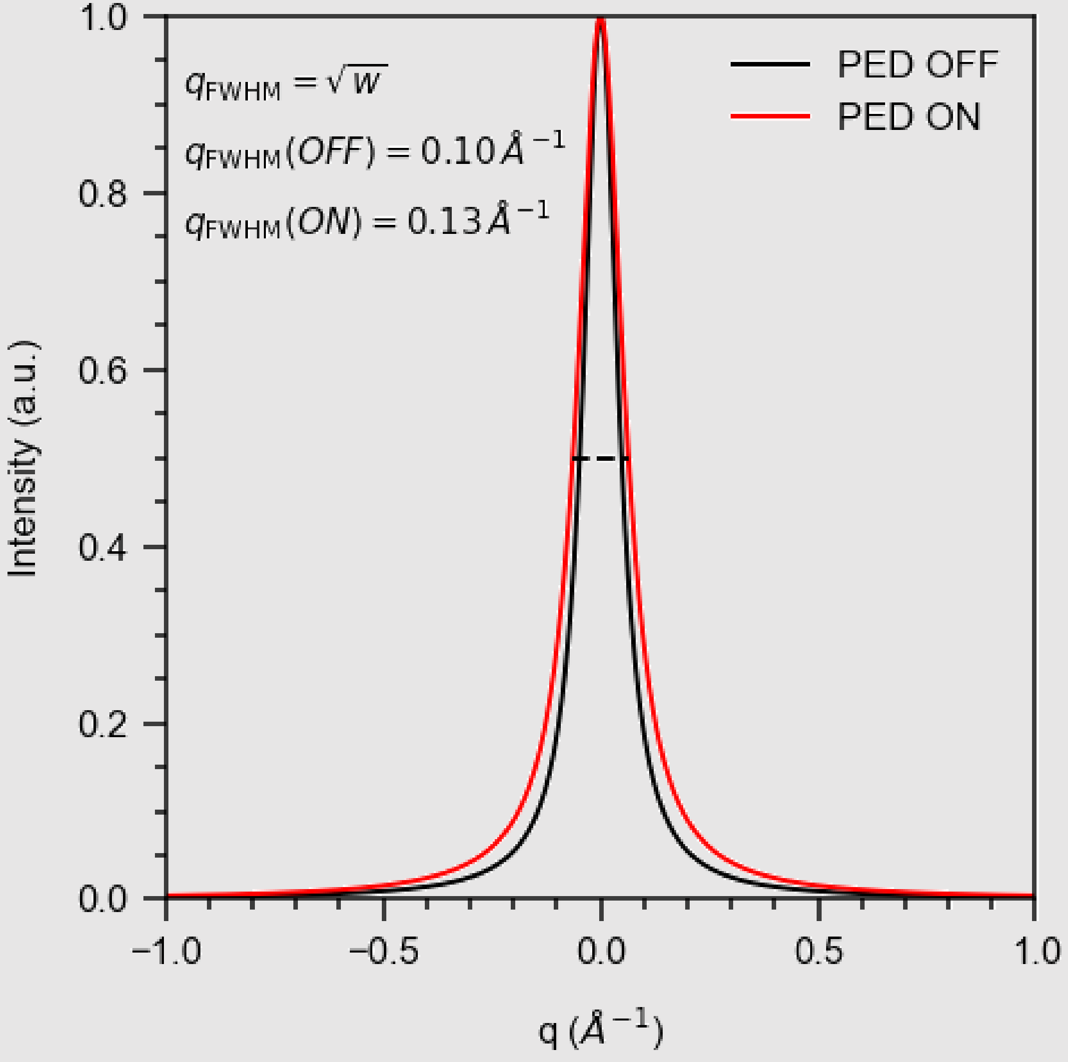
Fe_3O_4 ROIs: Refined Parameters (mean ± σ)

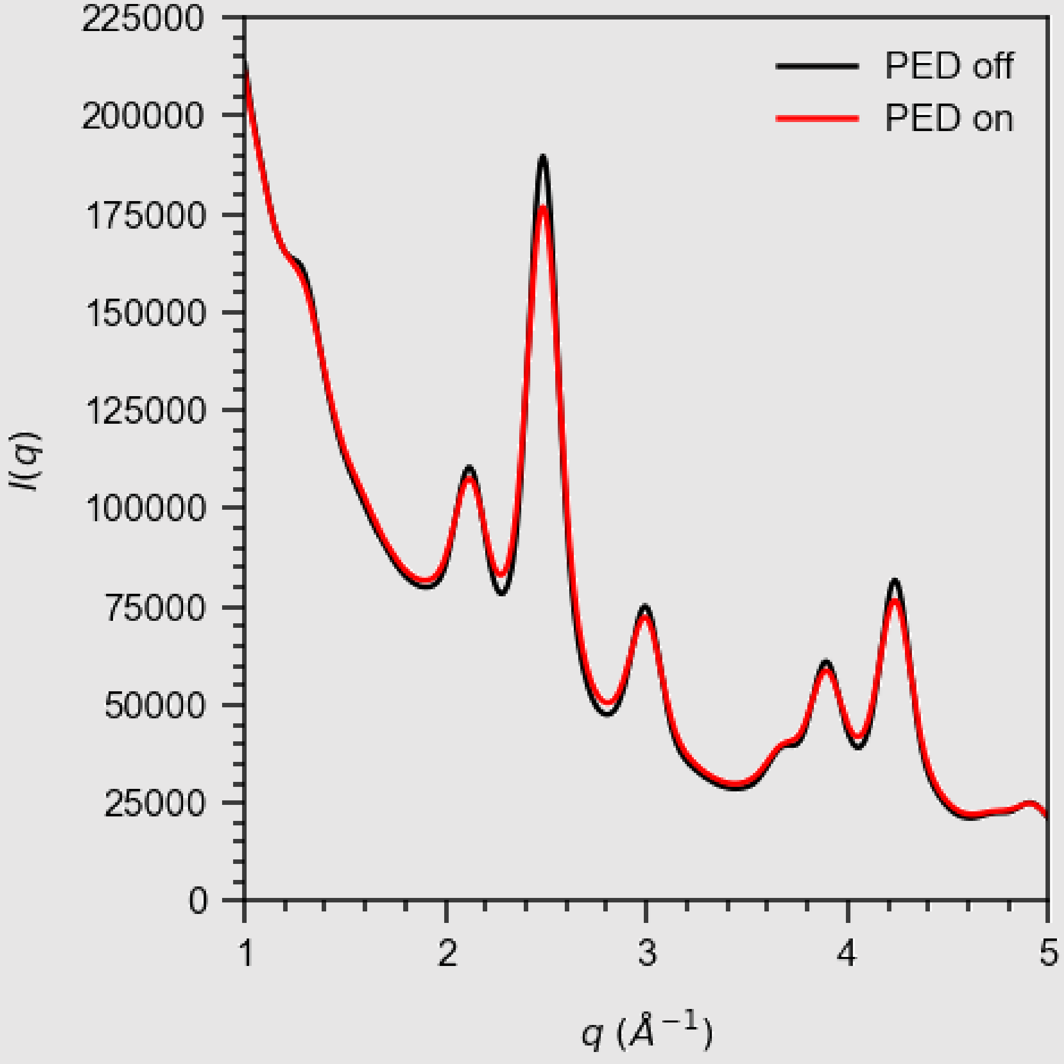
F30: spot 2, 400 nm beam, 380 mm KL

Parameter	4.3 nm PED OFF	4.3 nm PED ON	5.3 nm PED OFF	5.3 nm PED ON
w (Å^{-1})	2e-03 ± 6e-04	3e-03 ± 2e-04	2e-03 ± 6e-04	3e-03 ± 1e-04
η	0.9999 ± 0.0002	0.99993 ± 0.00005	0.99 ± 0.02	0.96 ± 0.04
B_{metal}	1.3 ± 0.3	1.31 ± 0.05	1.0 ± 0.1	0.7 ± 0.3
B_{anions}	0.3 ± 0.1	0.31 ± 0.03	1.3 ± 0.2	1.1 ± 0.2
R_w (%)	2.8 ± 0.9	2.8 ± 0.2	1.8 ± 0.3	1.6 ± 0.2

$$\mathrm{FWHM}_Q^2 = w$$

Instrument Function





ePDF Calculation

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Exp/Calc Intensity

↓ Subtract refined background

Background subtracted

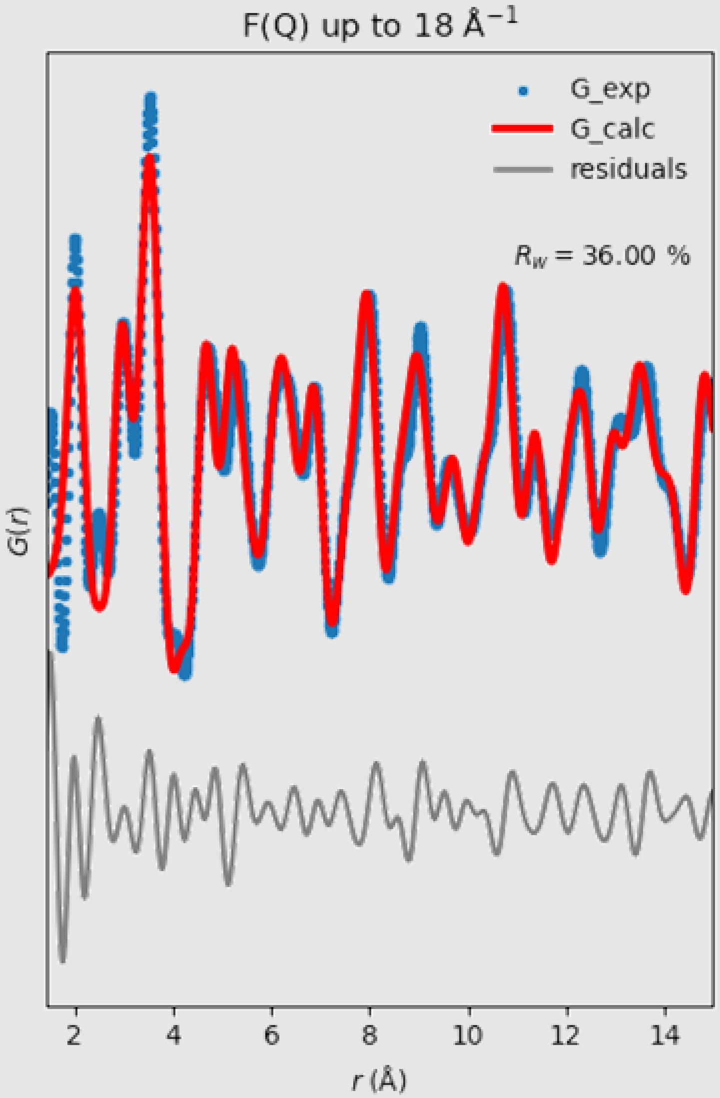
↓ Electron form factors normalization

Structure function F(Q)

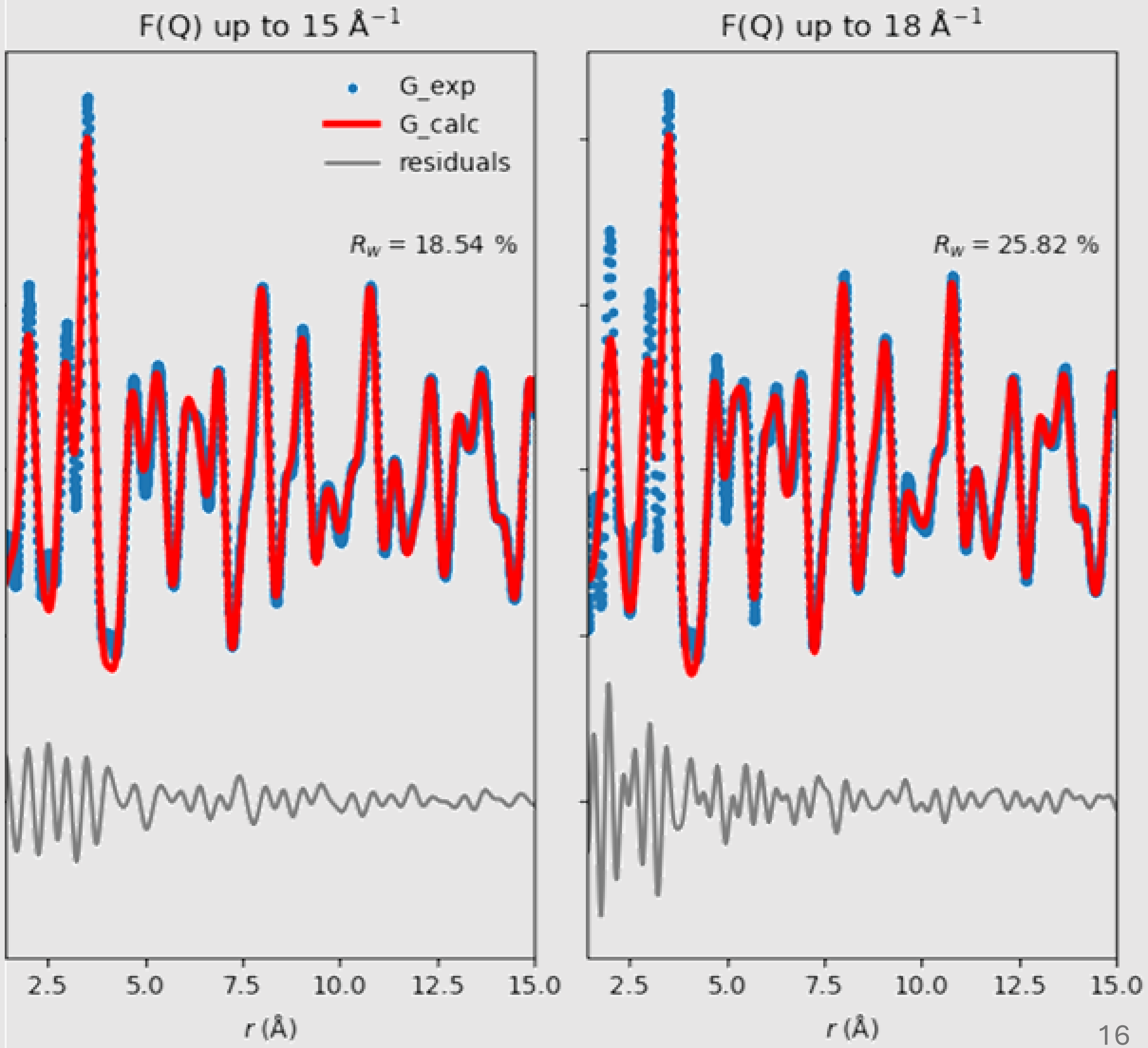
↓ Sine Fourier Transform

ePDF

Fe_3O_4 4.3 nm



Fe_3O_4 5.3 nm



Conclusions and Perspectives

- The crystalline particle model is a good approximation.
- Debye calculation presented good agreement for diffraction intensities.
- Lorentzian convolution approximates TEM instrument function.
- Precession alignment increases instrument FWHM but improves reproducibility.

❑Unit cell and thermal parameters input from X-ray and Neutron diffraction.
❑Refine instrument function for LaB_6 source and third particle size.
❑Improve model with ligand simulation.
❑Isolate contributions of beam convergence and detector point spread function.

Acknowledgements

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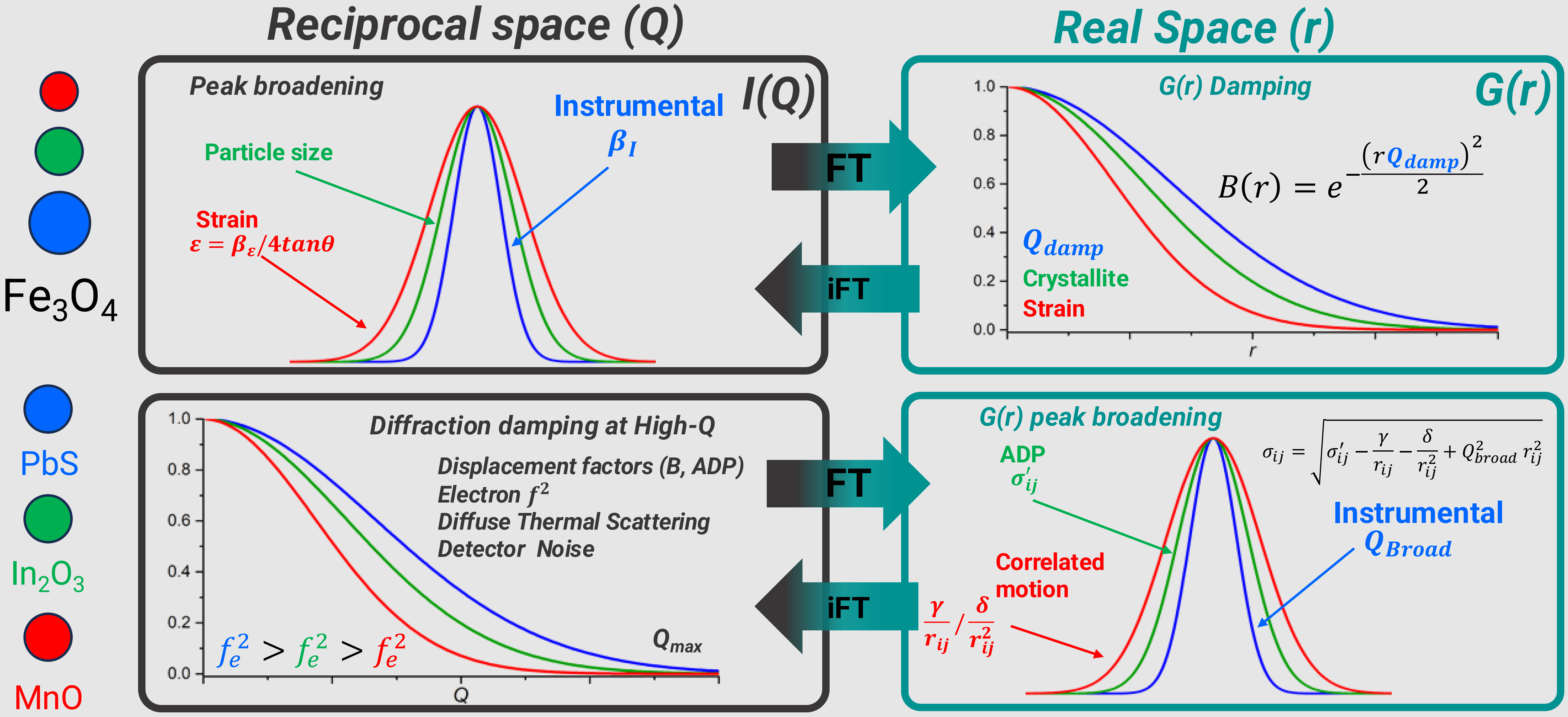
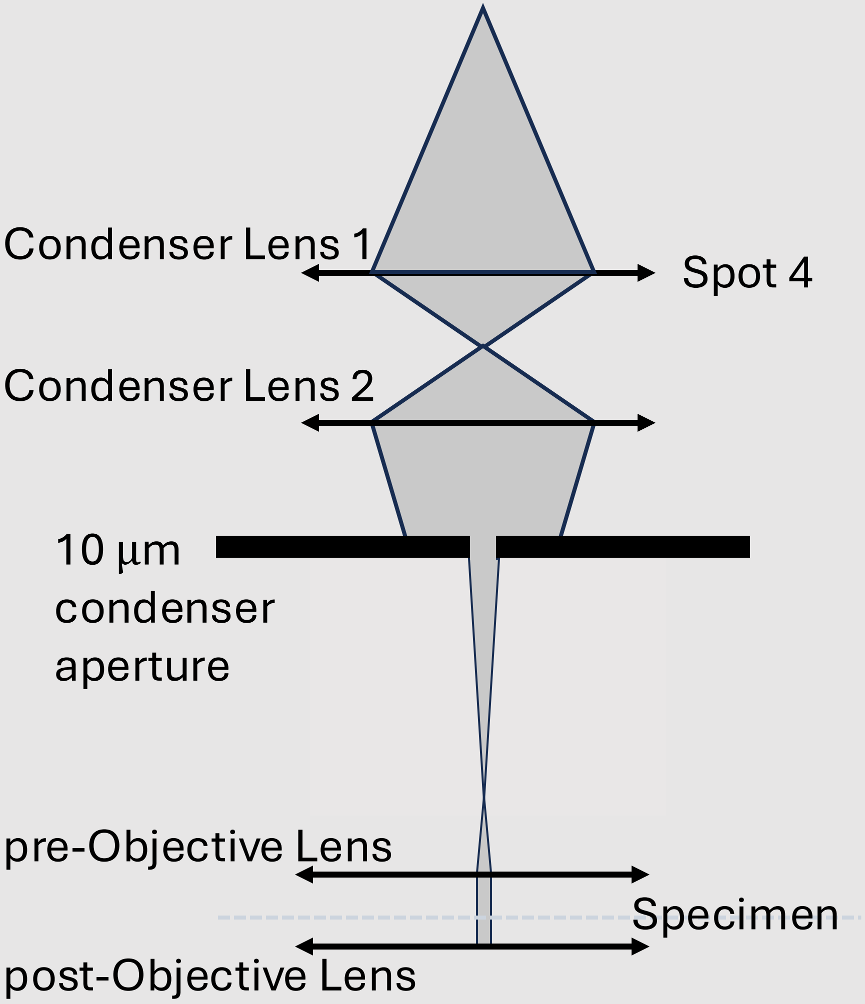
TEM Instrumental Contribution




Condenser Lens 1
Spot 4
Condenser Lens 2
10 µm condenser aperture
pre-Objective Lens
Specimen
post-Objective Lens