Modelling the PDF of Crystalline Materials with RMCProfile

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China Spallation Neutron Source

Institute of High Energy Physics, Dongguan, China

7th November 2016

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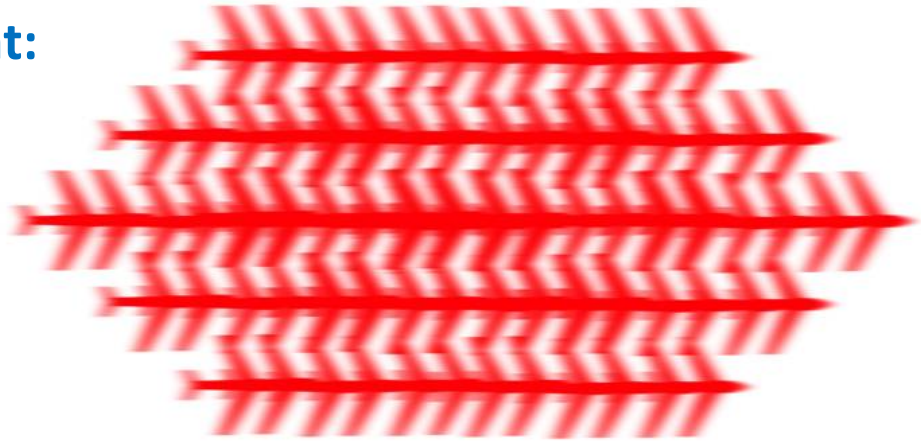
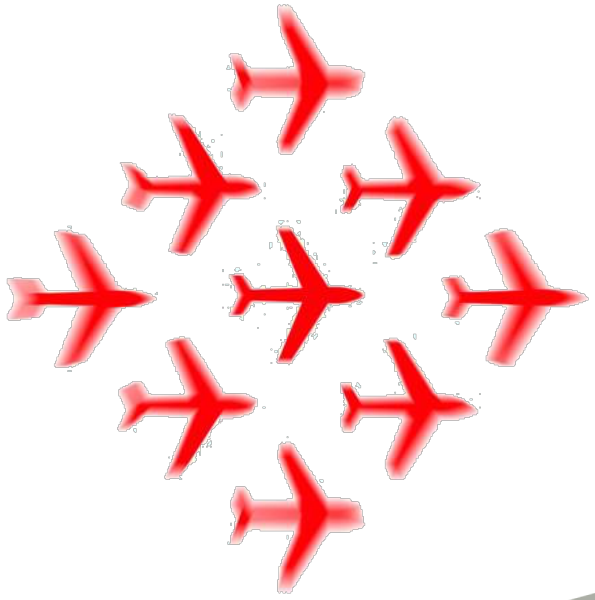
Local and Average Viewpoints

Average viewpoint:



Local viewpoint:



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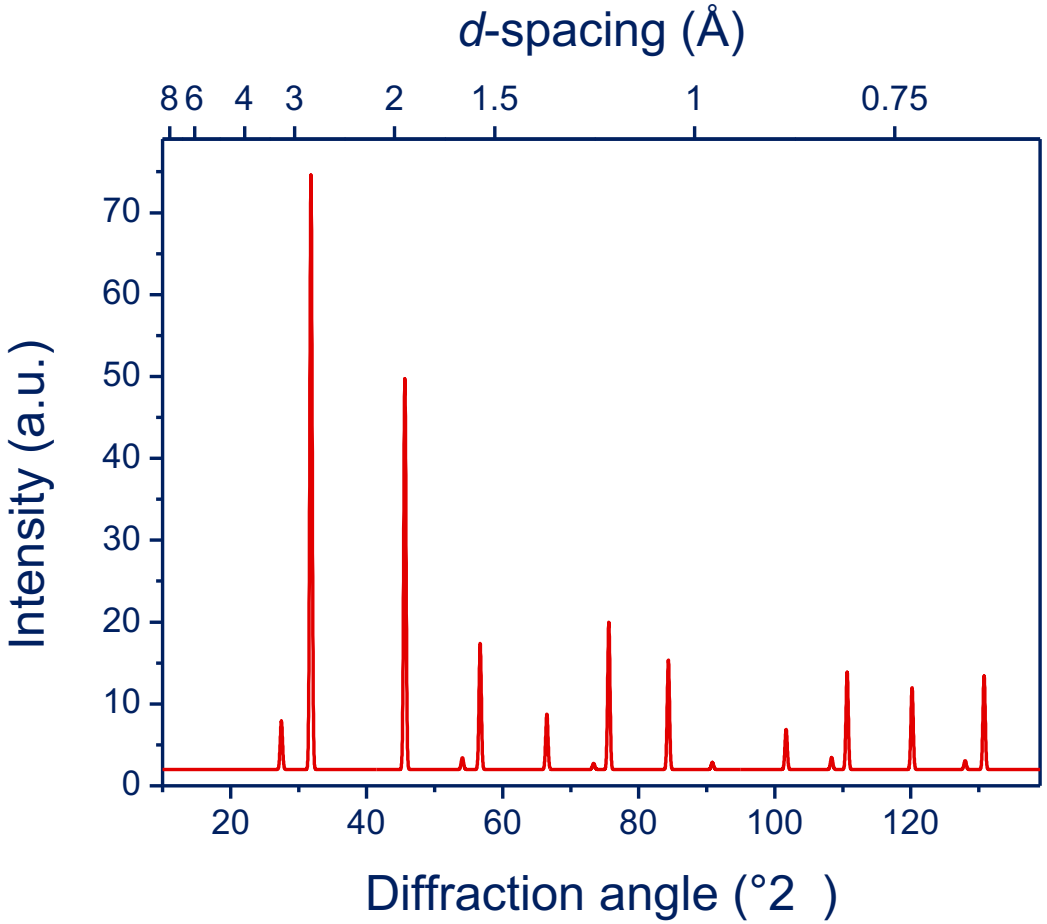
Diffraction as a Structural Probe



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

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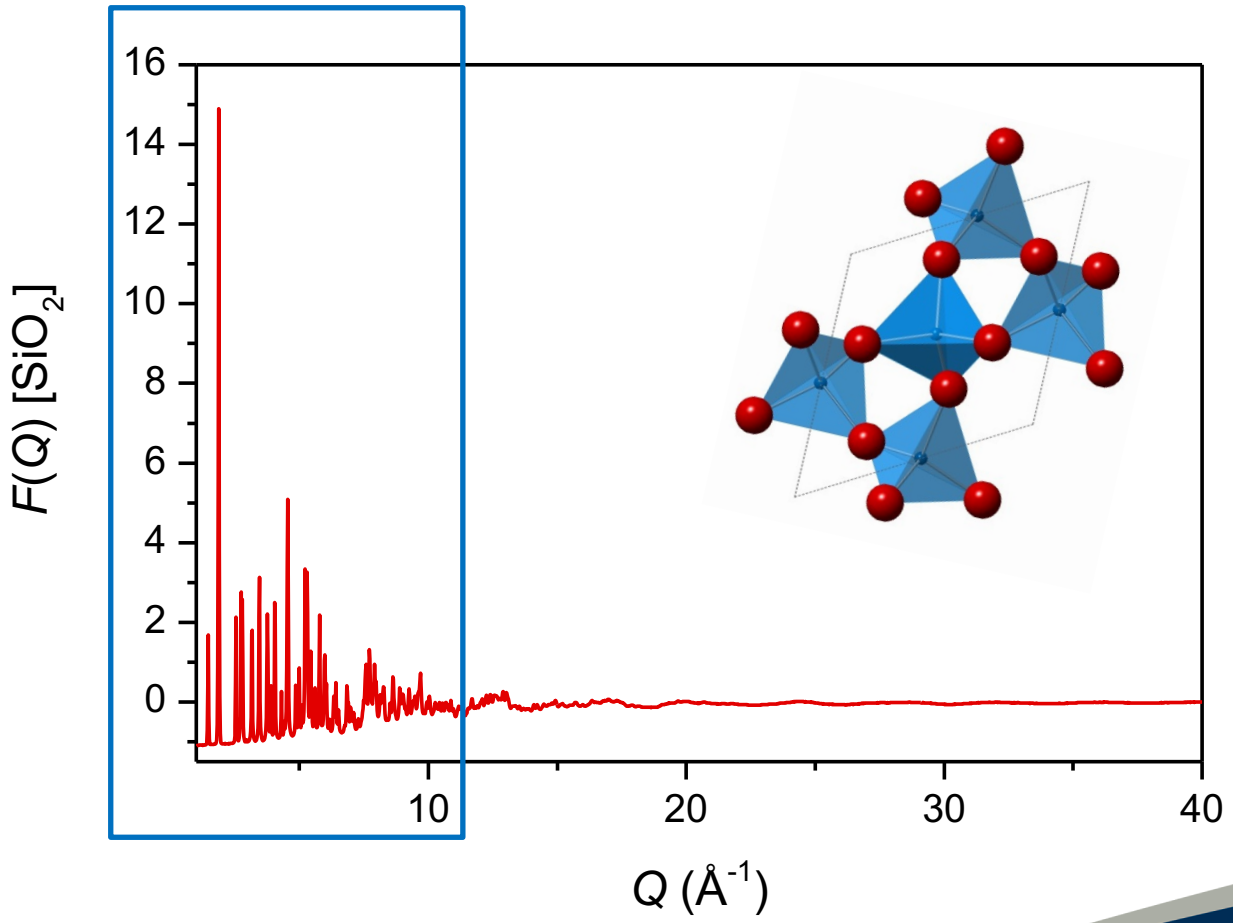
Introduction to Total Scattering

What is total scattering?

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



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

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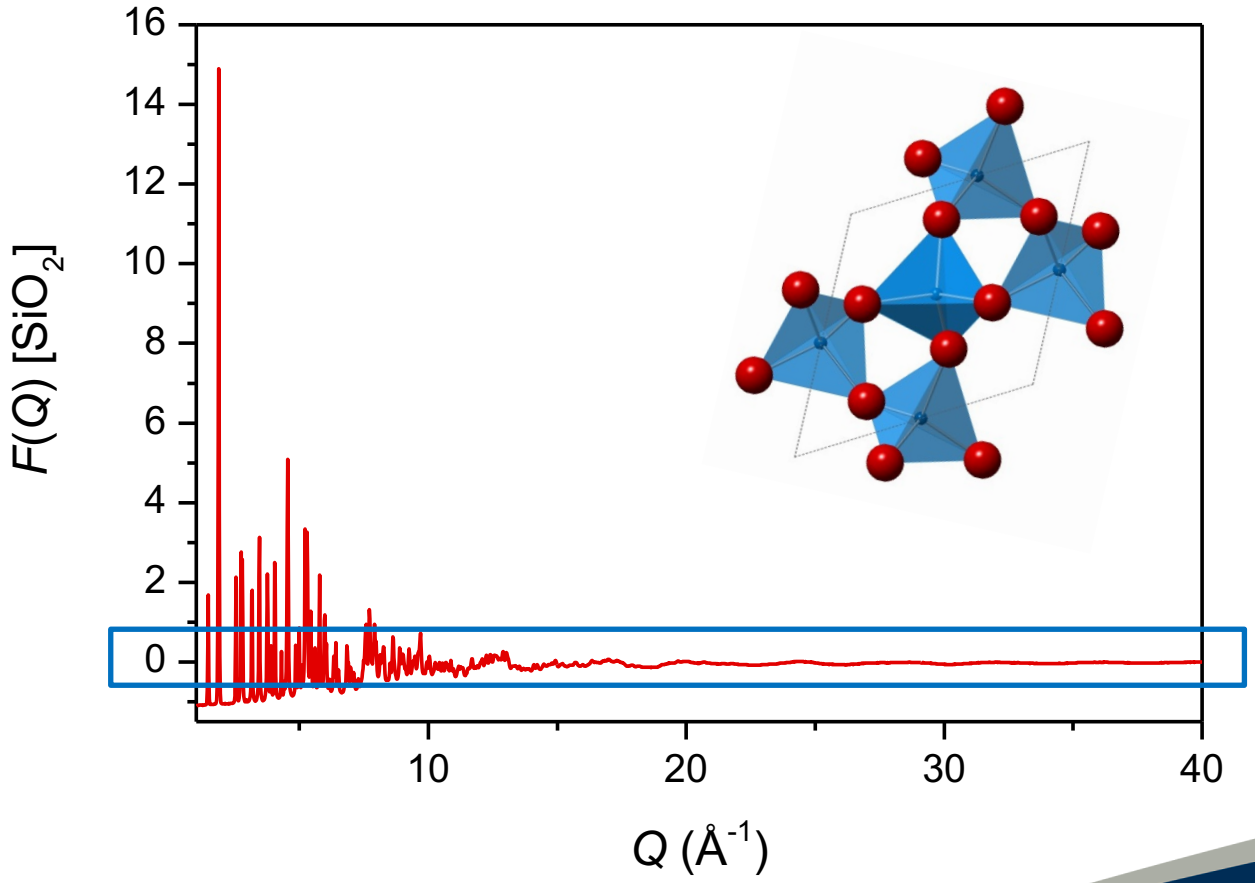

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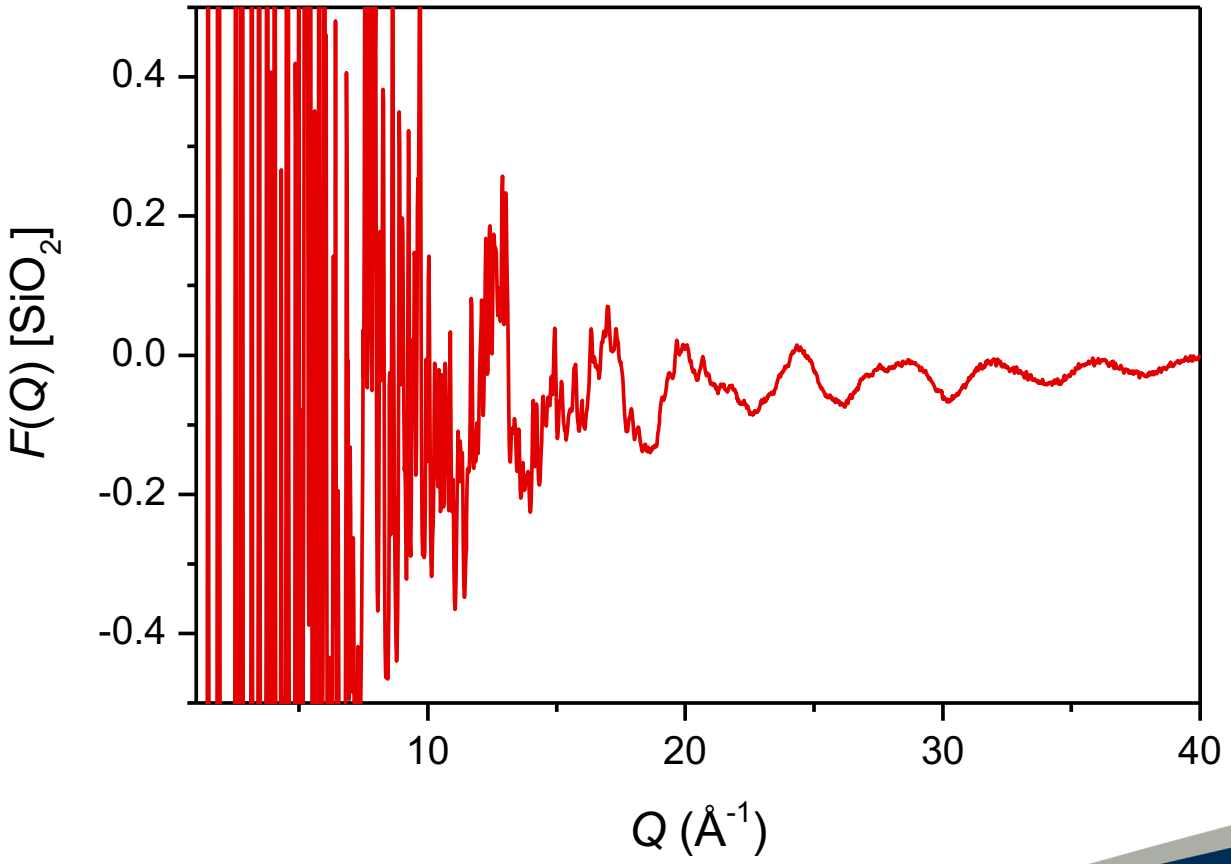

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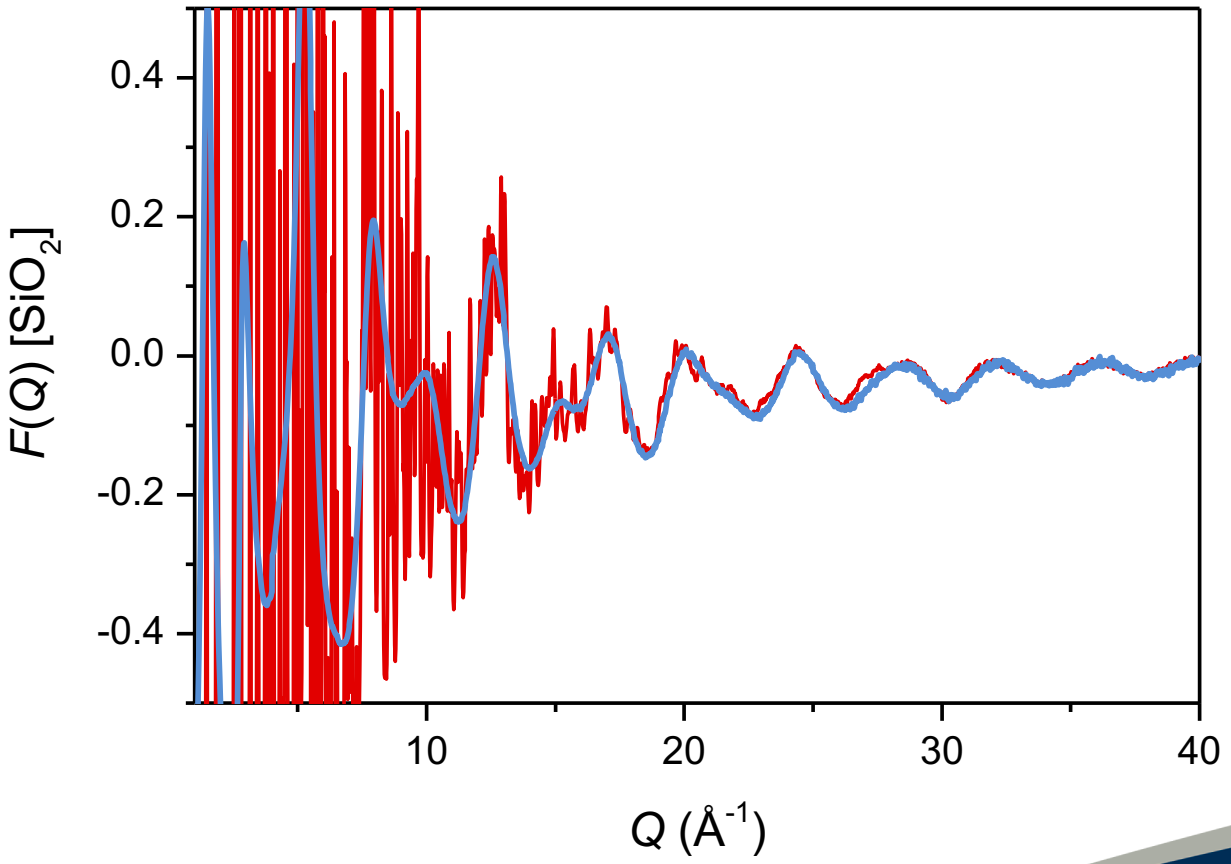

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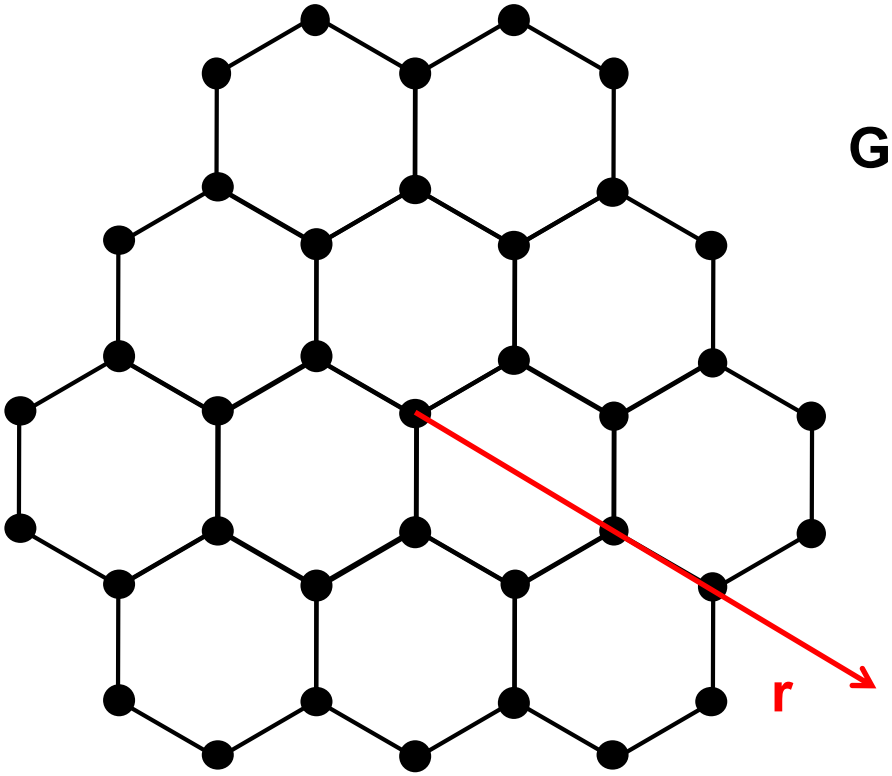
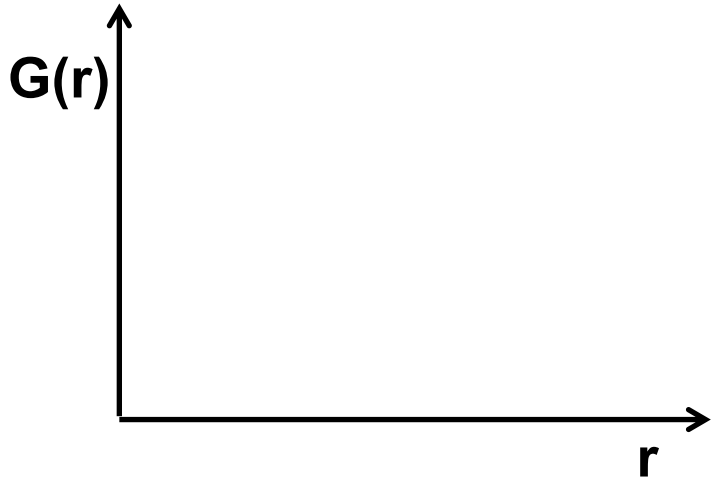
Introduction to Total Scattering

The pair distribution function (PDF)

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





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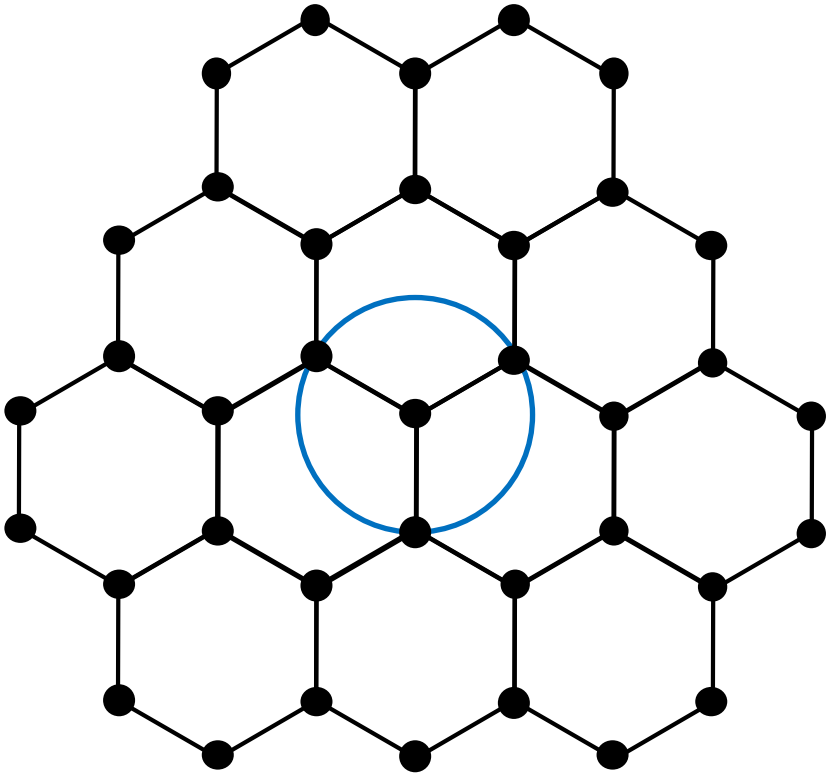

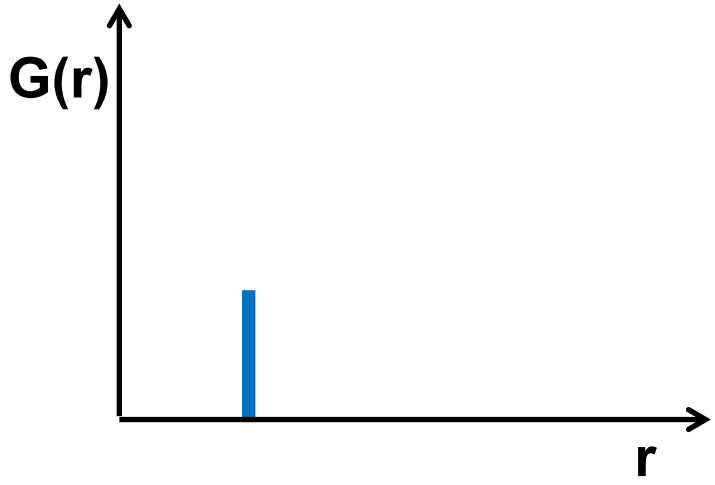

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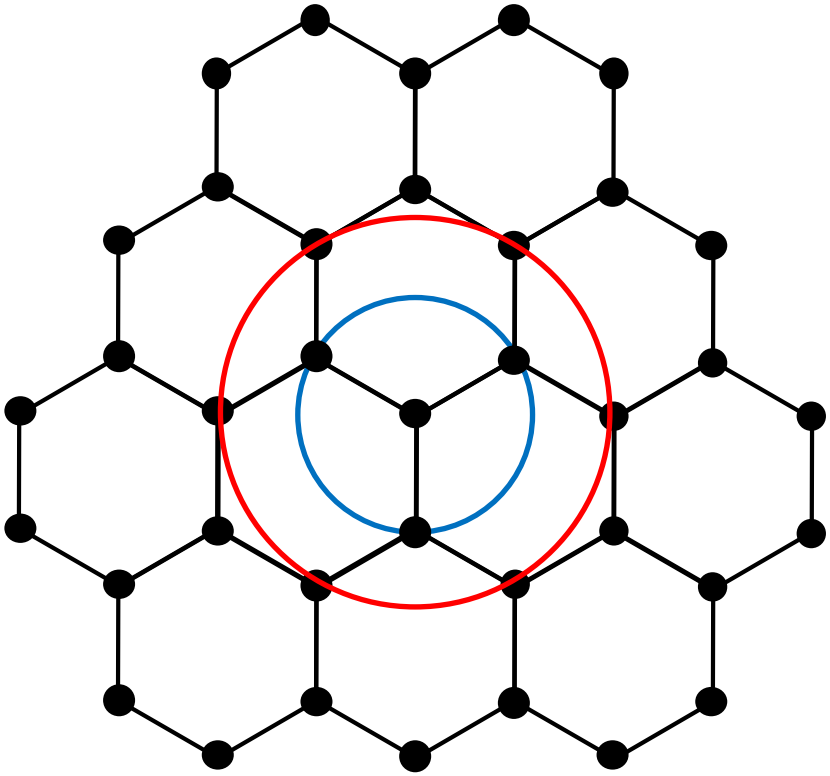

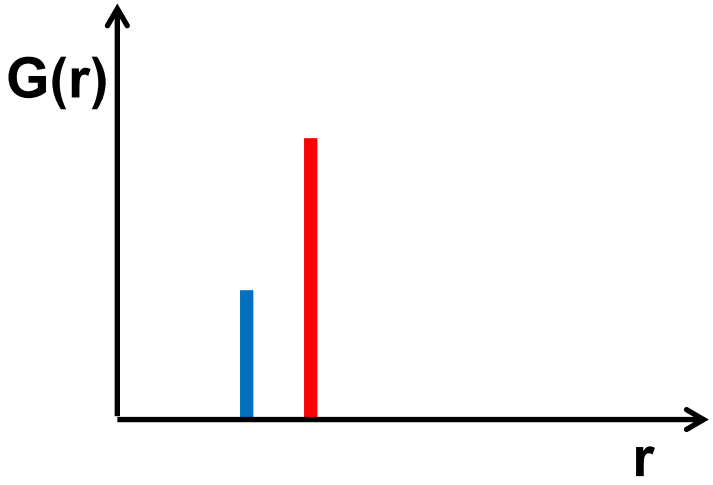

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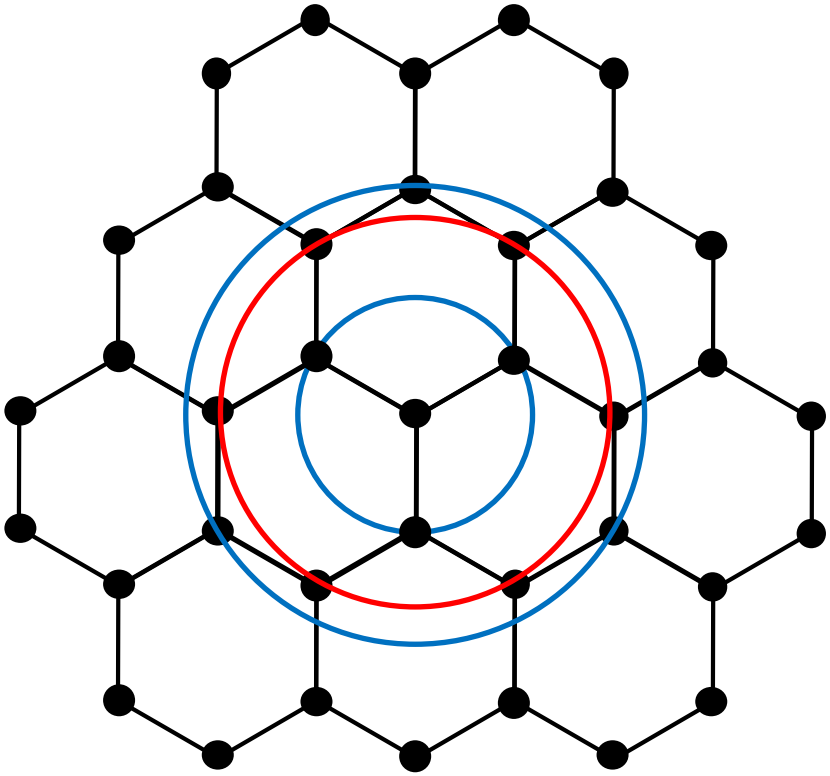

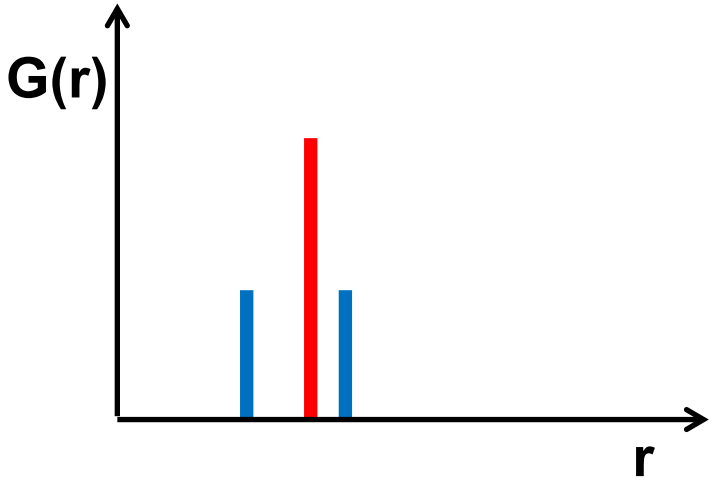

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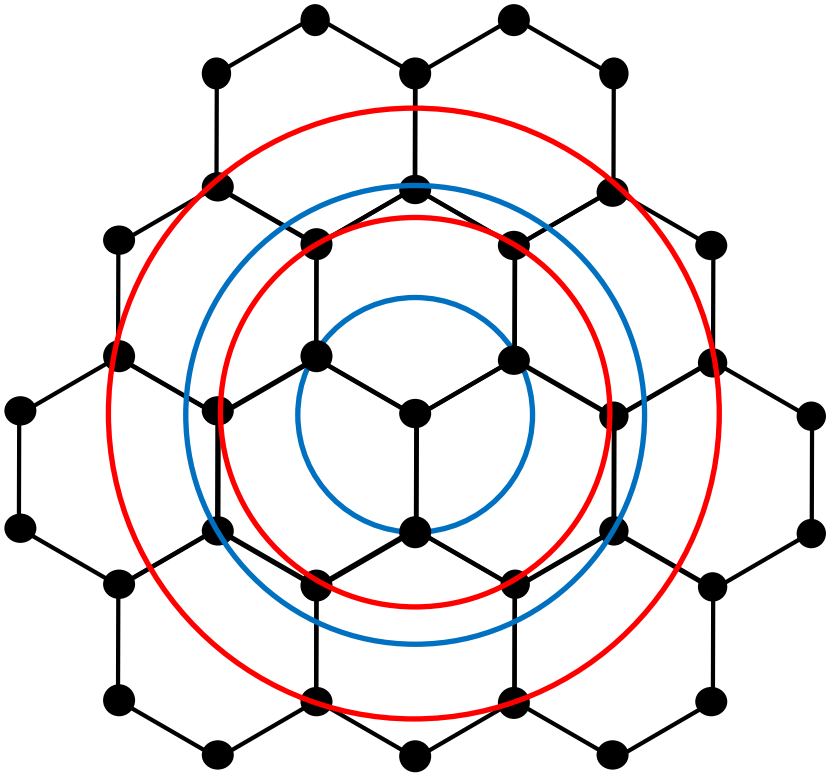

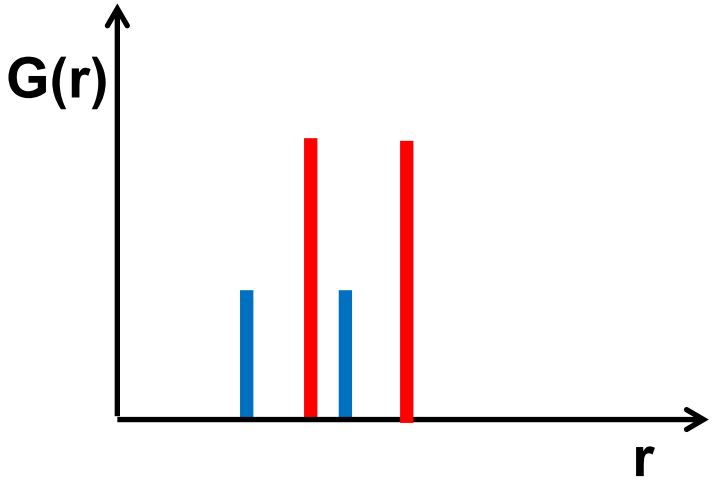

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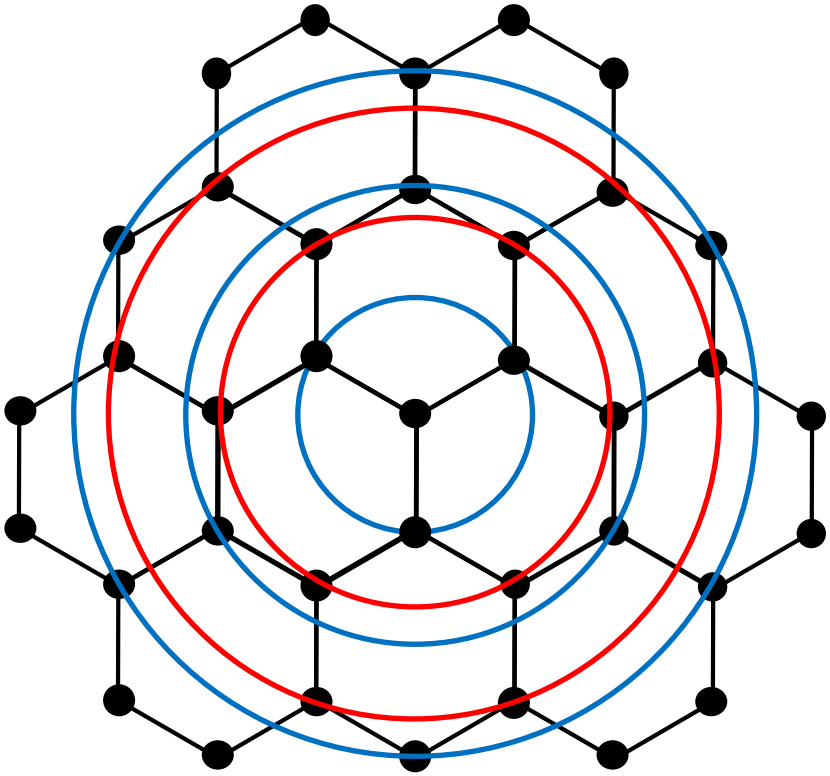

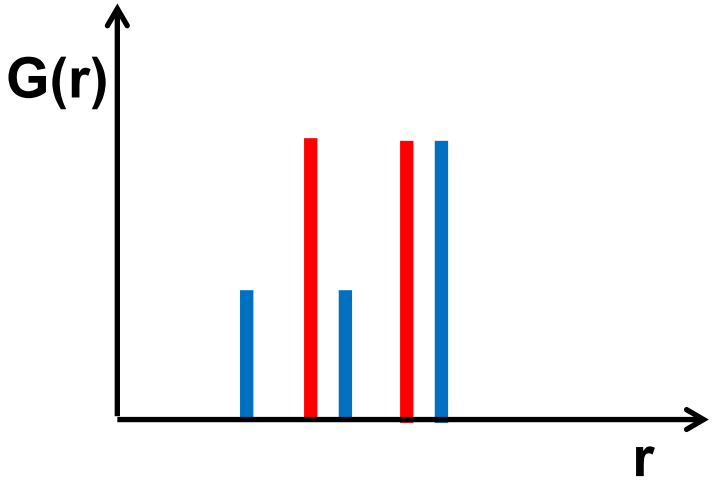

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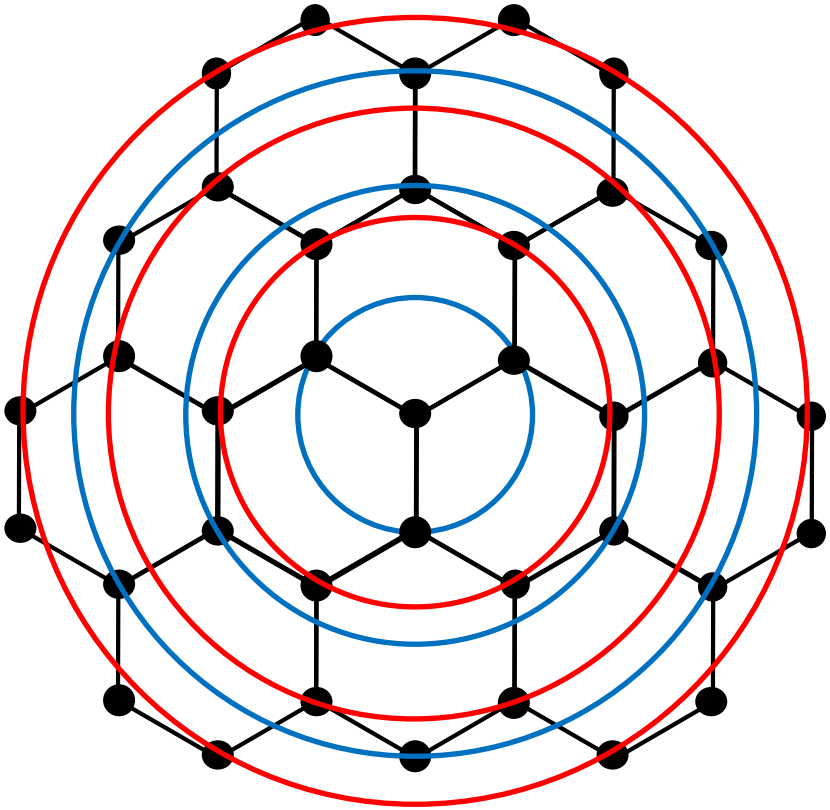

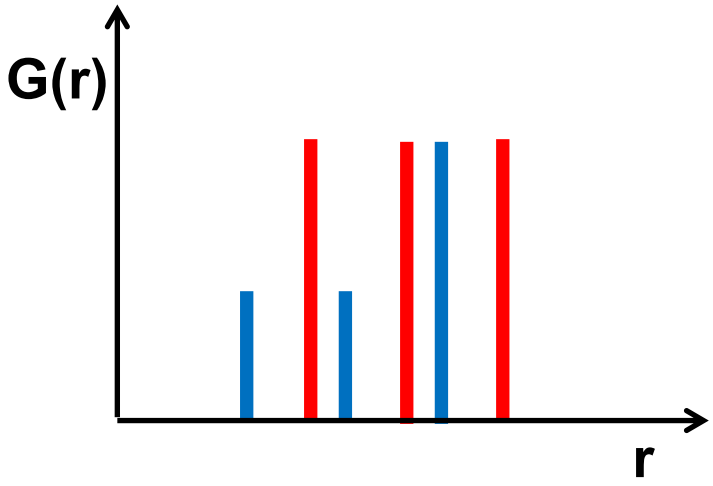

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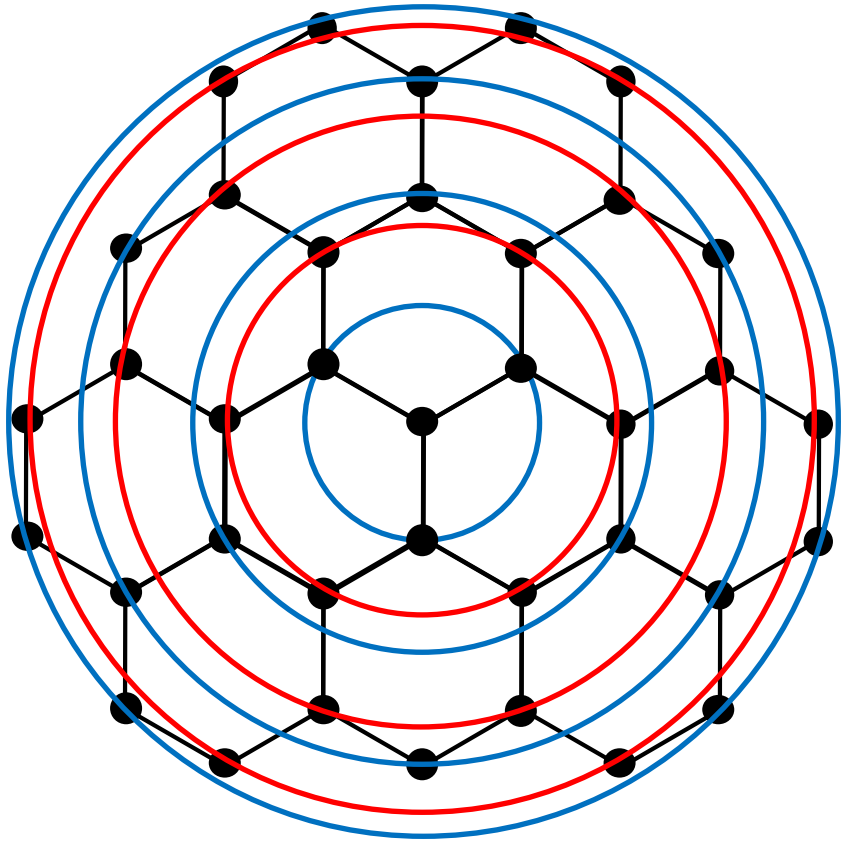

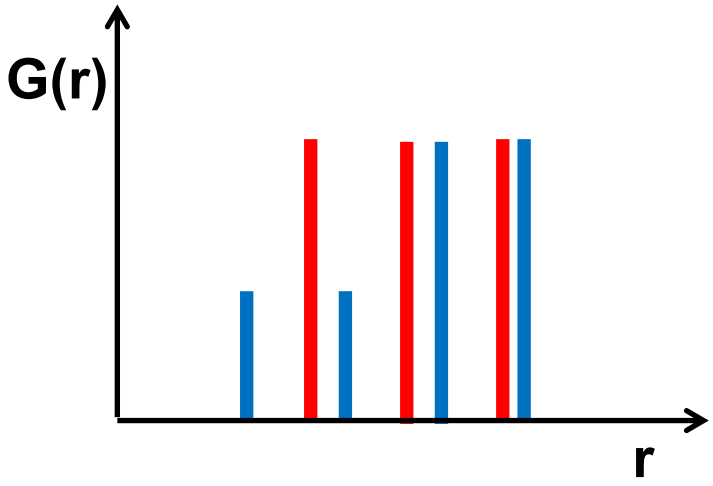

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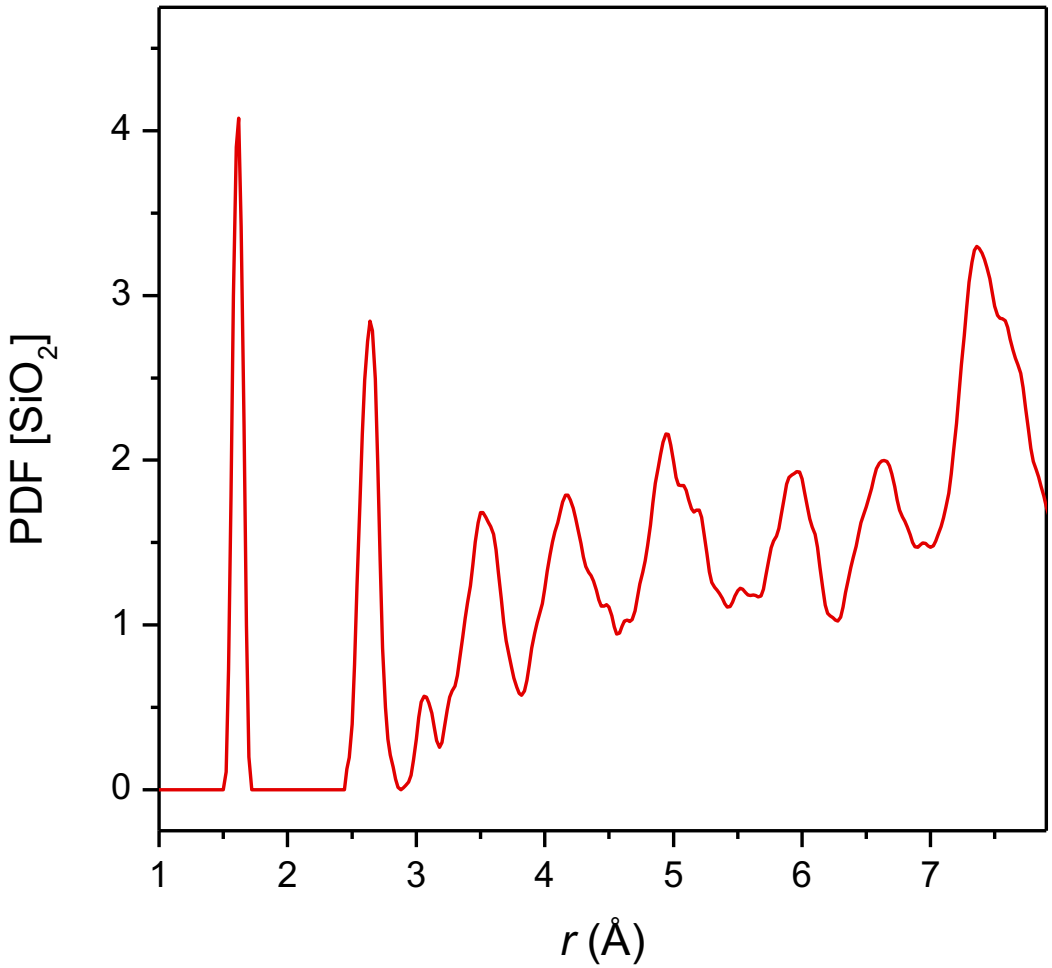

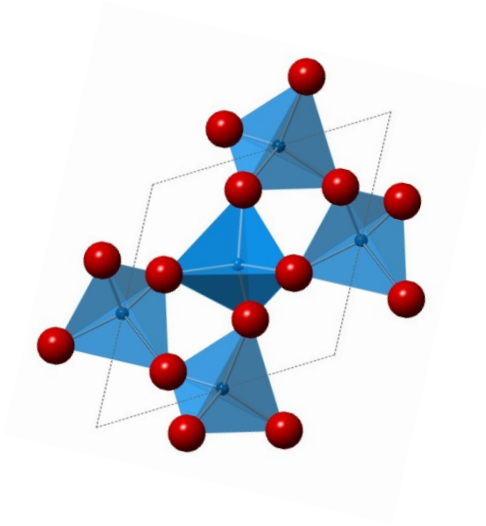

This is the neutron PDF for quartz type SiO_2.

Introduction to Total Scattering

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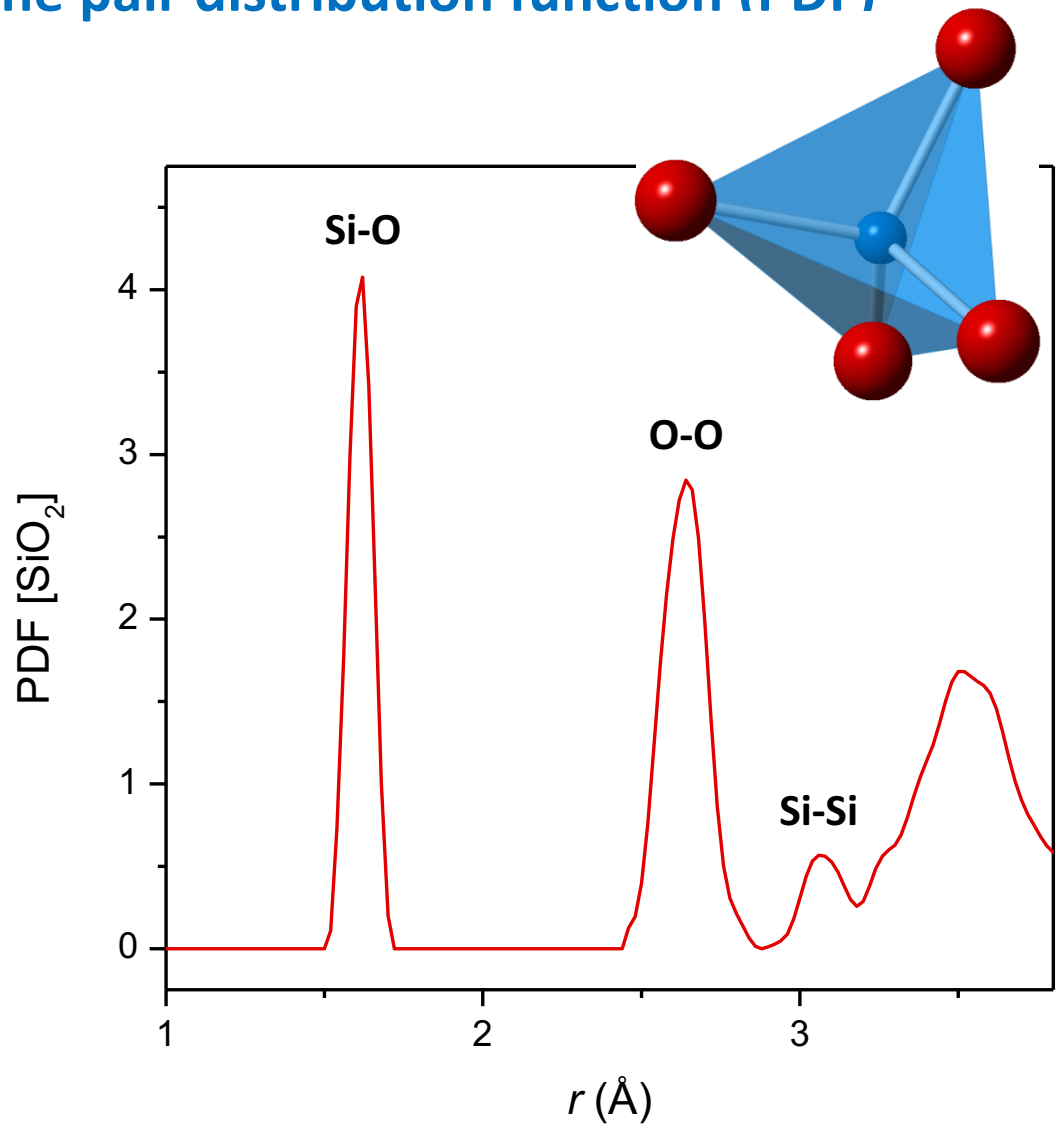
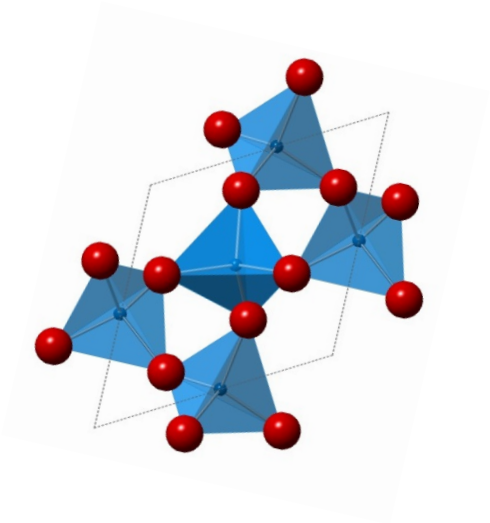


Visual inspection can provide information about:

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

…more detail comes from modelling!



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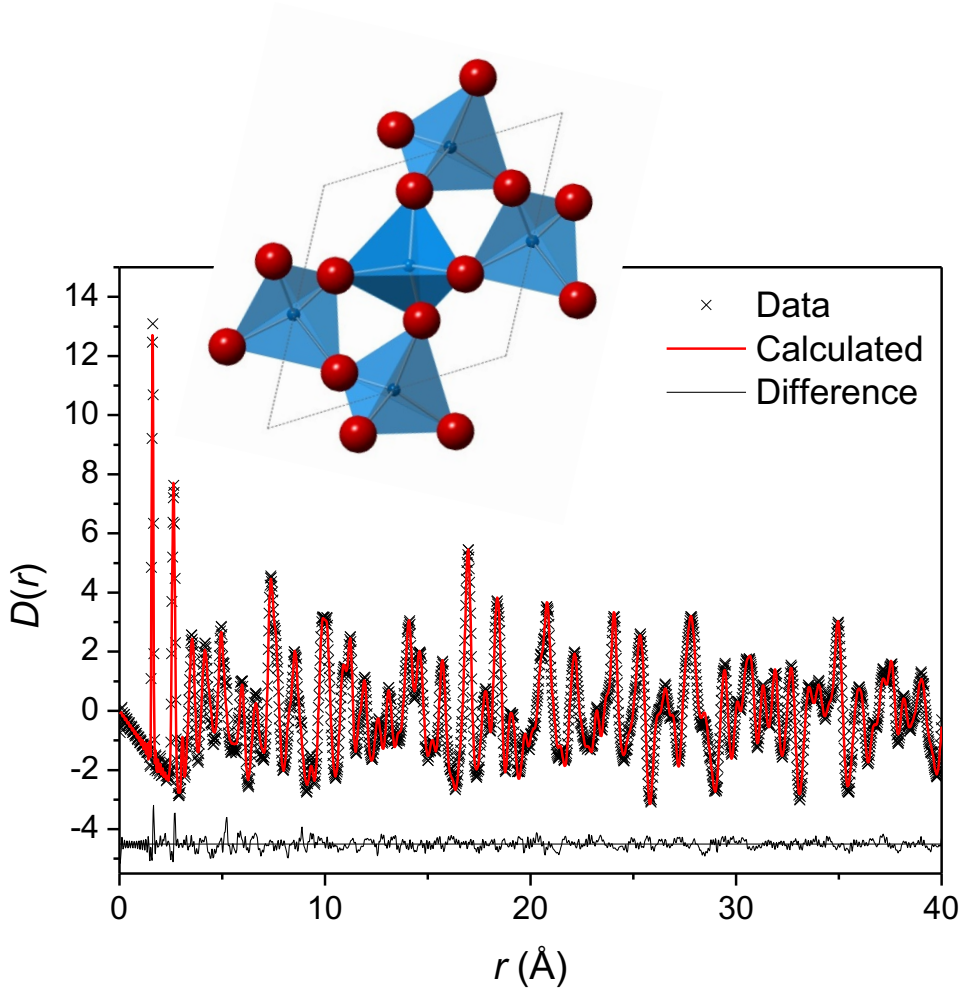
Introduction to total scattering

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.

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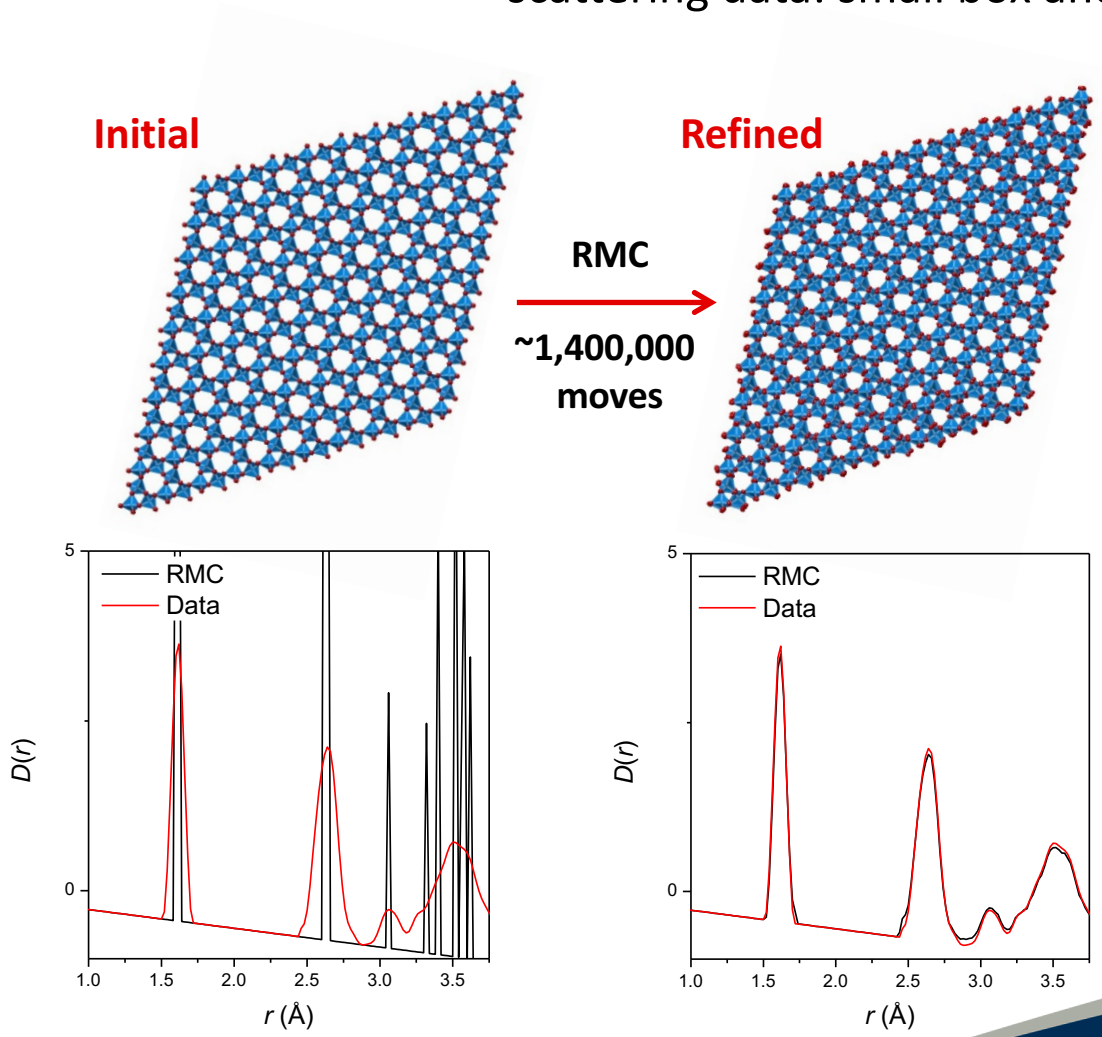
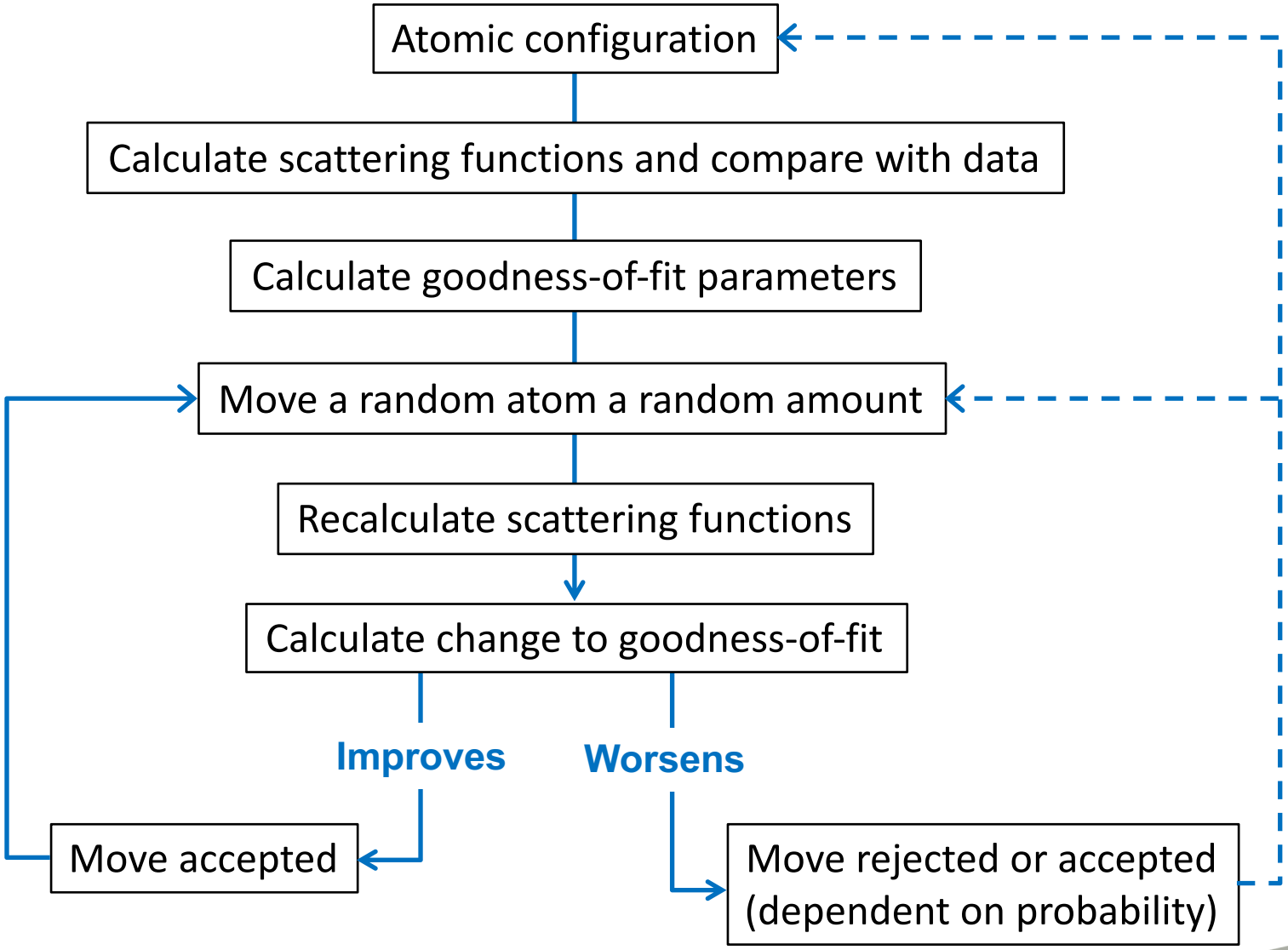
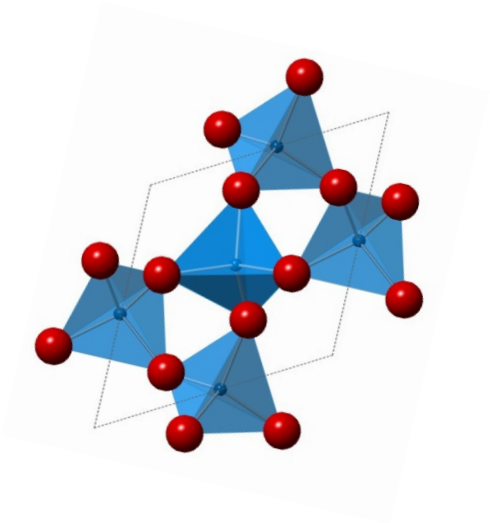


Big box modelling:

- 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 average and local structure.
- Not constrained by symmetry.

The Reverse Monte Carlo Technique

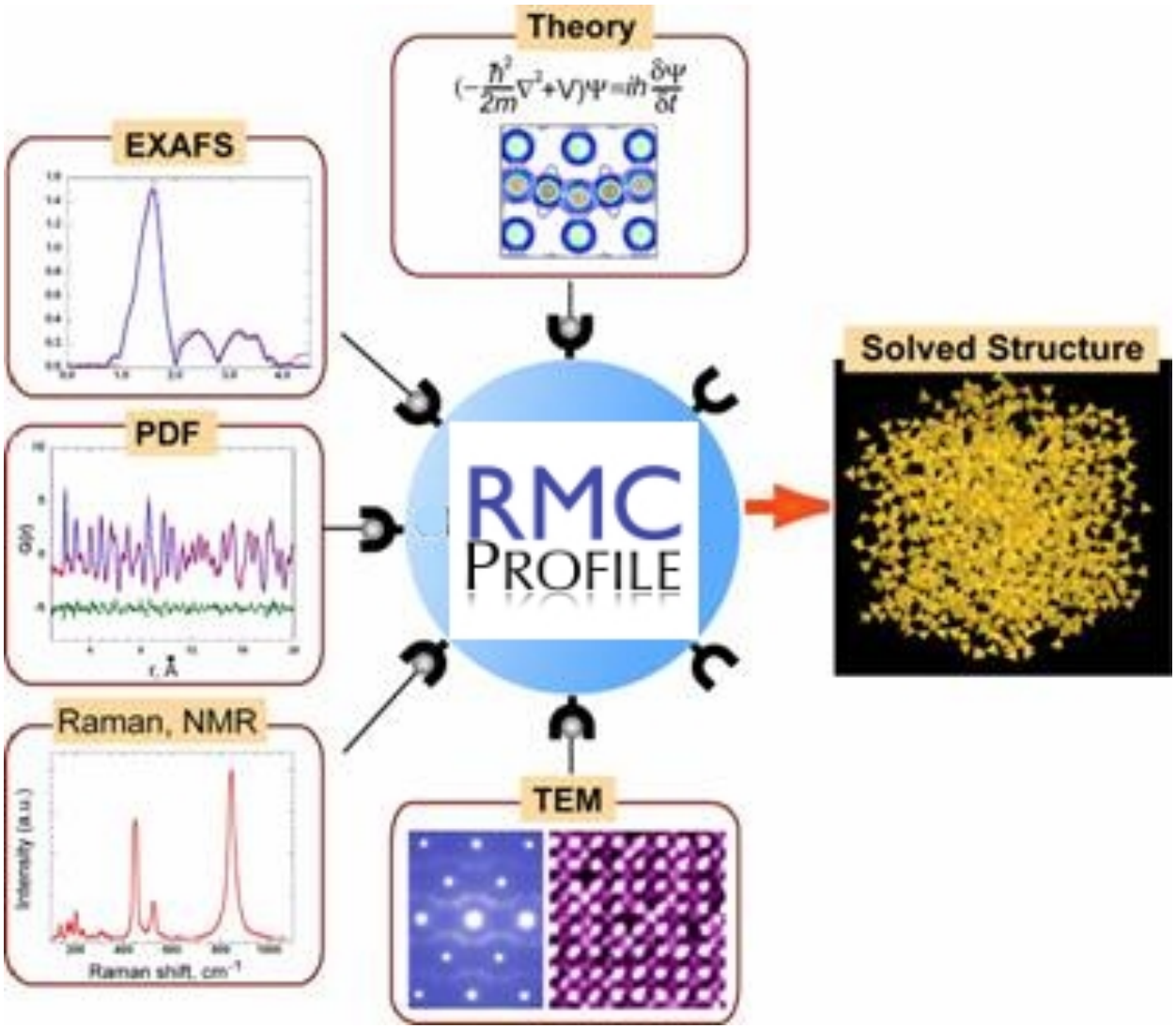




RMCProfile

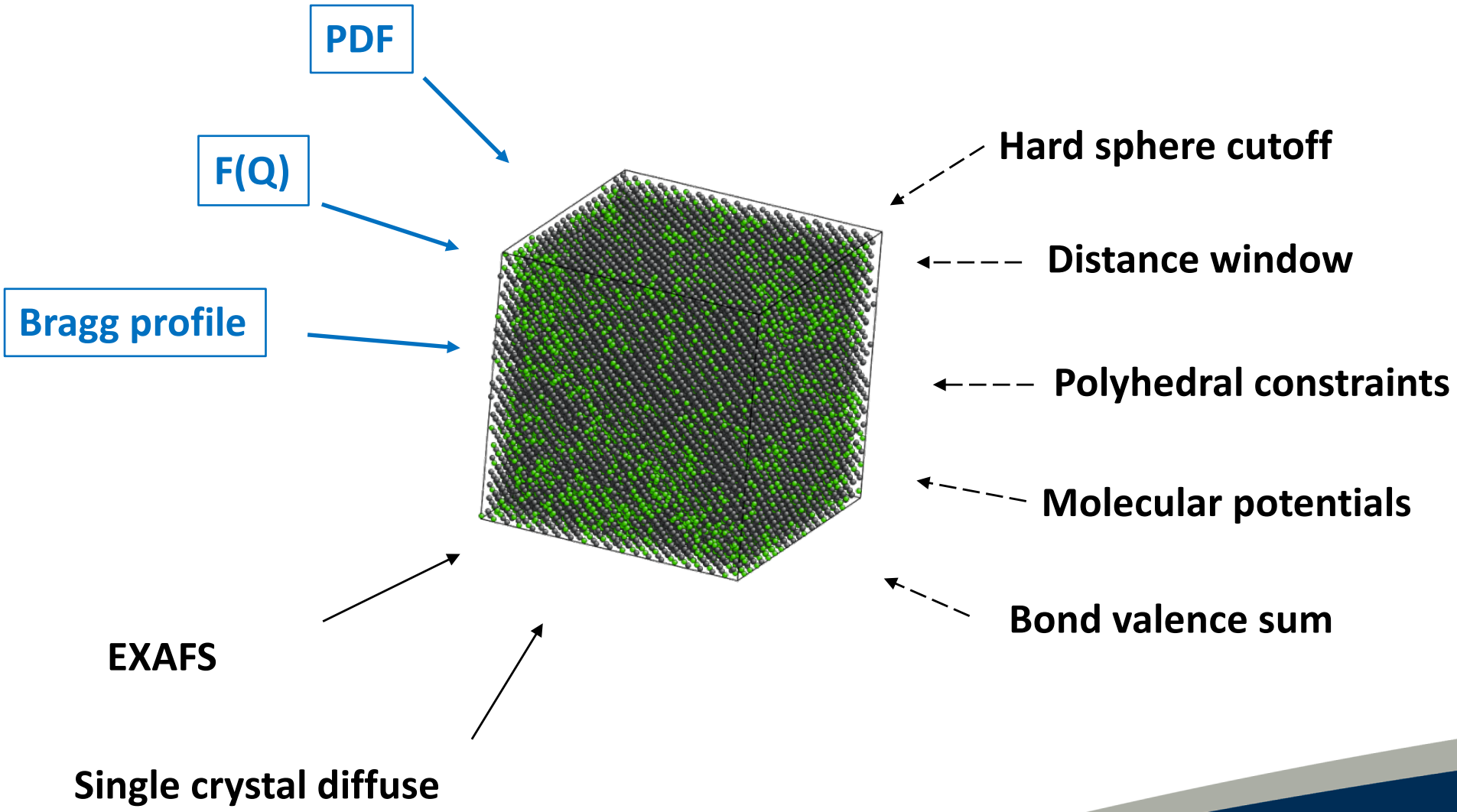
- Implementation of the RMC algorithm particularly suited to crystalline materials.
- "Profile" refers to the Bragg profile – a very important constraint for average structure.
- Based on the original RMCA code of McGreevy and Puzstai, extended by Matt Tucker (now at ORNL).
- Developers: Dave Keen (ISIS), Martin Dove (QMUL), Andrew Goodwin (Oxford), Helen Playford (ISIS), Wojciech Slawinski (ISIS), and many others.
- 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



Adapted from:
S. J. L. Billinge and I. Levin, *Science,* 2007, **316**, 561–565.

RMCProfile



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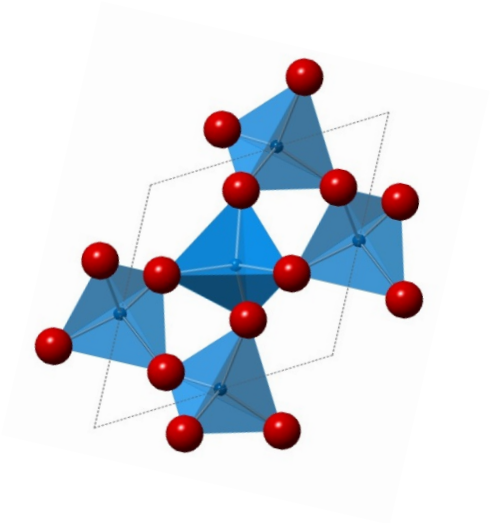
RMCProfile

Requirements for 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

RMCProfile

- RMCProfile 6.6
  - developed at ISIS by Wojciech Slawinski
  - arbitrary scattering length inputs
  - multiple atom swapping
  - bugfixes
  - usability improvements
  - release date: ASAP
- 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 and colleagues**
  - (beta) release date: February 2017
- RMCProfile 7.1 and later **
  - incorporation of small-box modelling (with colleagues at SNS)
  - developments for nanoparticles, low-dimensional systems & networks (with QMUL and University of Oxford)
  - release date: future



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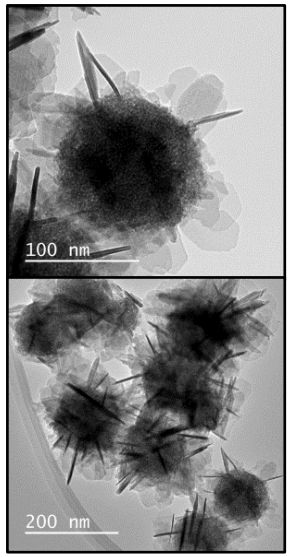
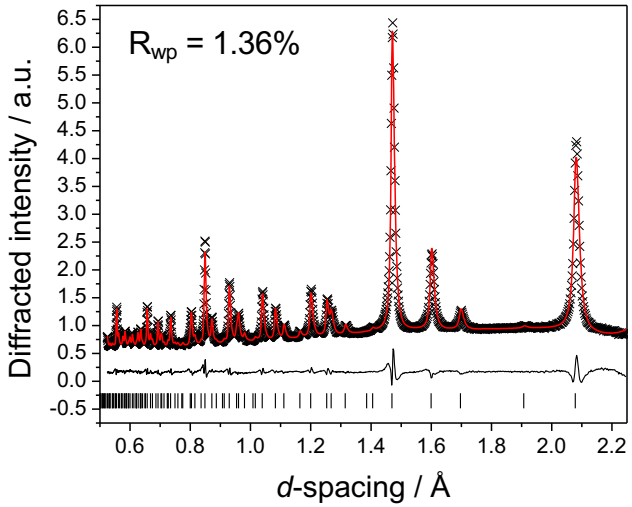
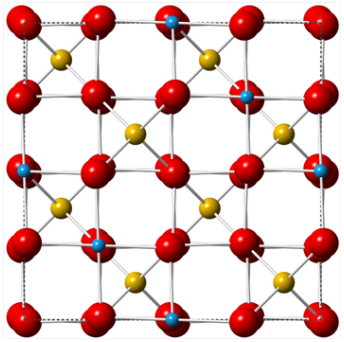
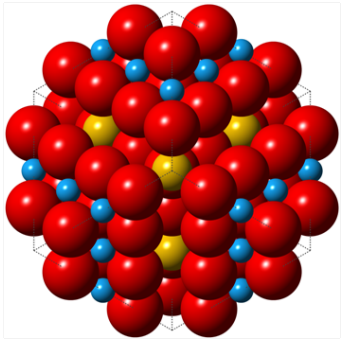
Case Study: Gallium Oxide

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.

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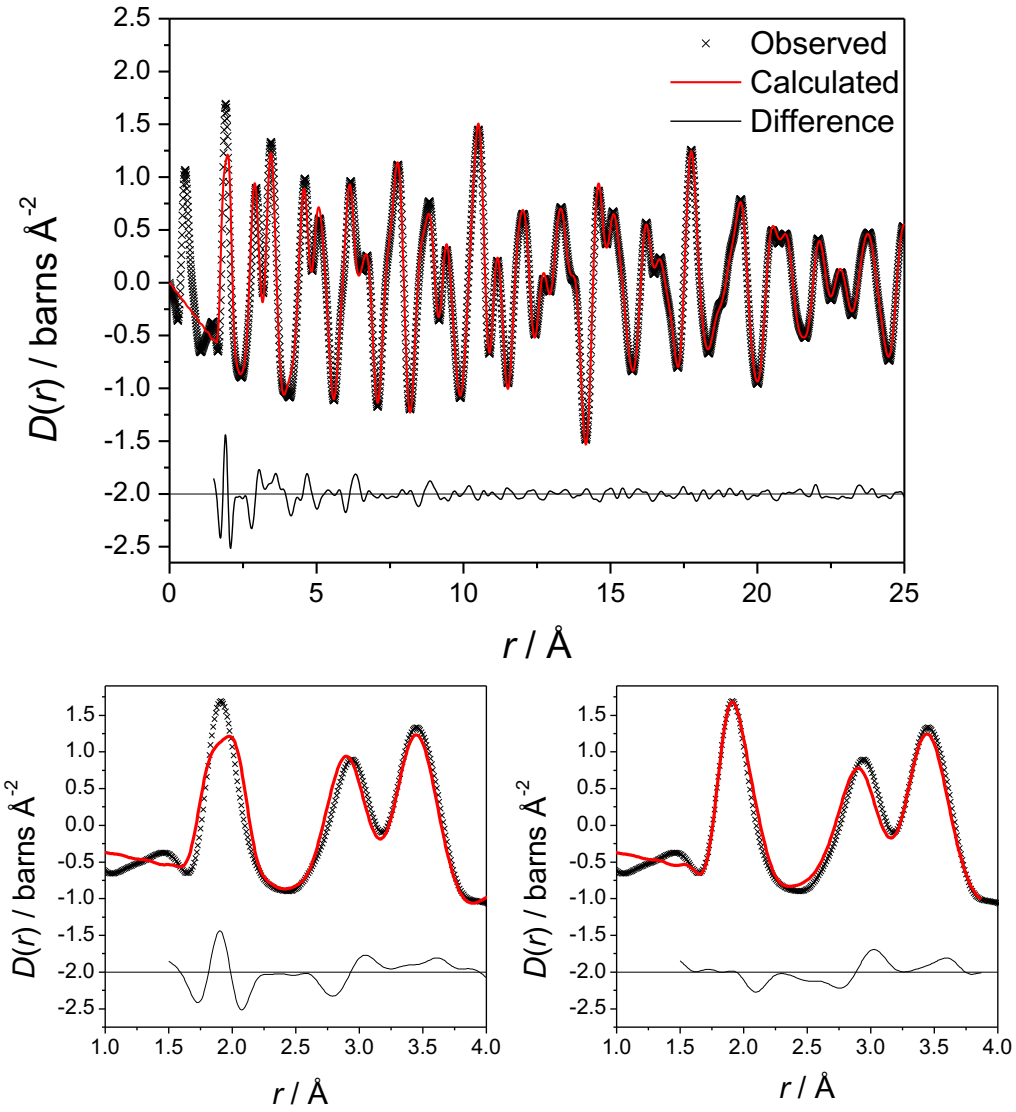

- Small-box modelling of the PDF
- Medium-to-high *r* agrees well with average crystal structure
- Large discrepancies in local structure
- Improved fit when lower symmetry model is used, but it is a purely local effect

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

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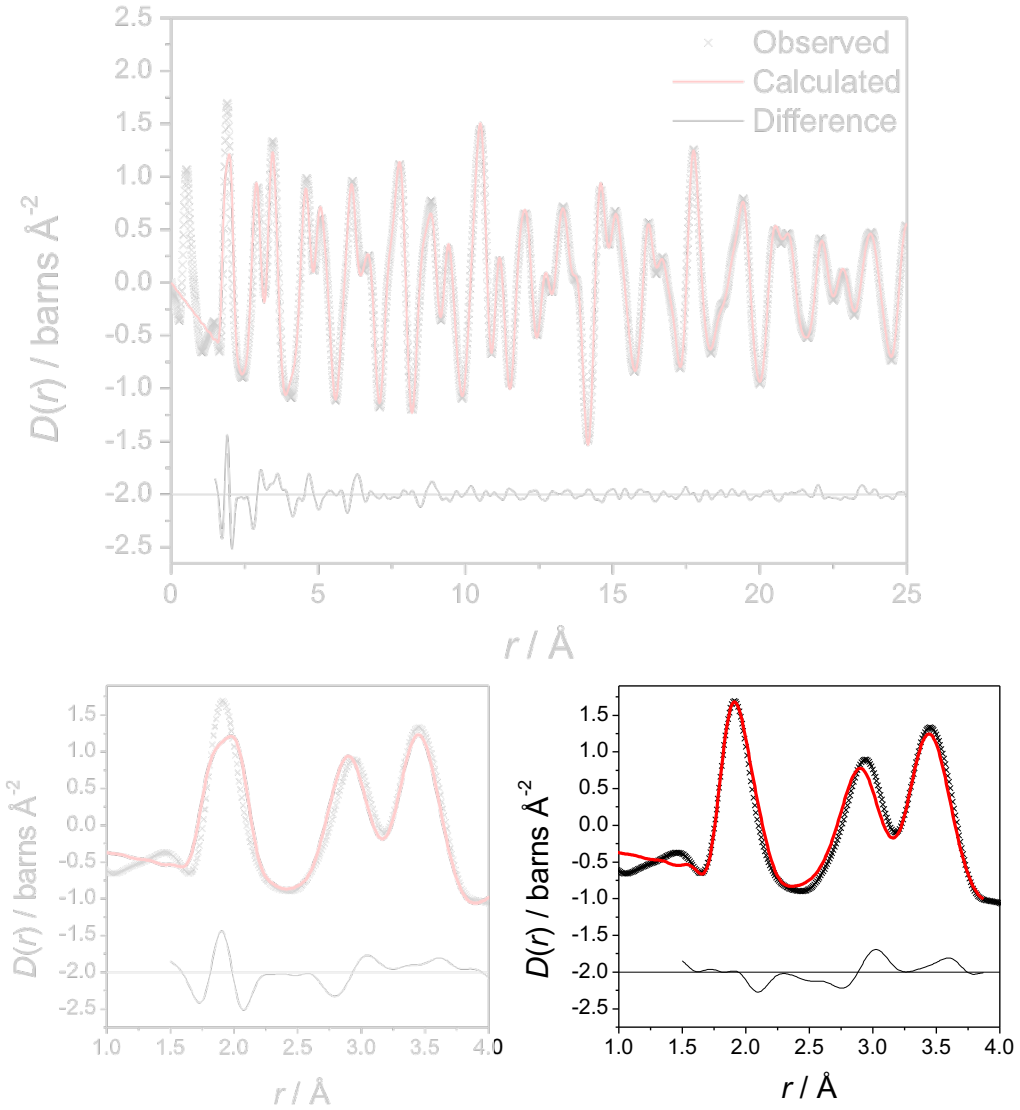

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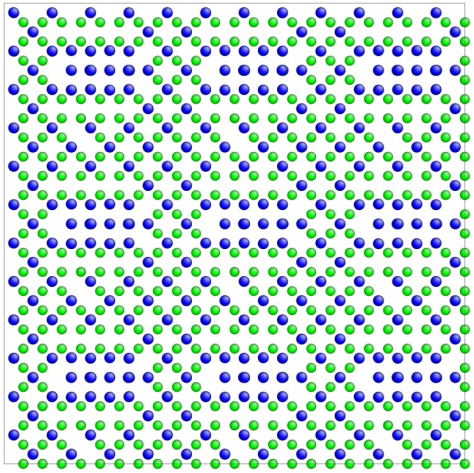
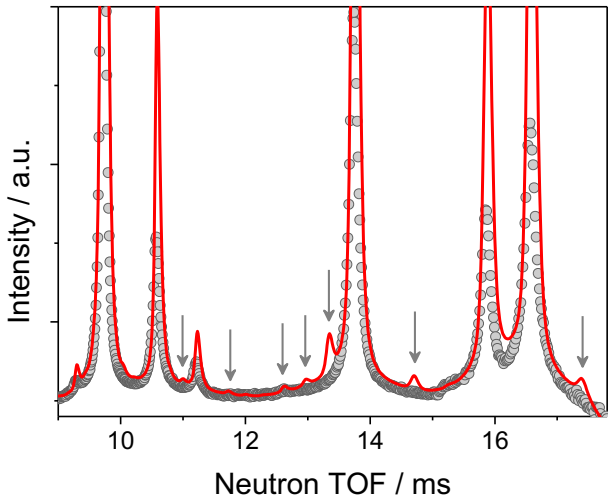
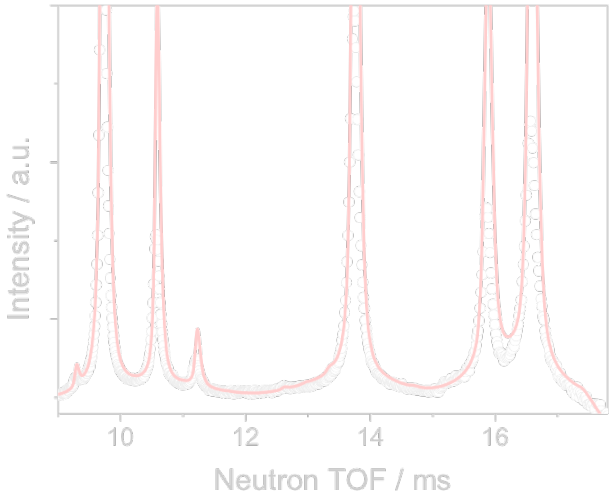


Green = octahedral Ga
Blue = tetrahedral Ga





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.

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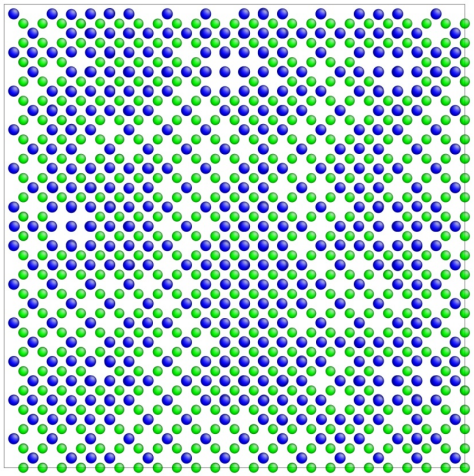

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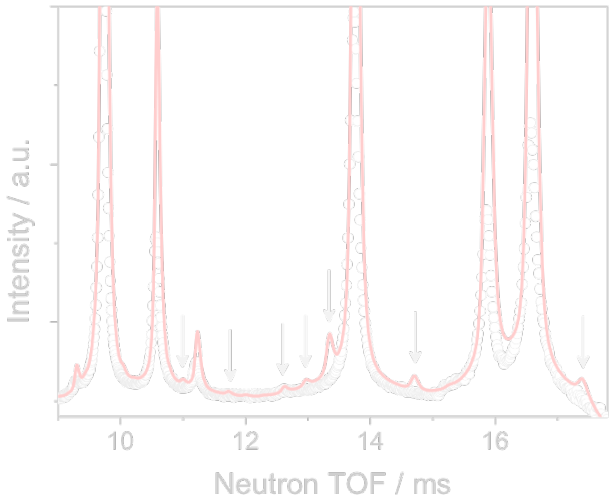

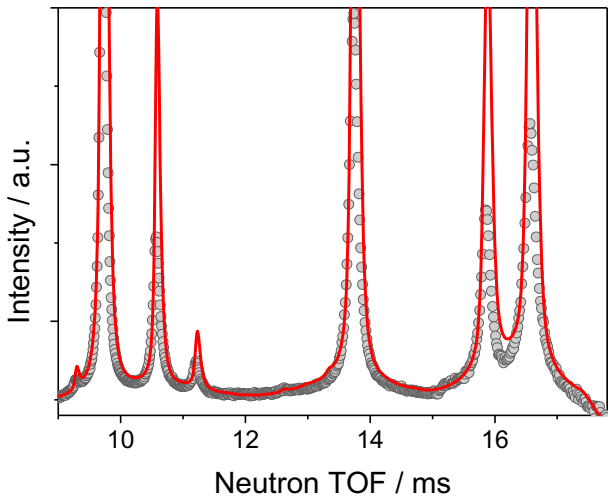

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Physically and chemically sound starting model(s) for full RMC refinement

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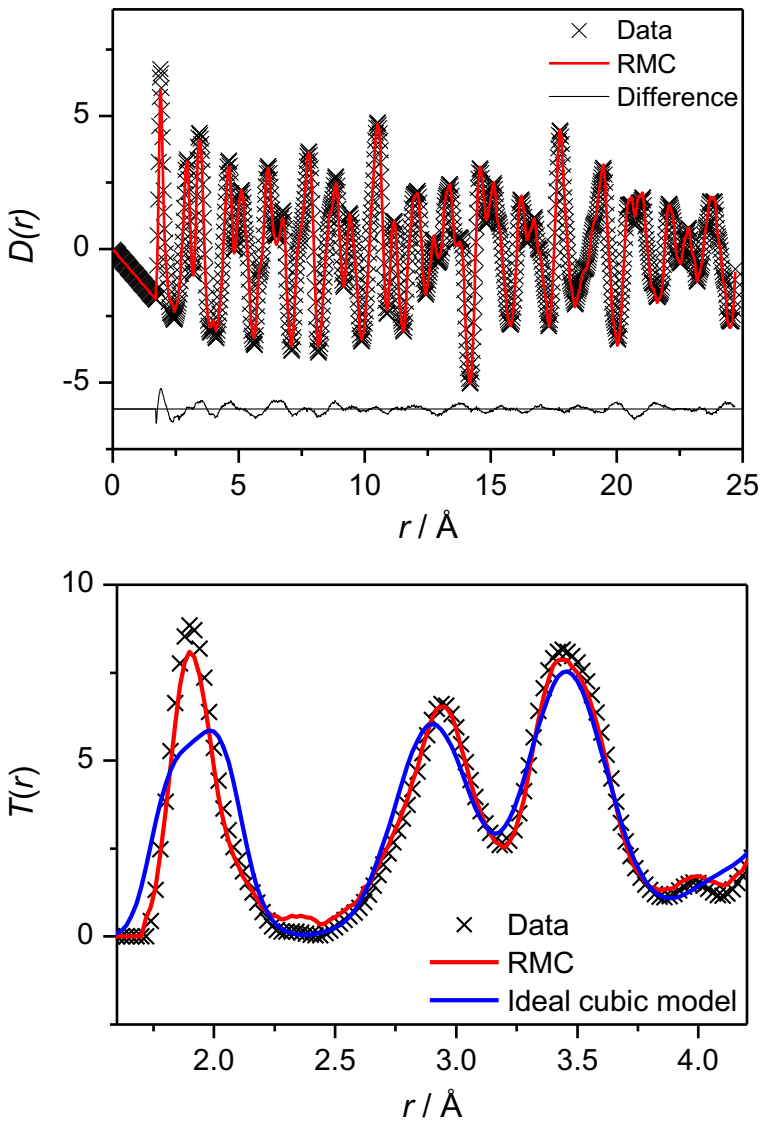
Case Study: Gallium Oxide



RMC refinement using 6x6x6 supercell

- vastly improved fit to local structure

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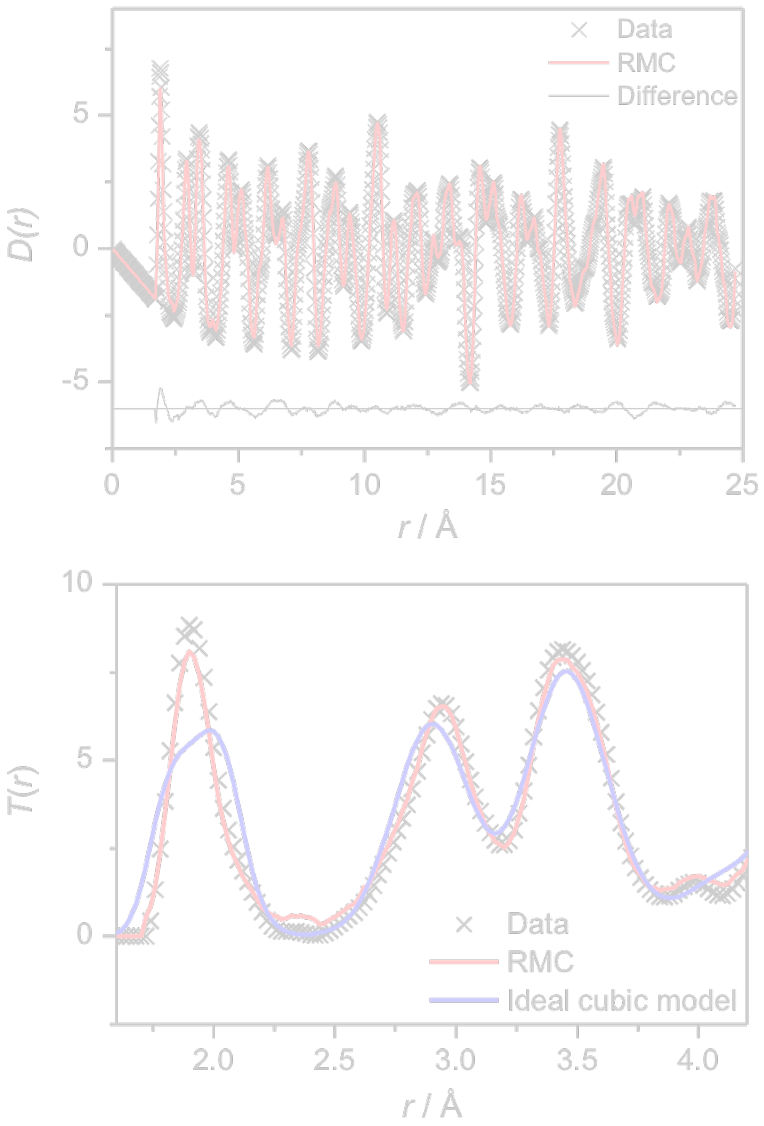
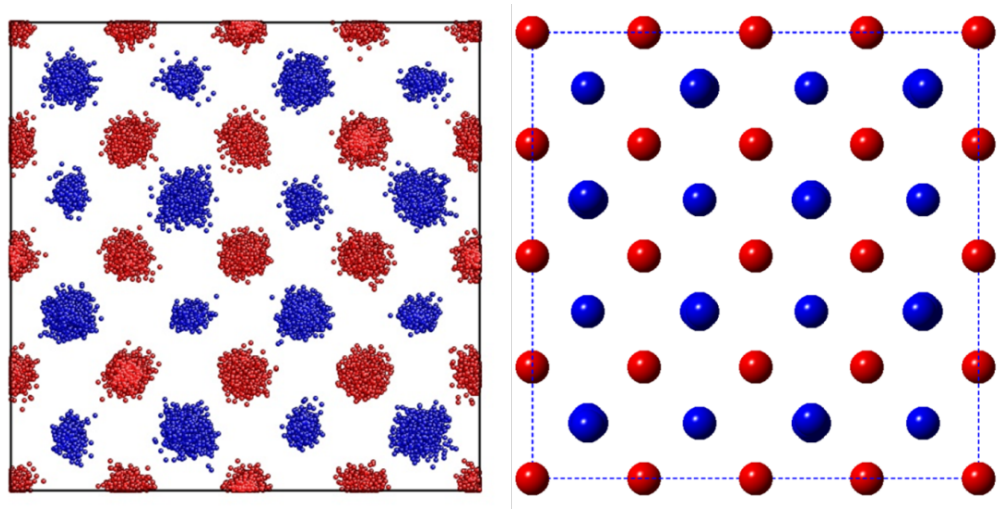


RMC refinement using 6x6x6 supercell

- vastly improved fit to local structure
- maintains correct average



Collapsed RMC box

Unit cell

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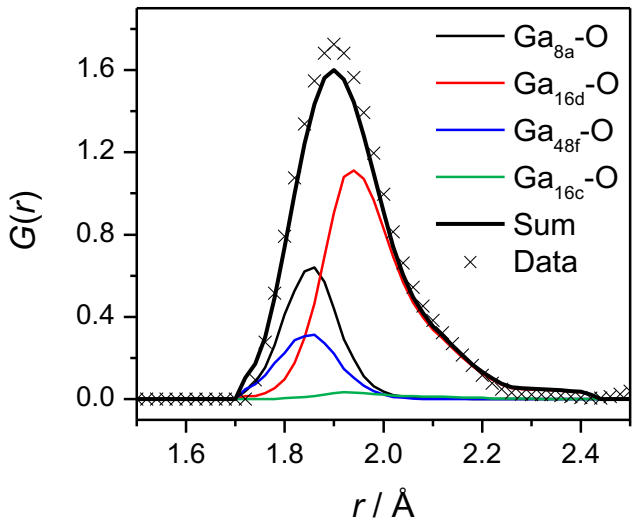
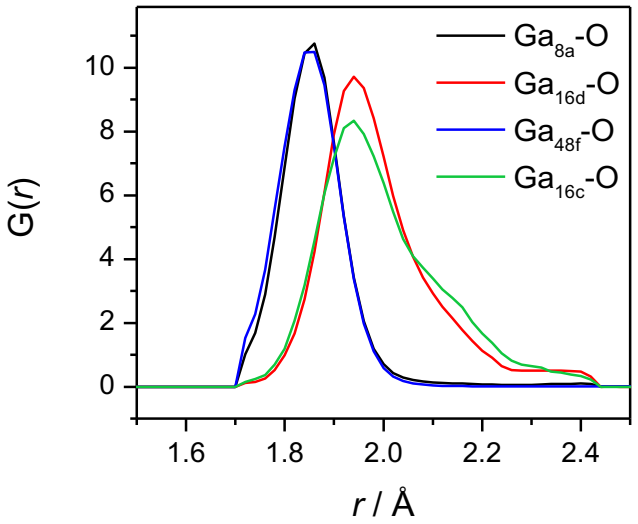
Weighted Ga-O partials



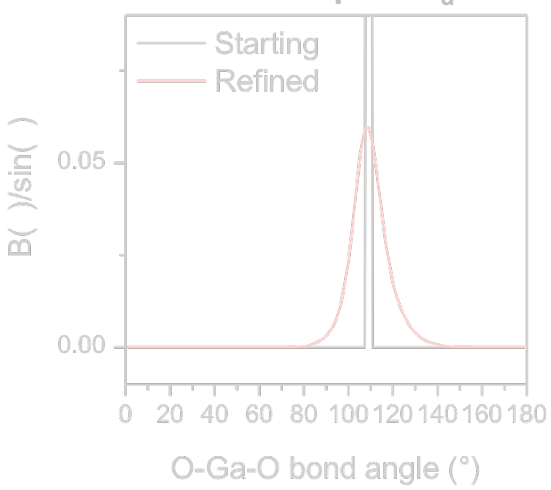
Non-weighted Ga-O partials



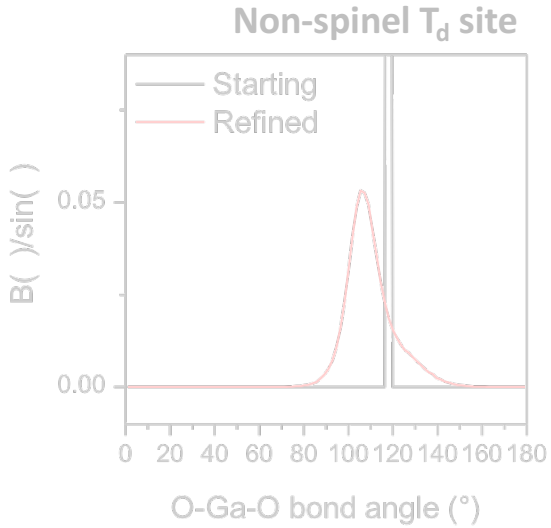
RMC provides bond length and angle distributions:

- 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



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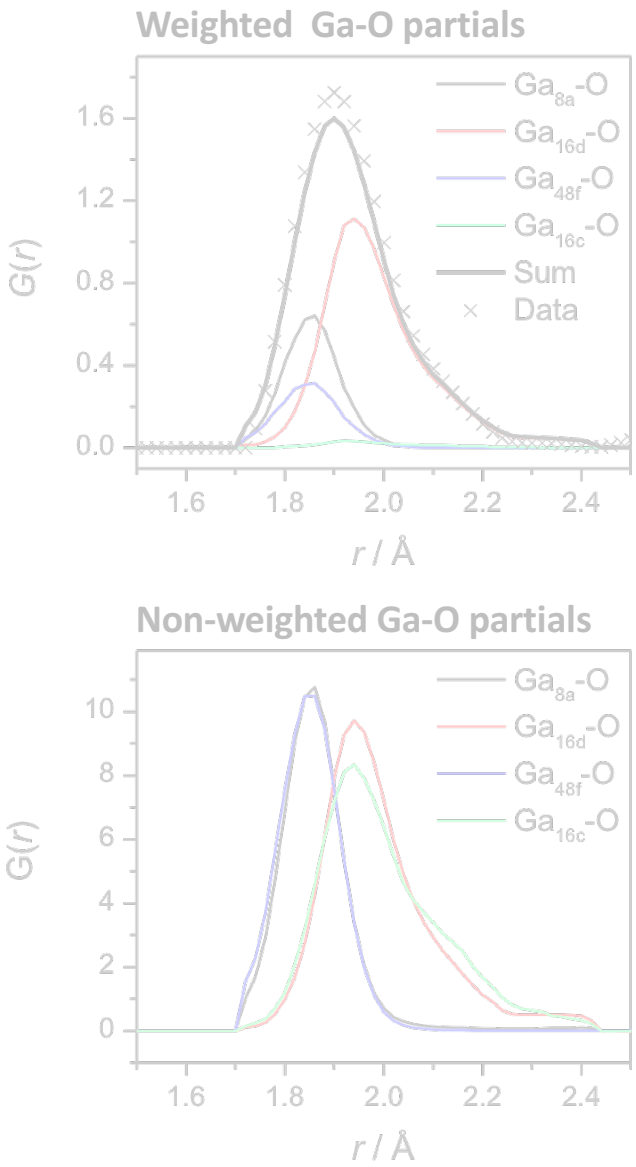

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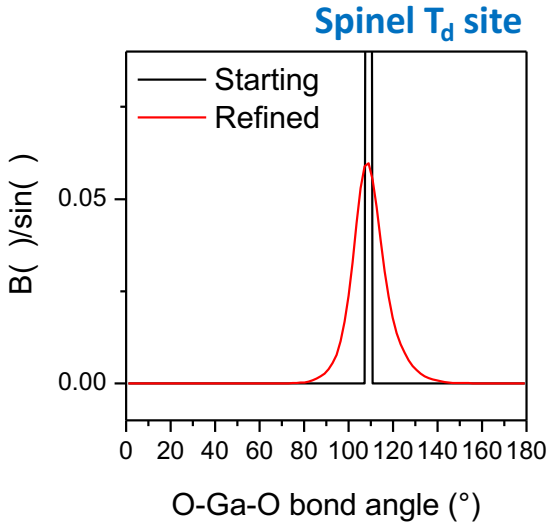

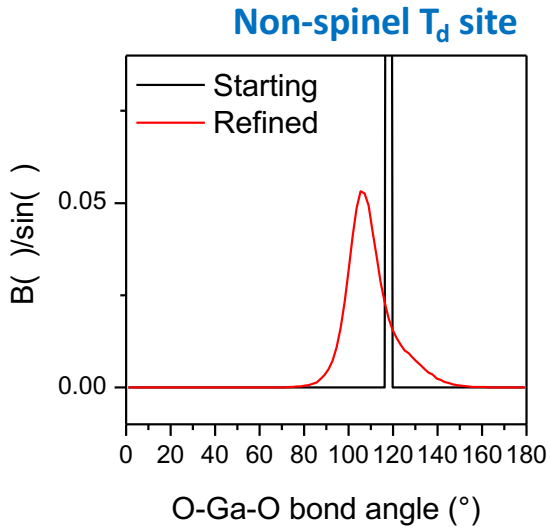

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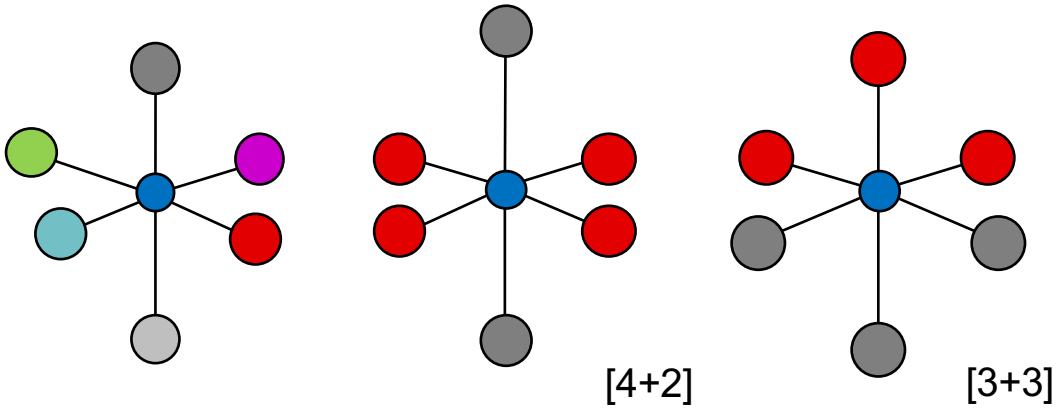
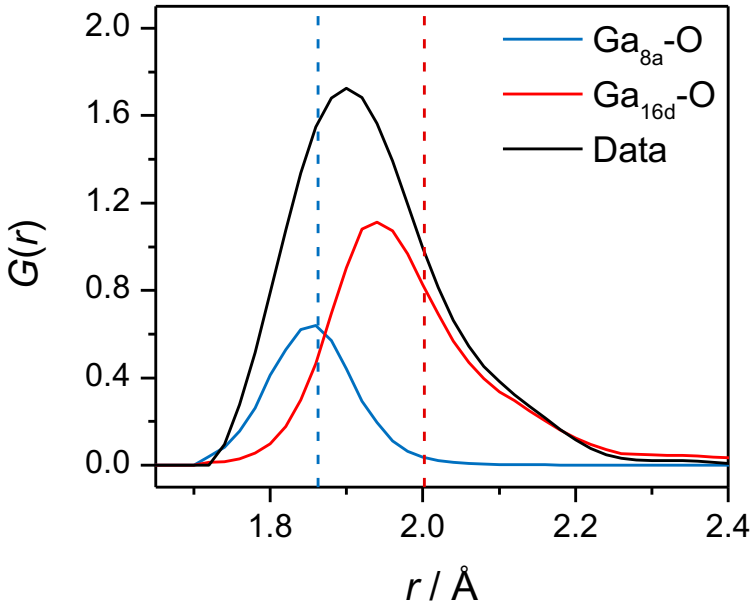
Case Study: Gallium Oxide

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

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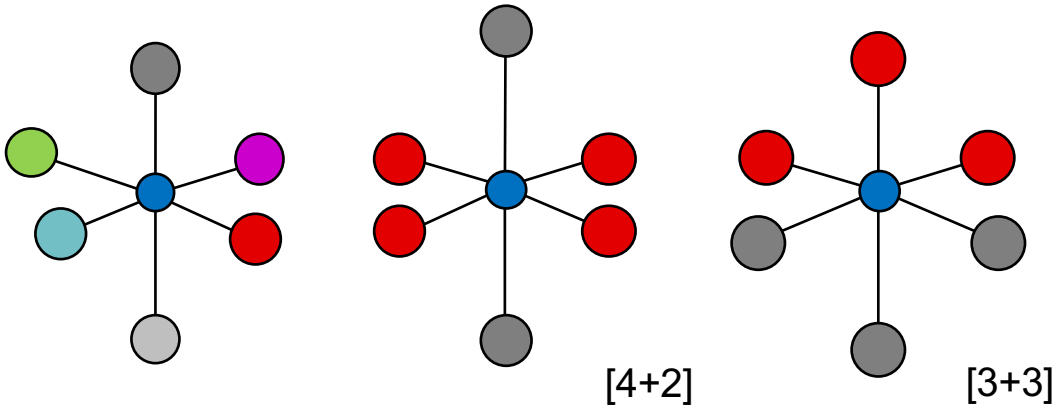

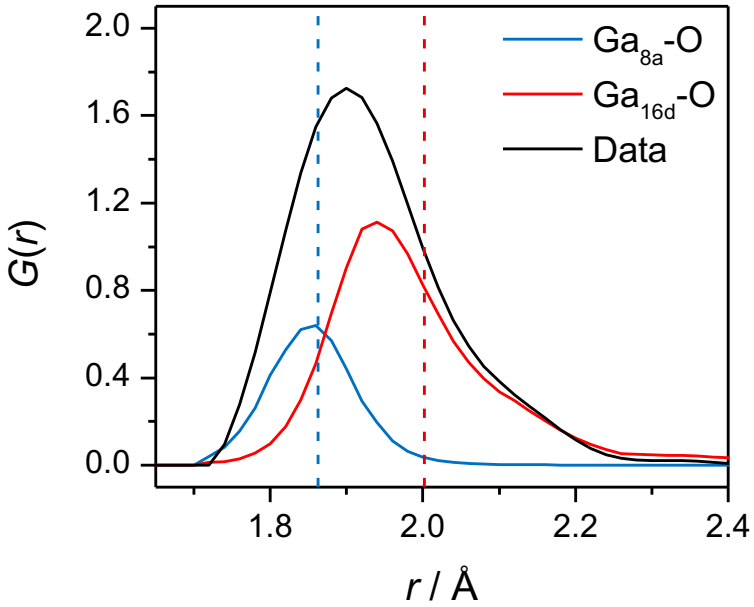

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Thermodynamically stable β-Ga_2O_3 has [3+3] type…

Locally, cubic γ-Ga_2O_3 = monoclinic β-Ga_2O_3

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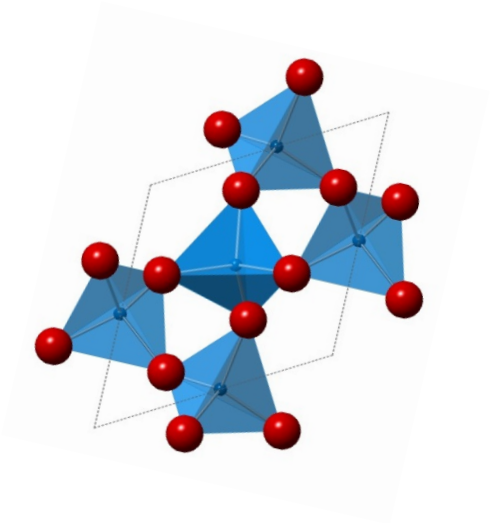
Why was the Case Study successful?

Requirements for 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 ✓



Conclusions

- Total scattering is an extension of powder diffraction that changes the viewpoint from average to local.
- 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!
- The program is always being developed and we always want to hear from you!
- www.rmcprofile.org

Thank you!

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