Introduction to Total Scattering and Reverse Monte Carlo Methods

Dr Helen Y. Playford

ISIS Neutron and Muon Source

Neutrons for Chemistry and Materials Science Applications

4th-13th July 2018

Science & Technology Facilities Council
ISIS

Outline

- About me.
- Introduction to total scattering.
- Instrument requirements for total scattering/PDF methods.
- Modelling total scattering data.
- Scientific case studies.
- A closer look at RMCProfile.
- Conclusions & discussion points

Part 1

Part 2

About Me

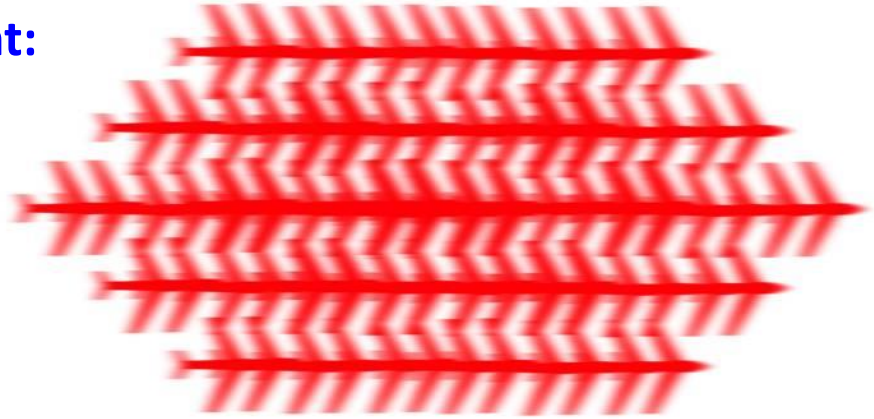
I am a materials chem **rument scientist.**

- **MChem at Warwick Un**
  - Final year project on h oxides
- **PhD in Chemistry at Wa & Dr. Alex Hannon)**
  - Hydro/solvothermal sy terials
  - Structural refinement
  - Total scattering metho
- **Postdoctoral fellowship**
  - Structure and propert
- **Postdoctoral researche**
  - RMCProfile developm d Polaris
- **Instrument scientist at**
  - Responsible for total s

Science & Technology Facilities Council
ISIS

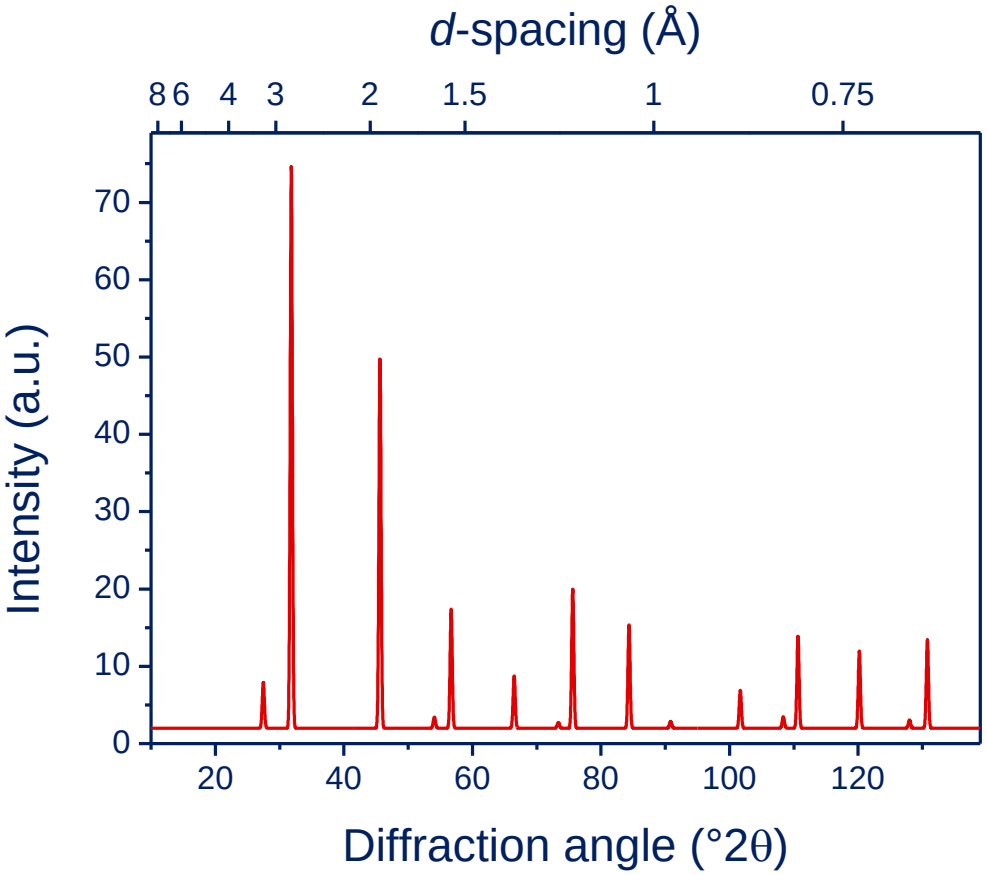
Local and Average Viewpoints

Average viewpoint:



Local viewpoint:

Introduction



Information contained in a diffraction pattern:

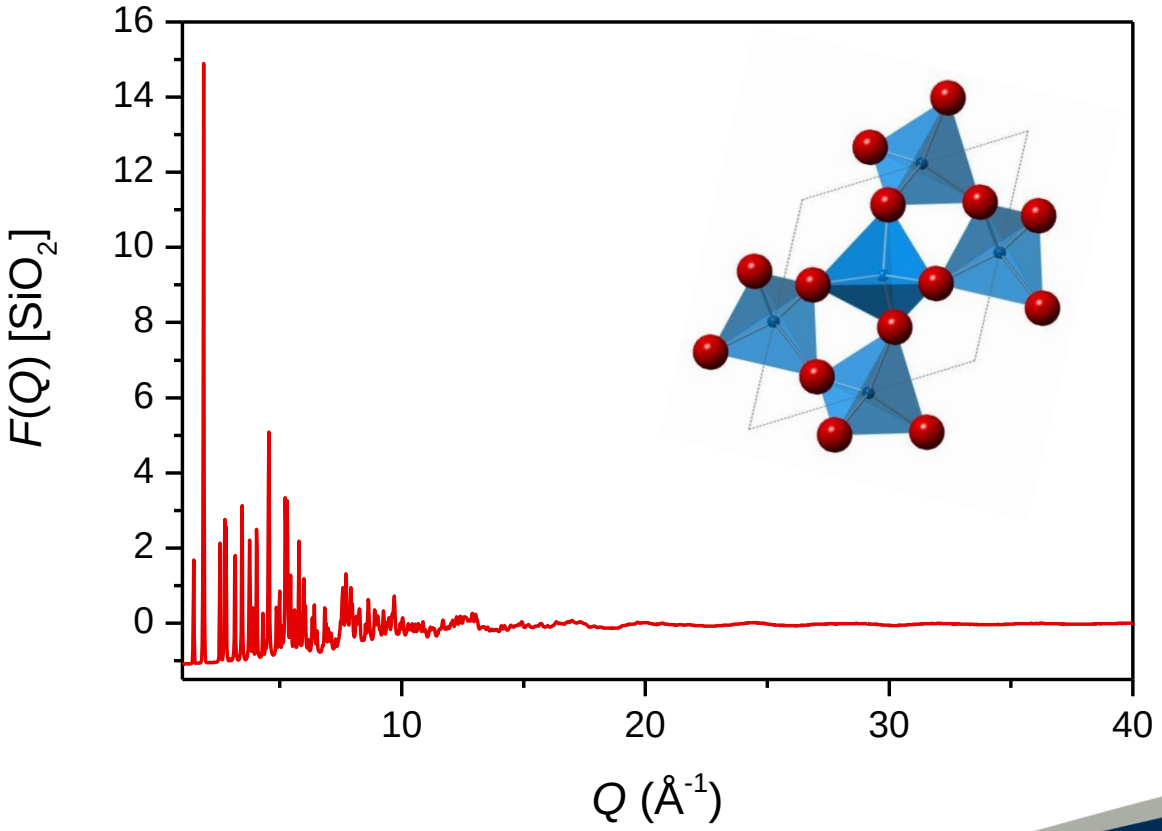
- Size and shape of unit cell (peak positions)
- Symmetry within the unit cell (absences)
- Contents of the unit cell (relative intensities)

- Thermal motion
- Particle size
- Strain
- Texture

Introduction

What is total scattering?

A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.

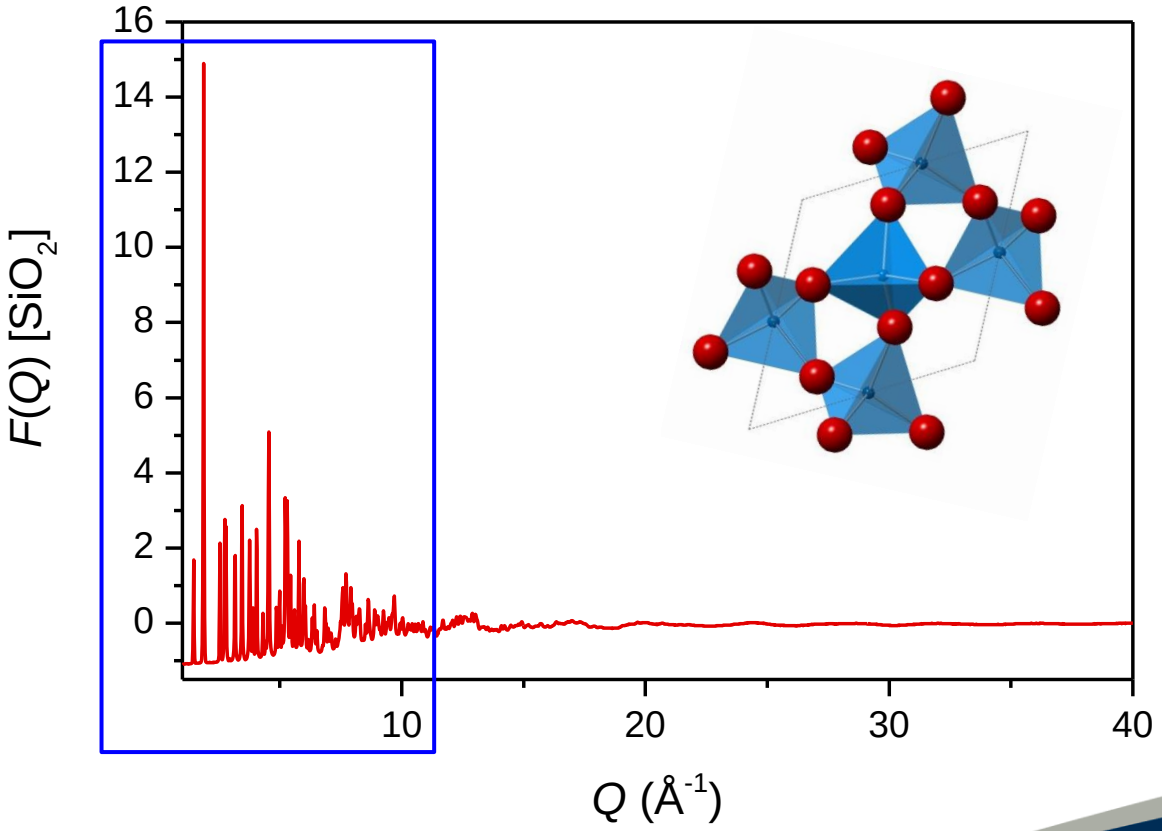


$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda}$$

Introduction

What is total scattering?

A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.

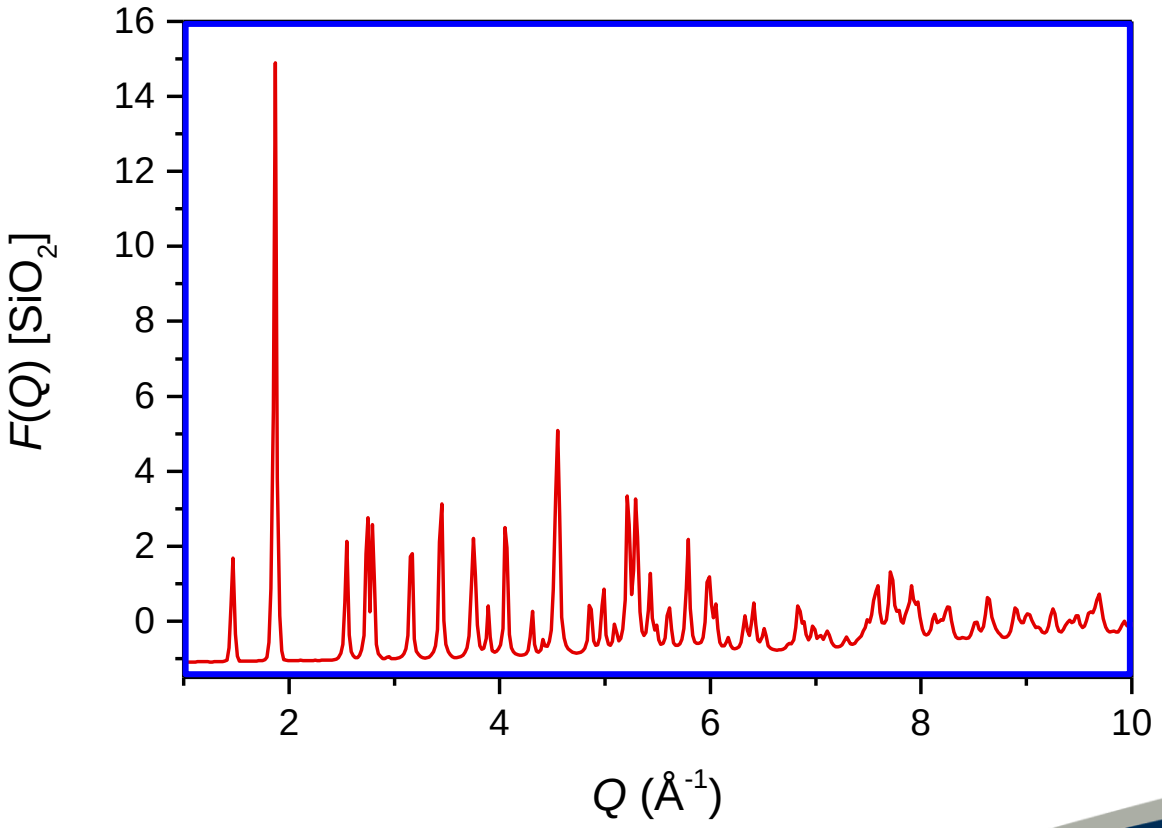


$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda}$$

Introduction

What is total scattering?

A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.



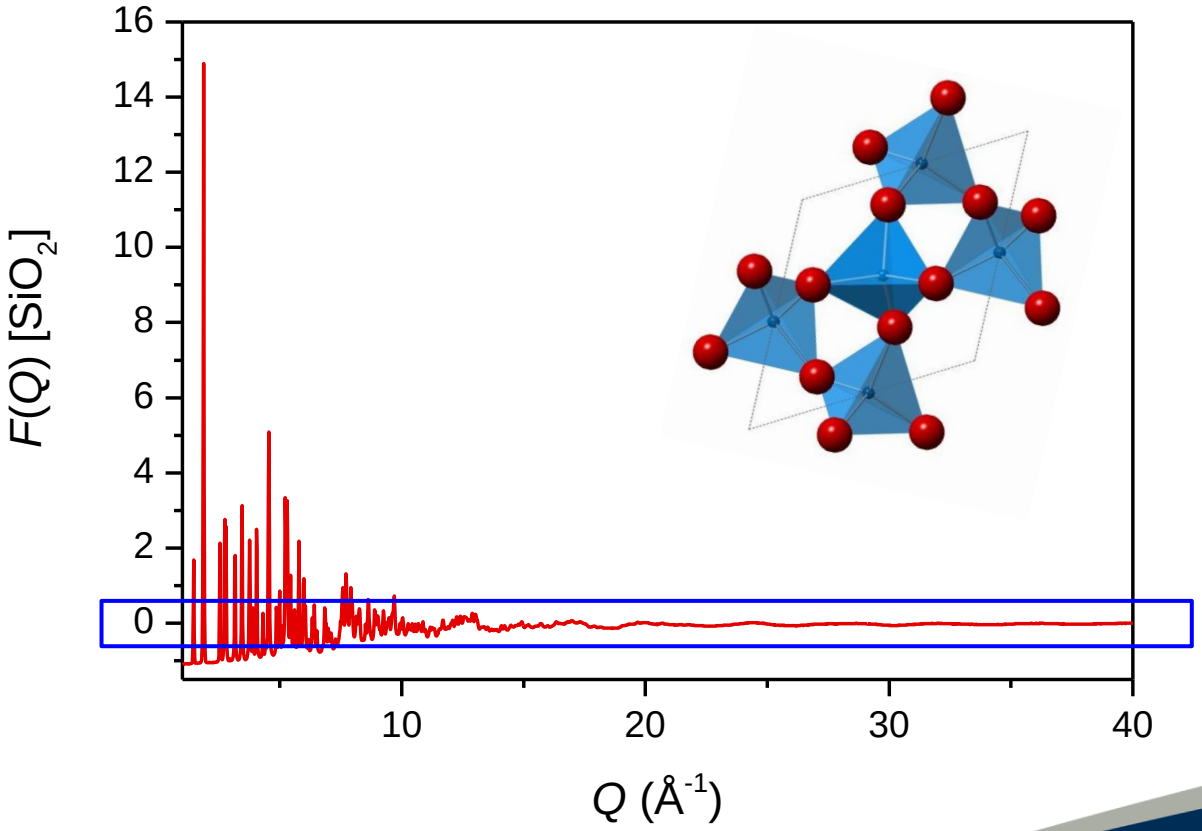
$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda}$$

Science & Technology Facilities Council
ISIS

Introduction

What is total scattering?

A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.

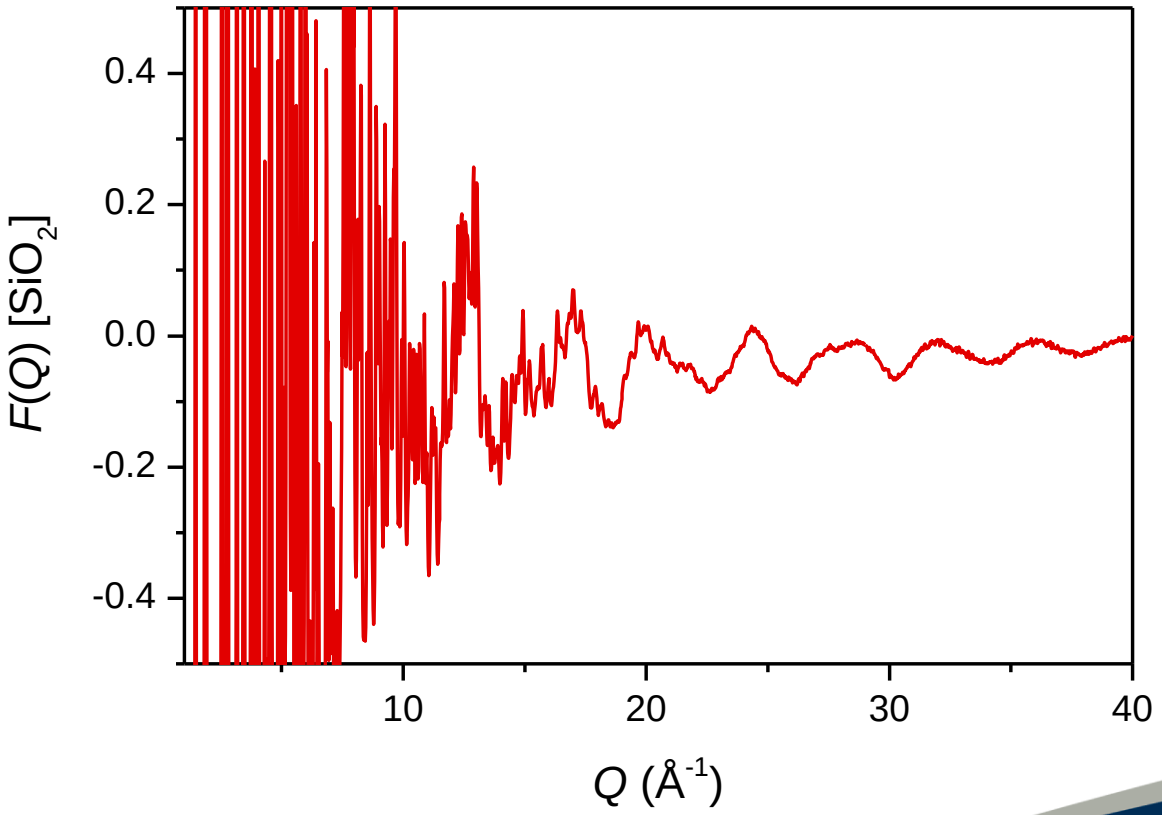


$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda}$$

Introduction

What is total scattering?

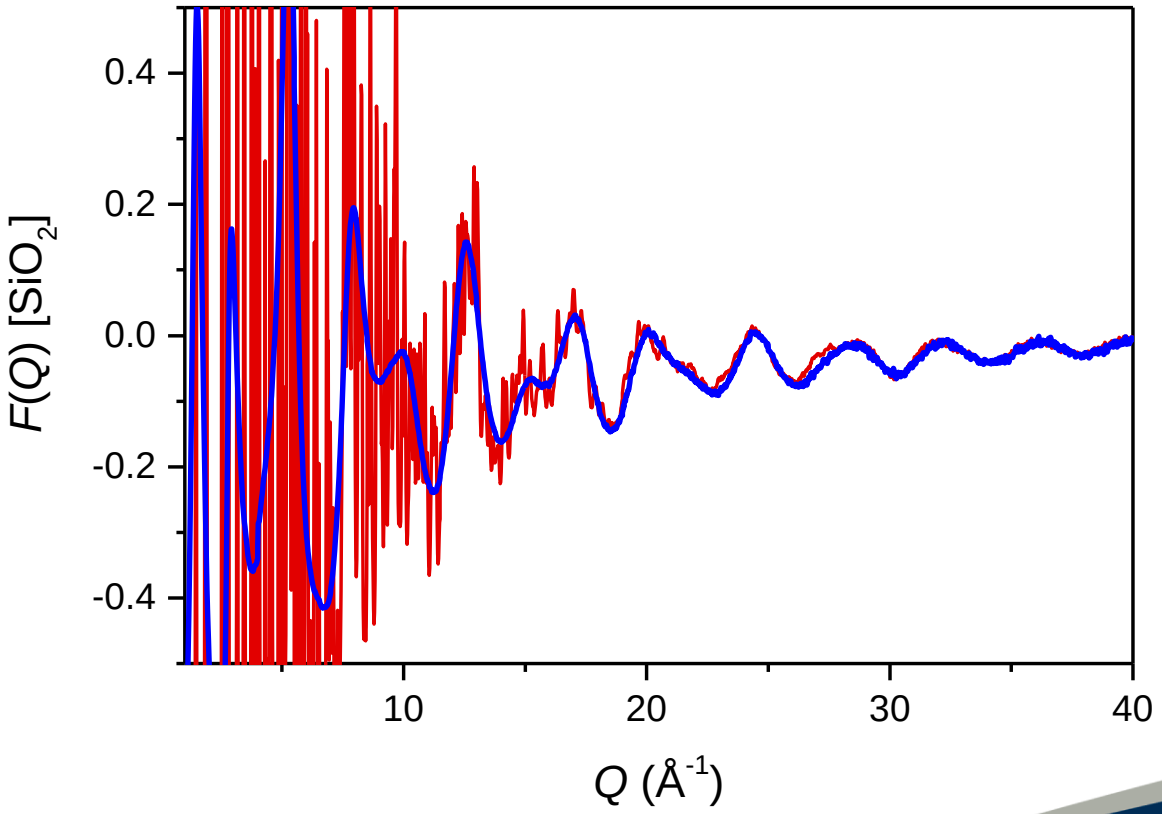
A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.



Introduction

What is total scattering?

A powder diffraction based technique in which the Bragg and diffuse scattering are measured and analysed simultaneously.



Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

Differential cross section

$$\frac{1}{N}\frac{d\sigma}{d\Omega} = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j \left[A_{ij}(Q) - 1\right] + \sum_{i=1}^{n} c_i \bar{b}_i{}^2$$

"Distinct scattering"

$$F(Q) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j \left[A_{ij}(Q) - 1\right]$$

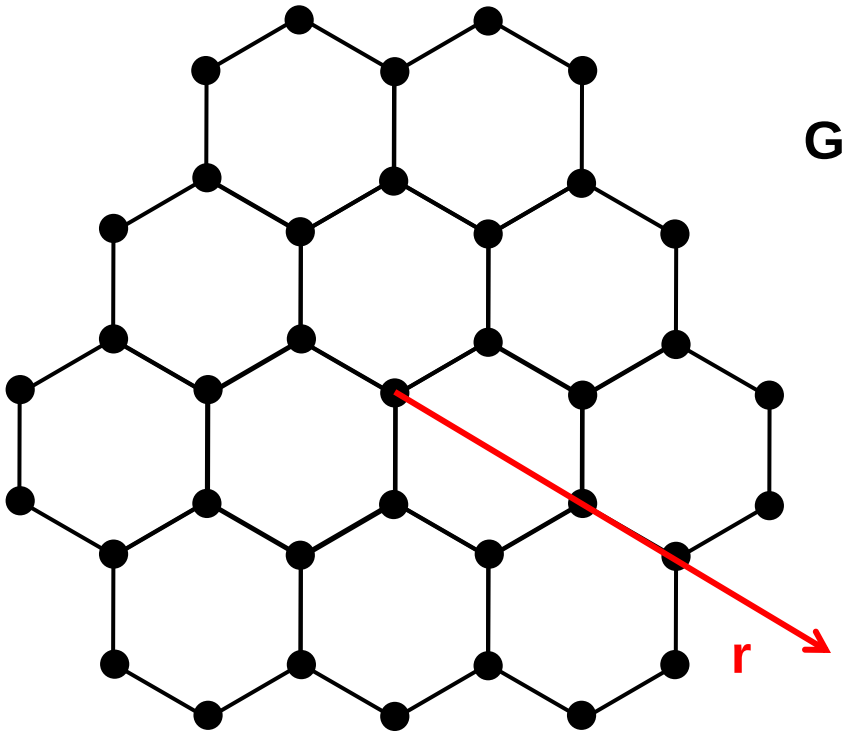
Pair distribution function or PDF

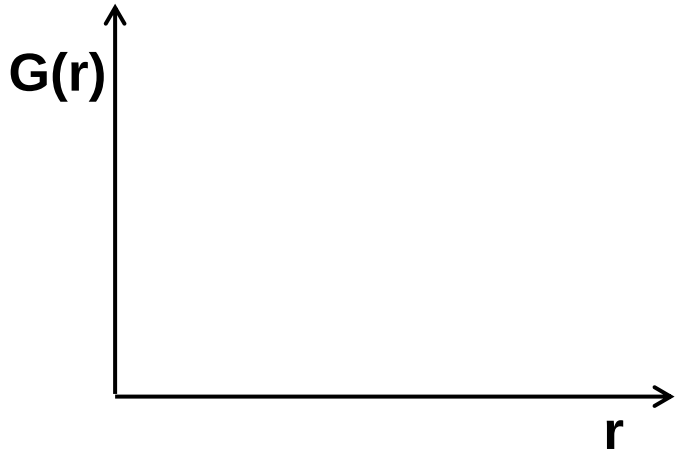
$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^{\infty} 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} dQ$$

Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

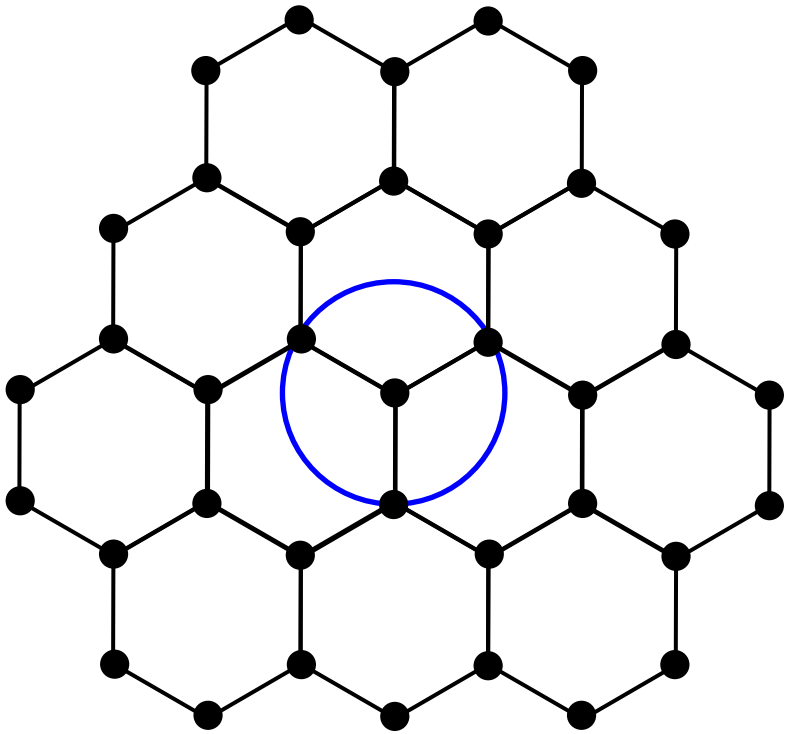


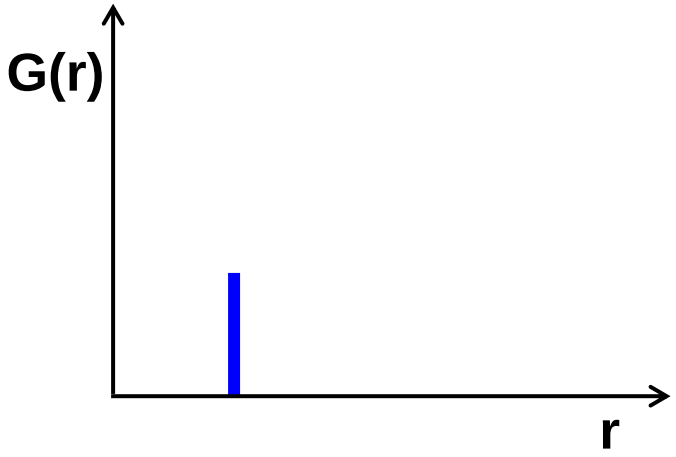


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

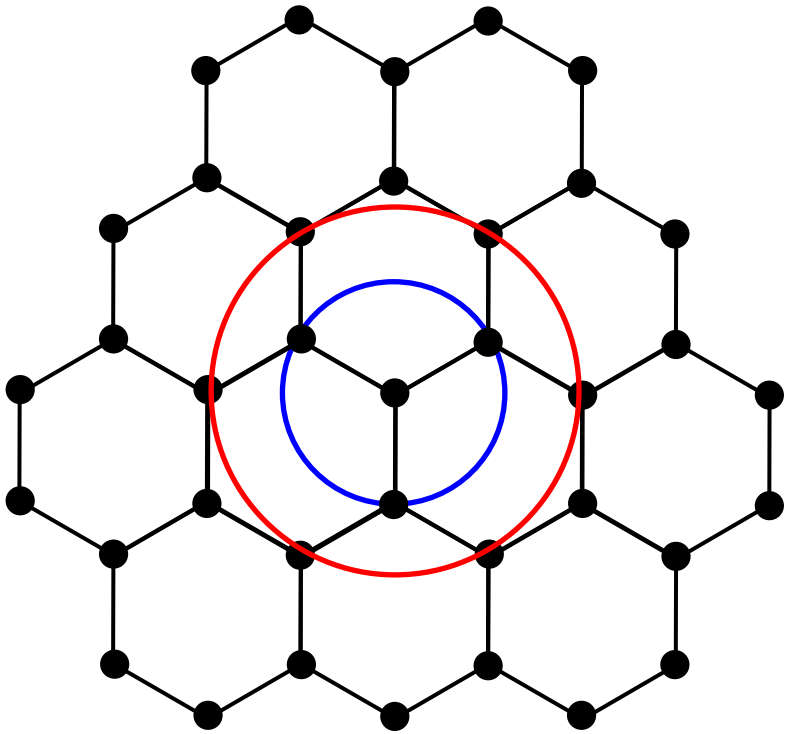


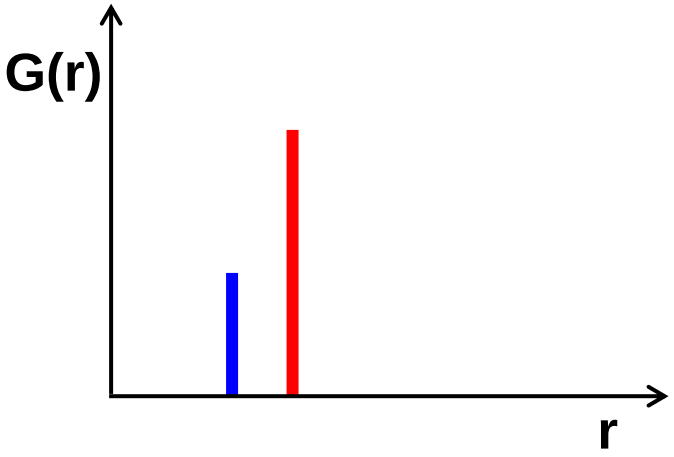


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

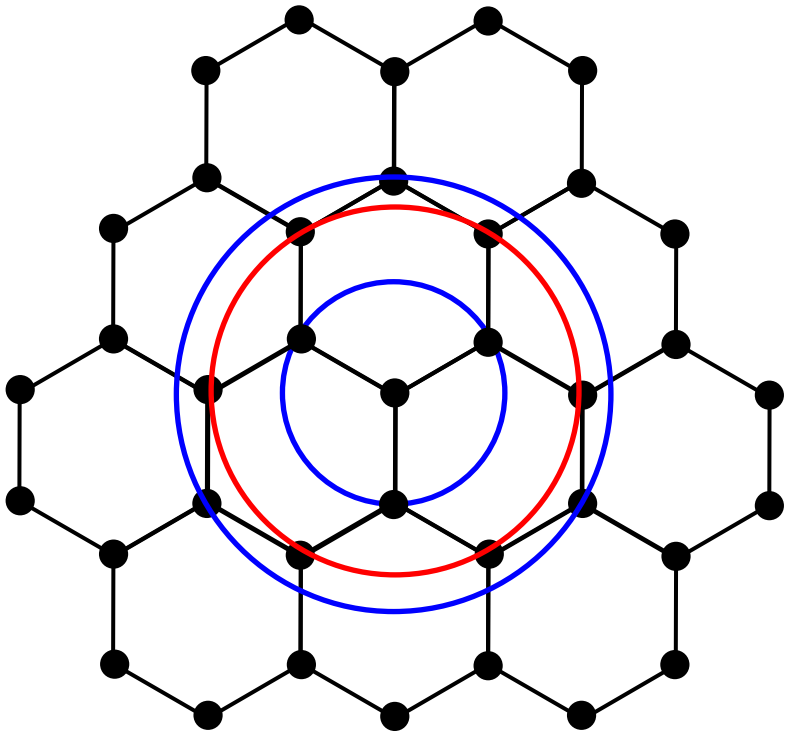


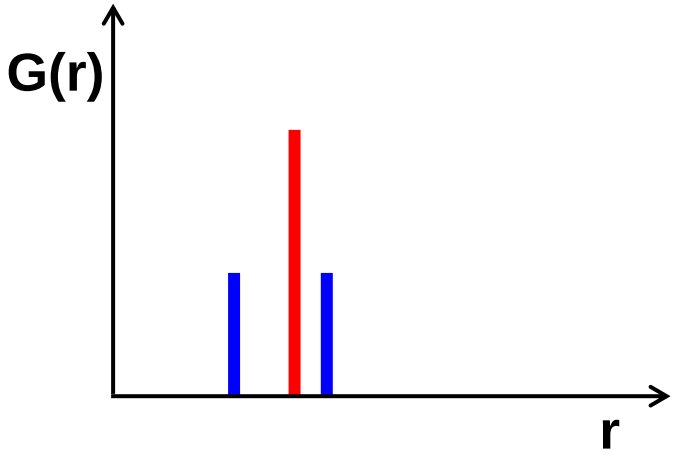


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

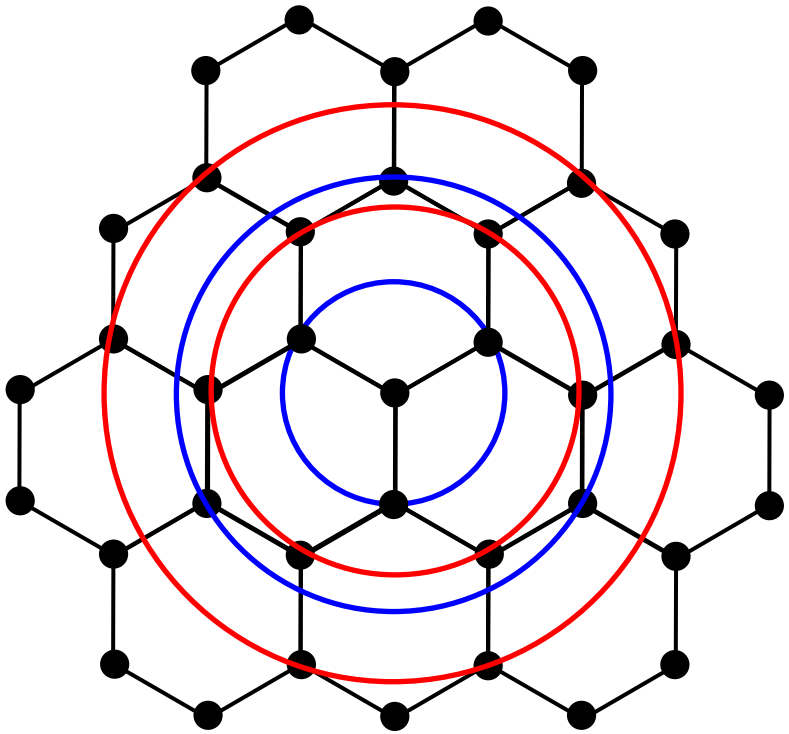


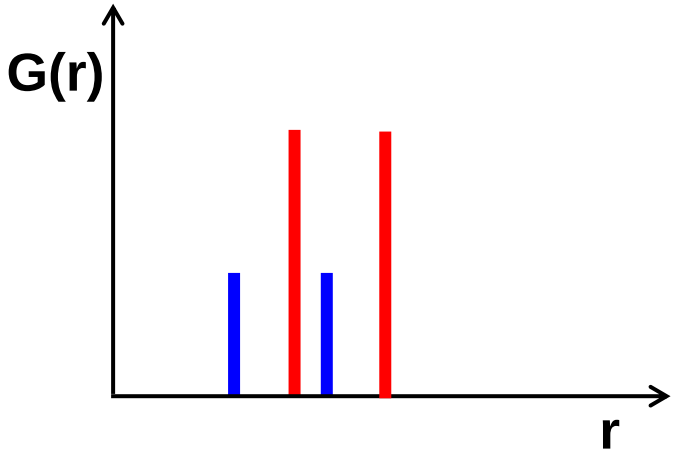


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

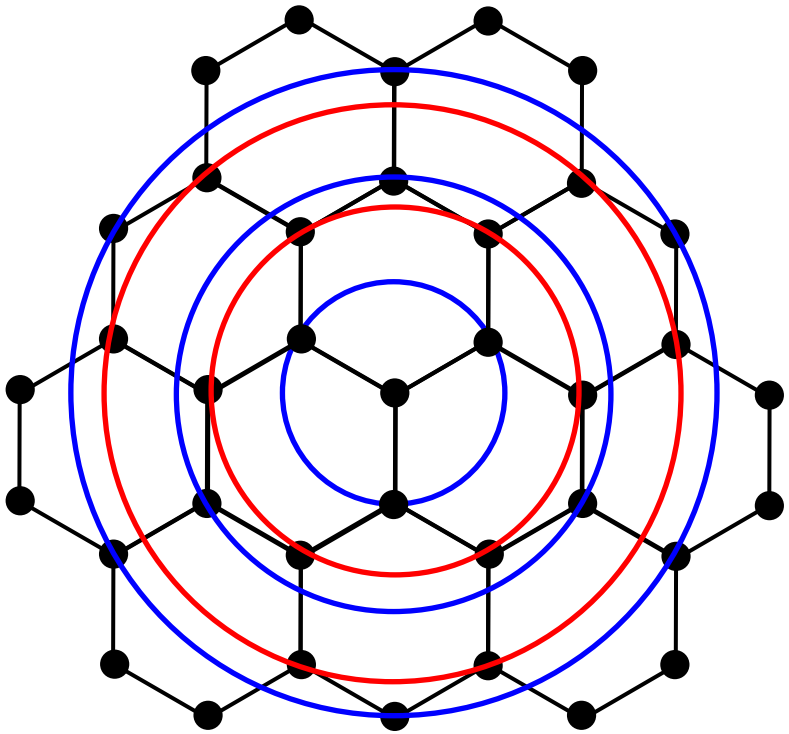


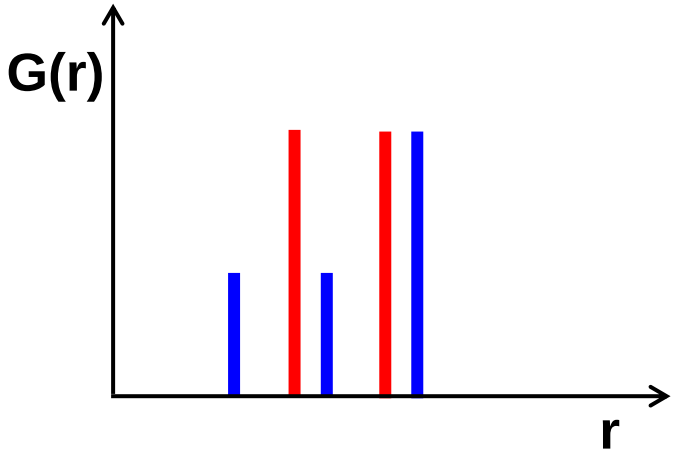


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

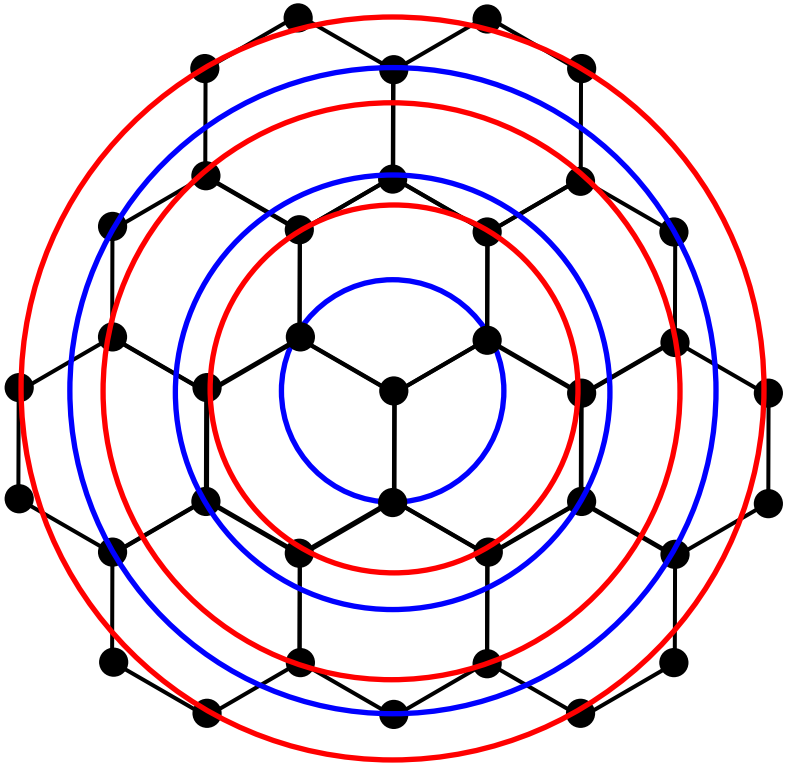


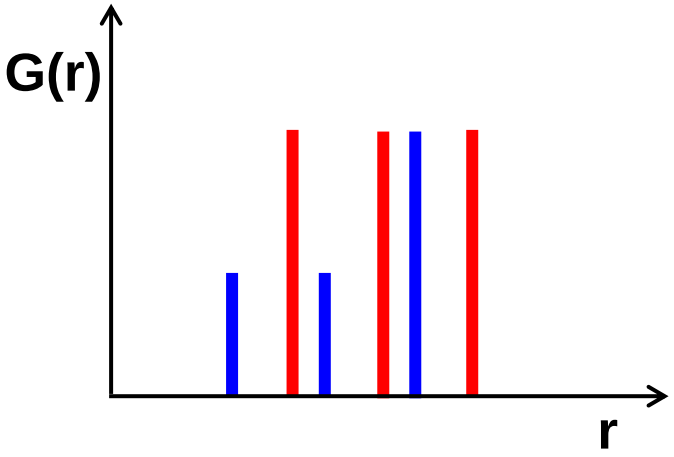


Introduction

The pair distribution function (PDF)

A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

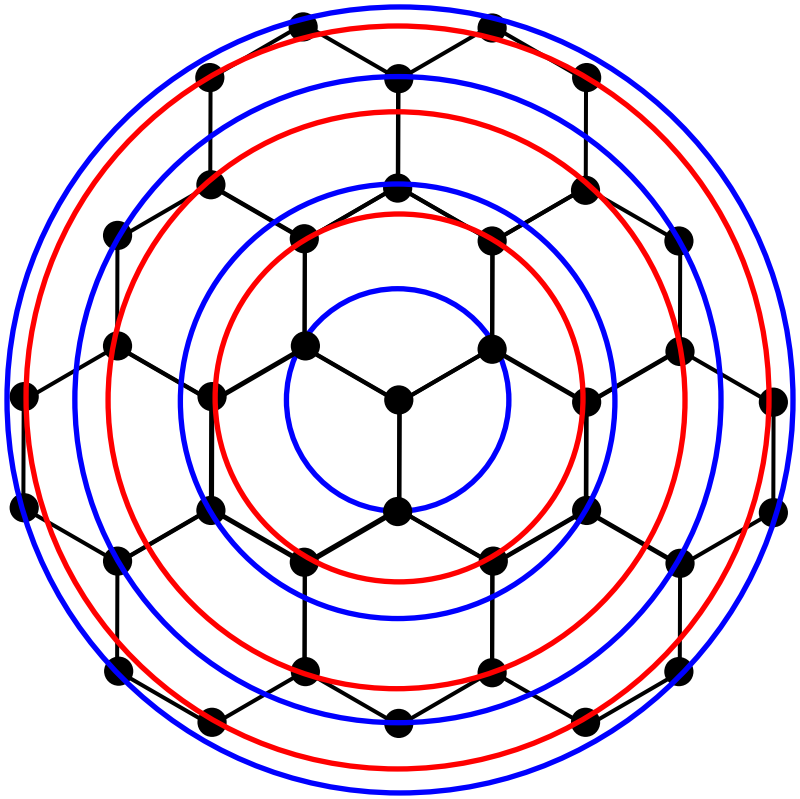


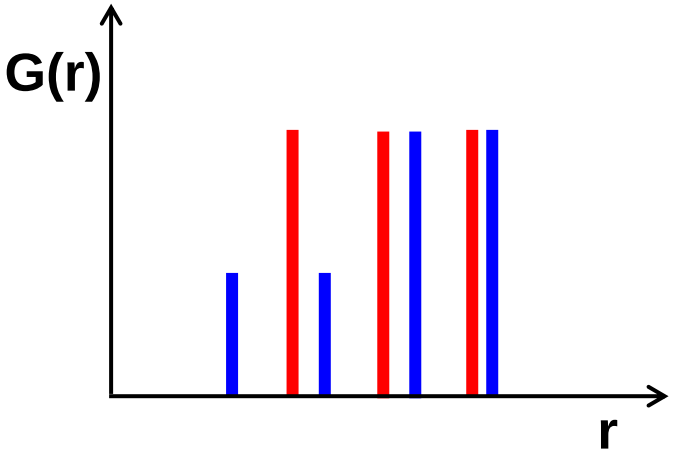


Introduction

The pair distribution function (PDF)

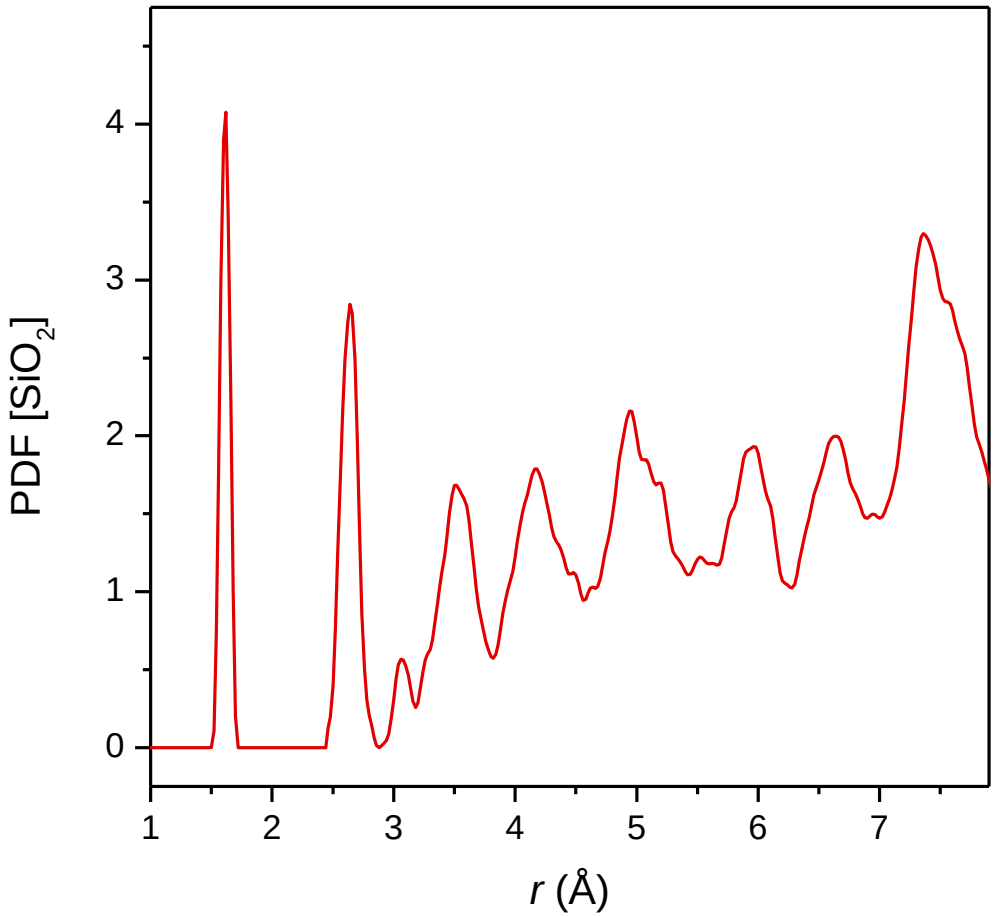
A histogram of pairwise interatomic distances produced by Fourier transformation of the total scattering function.

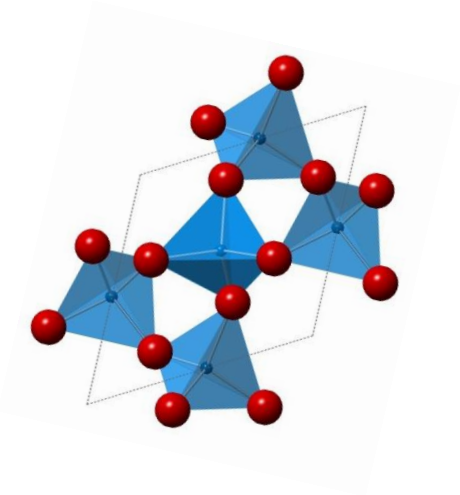




Introduction

The pair distribution function (PDF)

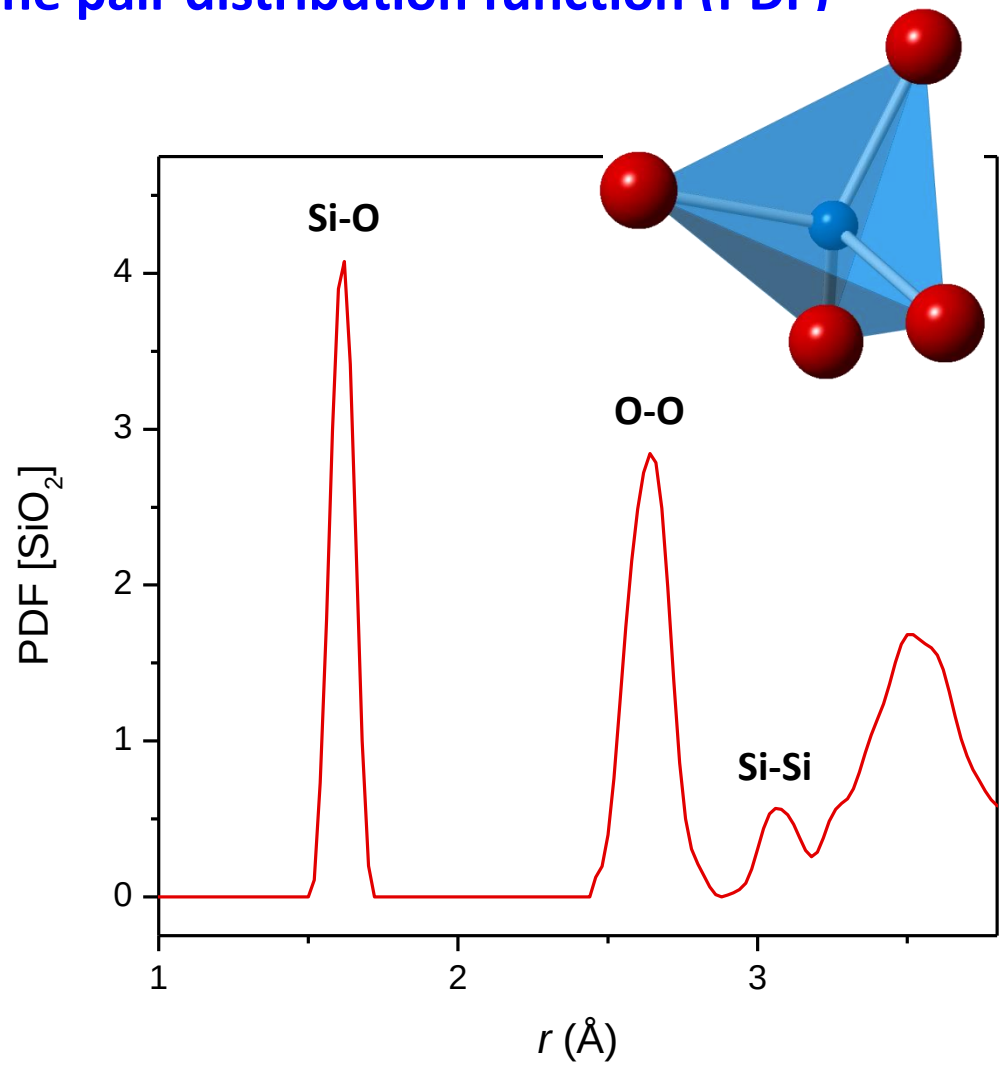




This is the neutron PDF for quartz-type SiO_2 (measured on Polaris).

Introduction

The pair distribution function (PDF)



Visual inspection can provide information about:

- bond lengths
- coordination numbers
- level of disorder
- identities of species involved

…more detail comes from **modelling**!

Measuring total scattering data

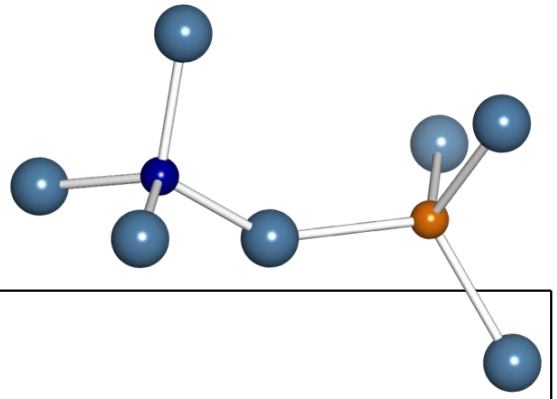
Measuring total scattering data

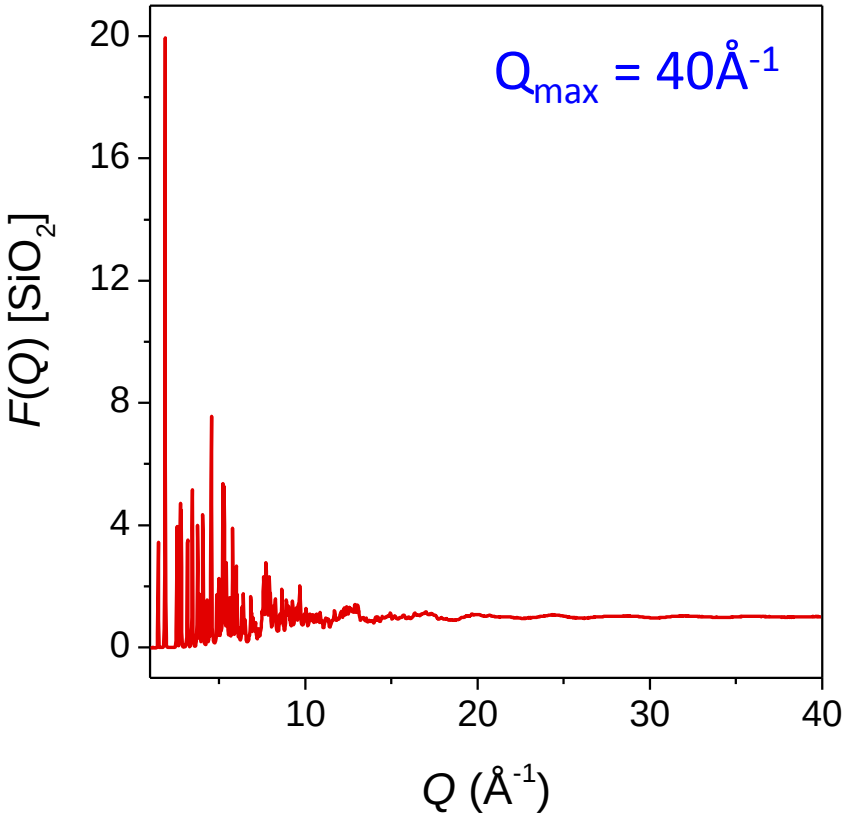
Measure diffraction data to a high maximum *Q*

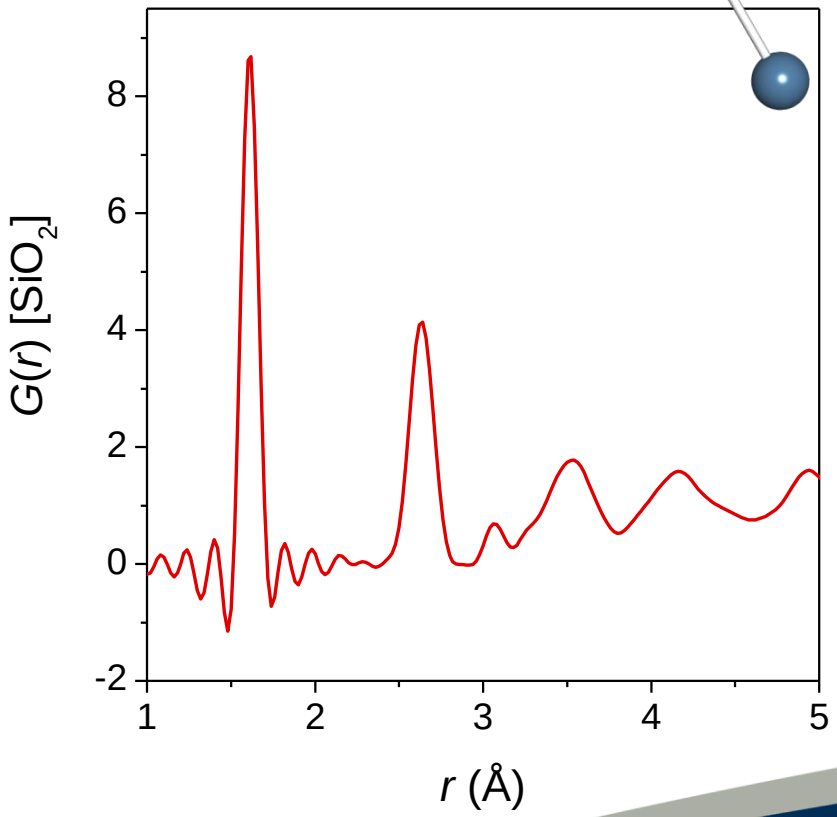
- the spatial resolution of the PDF depends on Q_{max}
- need high energy (short wavelength) X-rays or spallation neutrons

Measuring total scattering data

The importance of Q-range

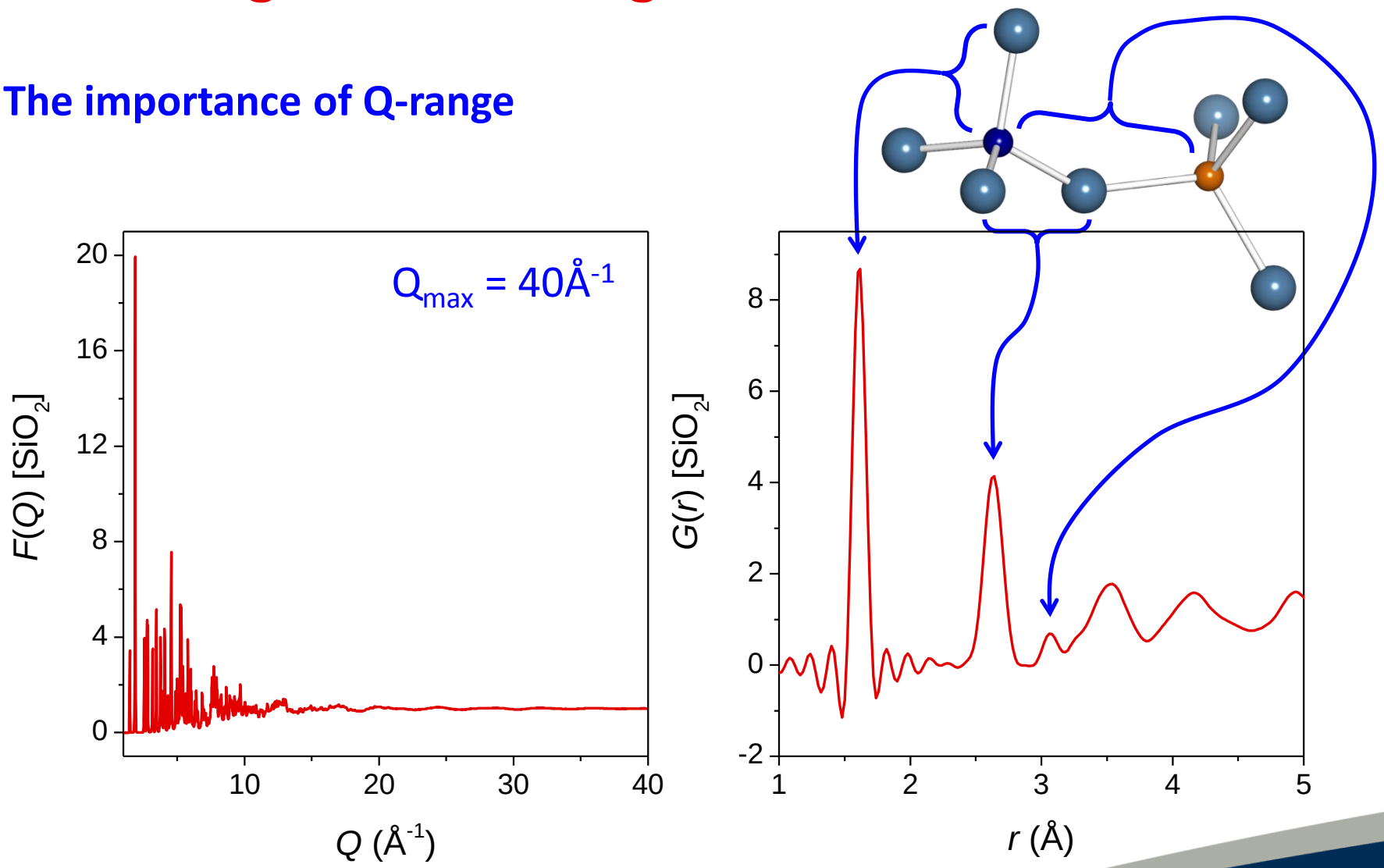






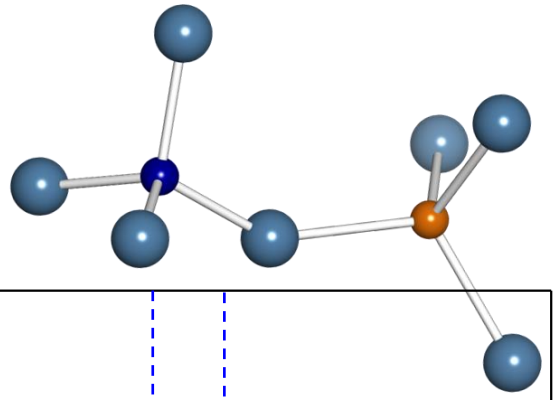
Measuring total scattering data

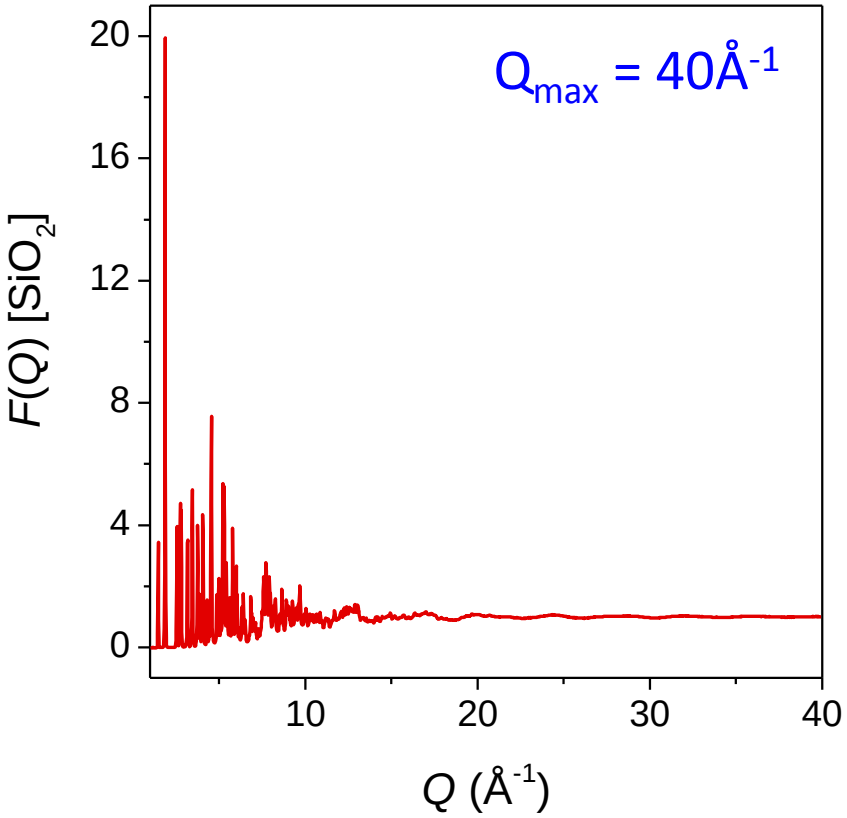
The importance of Q-range

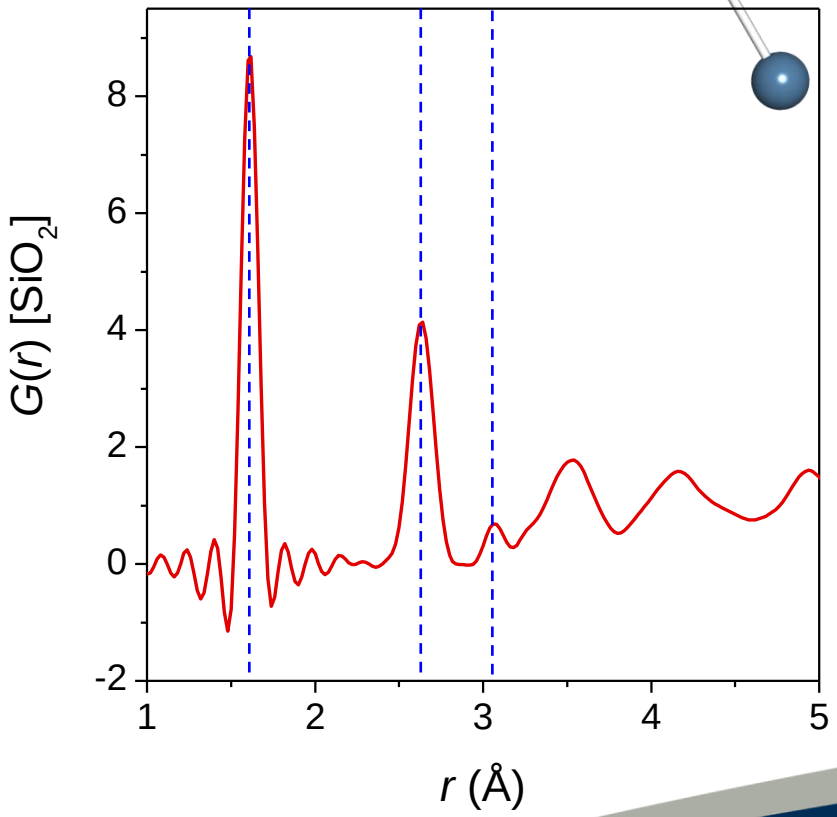


Measuring total scattering data

The importance of Q-range

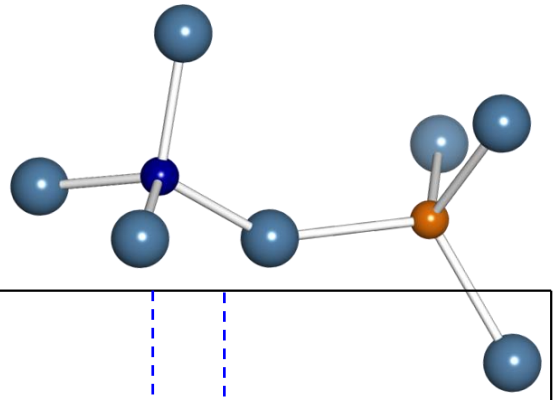


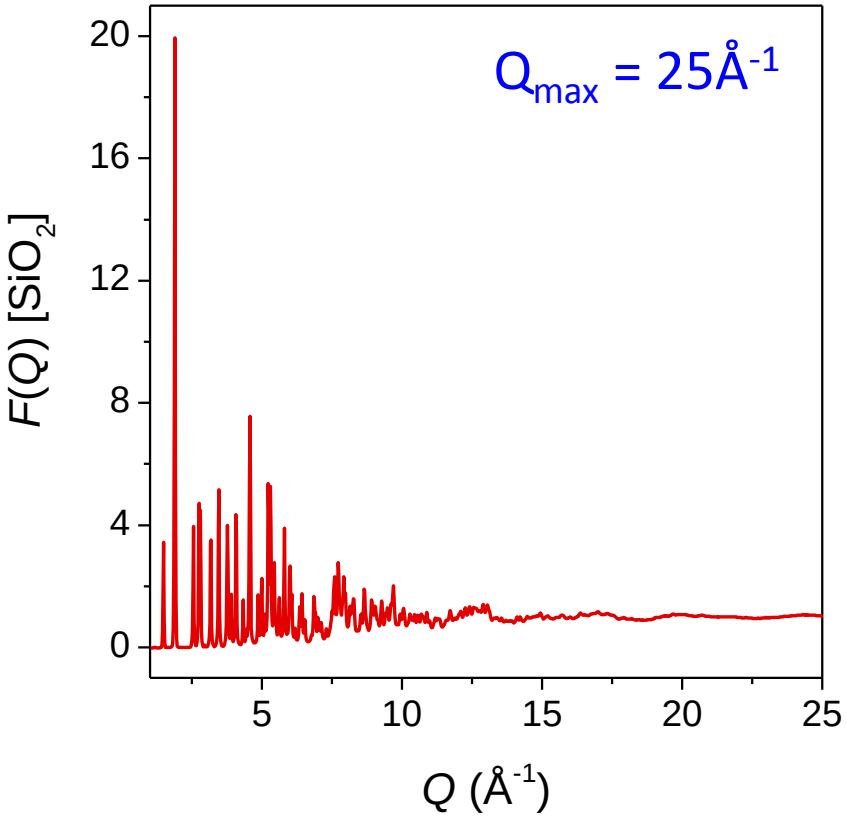


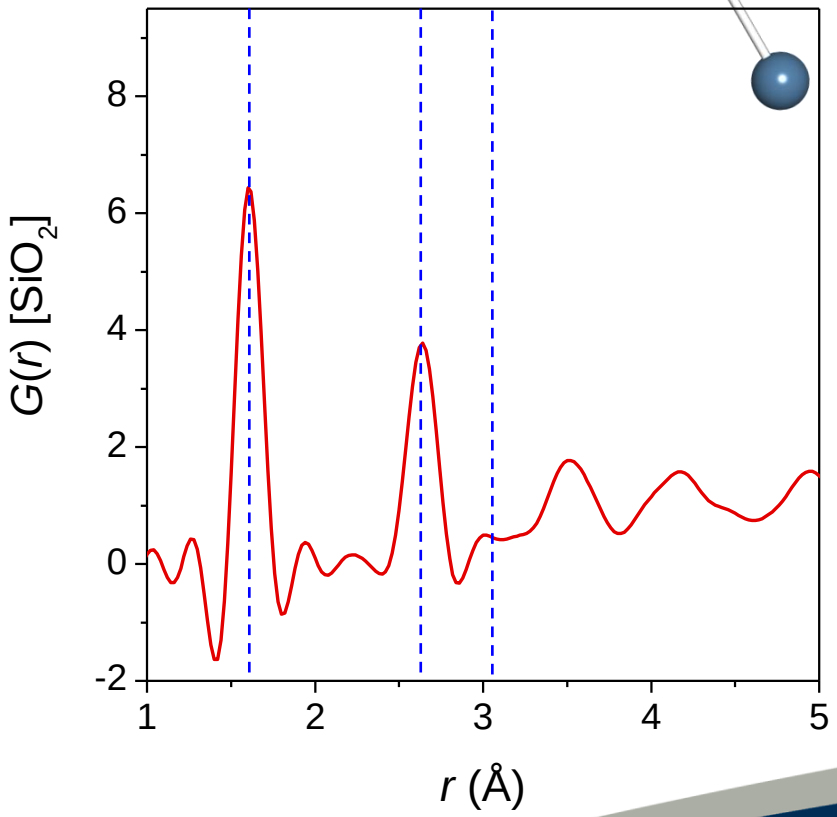


Measuring total scattering data

The importance of Q-range

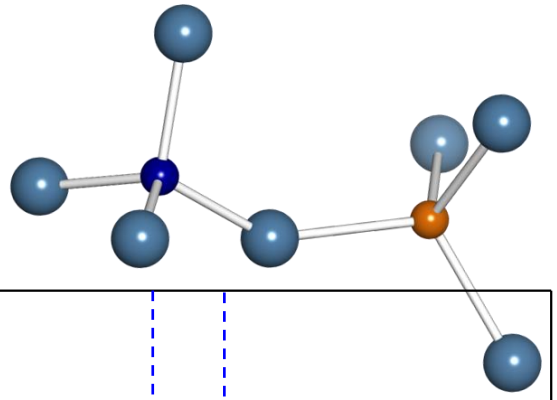


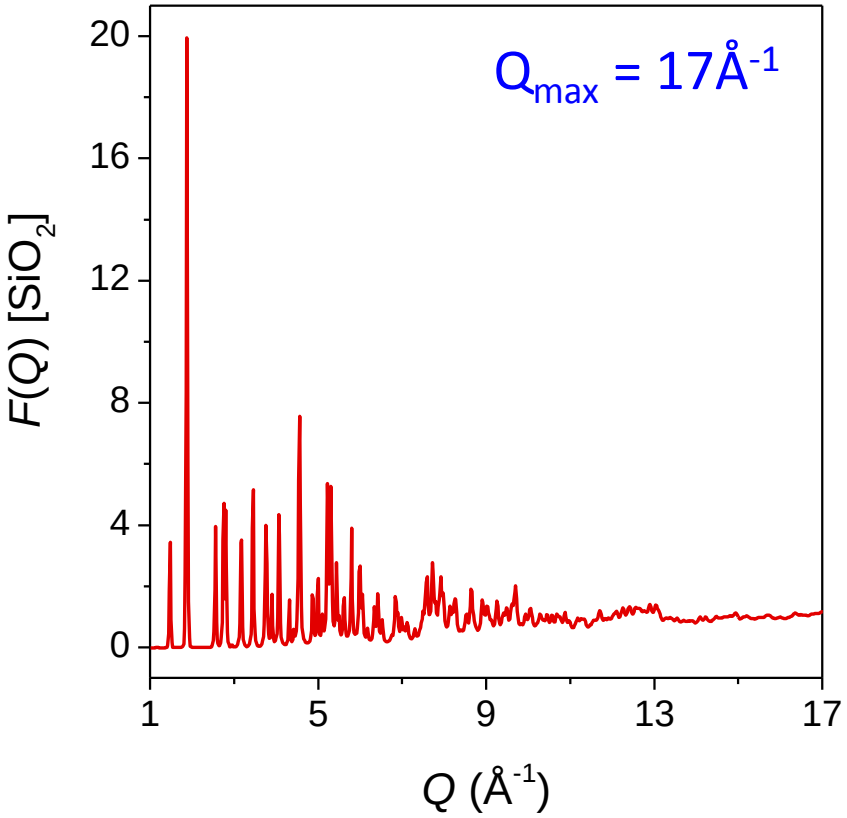


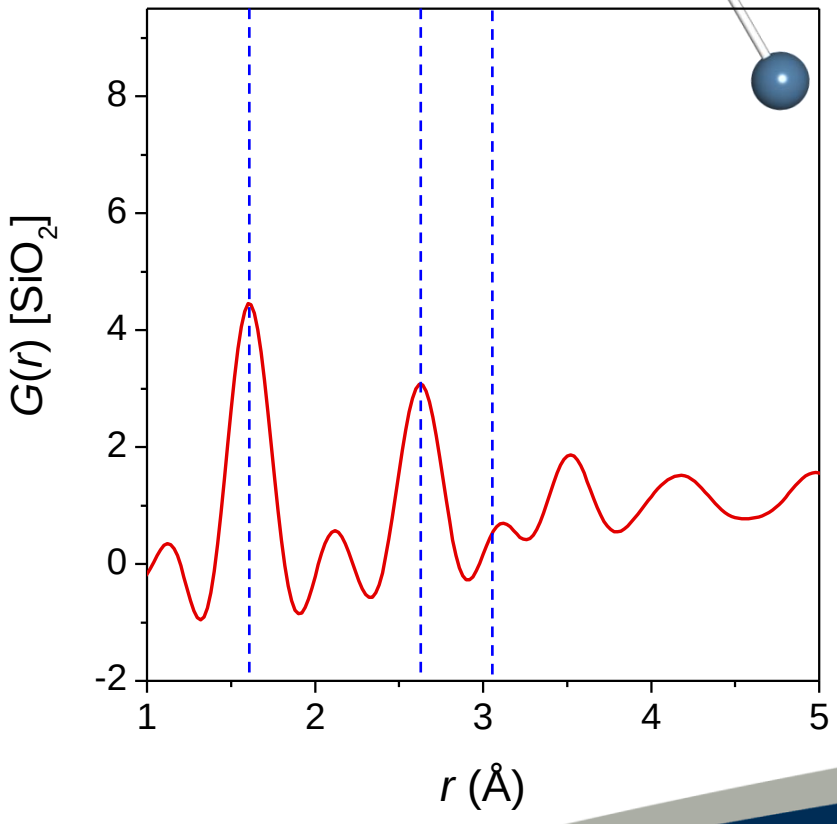


Measuring total scattering data

The importance of Q-range

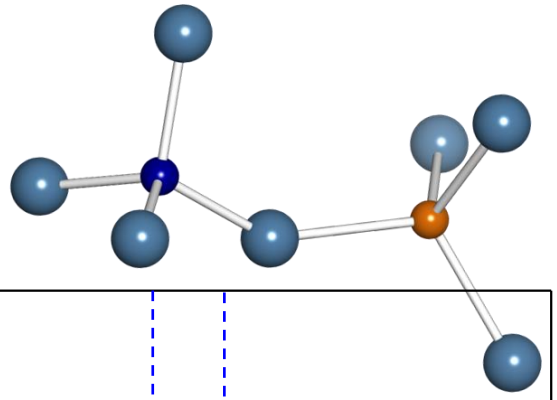


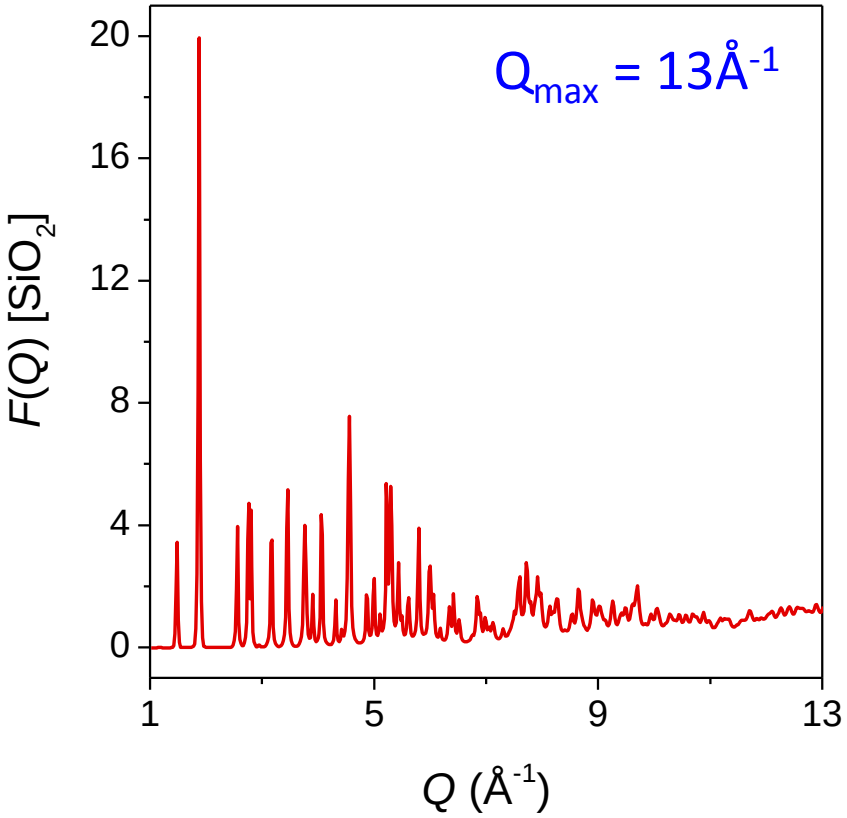


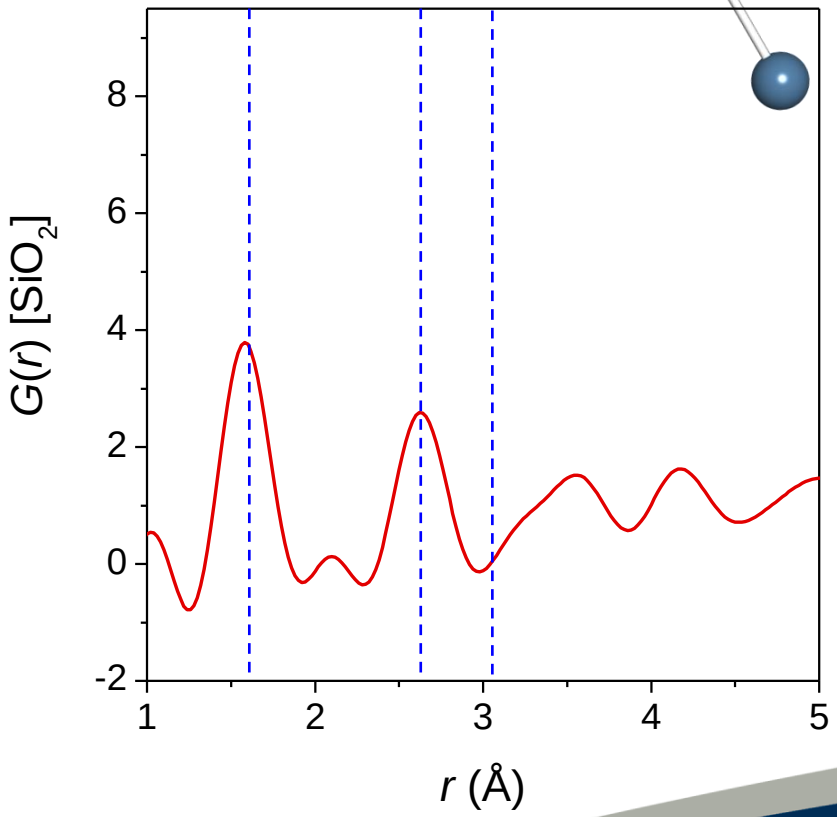


Measuring total scattering data

The importance of Q-range

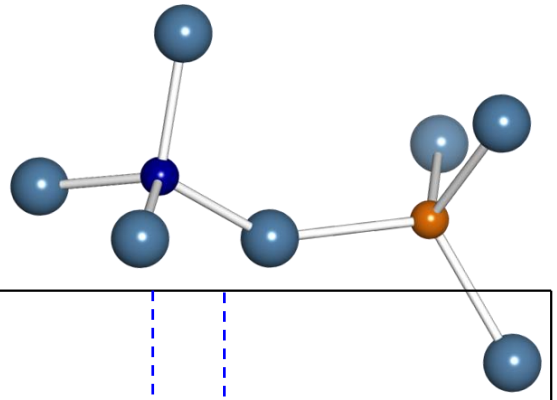


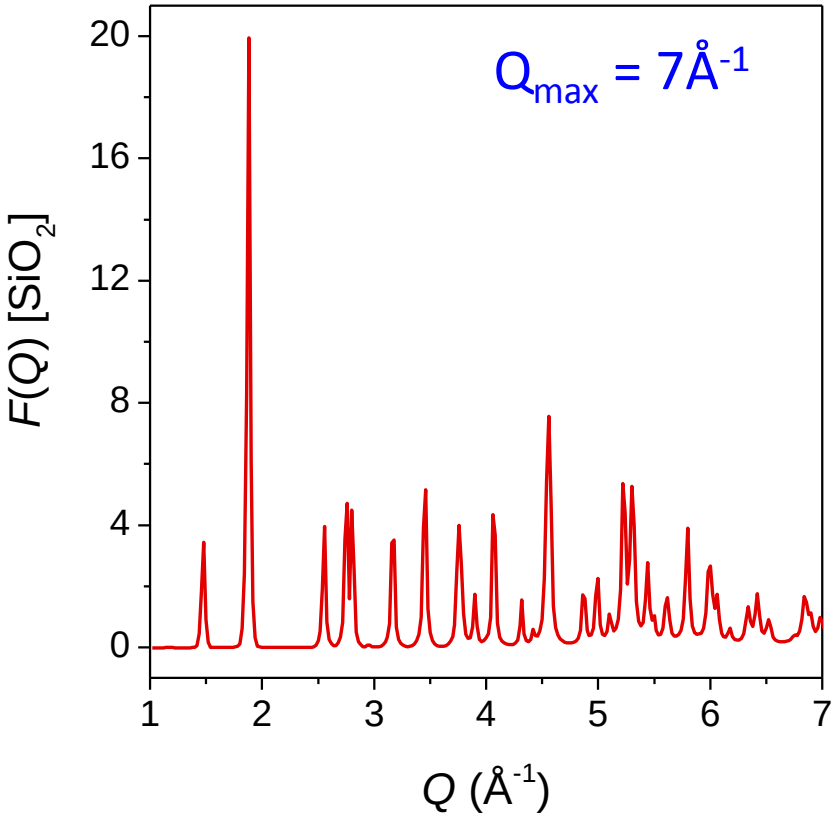


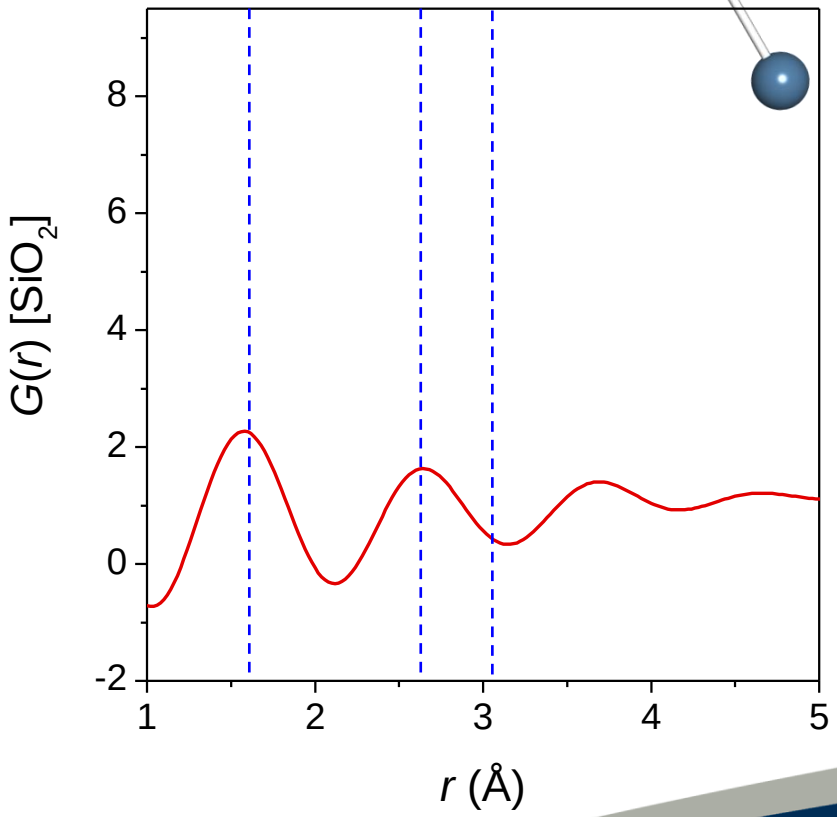


Measuring total scattering data

The importance of Q-range

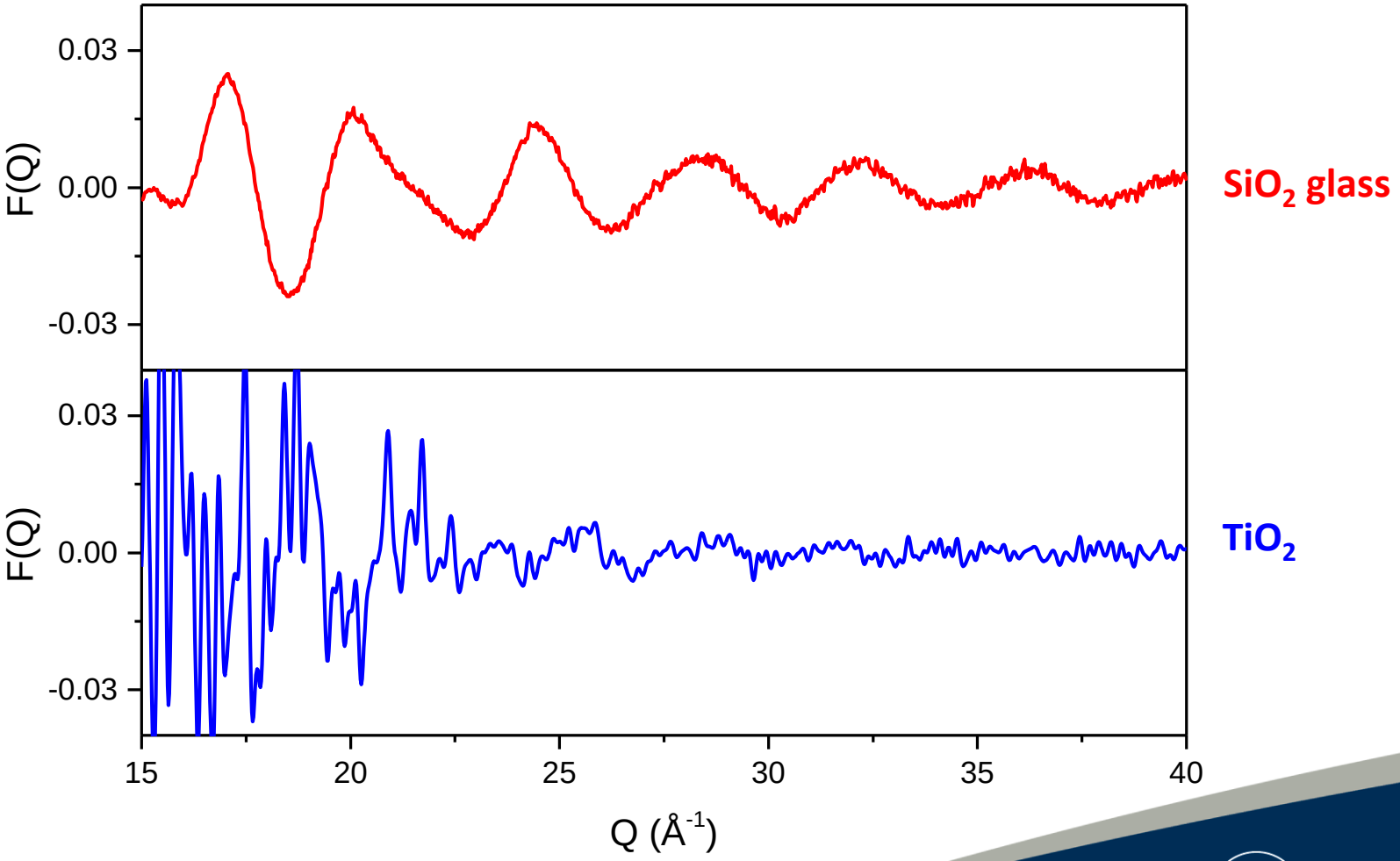






Measuring total scattering data

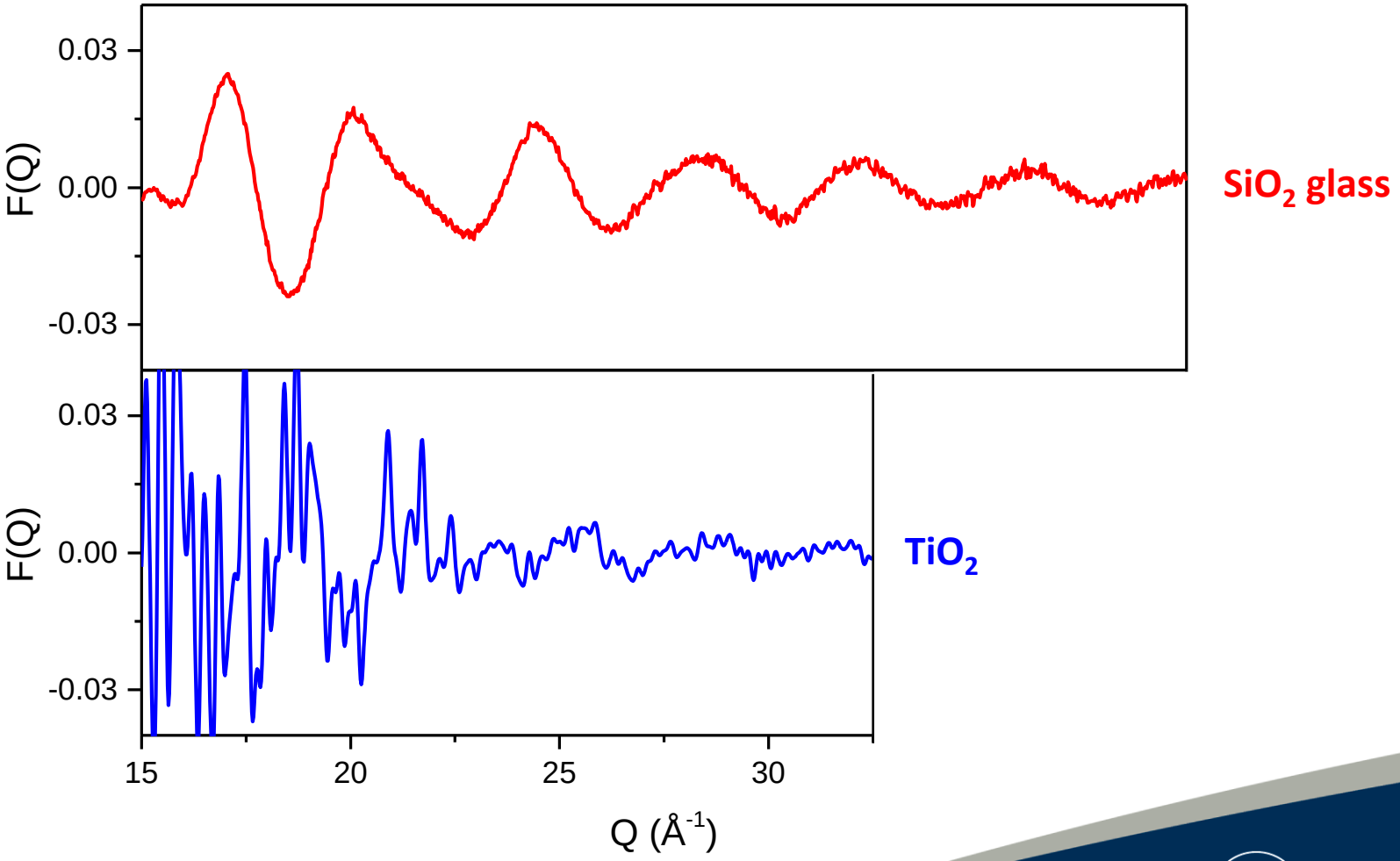
Choose the Q-range that is right for YOUR sample



Science & Technology Facilities Council
ISIS

Measuring total scattering data

Choose the Q-range that is right for YOUR sample



Science & Technology Facilities Council
ISIS

Measuring total scattering data

Measure diffraction data to a high maximum *Q*

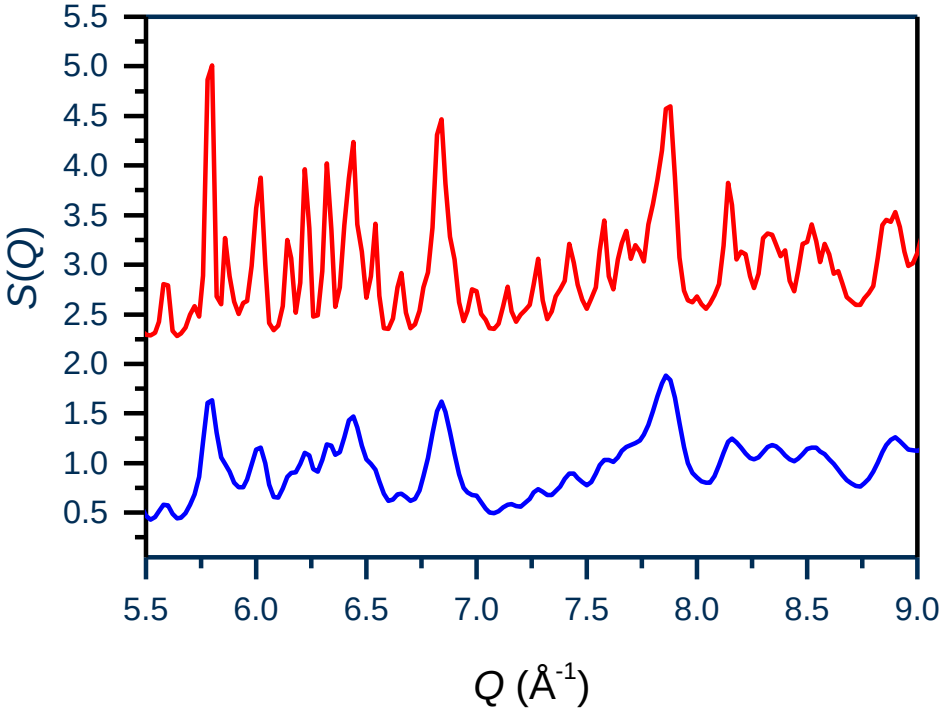
- the spatial resolution of the PDF depends on Q_{max}
- need high energy (short wavelength) X-rays or spallation neutrons

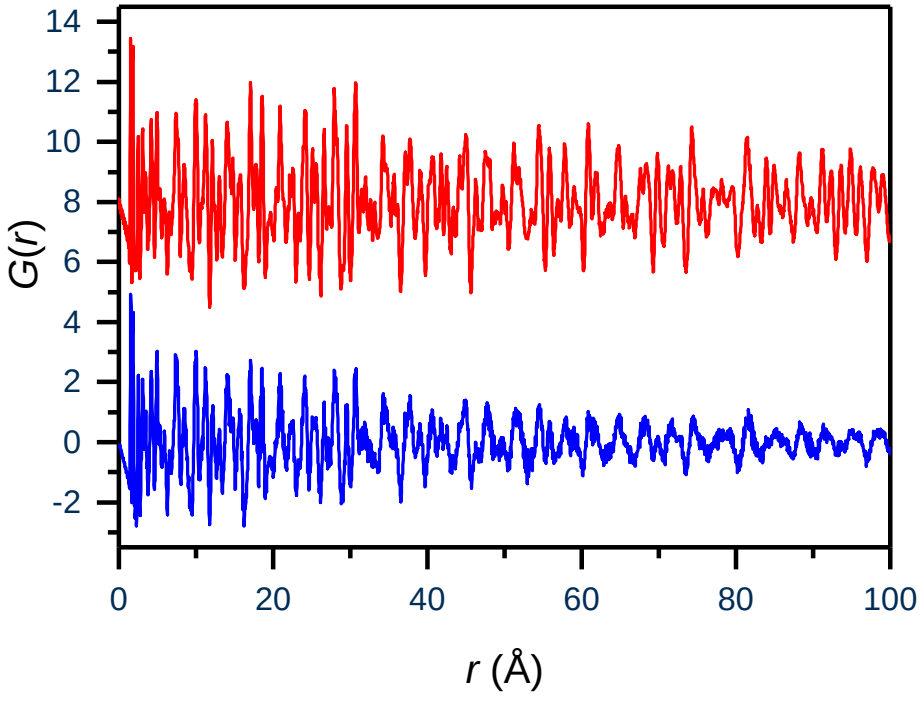
Use an instrument with good reciprocal space resolution

- broadened Bragg peaks result in a dampened PDF

Measuring total scattering data

The effect of Q-space resolution





Higher resolution in reciprocal space = less damping in PDF

Measuring total scattering data

Measure diffraction data to a high maximum Q

- the spatial resolution of the PDF depends on Q_{max}
- need high energy (short wavelength) X-rays or spallation neutrons

Use an instrument with good reciprocal space resolution

- broadened Bragg peaks result in a dampened PDF

Maximise signal-to-noise ratio

- brighter sources
- lots of detectors
- long (enough) measurement times

Measuring total scattering data

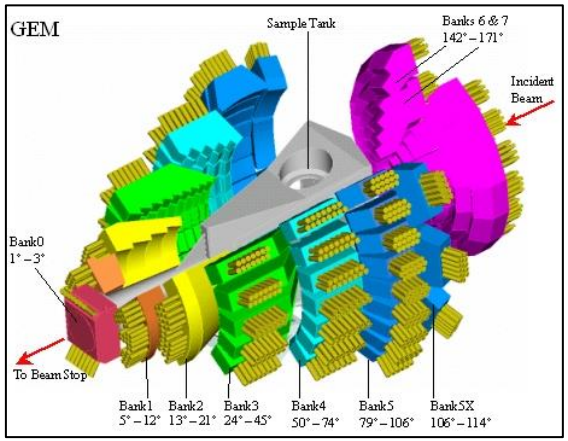
Maximising signal-to-noise ratio

- New, brighter neutron sources offer a much greater flux of neutrons.
- They will only be useful for total scattering if the right instruments are built!
- SNS has NOMAD, also second target station coming?
- J-PARC has NOVA.
- ESS ???

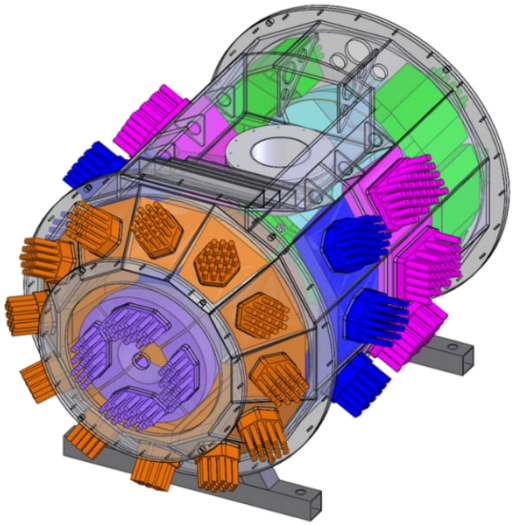
Measuring total scattering data

Maximising signal-to-noise ratio

- Less bright sources can maximise count-rate by using as many detectors as possible around the sample.
- This also increases the d/Q range accessible, BUT…
- …the instrument resolution varies with 2θ and flight path.
- Which makes data processing somewhat more complicated!



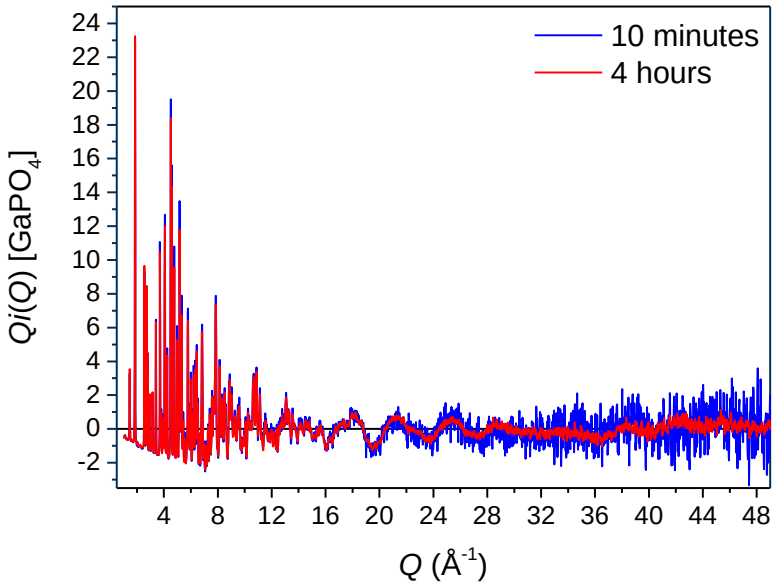
GEM
Since 1999

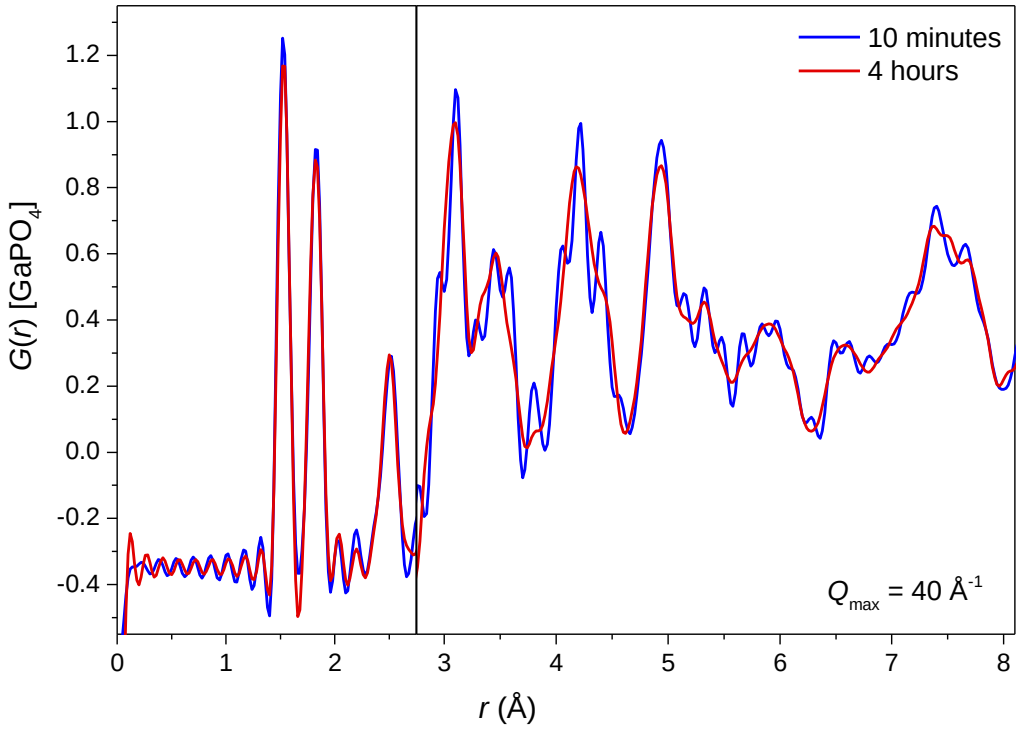


Polaris upgrade
Since 2012

Measuring total scattering data

Maximising signal-to-noise ratio





- It is not surprising that shorter measurements produce noisier data.

- How much of a problem this is will depend on the specifics of the sample and experiment!

Measuring total scattering data

Measure diffraction data to a high maximum Q

- the spatial resolution of the PDF depends on Q_{max}
- need high energy (short wavelength) X-rays or spallation neutrons

Use an instrument with good reciprocal space resolution

- broadened Bragg peaks result in a dampened PDF

Maximise signal-to-noise ratio

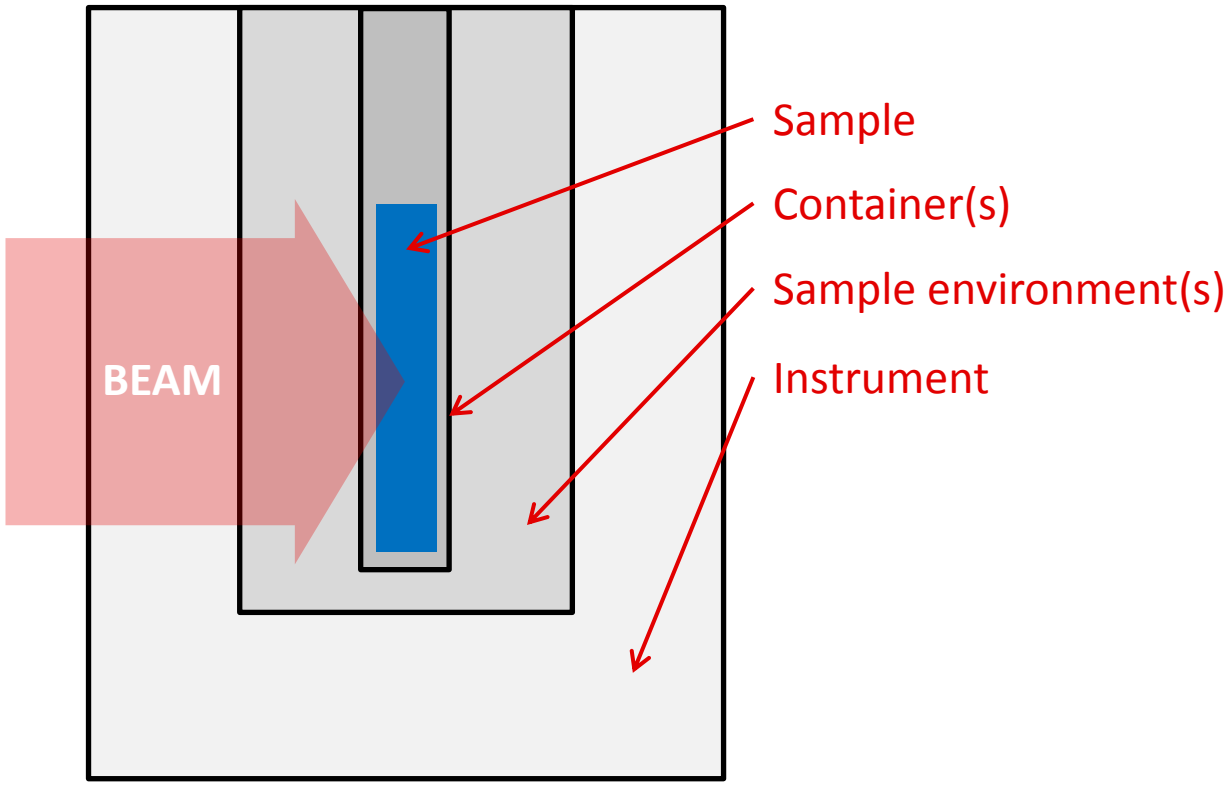
- brighter sources
- lots of detectors
- long (enough) measurement times

Measure all background contributions carefully

- non-sample scattering must be removed

Measuring total scattering data

In an ideal situation we would have a sample floating in "mid-air", but in most cases this isn't going to be possible…

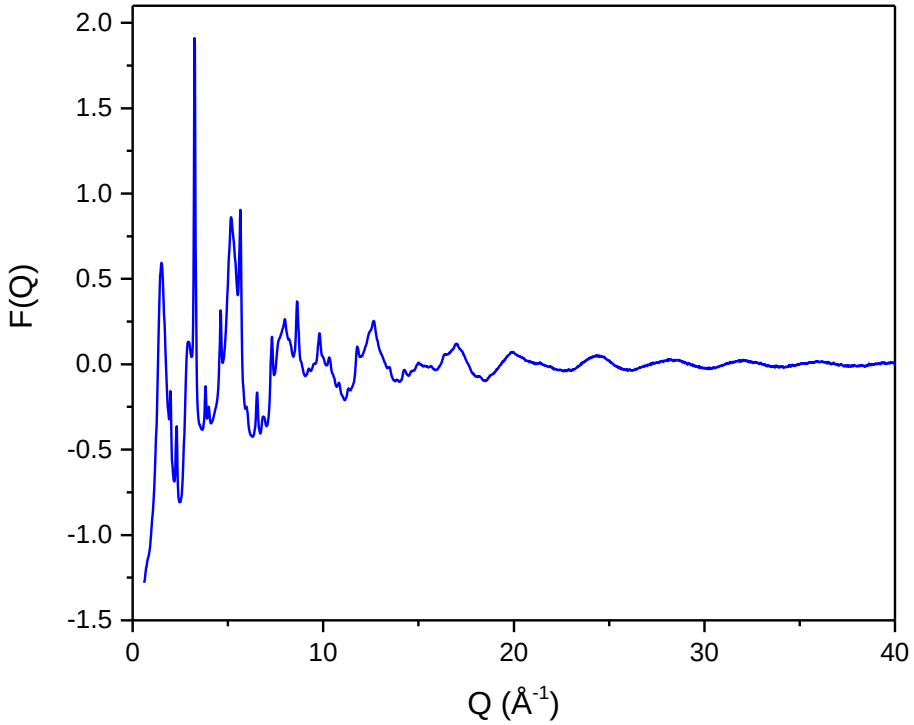


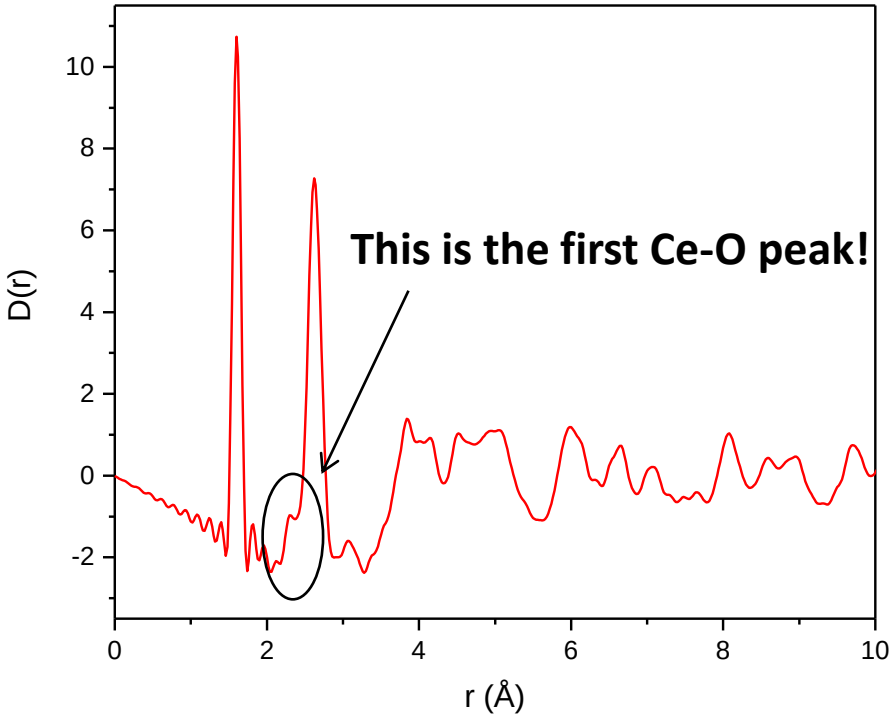
Measuring total scattering data

- Removing “background” is easy if the sample is in a thin vanadium can or TiZr cell.
- It is much more difficult when the environment is more complicated, e.g. in situ cells or the Paris Edinburgh press.
- More, and longer, background measurements will be required.
- SE design should seek to minimise background contributions.
- Data quality may always be compromised?

Measuring total scattering data

Minimising and removing background scattering





- These data are from several grams of CeO_2 in a glass tube.
- Although CeO_2 Bragg peaks are clearly visible, the total scattering is dominated by the tube!

Measuring total scattering data

Measure diffraction data to a high maximum Q

- the spatial resolution of the PDF depends on Q_{max}
- need high energy (short wavelength) X-rays or spallation neutrons

Use an instrument with good reciprocal space resolution

- broadened Bragg peaks result in a dampened PDF

Maximise signal-to-noise ratio

- brighter sources
- lots of detectors
- long (enough) measurement times

Measure all background contributions carefully

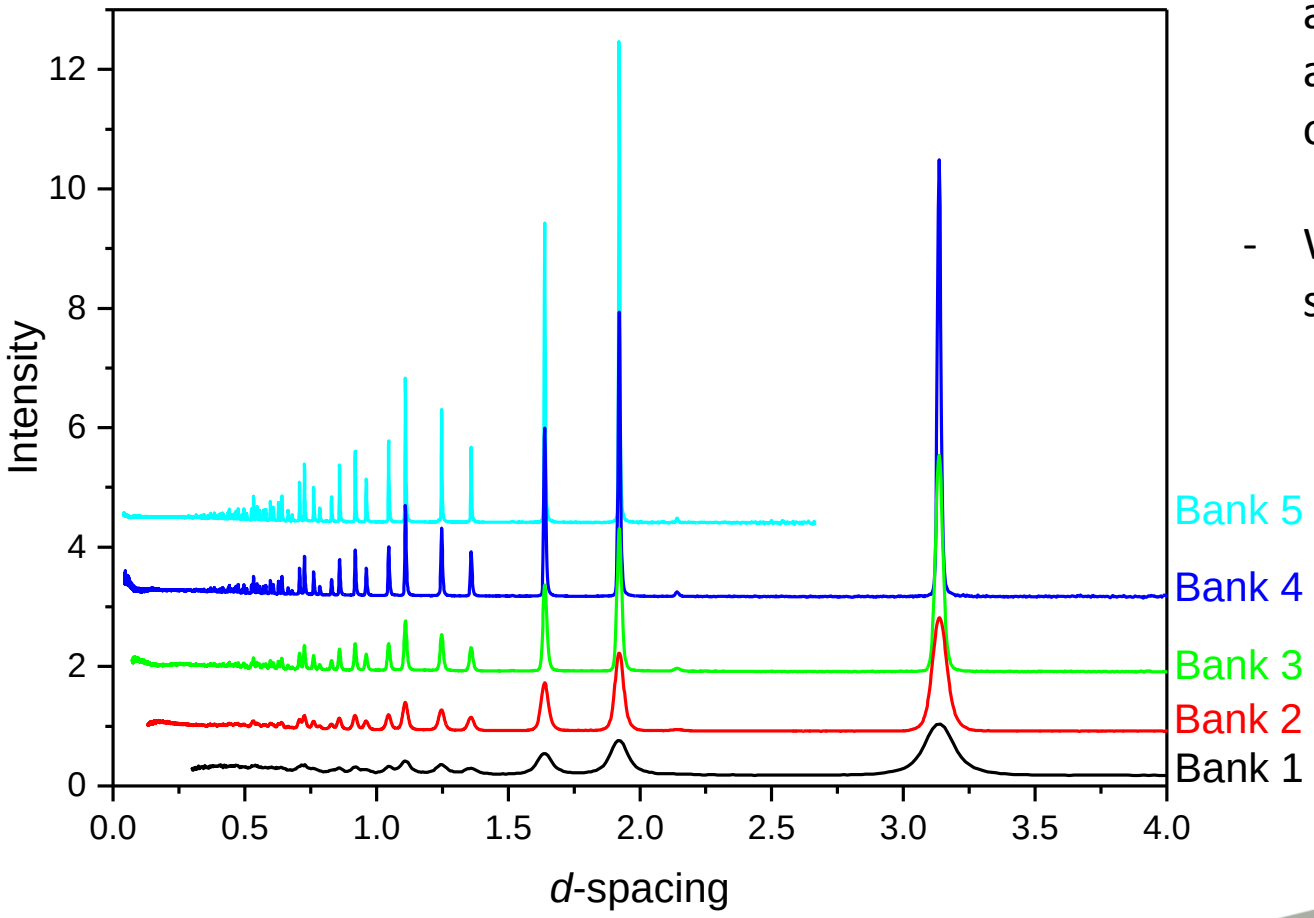
- non-sample scattering must be removed

Process the data carefully and appropriately

- put the data on an absolute scale
- understand instrument geometry and calibration

Measuring total scattering data

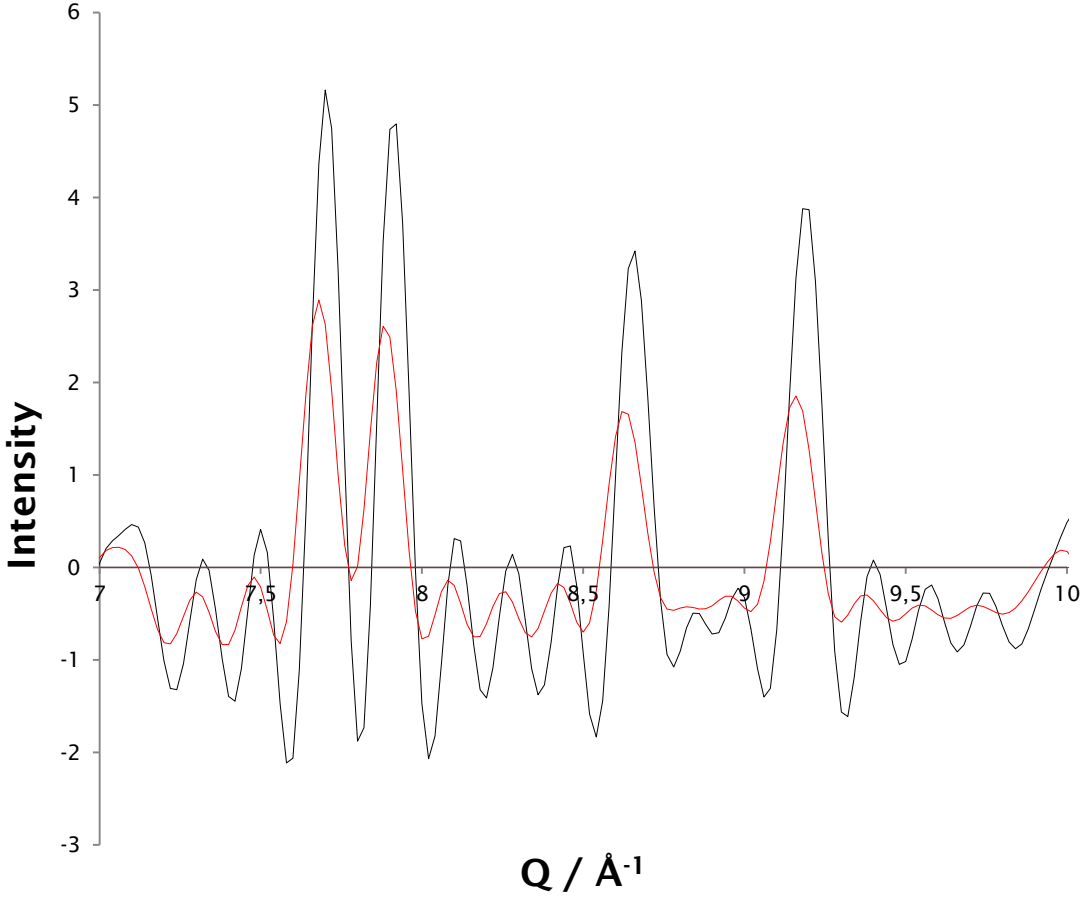
Going from raw counts to F(Q)

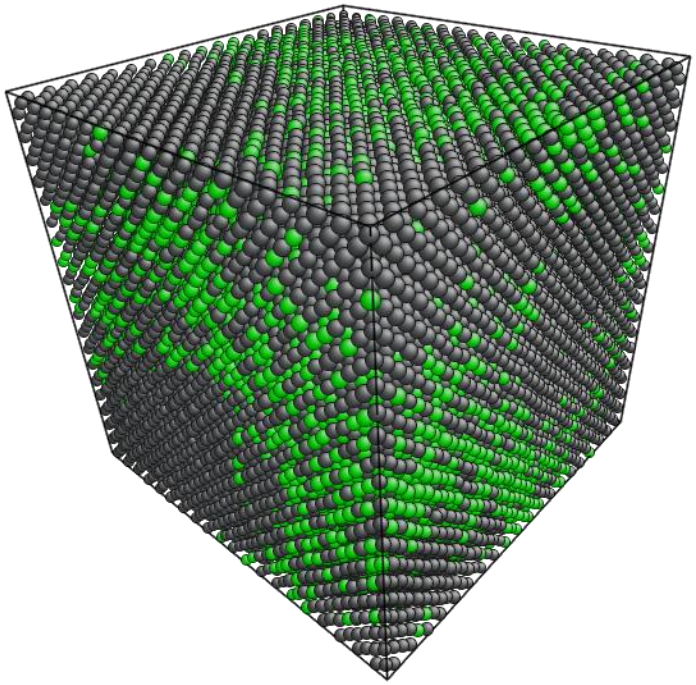


- Generally for diffraction analysis, the raw spectra are grouped into “banks” of similar scattering angle.
- What about total scattering?

Measuring total scattering data

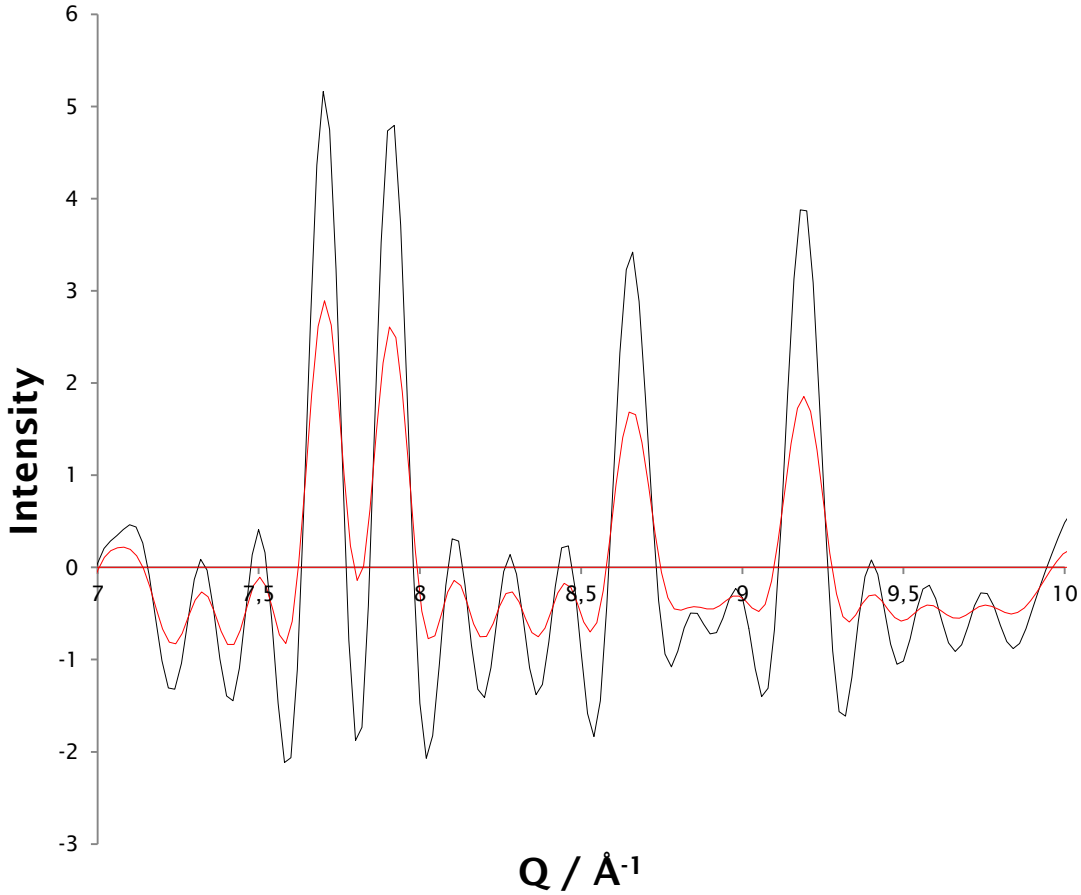
The dangers of incorrect calibration

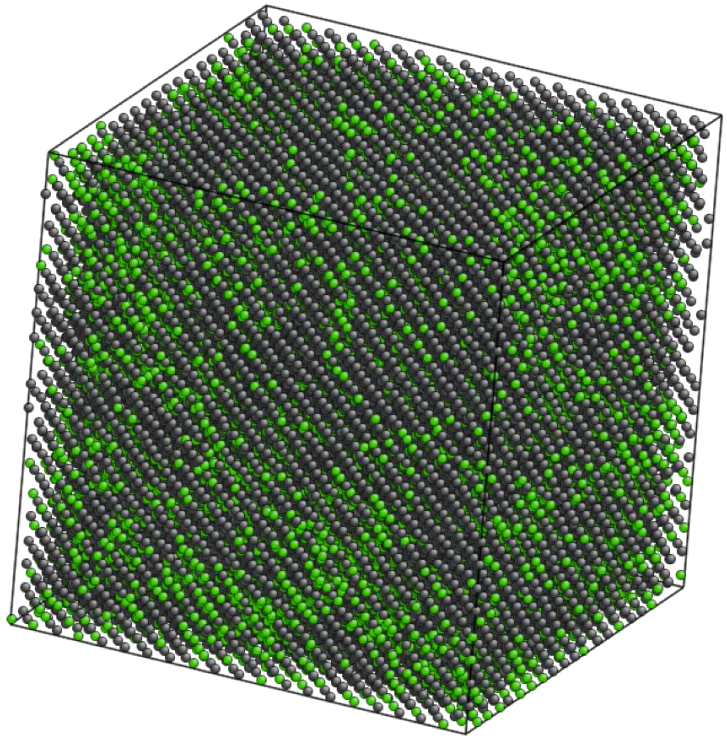




Measuring total scattering data

The dangers of incorrect calibration



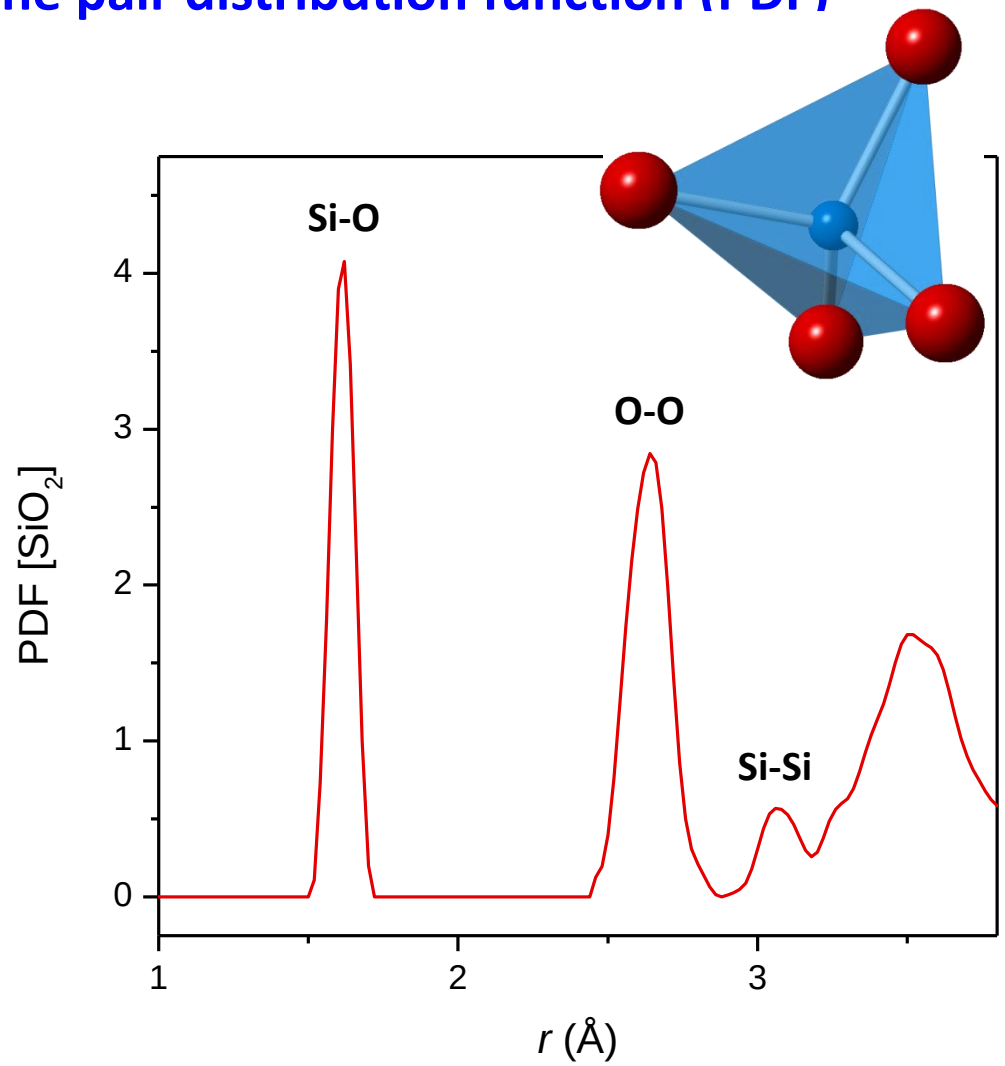


Modelling total scattering data

Science & Technology Facilities Council
ISIS

Introduction

The pair distribution function (PDF)



Visual inspection can provide information about:

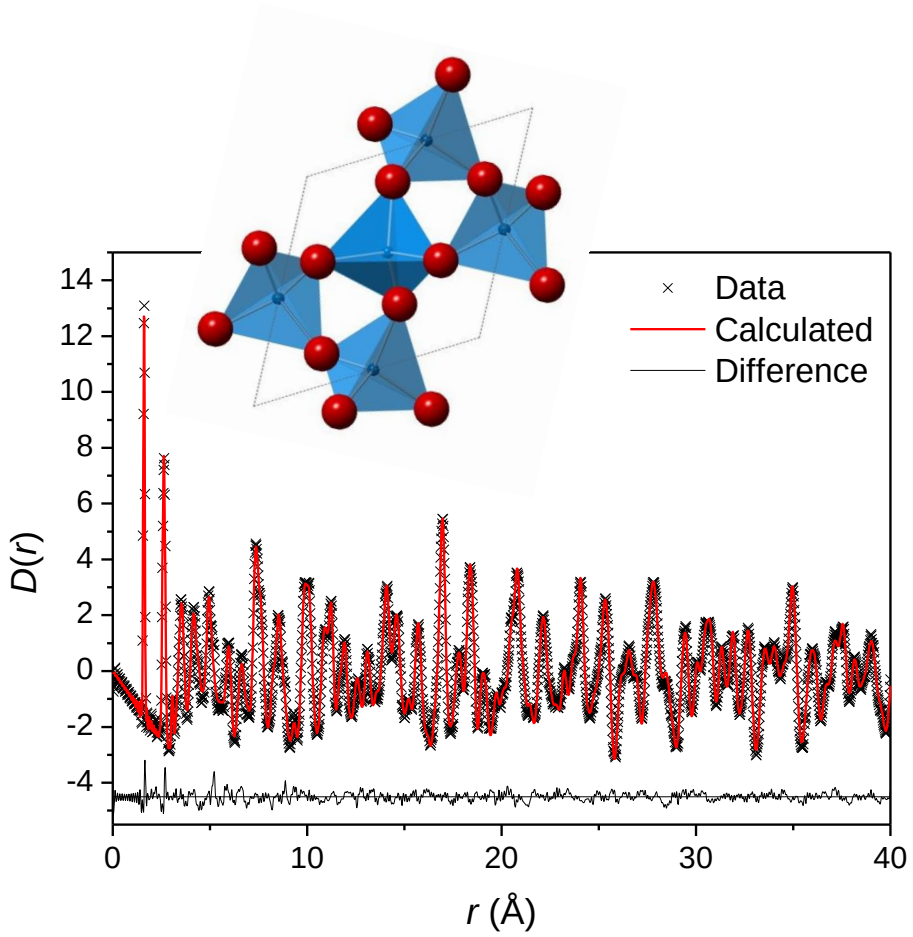
- bond lengths
- coordination numbers
- level of disorder
- identities of species involved

…more detail comes from **modelling**!

Modelling total scattering data

Modelling techniques

There are two main ways in which detailed structural information can be extracted from total scattering data: **small box** and big box modelling.



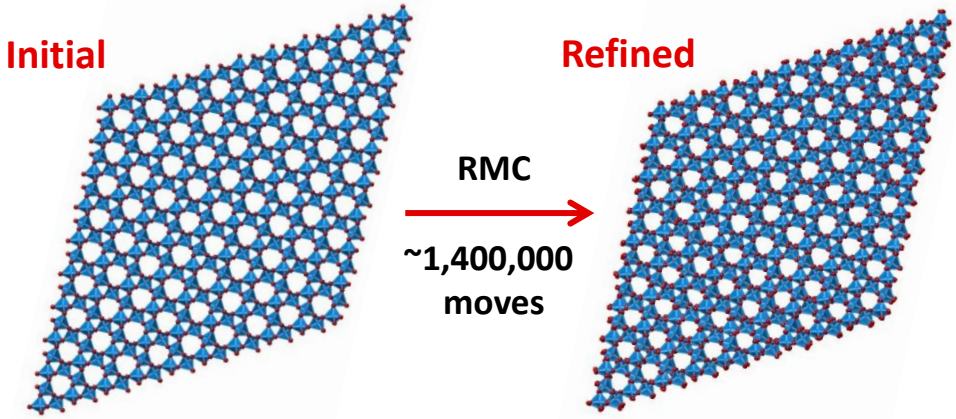
Small box modelling:

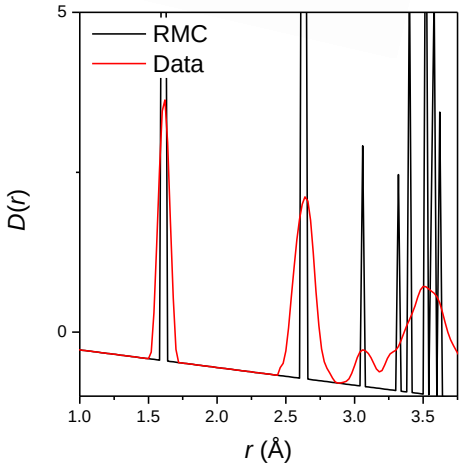
- Crystal structure refined to fit the PDF: **"real-space Rietveld"**
- Limited to crystallographic descriptions of structural parameters.
- Identify discrepancies between average and local structure.

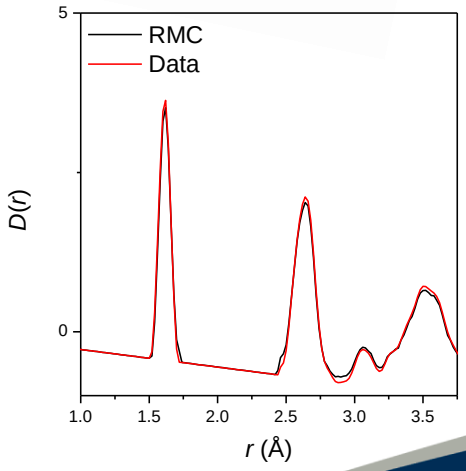
Modelling total scattering data

Modelling techniques

There are two main ways in which detailed structural information can be extracted from total scattering data: small box and **big box** modelling.



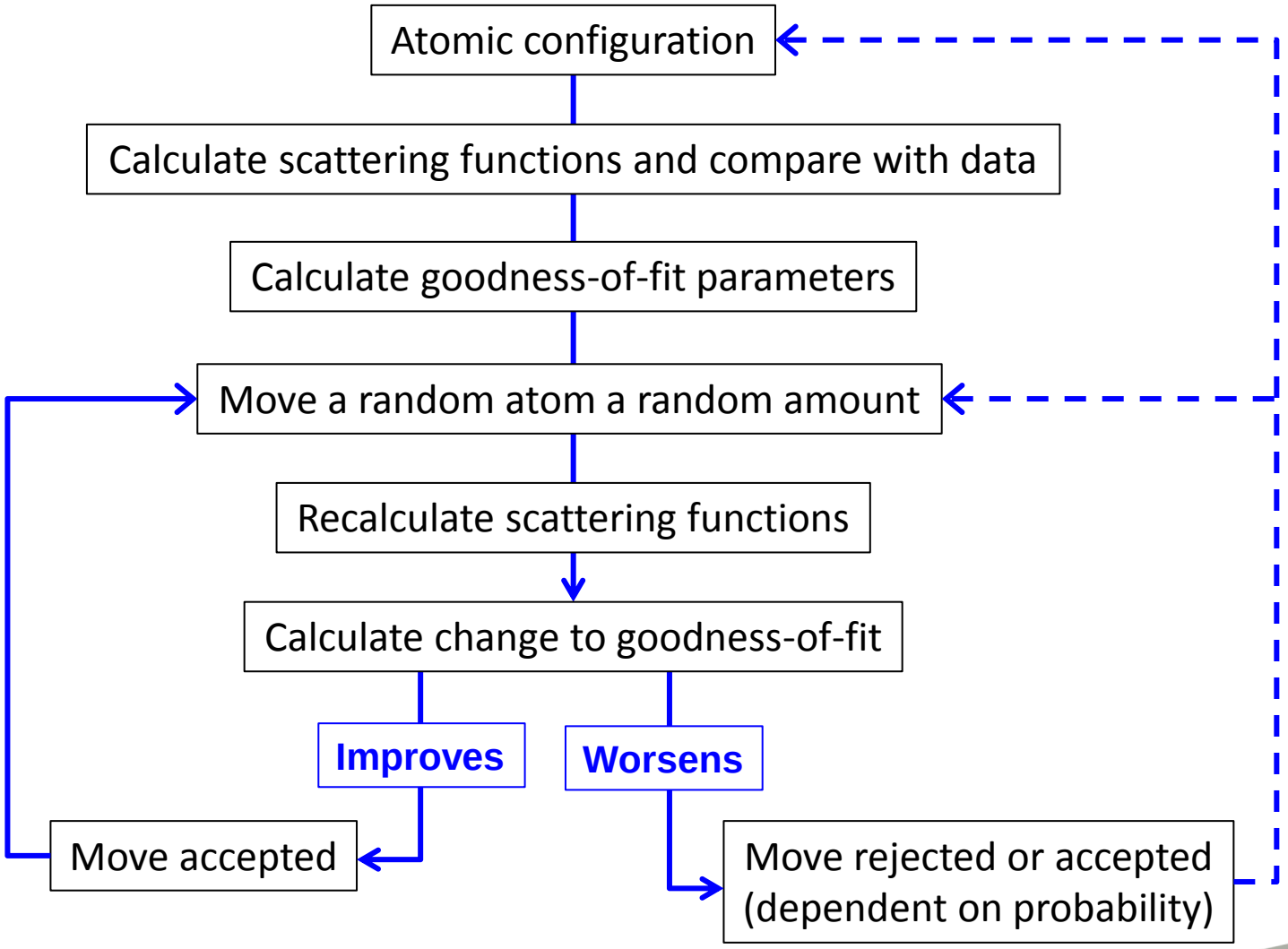




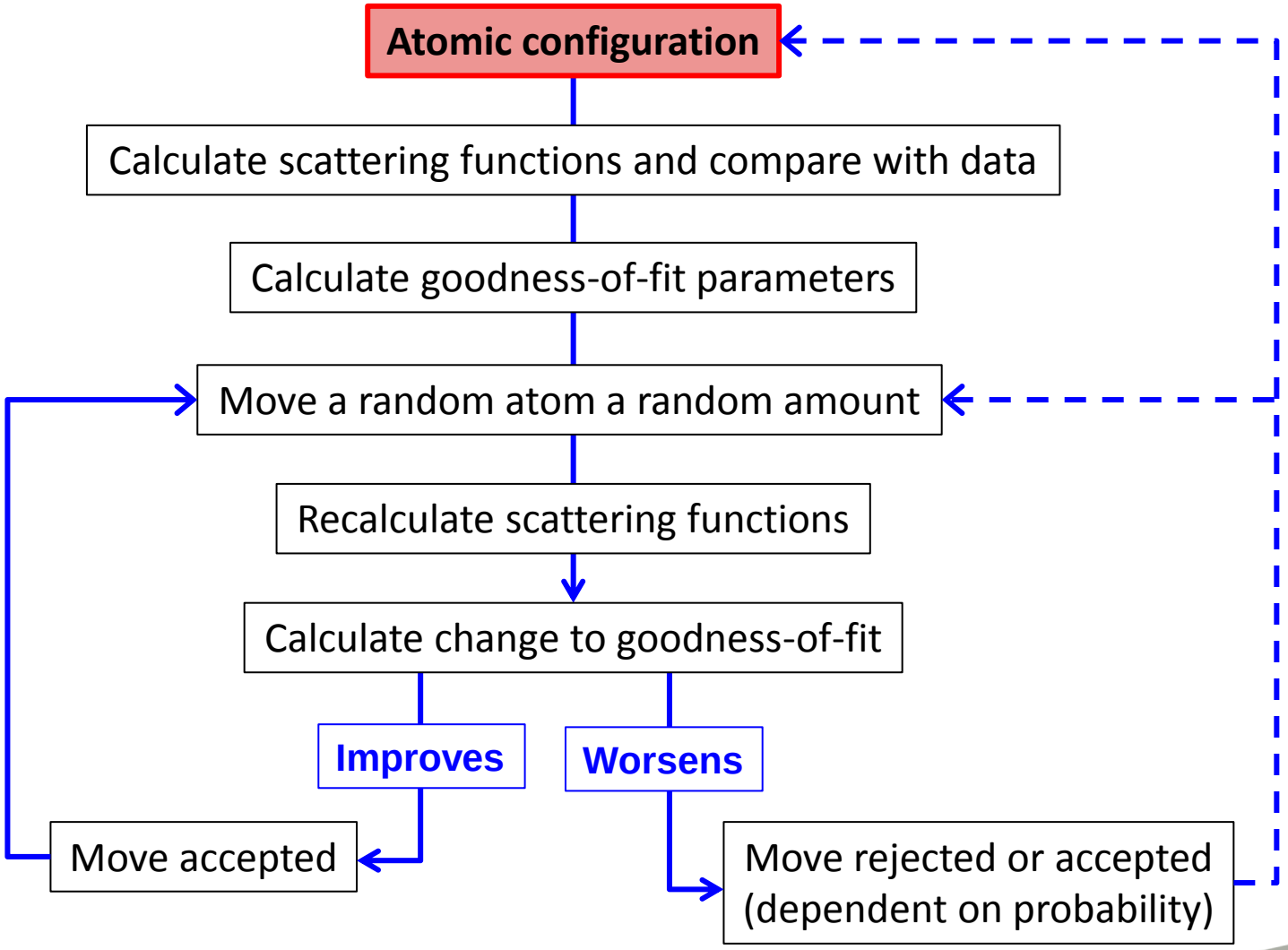
Big box modelling:

- Reverse Monte Carlo (RMC).
- Supercell of >10,000 atoms, moved at random to obtain best possible agreement with all data.
- **Atomistic model that is consistent with input data.**
- Not constrained by symmetry.

The Reverse Monte Carlo Algorithm



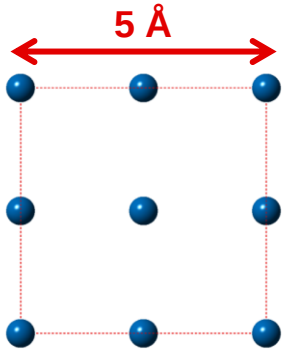
The Reverse Monte Carlo Algorithm



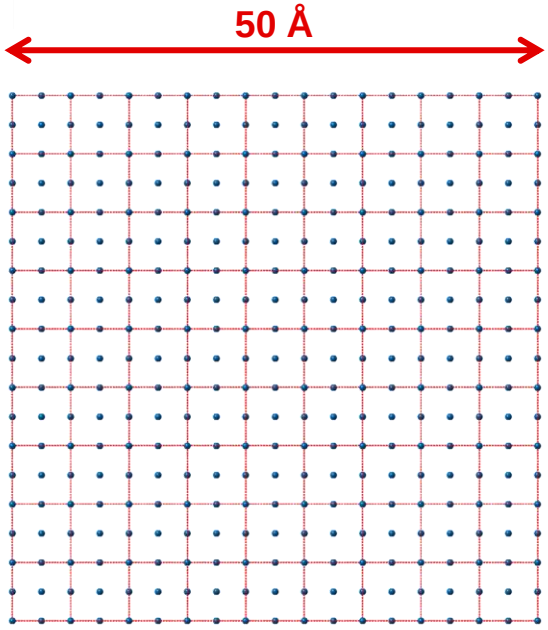
The Reverse Monte Carlo Algorithm

Atomic configuration

- This is a “box of atoms”
- Needs to be fairly large: 10,000 – 100,000 atoms
- Crystalline material:
  - supercell of the (refined) unit cell
  - careful if partial/mixed occupancy
  - check for unphysical distances
- Amorphous material:
  - distribute atoms randomly
  - molecular dynamics simulation
  - other possibilities?

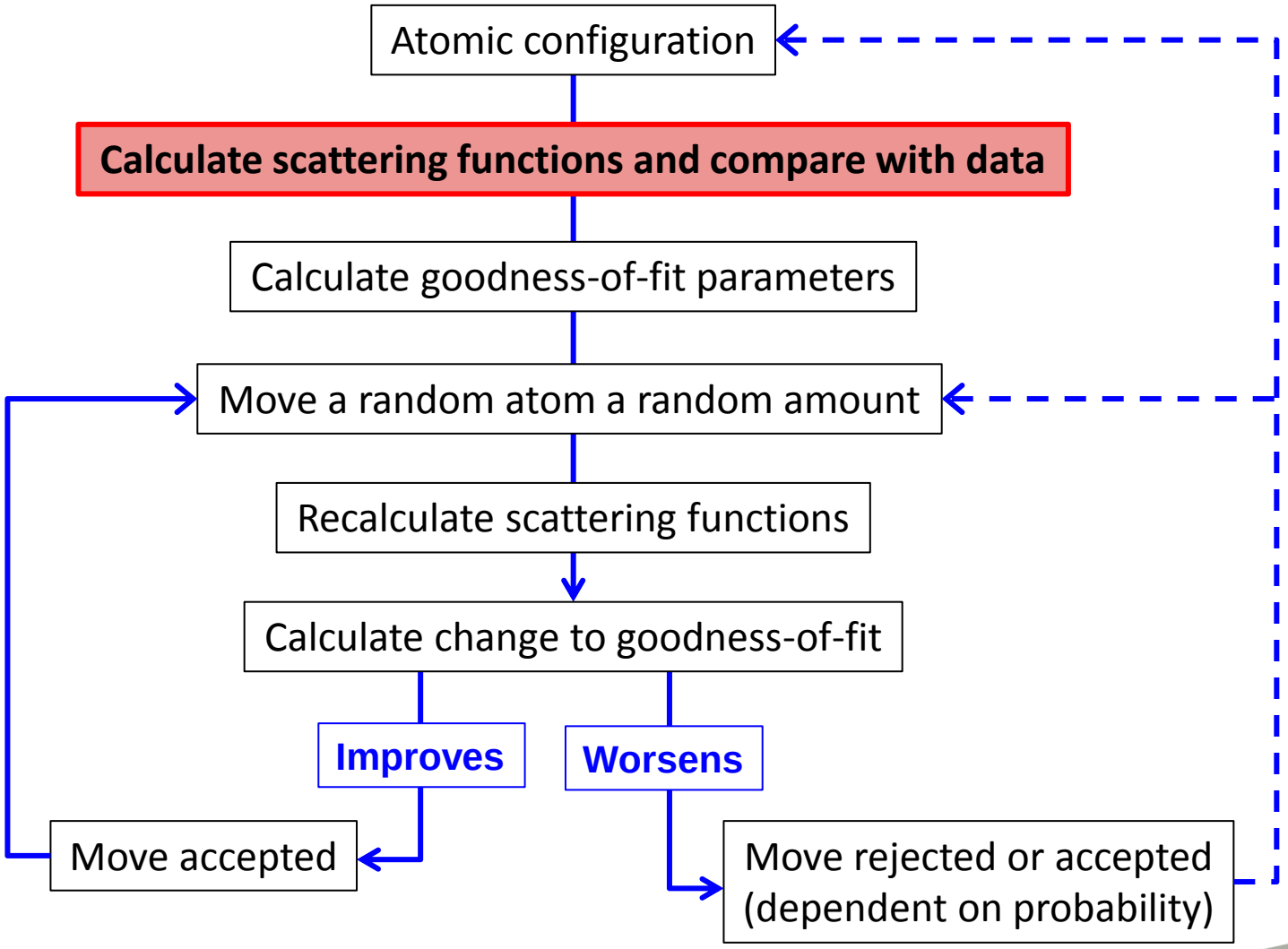


Single unit cell

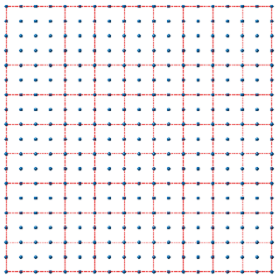


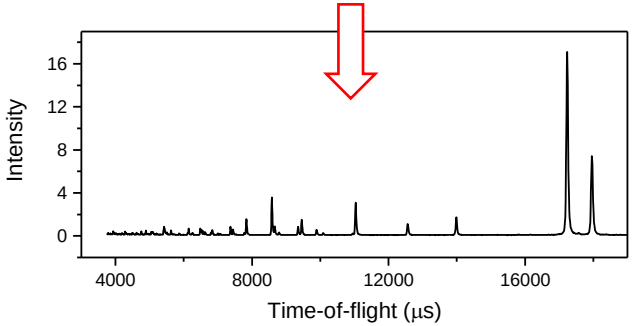
10 x 10 x 10 supercell

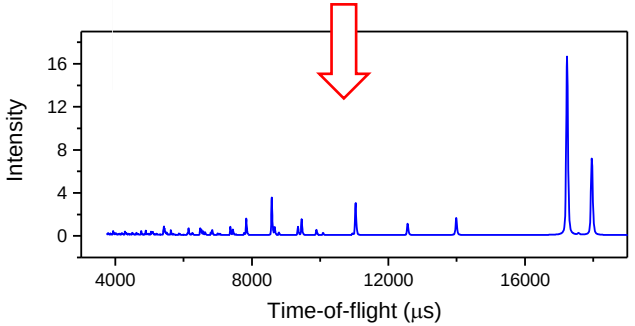
The Reverse Monte Carlo Algorithm

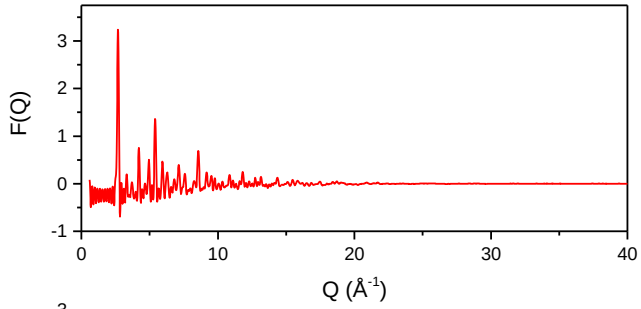


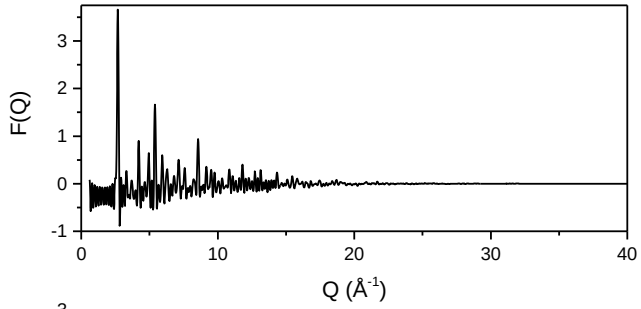
The Reverse Monte Carlo Algorithm

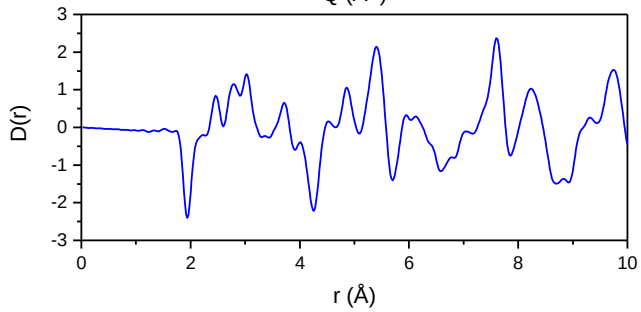


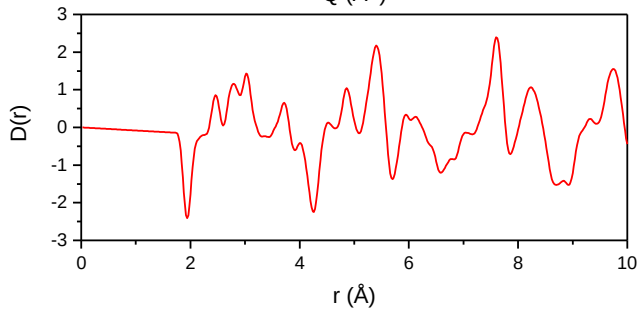




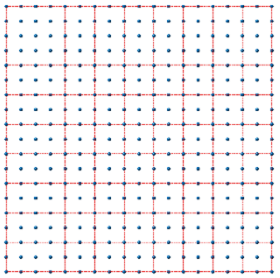


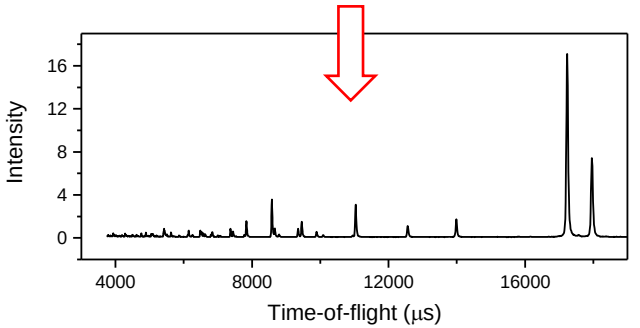


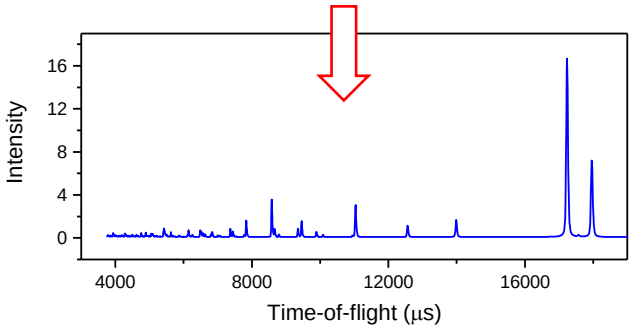


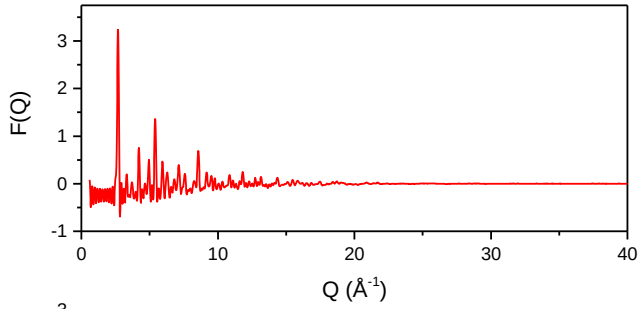


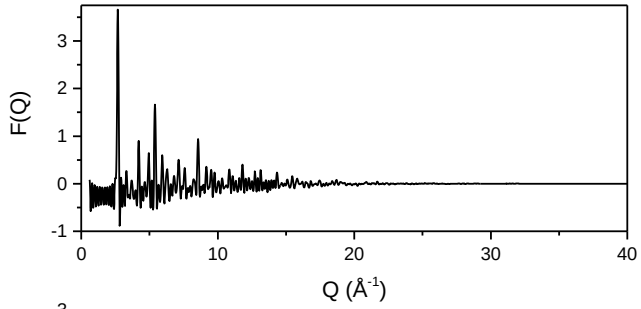
The Reverse Monte Carlo Algorithm

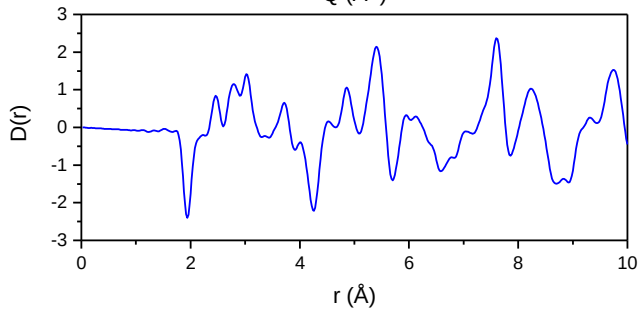


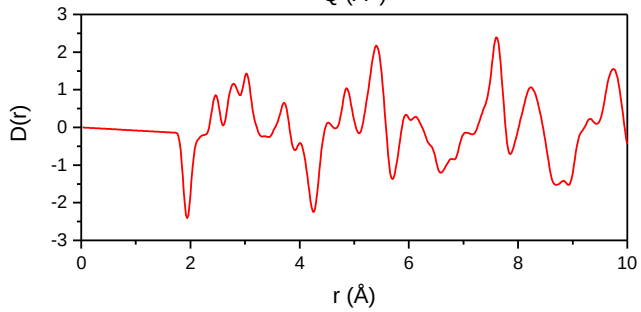




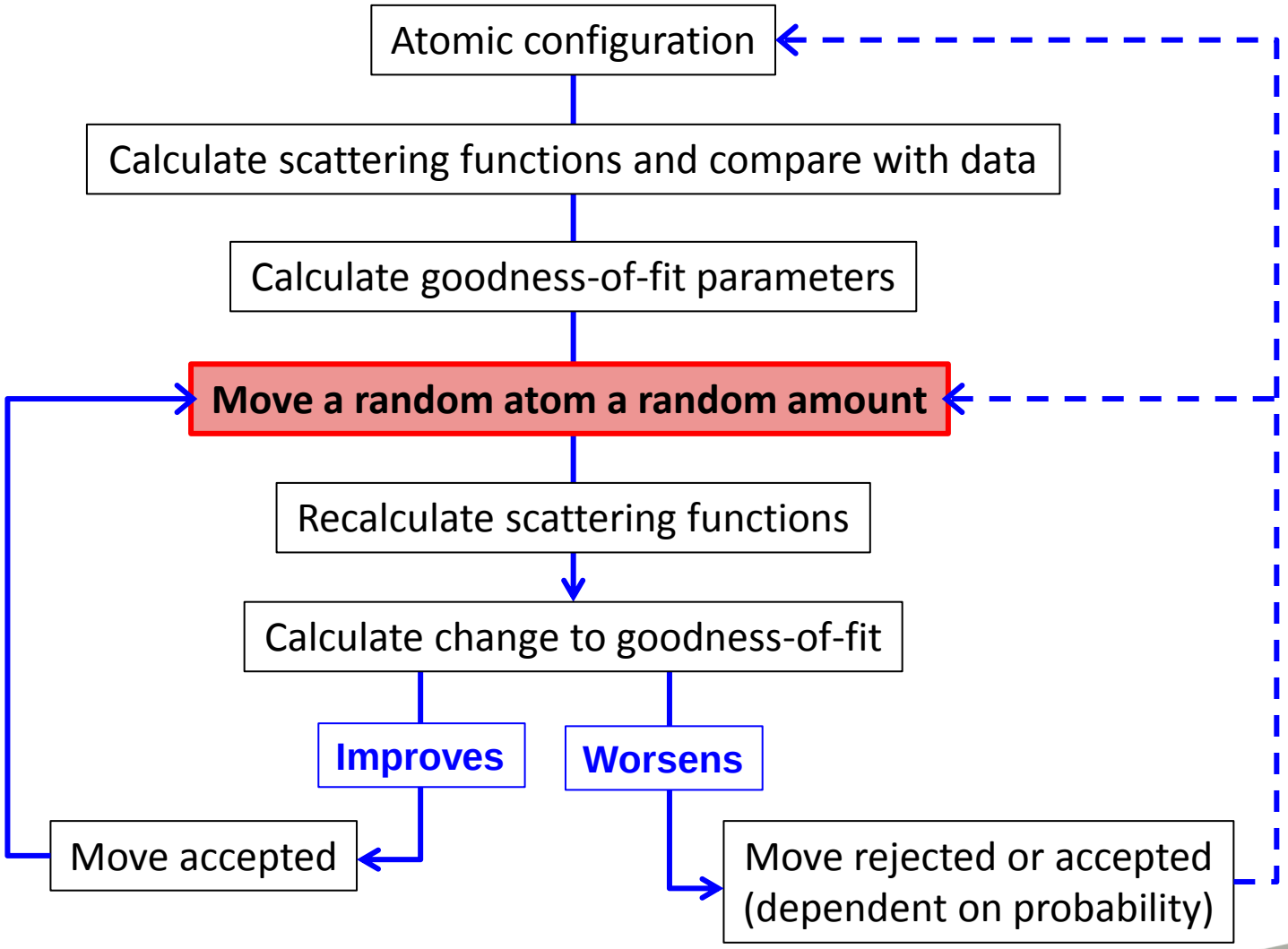








The Reverse Monte Carlo Algorithm



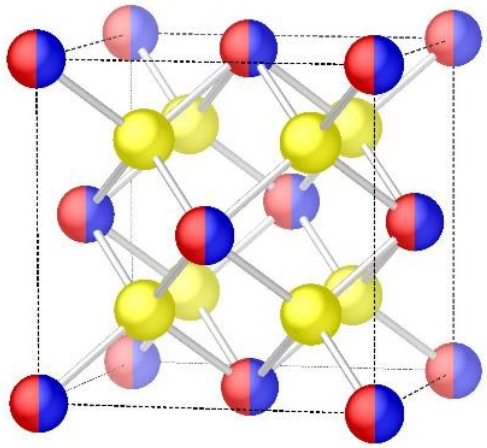
The Reverse Monte Carlo Algorithm

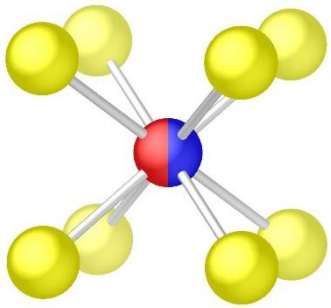
The power of randomness

- Without the constraints of symmetry, the RMC algorithm can explore more of phase space.

- This can be necessary to model certain types of systems.

- Take this doped CeO_2 as an example…

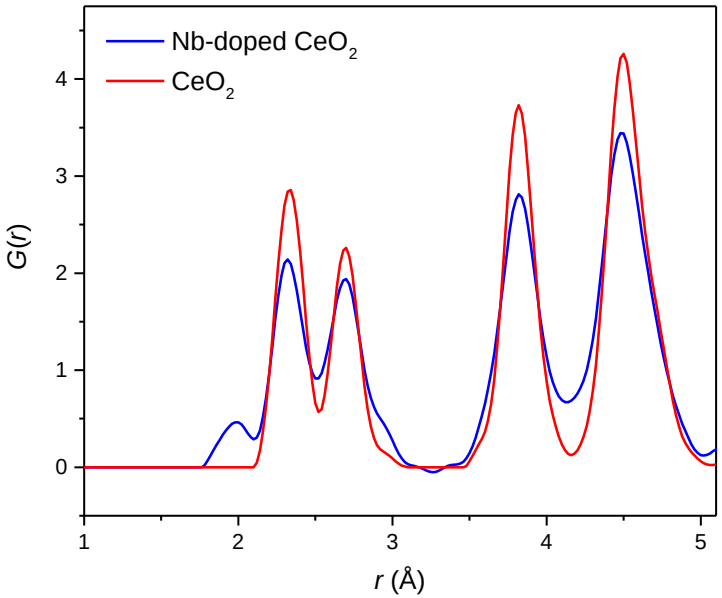


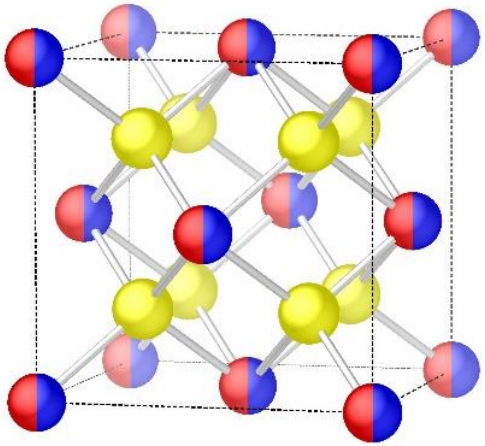


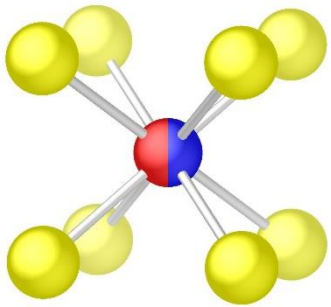
The Reverse Monte Carlo Algorithm

The power of randomness

- Without the constraints of symmetry, the RMC algorithm can explore more of phase space.
- This can be necessary to model certain types of systems.
- Take this doped CeO_2 as an example…



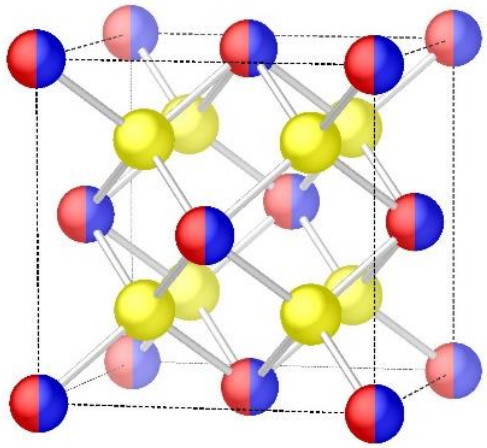


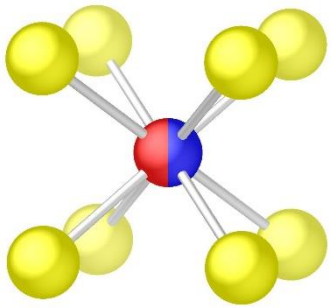


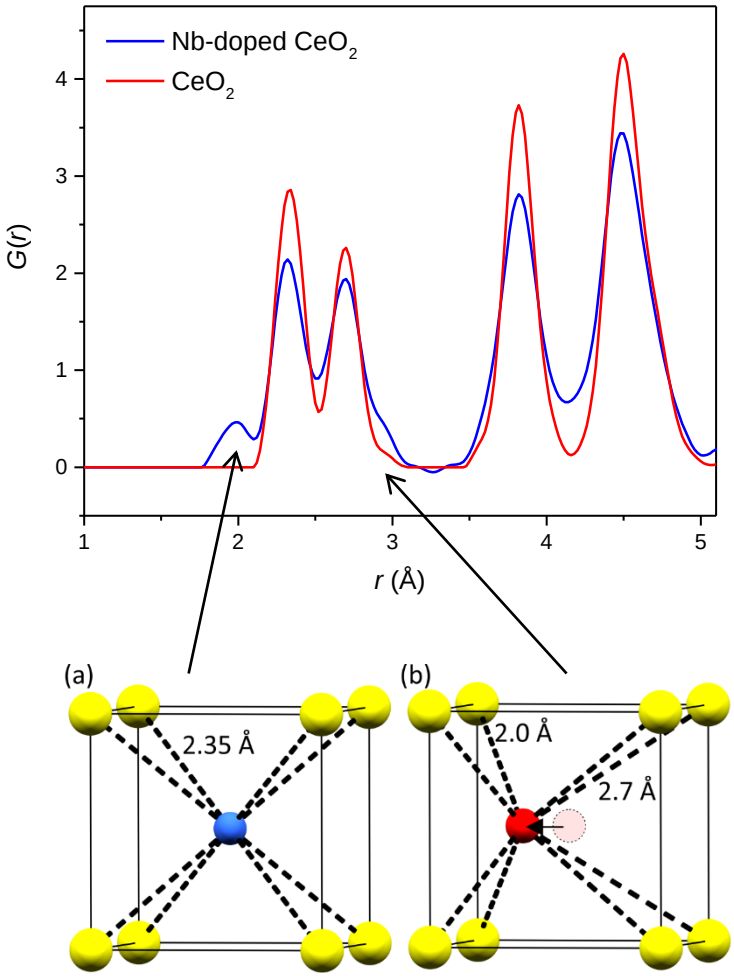
The Reverse Monte Carlo Algorithm

The power of randomness

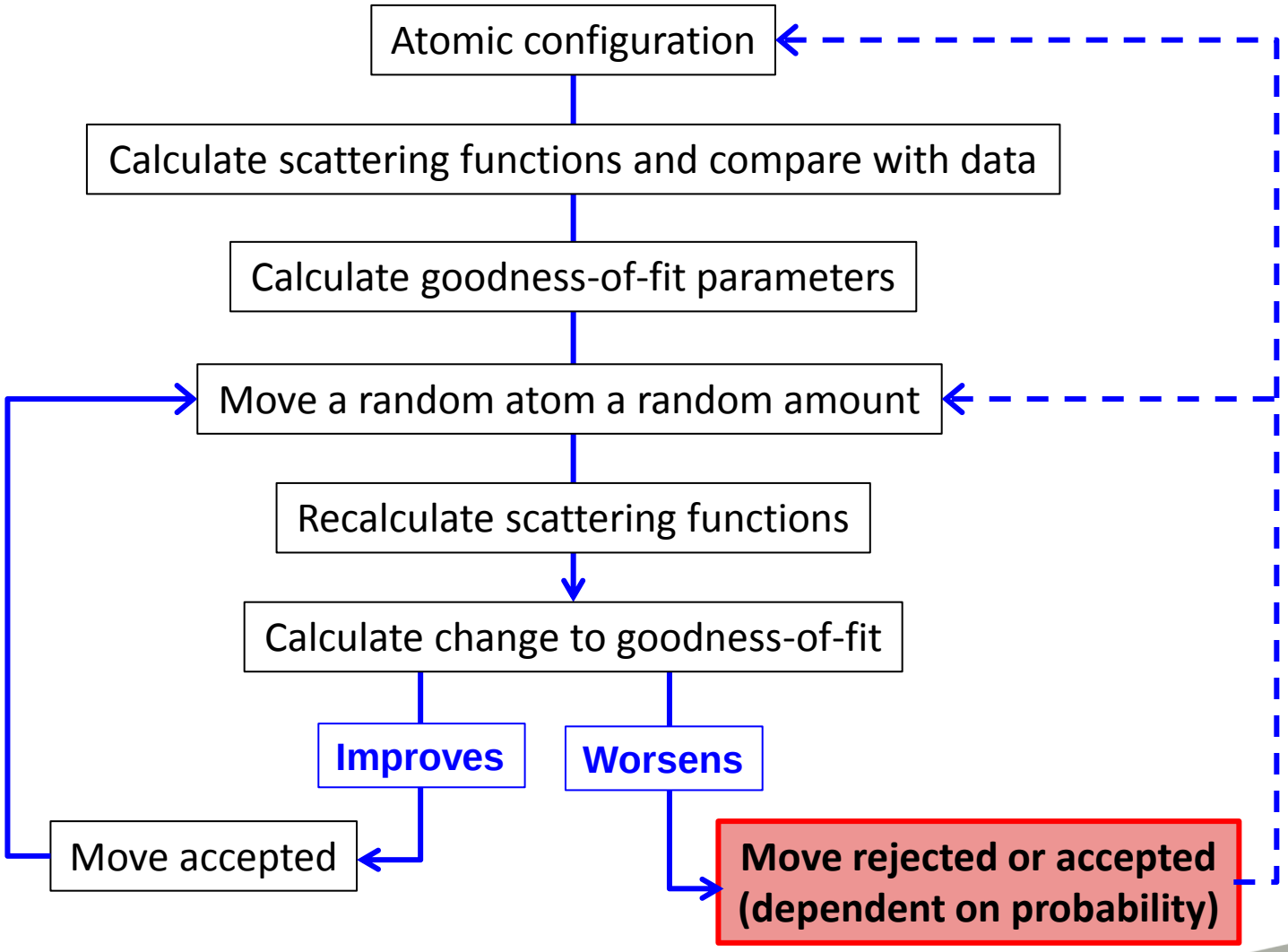
- Without the constraints of symmetry, the RMC algorithm can explore more of the phase space.
- This can be necessary to model certain types of systems.
- Take this doped CeO_2 as an example…







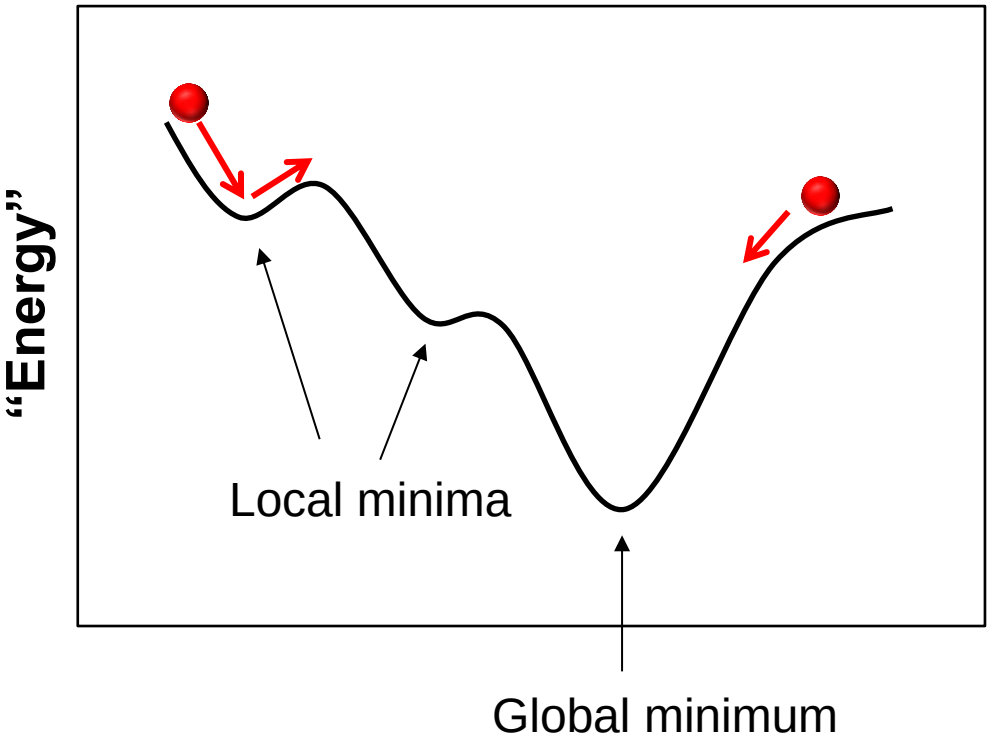
The Reverse Monte Carlo Algorithm



The Reverse Monte Carlo Algorithm

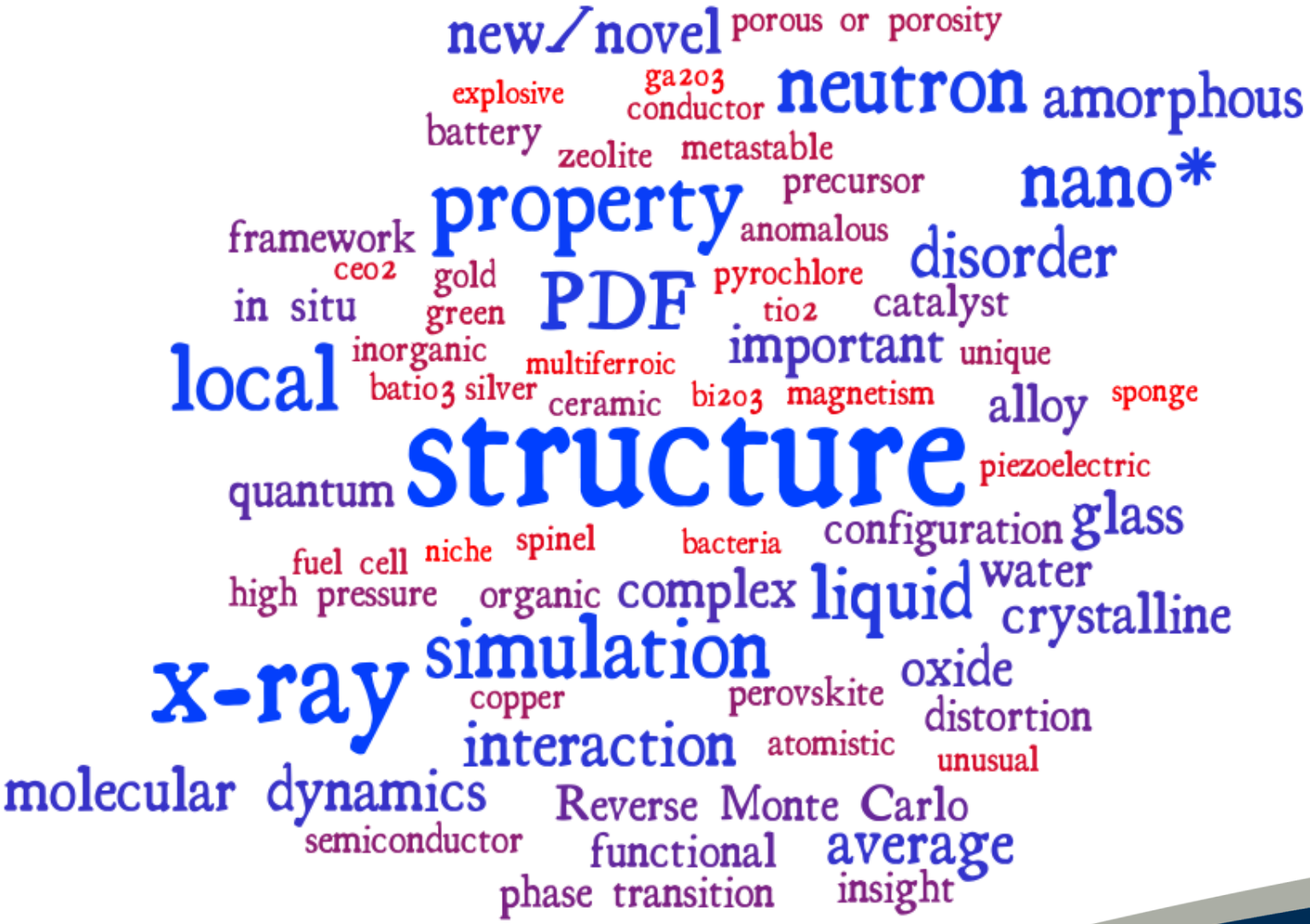
Why accept some "bad" moves?

- If only "good" moves are accepted, you risk getting stuck in a local minimum.
- The probability of accepting a "bad" move depends on how much it worsens the goodness-of-fit.
- Moves that violate hard constraints are always rejected.



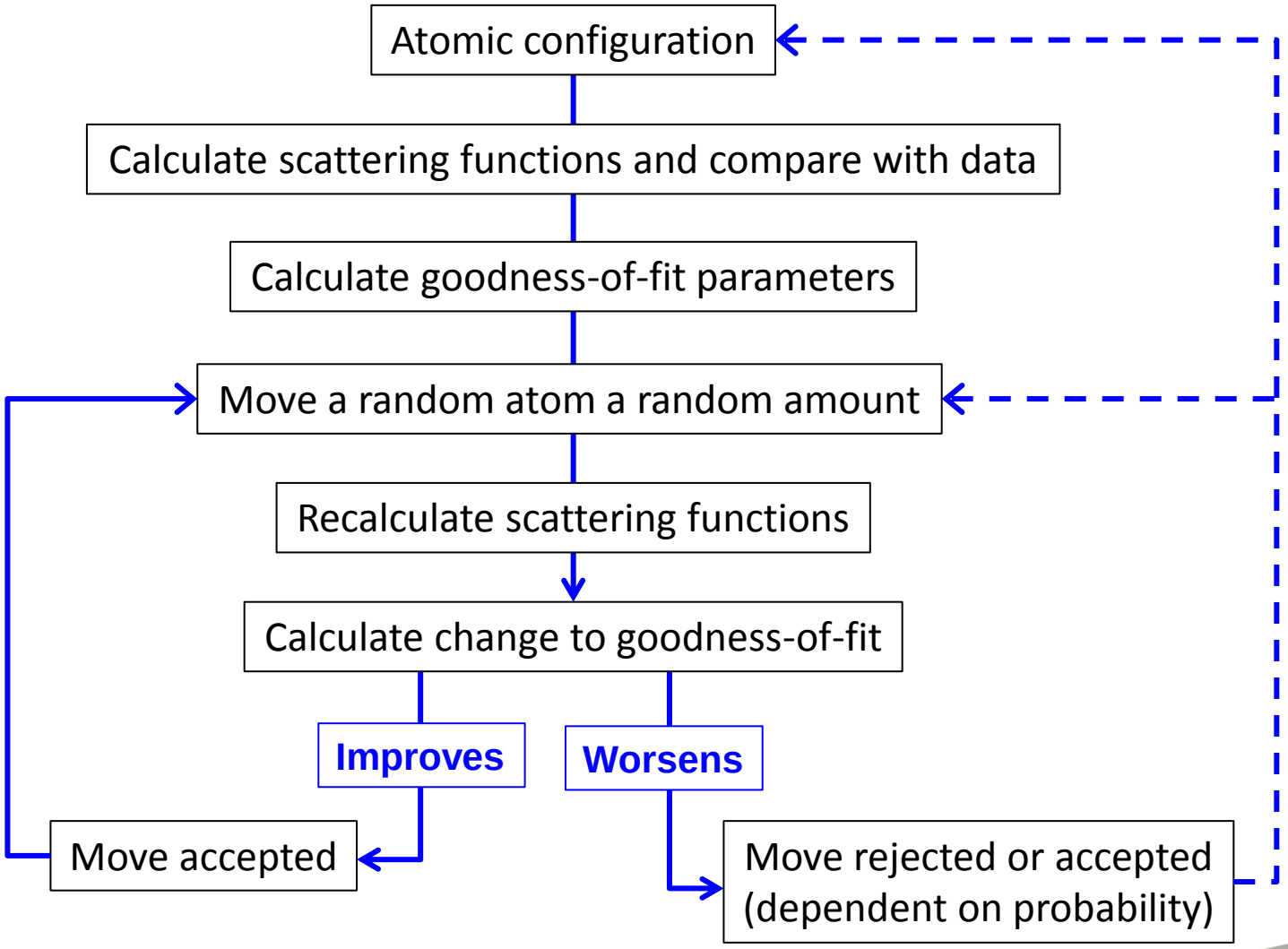
Time for a break!

Science & Technology Facilities Council
ISIS



Science & Technology Facilities Council
ISIS

The Reverse Monte Carlo Algorithm

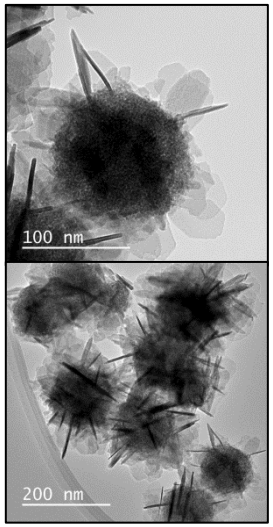


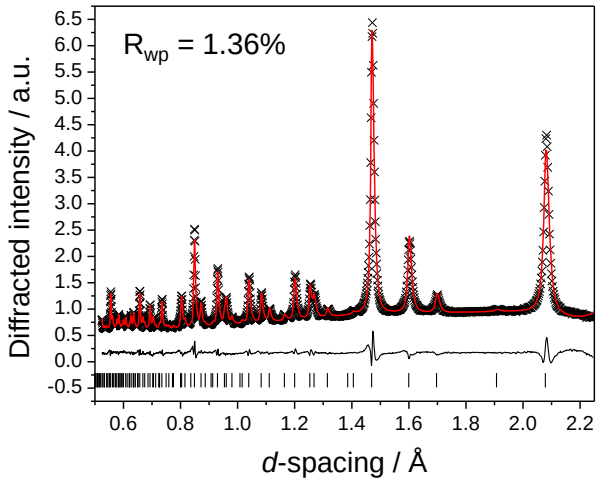
Case Study: Gallium Oxide

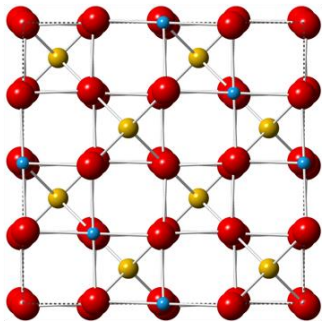
Science & Technology Facilities Council
ISIS

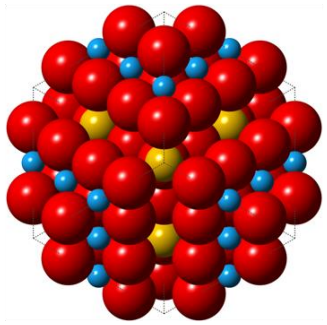
Case Study: Gallium Oxide

A disordered polymorph of Ga_2O_3





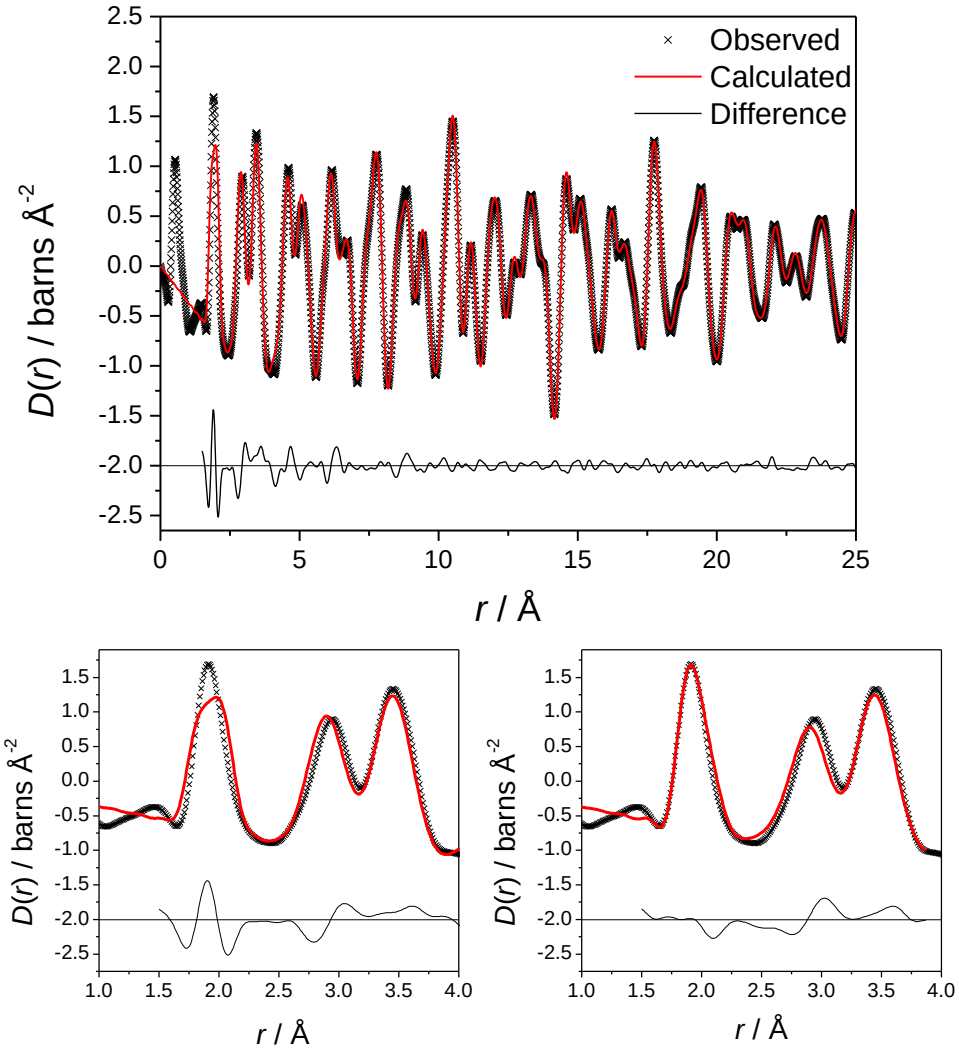




- Potential photocatalyst and catalyst support
- Structure poorly understood
- Cubic spinel structure
- Rietveld refinement reveals four partially occupied Ga sites
- Nanocrystalline

H. Y. Playford, A. C. Hannon, E. R. Barney, and R. I. Walton, *Chem. Eur. J.*, 2013, **19**, 2803–2813.

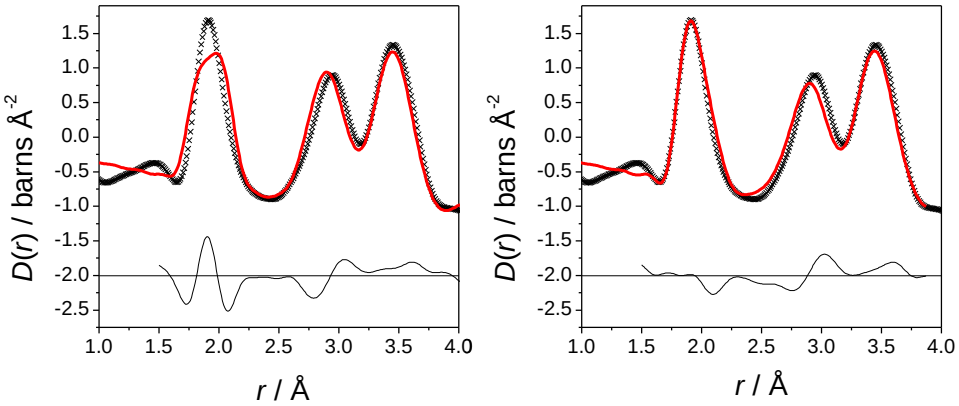
Case Study: Gallium Oxide



- Small-box modelling of the PDF
- Medium-to-high *r* agrees well with average crystal structure
- Large discrepancies in local structure
- Improved fit when lower symmetry model is used, but it is a purely local effect

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Case Study: Gallium Oxide

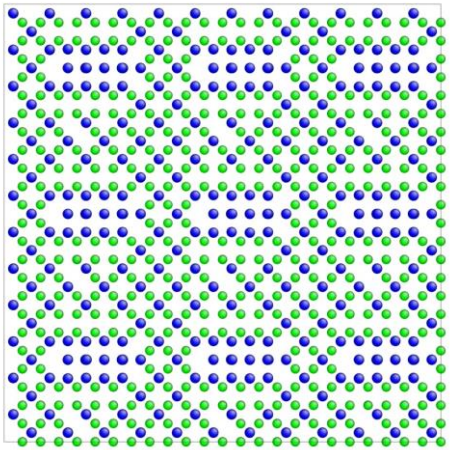


- Small-box modelling of the PDF
- Medium-to-high *r* agrees well with average crystal structure
- Large discrepancies in local structure
- Improved fit when lower symmetry model is used, but it is a purely local effect

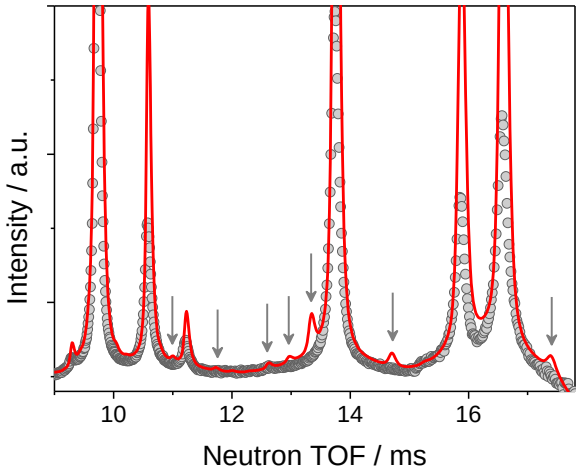
H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Science & Technology Facilities Council
ISIS

Case Study: Gallium Oxide



Green = octahedral Ga
Blue = tetrahedral Ga



Random starting model:
Ga-Ga < 1Å

↓

Handmade 2x2x2 cell with reasonable distances: supercell with artificial superstructure

↓

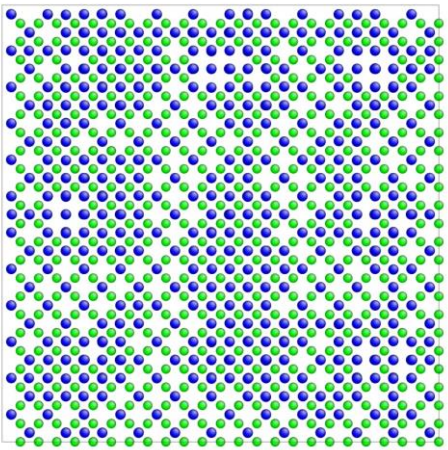
Re-randomised supercell using atom swapping & fit to Bragg pattern

↓

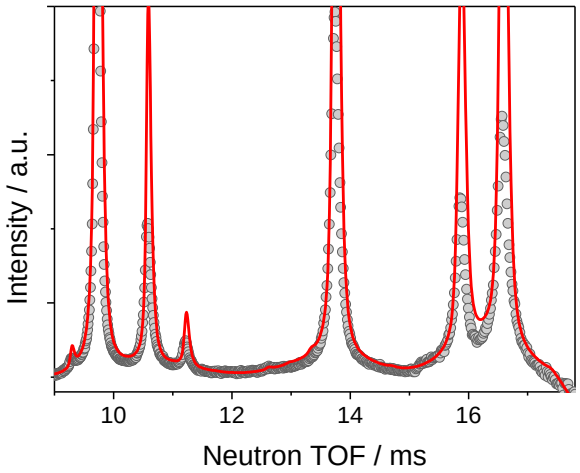
Physically and chemically sound starting model(s) for full RMC refinement

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Case Study: Gallium Oxide



Green = octahedral Ga
Blue = tetrahedral Ga



Random starting model:
Ga-Ga < 1Å

↓

Handmade 2x2x2 cell with reasonable distances: supercell with artificial superstructure

↓

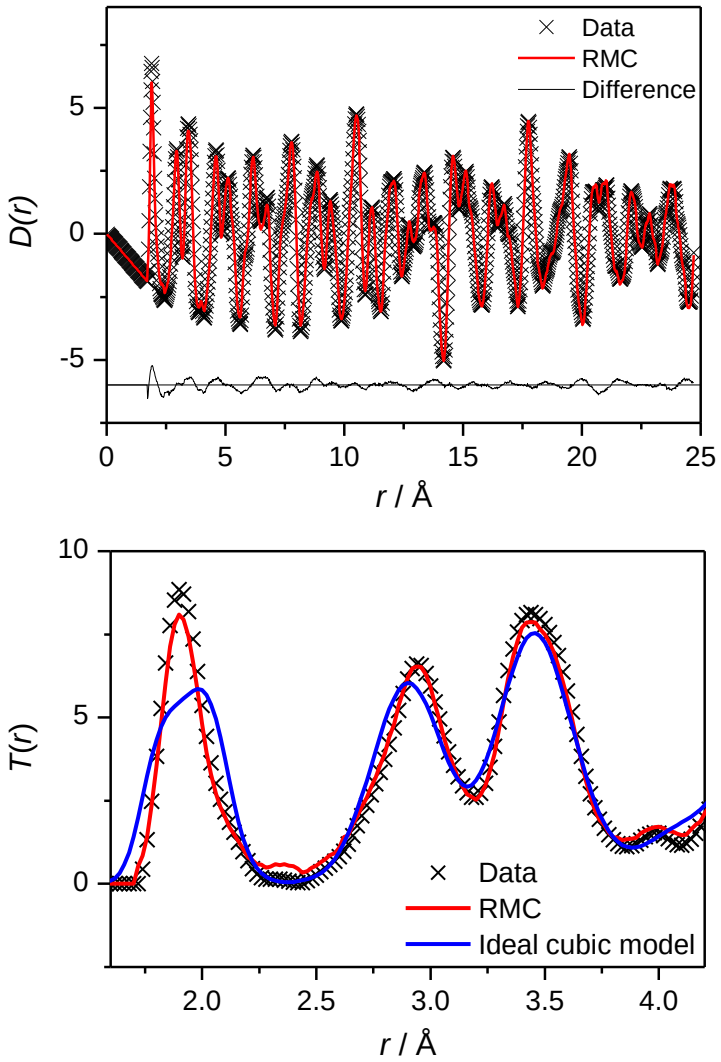
Re-randomised supercell using atom swapping & fit to Bragg pattern

↓

Physically and chemically sound starting model(s) for full RMC refinement

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Case Study: Gallium Oxide



RMC refinement using 6x6x6 supercell

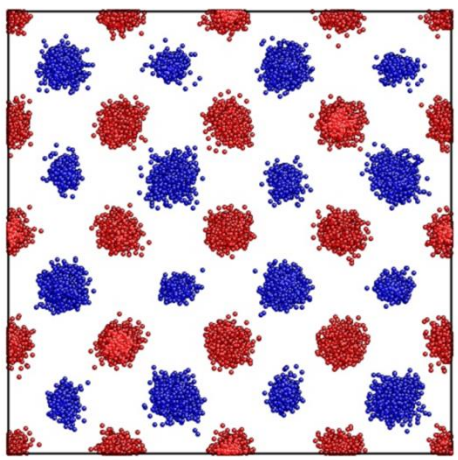
- vastly improved fit to local structure

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

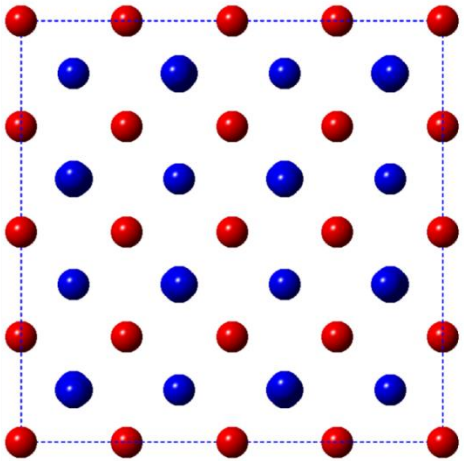
Case Study: Gallium Oxide

RMC refinement using 6x6x6 supercell

- vastly improved fit to local structure
- maintains correct average



Collapsed RMC box



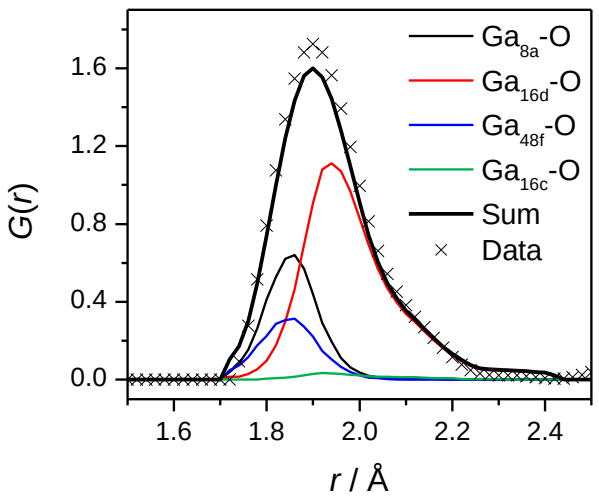
Unit cell

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

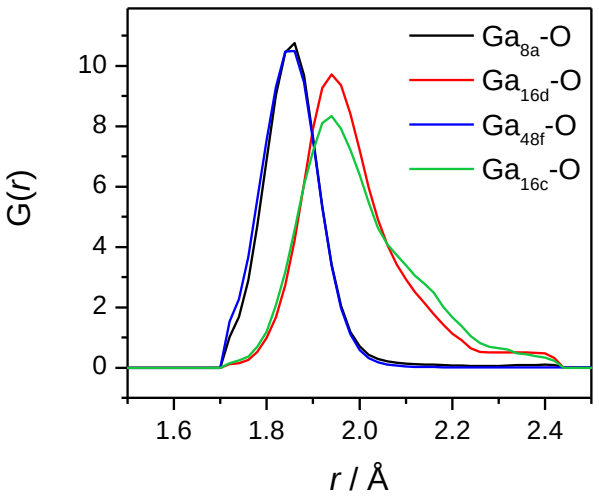
Science & Technology Facilities Council
ISIS

Case Study: Gallium Oxide

Weighted Ga-O partials



Non-weighted Ga-O partials



RMC provides bond length and angle distributions:

- these distributions are the sum of 200 refined "boxes of atoms"
- **the O_h sites are highly distorted**
- the crystal structure defines two very different T_d sites
- but locally these sites are very similar

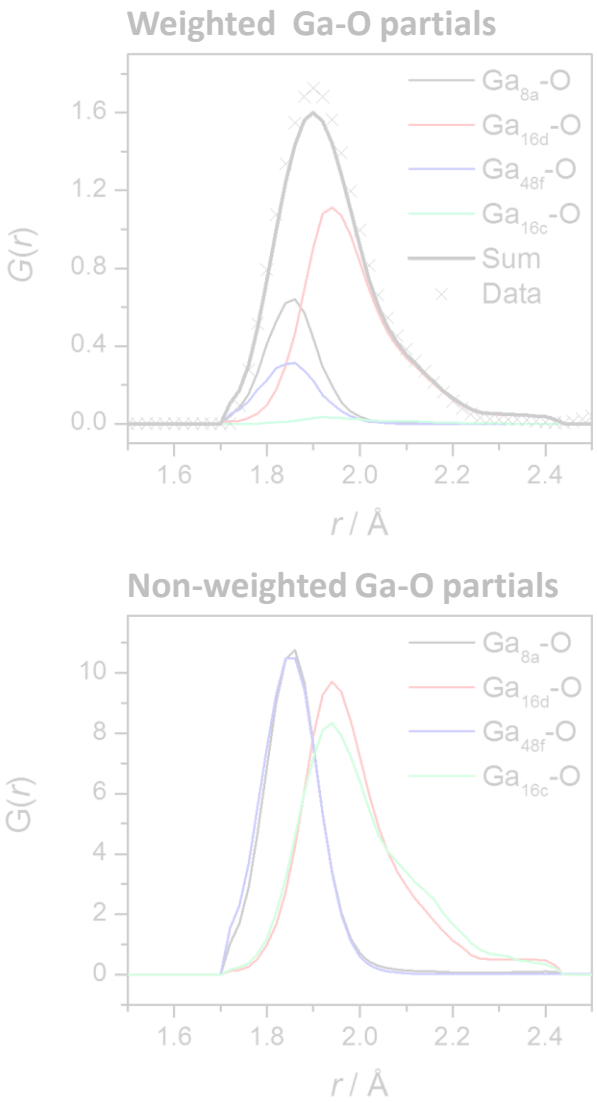
Spinel T_d site

Non-spinel T_d site

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

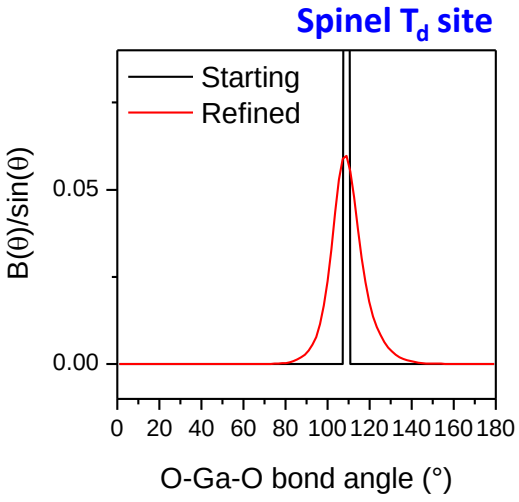
Science & Technology Facilities Council
ISIS

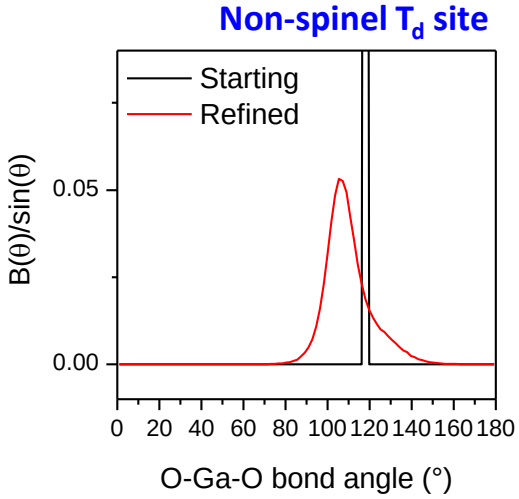
Case Study: Gallium Oxide



RMC provides bond length and angle distributions:

- these distributions are the sum of 200 refined "boxes of atoms"
- the O_h sites are highly distorted
- **the crystal structure defines two very different T_d sites**
- **but locally these sites are very similar**



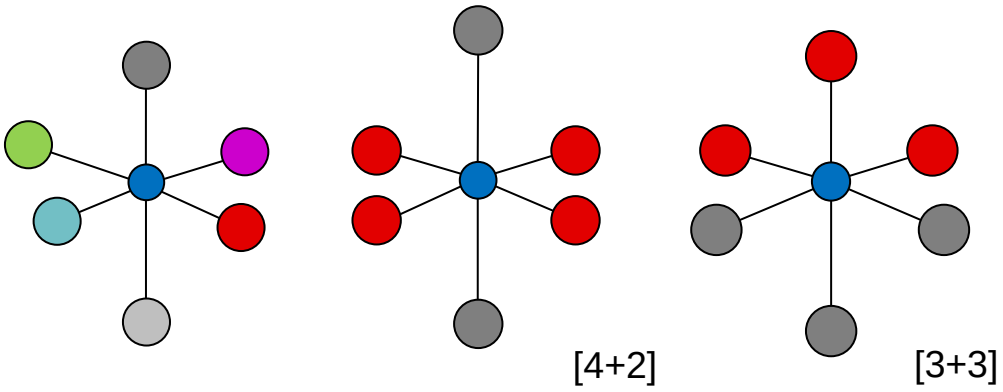


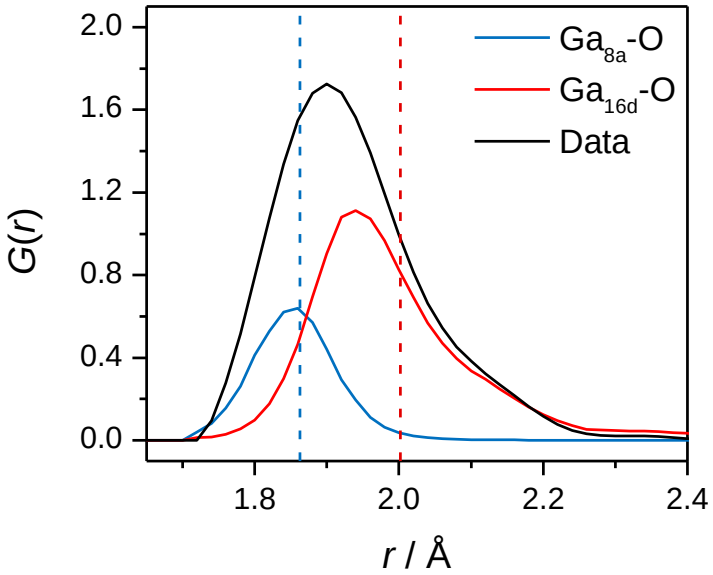
H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Science & Technology Facilities Council
ISIS

Case Study: Gallium Oxide

A disordered polymorph of Ga_2O_3





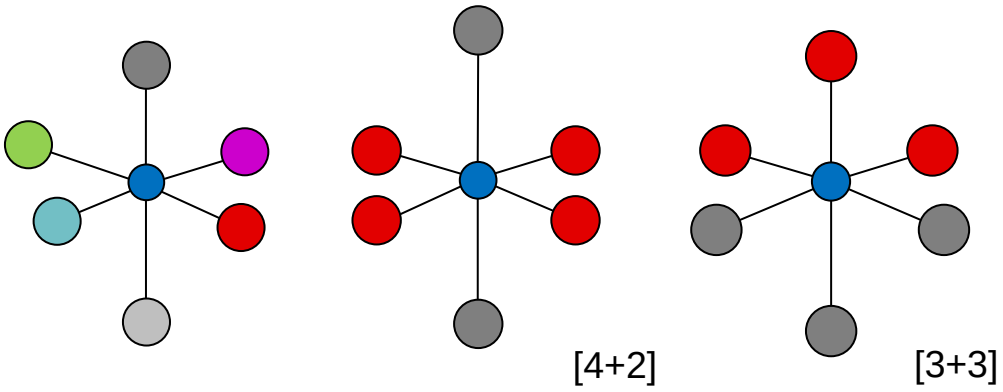
The data clearly show the octahedra are distorted, but what do they actually look like?

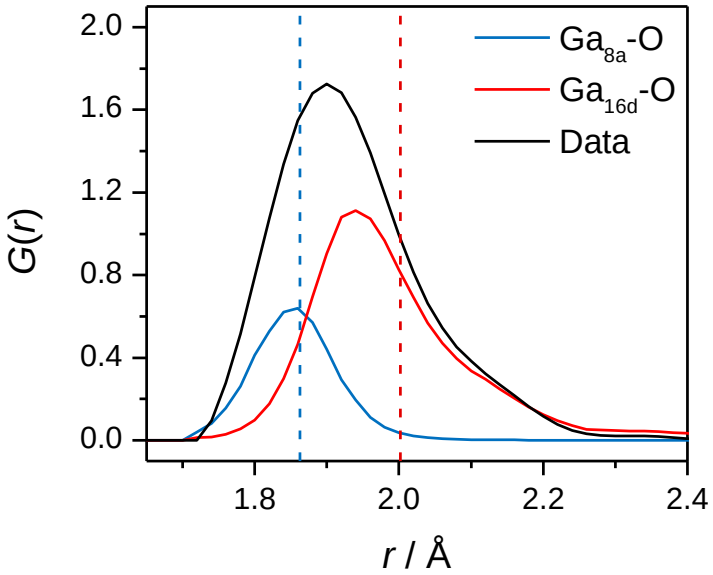
- multiple RMC runs provide ensemble of >700,000 polyhedra to analyse!
- 50% all 6 bonds shorter than the mean bond length
- 40% [3+3] type

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

Case Study: Gallium Oxide

A disordered polymorph of Ga_2O_3





The data clearly show the octahedra are distorted, but what do they actually look like?

- multiple RMC runs provide ensemble of >700,000 polyhedra to analyse!
- 50% all 6 bonds shorter than the mean bond length
- 40% [3+3] type

Thermodynamically stable β-Ga_2O_3 has [3+3] type…

Locally, cubic γ-Ga_2O_3 = monoclinic β-Ga_2O_3

H. Y. Playford, *et al.*, *J. Phys. Chem. C*, 2014, **118**, 16188–16198.

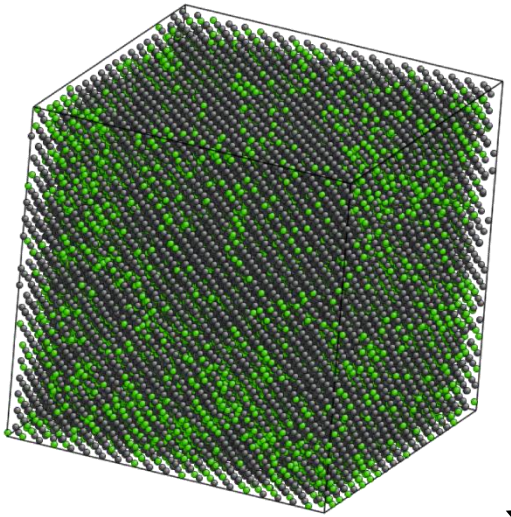
A closer look at RMCProfile

Science & Technology Facilities Council
ISIS

RMCProfile

- Implementation of the RMC algorithm particularly suited to crystalline materials.
- "Profile" refers to the Bragg profile – a very important constraint for average structure.
- Based on the original RMCA code of McGreevy and Puzstai, extended by Matt Tucker (now at ORNL).
- Developers from many institutions including ISIS, ORNL, QMUL, Oxford, Cambridge, NIST, Chalmers…
- The program is available online at www.rmcprofile.org
- It can fit multiple datasets (X-ray and neutron PDF, F(Q), Bragg)…
- …and use "chemical sense" in the application of appropriate constraints.

RMCProfile



PDF

F(Q)

Bragg profile

EXAFS

Single crystal diffuse

Hard sphere cutoff

Distance window

Polyhedral constraints

Molecular potentials

Bond valence sum

RMCProfile

- **Current version: RMCProfile 6.7.x**
  - was developed at ISIS by Wojciech Slawinski
  - incorporation of various user requested features
  - improved usability
- **RMCProfile 6.8**
  - final release of version 6 (coming soon)
  - incorporation of developments from Igor Levin's team at NIST
- **RMCProfile 7.0**
  - being developed at ISIS by Wojciech Slawinski
  - big news: multiphase RMC (multiple 'boxes' of atoms)
  - **currently in need of input from users**
  - available now for interested beta testers!
- **RMCProfile 7.1 and later**
  - speed and efficiency improvements
  - developments for nanostructured systems
  - improved support for X-ray data
  - regular incremental updates

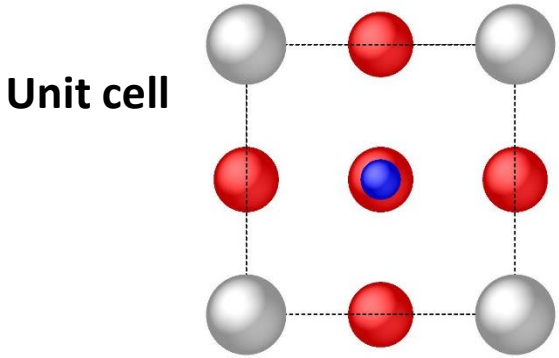
RMC PROFILE

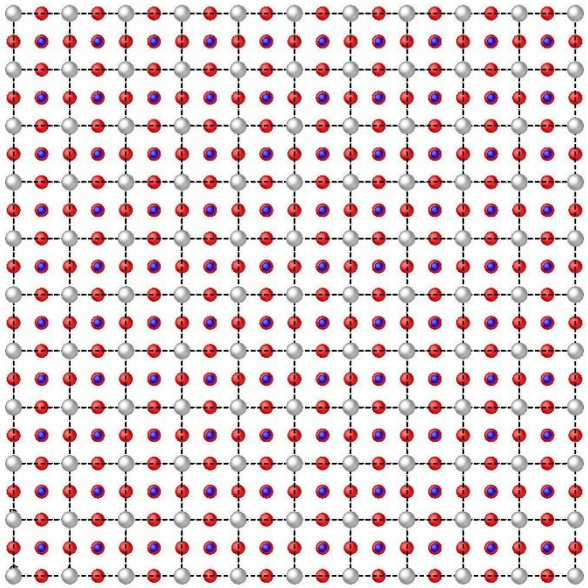
www.rmcprofile.org

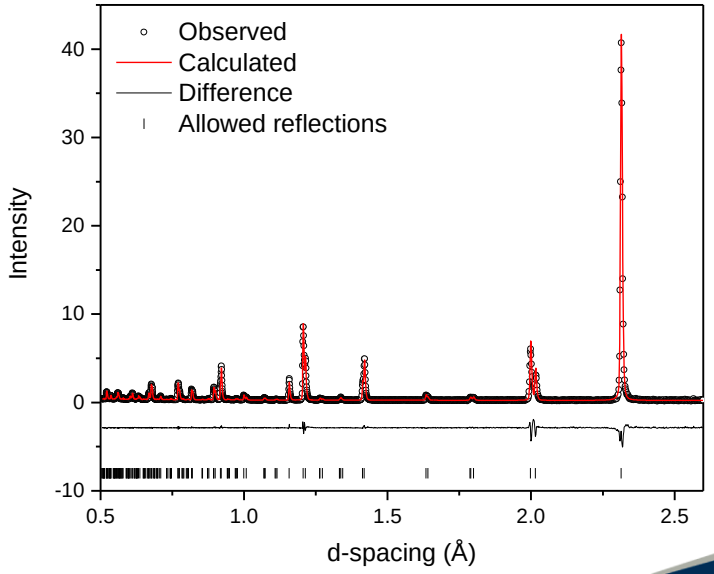
RMCProfile

A “live” demonstration

- Barium titanate, $BaTiO_3$
- Perovskite
- Surprisingly complex phase diagram!
- Neutron scattering data collected on Polaris
- Rietveld refinement using GSAS
- Total scattering data processed using GudrunN

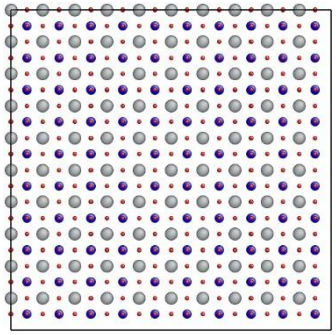


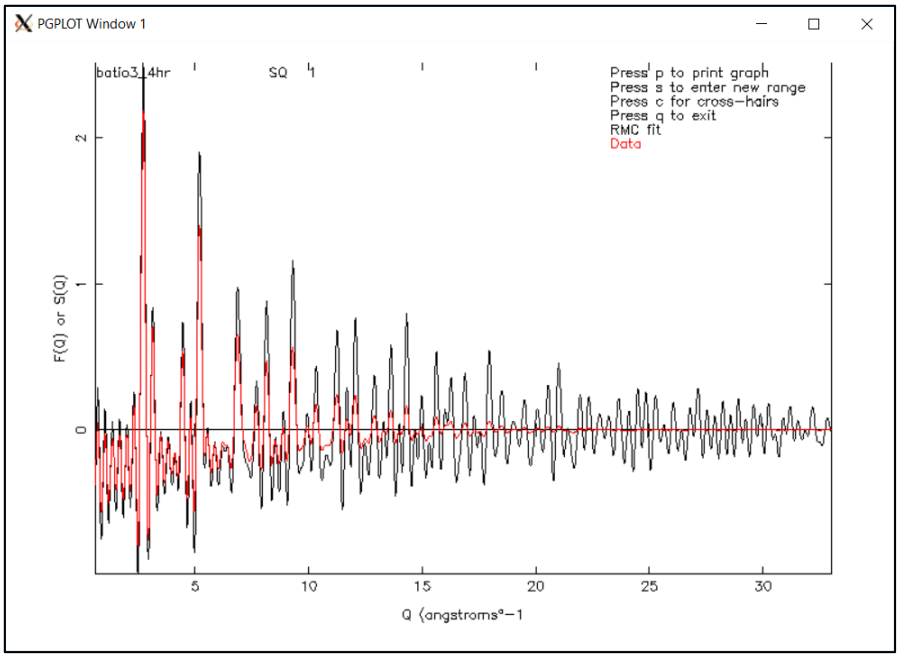




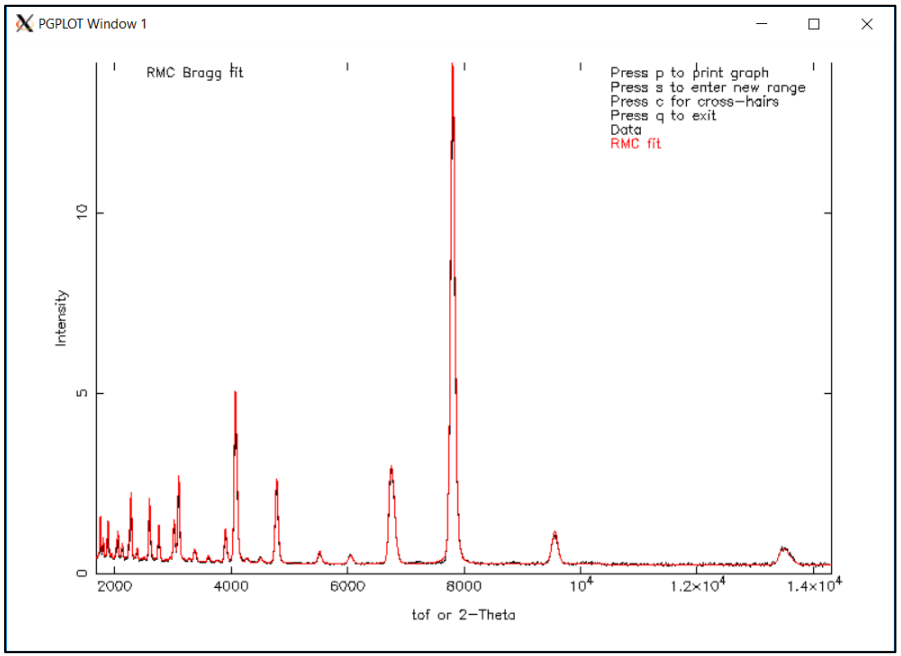
RMCProfile

A “live” demonstration





F(Q) initial fit

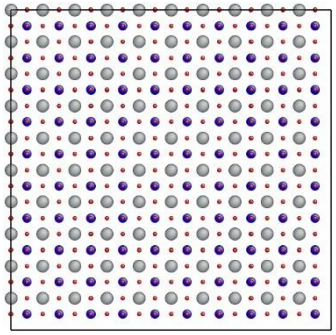


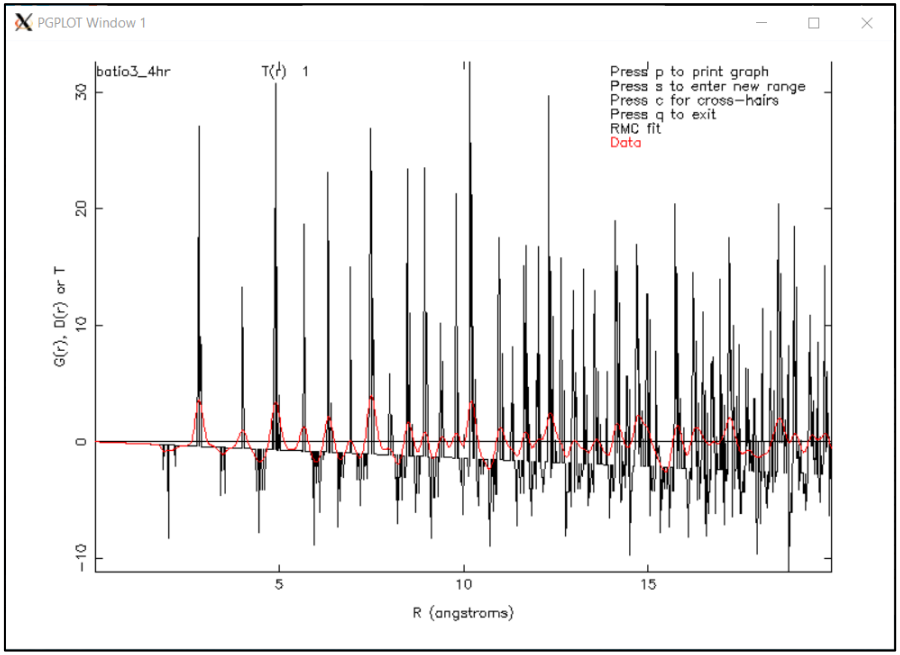
Bragg initial fit

Science & Technology Facilities Council
ISIS

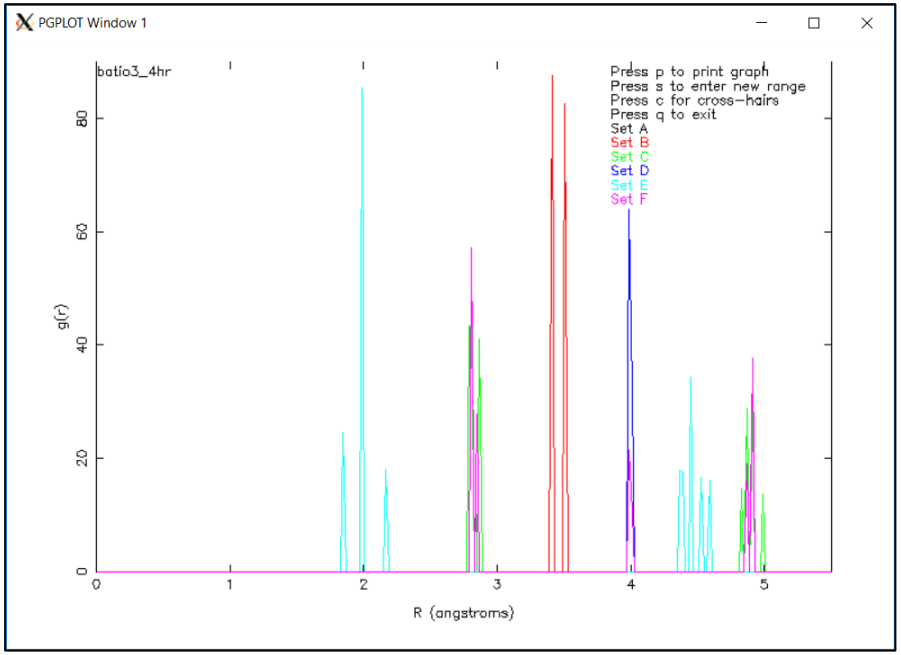
RMCProfile

A “live” demonstration





D(r) initial fit



Initial $g_{ij}(r)$

Science & Technology Facilities Council
ISIS

RMCProfile

batio3_4hr.dat

```
TITLE :: BaTiO3_4hr
MATERIAL :: BaTiO3
PHASE :: Tetragonal
TEMPERATURE :: 293
INVESTIGATOR :: HYP

MINIMUM_DISTANCES :: 1.68 1.68 1.68 1.68 1.68 1.68 Angstrom
MAXIMUM_MOVES :: 0.05 0.05 0.05 Angstrom
R_SPACING :: 0.0200 Angstrom
PRINT_PERIOD :: 1000
TIME_LIMIT :: 900.00 MINUTES
SAVE_PERIOD :: 10.00 MINUTES

INPUT_CONFIGURATION_FORMAT :: rmc6f
SAVE_CONFIGURATION_FORMAT :: cfg

IGNORE_HISTORY_FILE ::

ATOMS :: Ba Ti O

FLAGS ::
 > NO_MOVEOUT
 > NO_SAVE_CONFIGURATIONS
 > NO_RESOLUTION_CONVOLUTION
```

Number of partials =
n(n+1)/2

RMCProfile

```
25
26  NEUTRON_REAL_SPACE_DATA :: 1
27  > FILENAME :: batio3_rmc_4hr_32.99.gr
28  > DATA_TYPE :: G(r)
29  > FIT_TYPE :: D(r)
30  > START_POINT :: 1
31  > END_POINT :: 1000
32  > CONSTANT_OFFSET ::  0.00
33  > WEIGHT ::  0.005
34  > NO_FITTED_OFFSET
35  > NO_FITTED_SCALE
36
37  NEUTRON_RECIPROCAL_SPACE_DATA :: 1
38  > FILENAME :: batio3_rmc_4hr_32.99.fq
39  > DATA_TYPE :: F(Q)
40  > FIT_TYPE ::  F(Q)
41  > START_POINT :: 1
42  > END_POINT :: 1620
43  > CONSTANT_OFFSET ::  0.00
44  > CONVOLVE ::
45  > WEIGHT ::  0.100
46  > NO_FITTED_OFFSET
47  > NO_FITTED_SCALE
48
49  BRAGG ::
50  > BRAGG_SHAPE :: gsas3
51  > SUPERCELL ::  10 10 10
52  > RECALCULATE
53  > DMIN :: 0.5
54  > WEIGHT ::  0.005
55
56  END ::
57
```

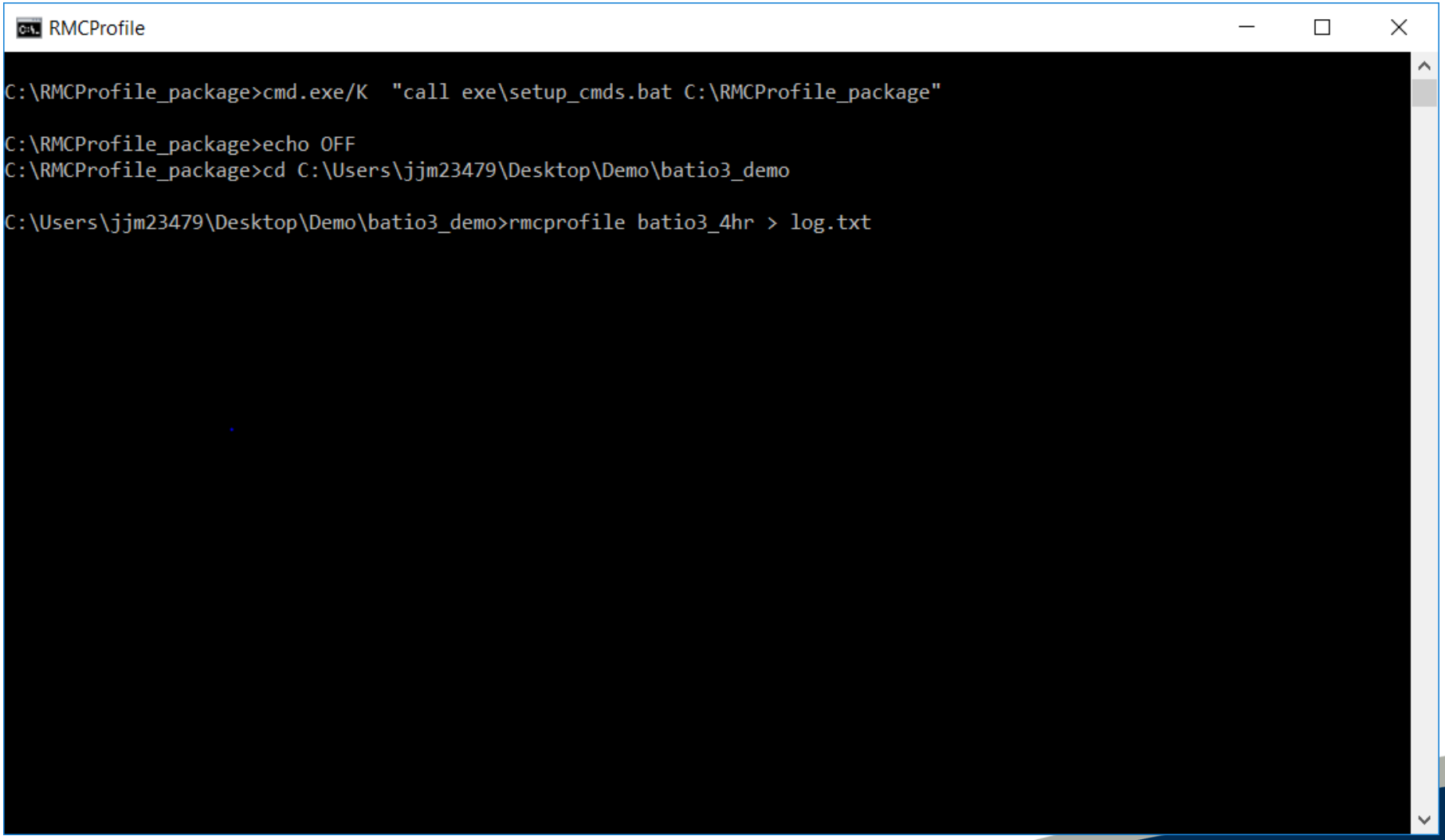
RMCProfile

```
68
69  DISTANCE_WINDOW ::
70    > MNDIST :: 0 1.750 0
71    > MXDIST :: 0 2.270 0
72
```

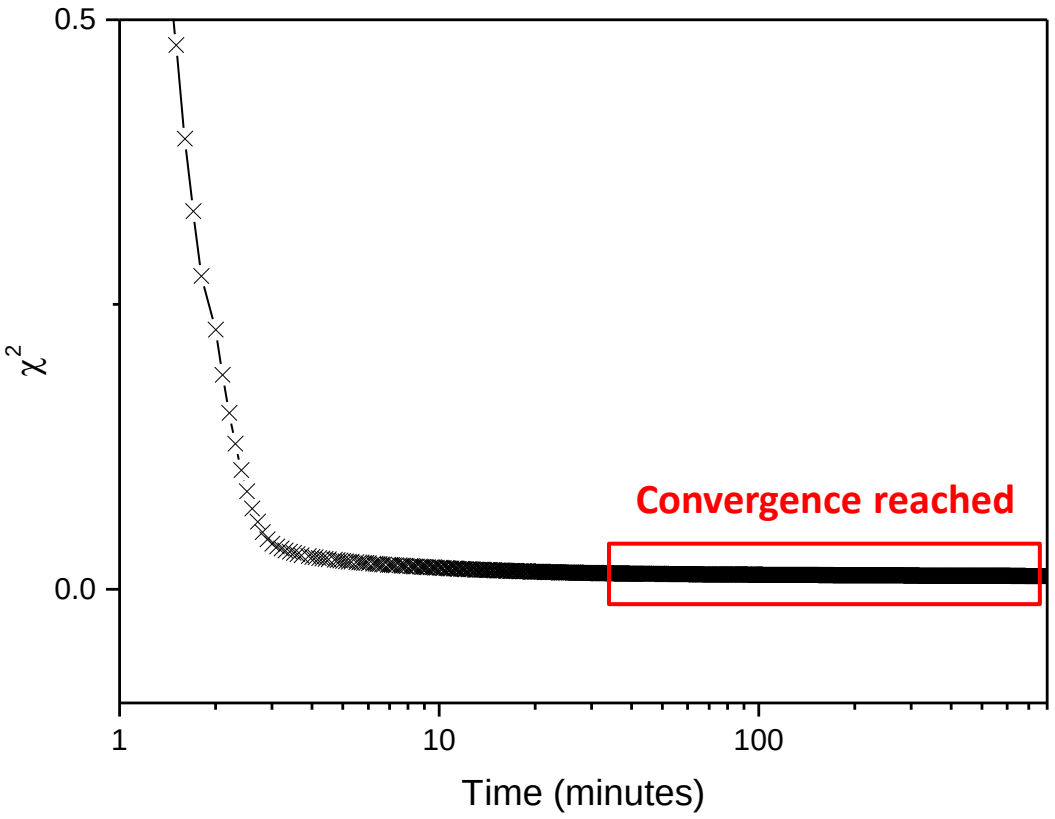
```
26
27  BVS ::
28    > ATOM :: Y Nb O
29    > OXID :: 3 5 -2
30    > WEIGHTS :: 0.001 0.001 0.1
31    > RIJ :: 0 2.019 1.911
32    > BVAL :: 0 0.37 0.37
33    > CUTOFF :: 0 3.0 2.5
34    > SAVE :: 400000
35    > UPDATE :: 200000
36
```

```
18
19  ATOMS :: Si O
20
21  FIXED_COORDINATION_CONSTRAINTS :: 2
22    > CSTR1 :: 1 2 1.497 1.717 4 1.0 0.00001
23    > CSTR2 :: 2 1 1.497 1.717 2 1.0 0.00001
24
```

RMCProfile


RMCProfile
C:\RMCProfile_package>cmd.exe/K "call exe\setup_cmds.bat C:\RMCProfile_package"
C:\RMCProfile_package>echo OFF
C:\RMCProfile_package>cd C:\Users\jjm23479\Desktop\Demo\batio3_demo
C:\Users\jjm23479\Desktop\Demo\batio3_demo>rmcprofile batio3_4hr > log.txt

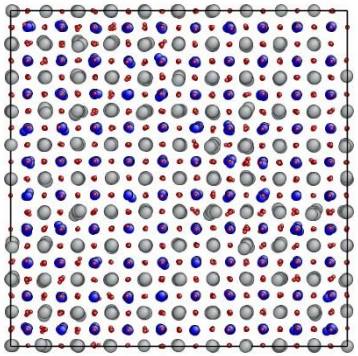
A "live" demonstration

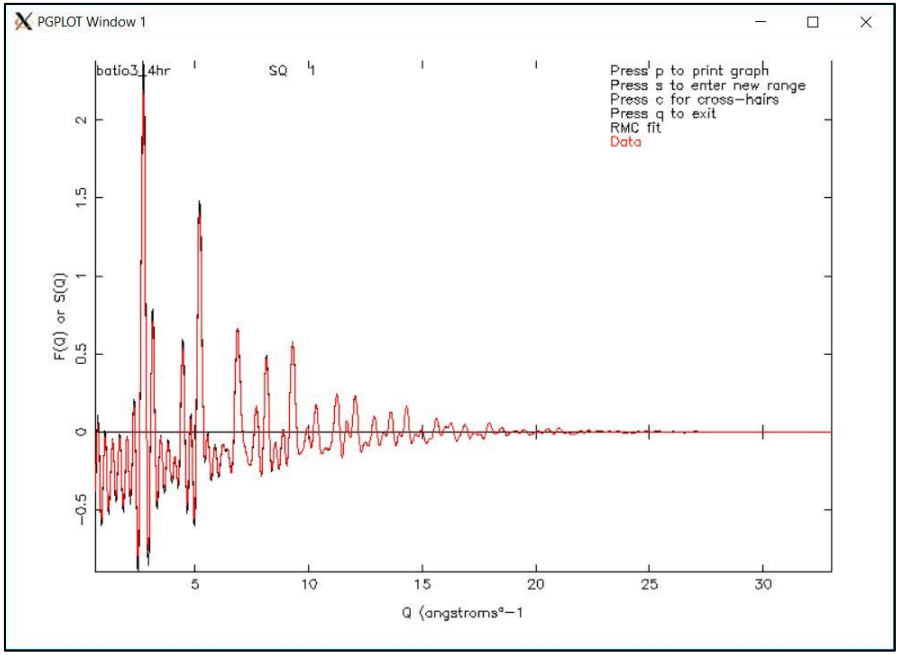


- In most cases, the χ^2 drops quickly at first, and then gradually approaches convergence.
- In this case, convergence is reached within an hour or so…
- Let's have a look at the results (live!)

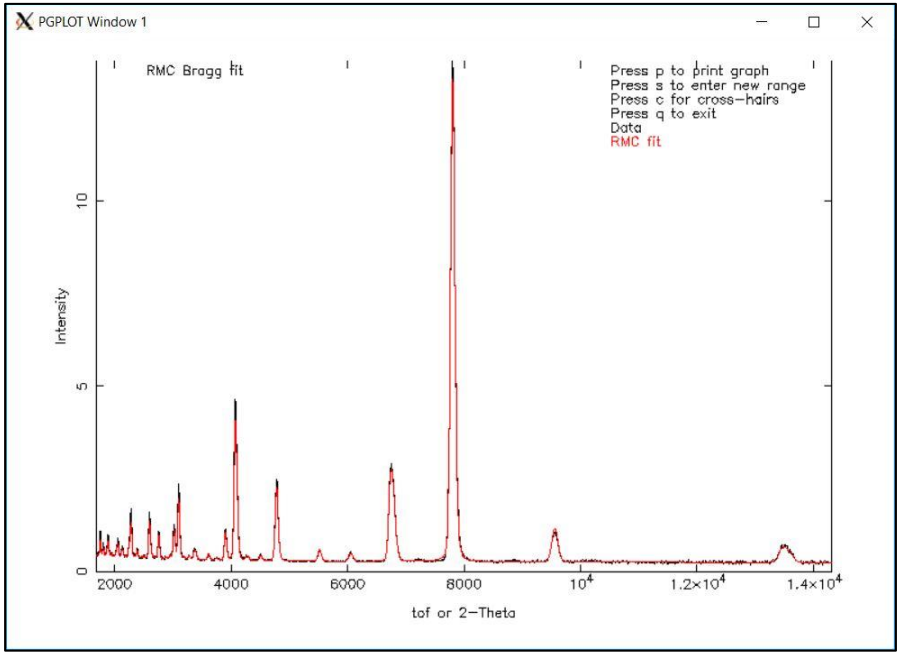
RMCProfile

A “live” demonstration





F(Q) final fit

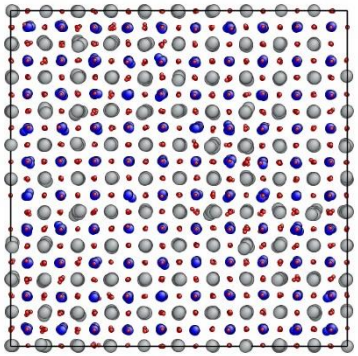


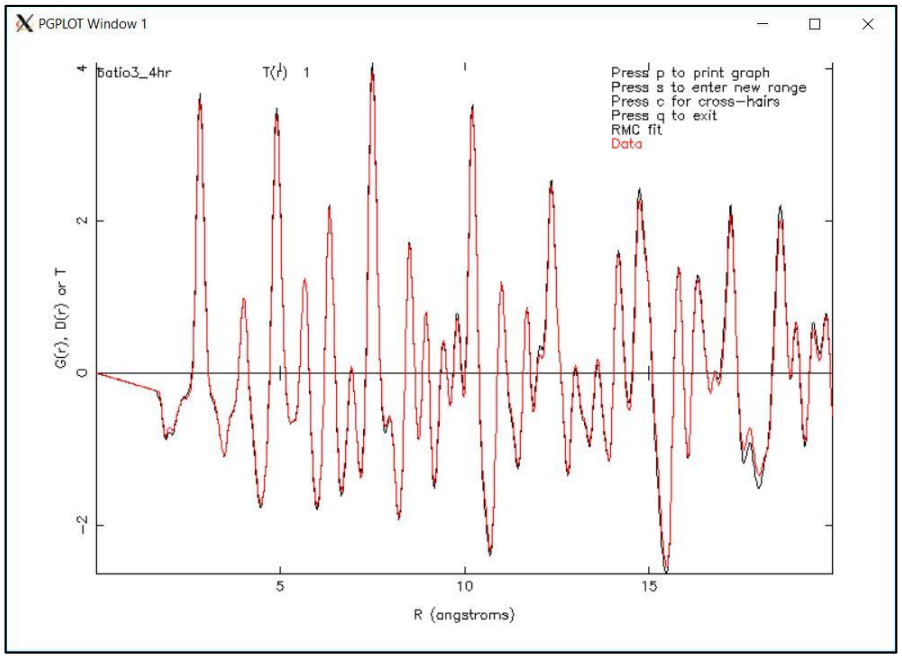
Bragg final fit

Science & Technology Facilities Council
ISIS

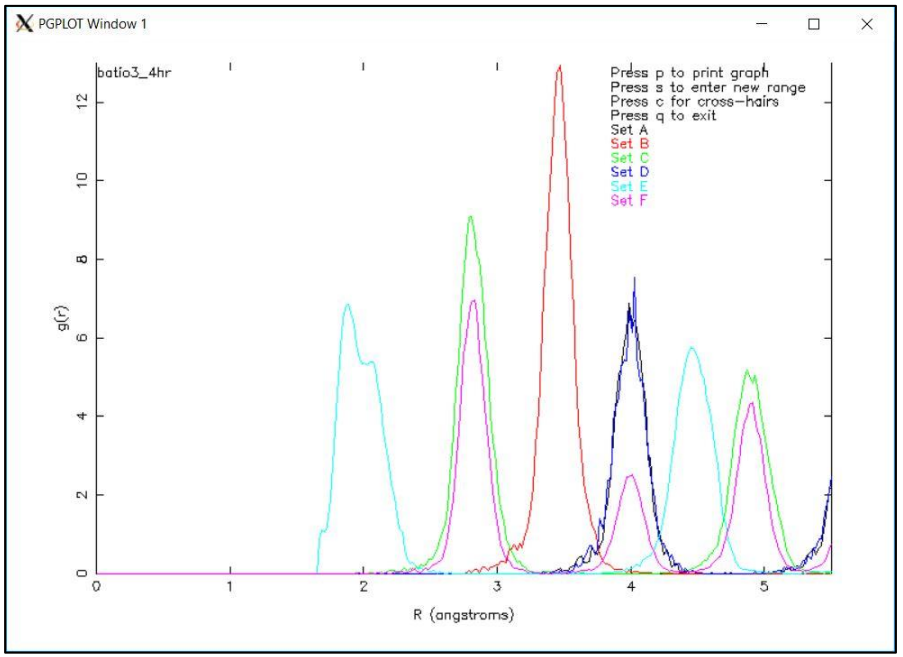
RMCProfile

A “live” demonstration





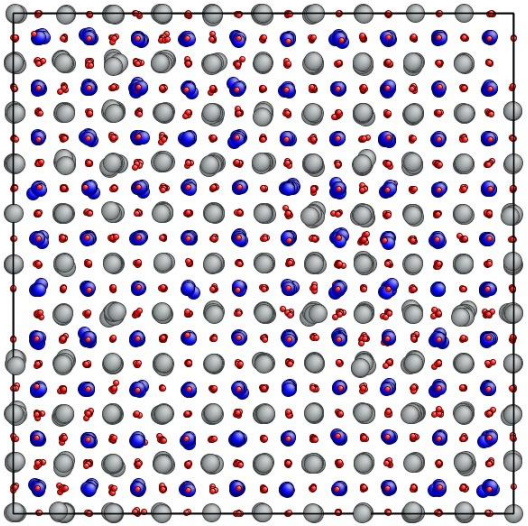
D(r) final fit



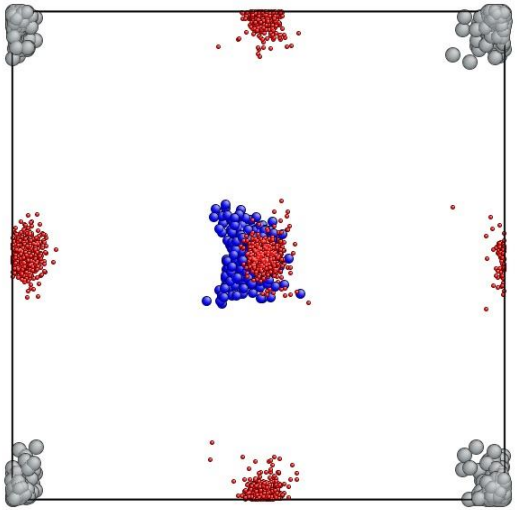
Refined $g_{ij}(r)$

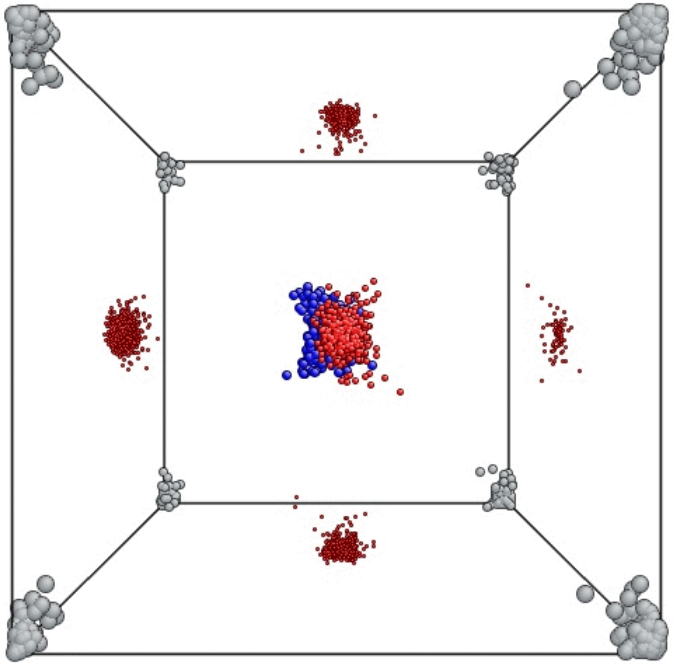
RMCProfile

A “live” demonstration



Supercell collapsed onto original unit cell





Requirements for a successful RMCProfile refinement:

- Quality data
- Multiple datasets
- Single phase sample
- Good powder average
- Average structure well-characterised
- Understanding of structural chemistry
- Targeted analysis of refined configurations

Why was the gallium oxide case study successful?

Why was the gallium oxide case study successful?

- Quality data ✓
  - Data were from GEM, a TOF diffractometer optimised for TS measurements
  - The instrument was well calibrated
  - The data were of good statistical quality

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓

  - Bragg diffraction pattern and TS data fitted simultaneously

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓
- Single phase sample ✓

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓
- Single phase sample ✓
- Good powder average ✓

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓
- Single phase sample ✓
- Good powder average ✓
- Average structure well-characterised ✓

  - I did a very thorough Rietveld investigation before beginning the PDF analysis

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓
- Single phase sample ✓
- Good powder average ✓
- Average structure well-characterised ✓
- Understanding of structural chemistry ✓

  - I knew what kinds of bonding environments Ga “preferred” and how close it could get to other atoms.

Why was the gallium oxide case study successful?

- Quality data ✓
- Multiple datasets ✓
- Single phase sample ✓
- Good powder average ✓
- Average structure well-characterised ✓
- Understanding of structural chemistry ✓
- Targeted analysis of refined configurations ✓

  - I wanted to understand how the octahedral sites were distorted, and my analysis reflected that.

And another thing…

Conclusions

- Total scattering is an extension of powder diffraction that changes the viewpoint from average to local.
- It is incredibly useful (and we have not yet found its limits) but it is NOT magic.
- The pair distribution function is simple and intuitive, but real structural information requires modelling!
- Reverse Monte Carlo refinements using RMCProfile produce atomistic models that are consistent with all available data
- Requirements for success include prior characterisation and an understanding of what you want to know about your structure.