RMCProfile:
Local structure of crystalline to amorphous materials

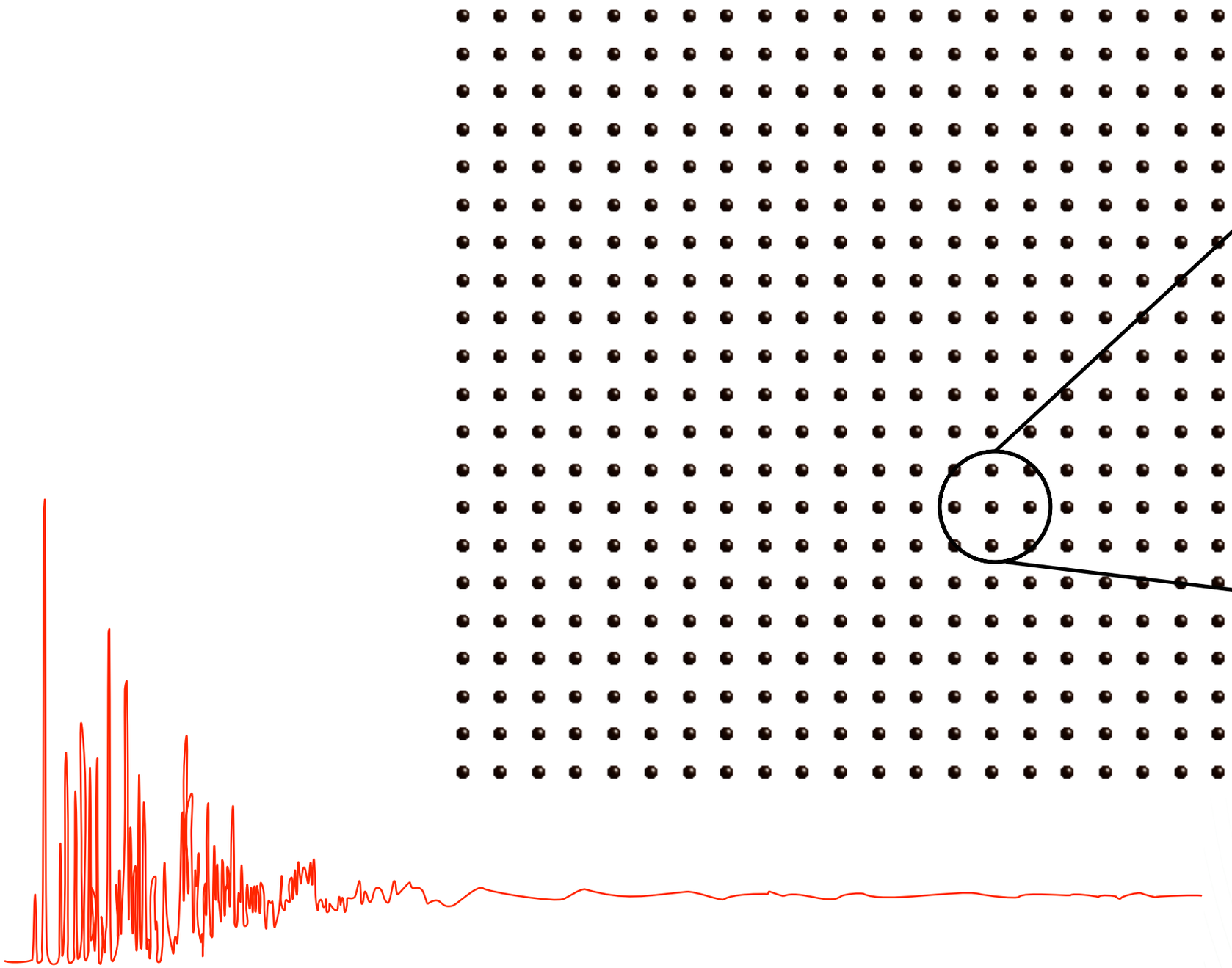
Matt Tucker & Helen Playford

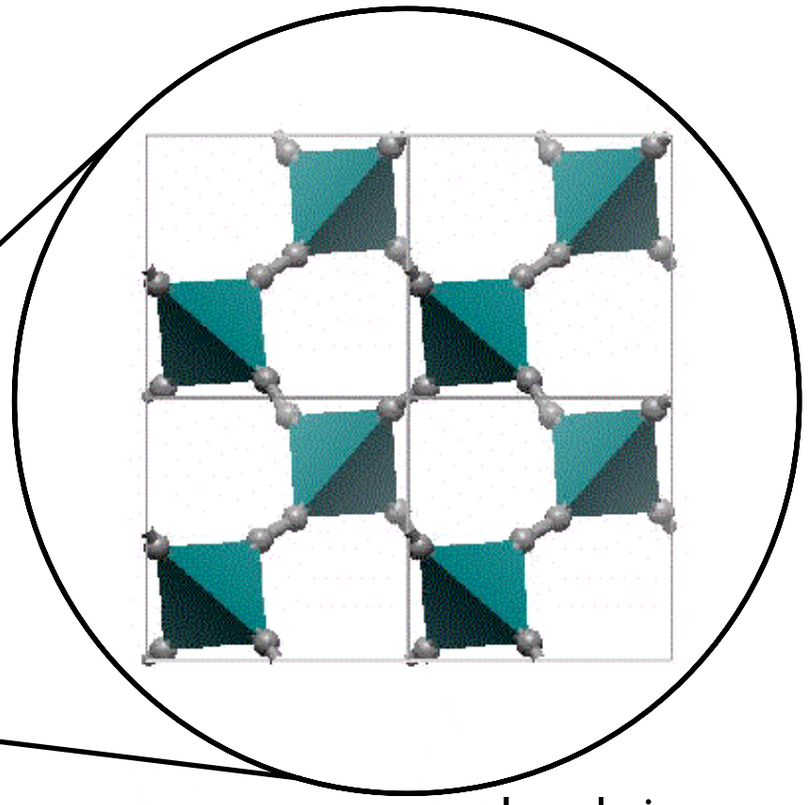
(ORNL, USA & ISIS, UK)

ADD2019, Grenoble

The local view

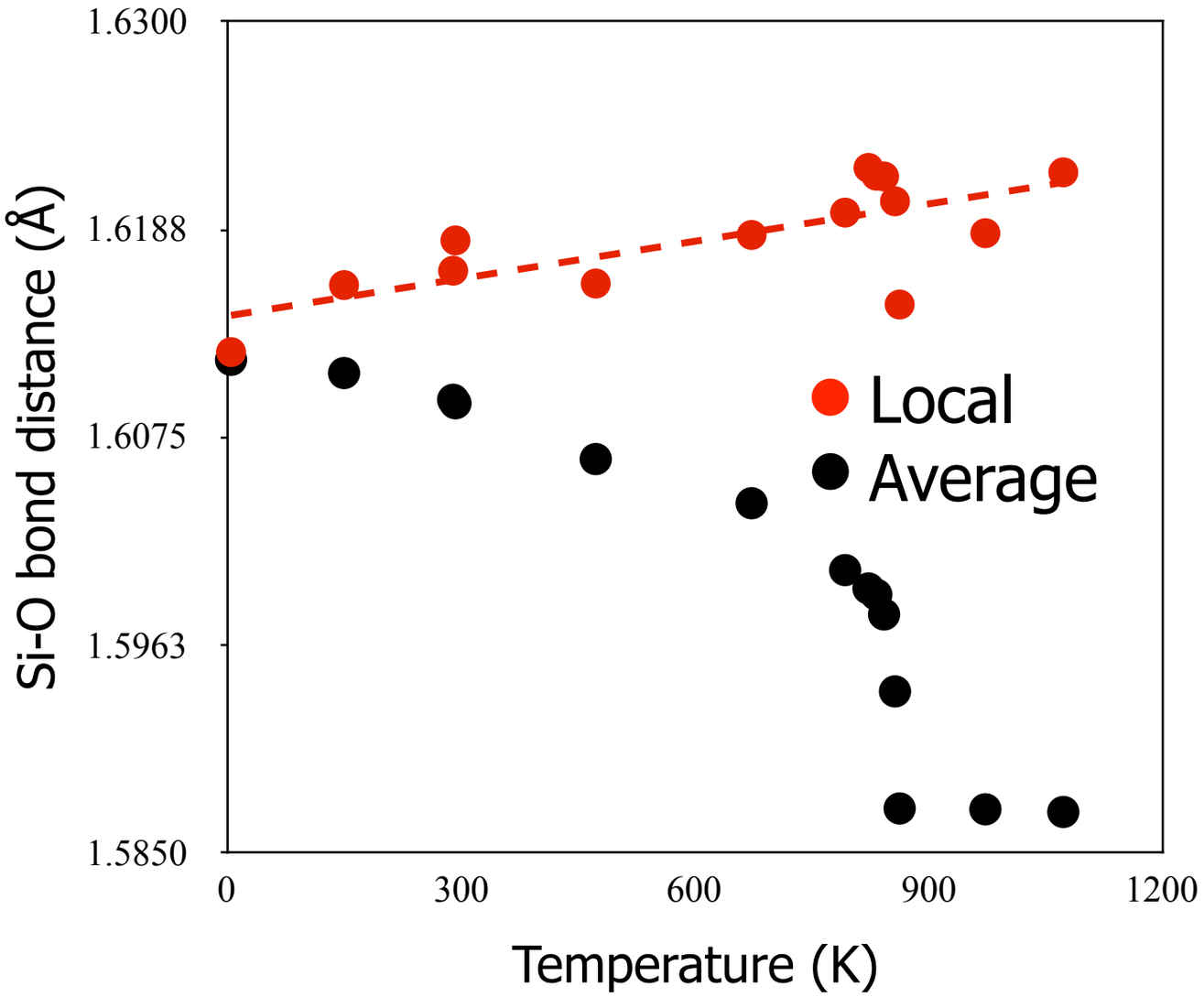
Conventional view

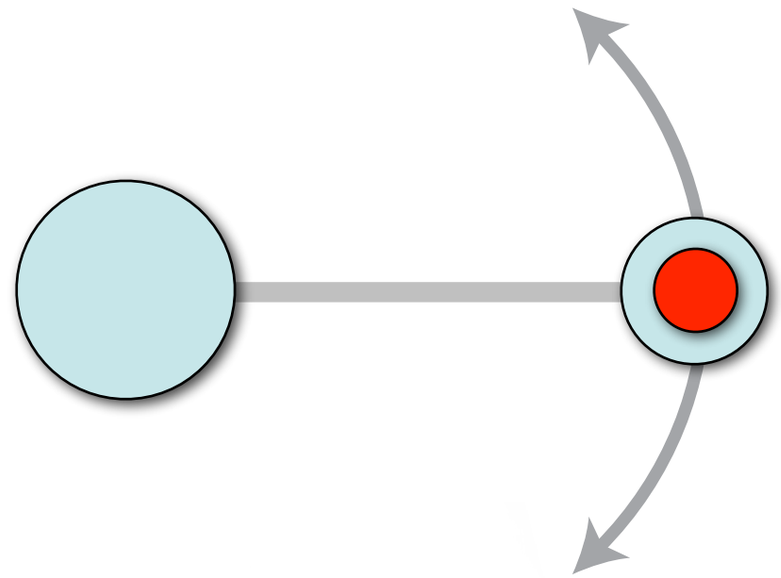




Local view

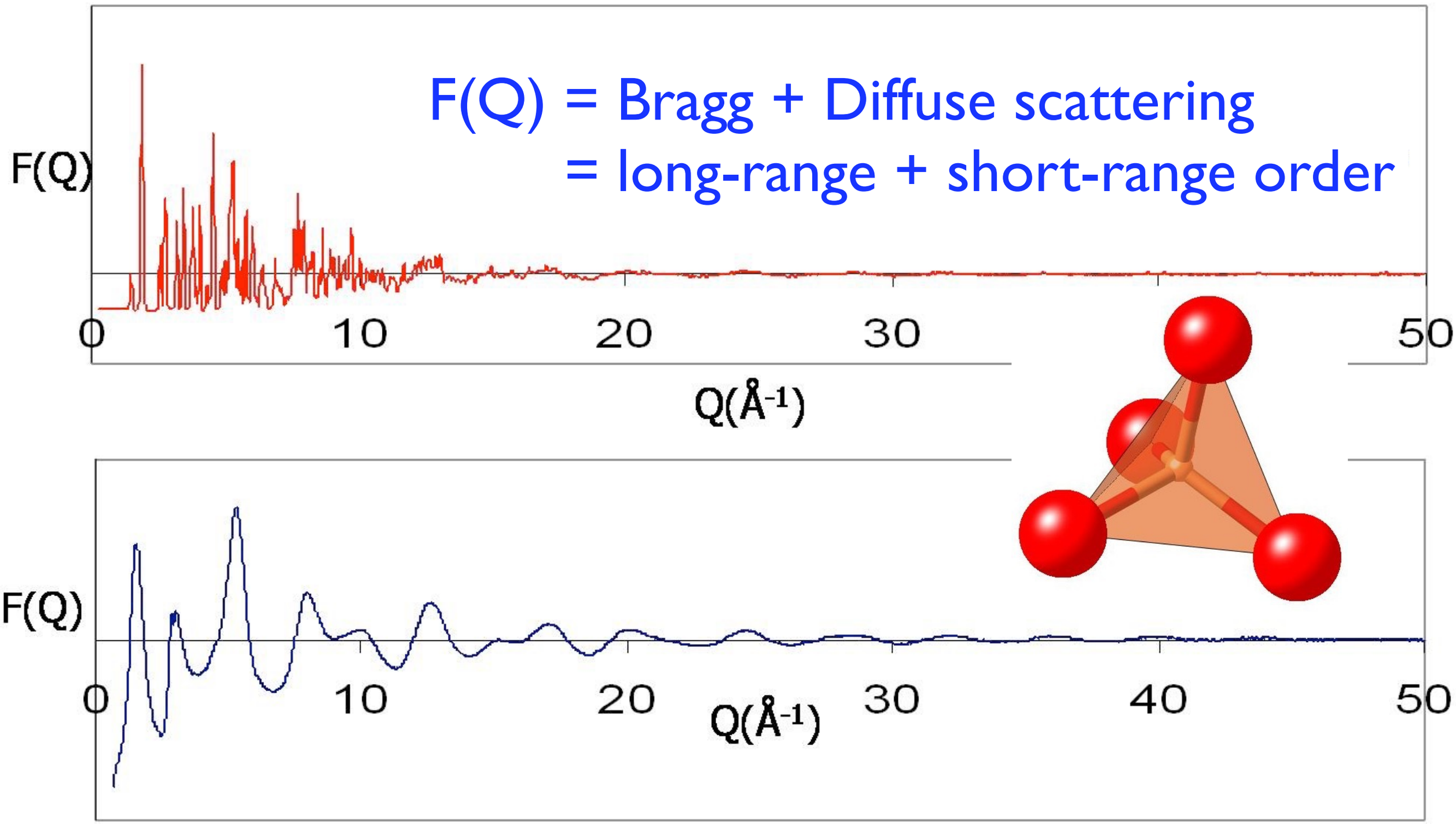
Local vs Average





Total scattering

F(Q) = Bragg + Diffuse scattering
= long-range + short-range order



Total scattering

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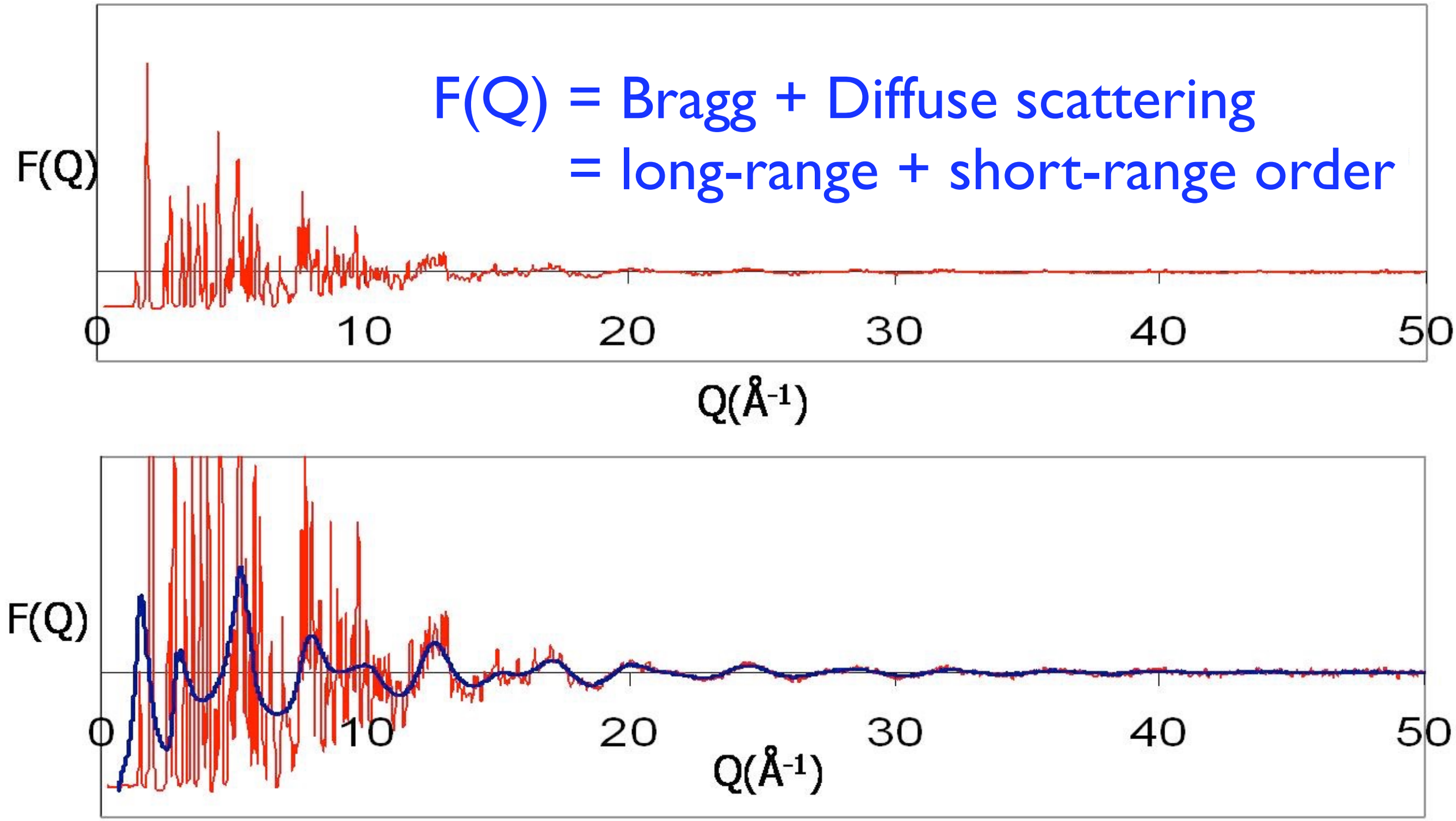
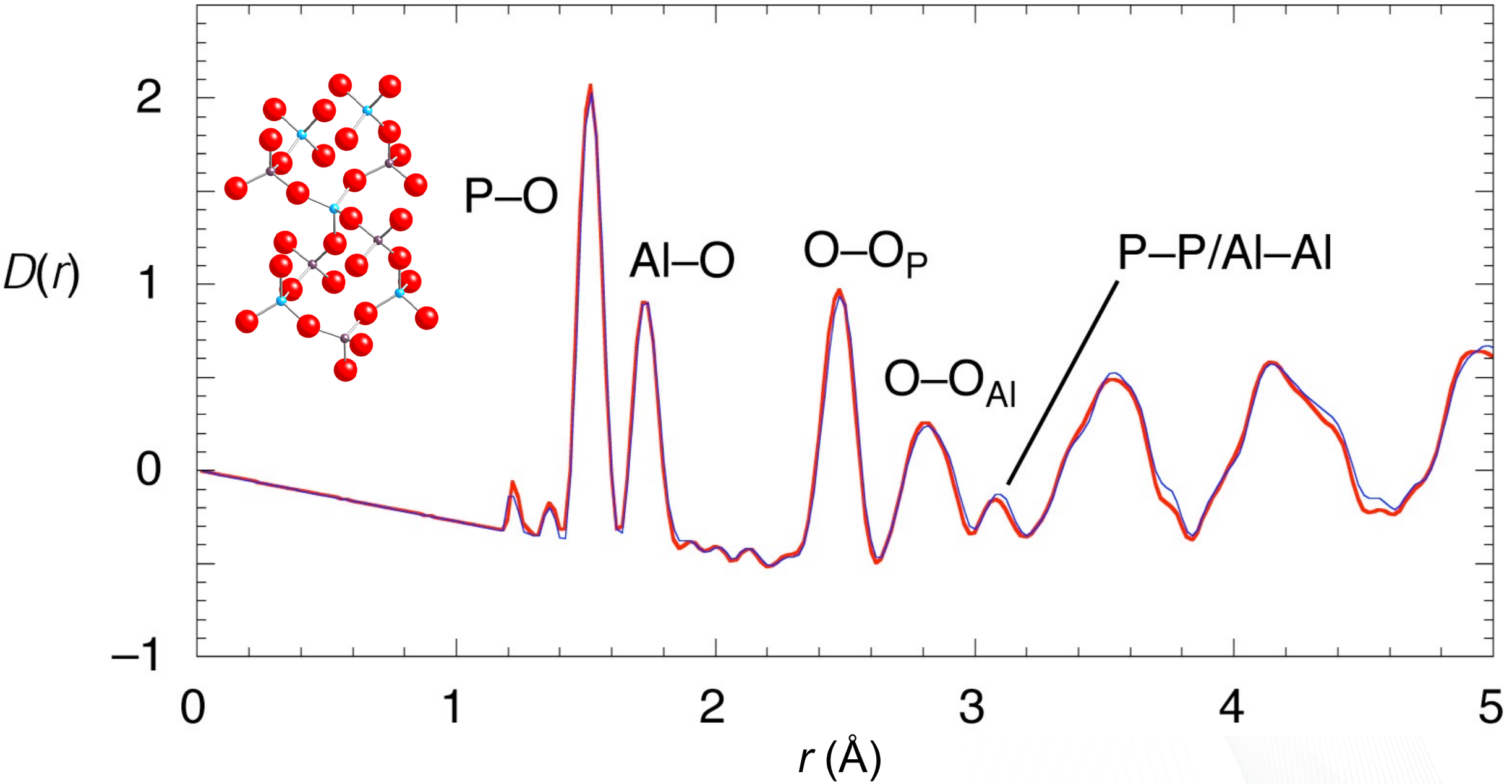
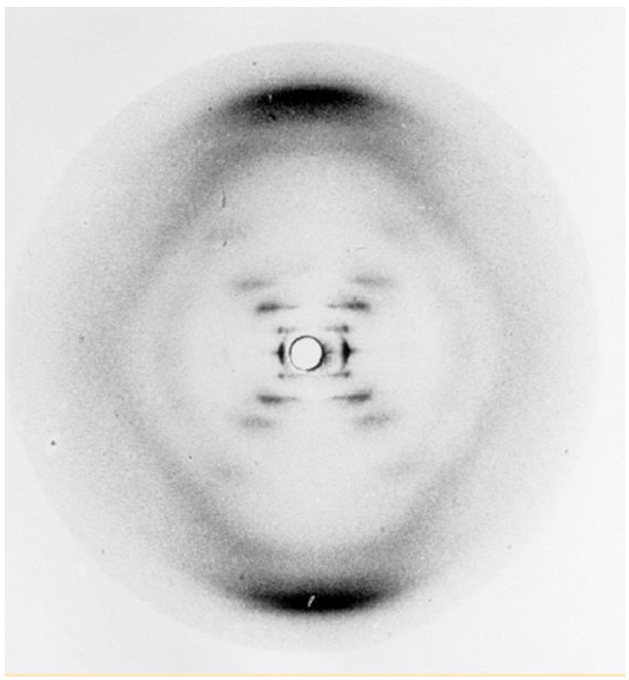


Pair distribution function



Rosalind Franklin and Total Scattering



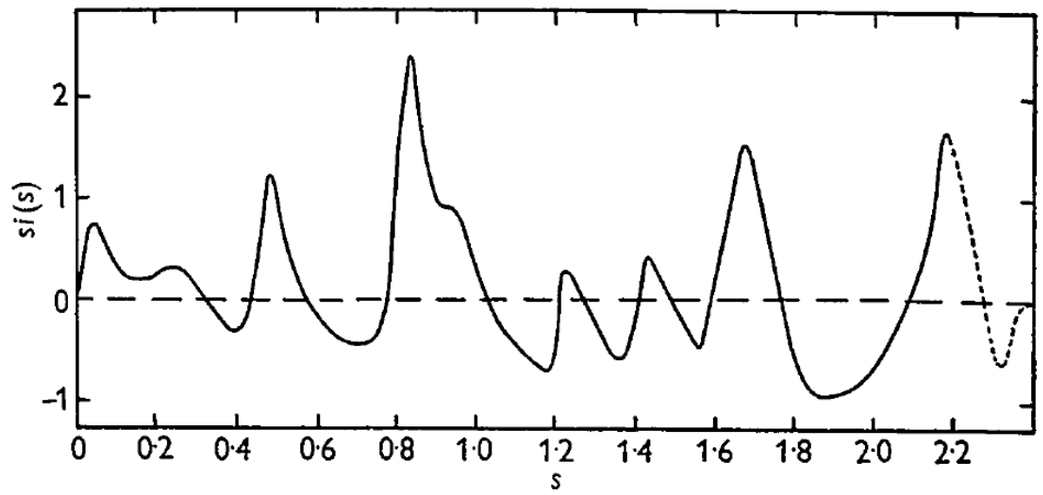


Fig. 3. The function $si(s)$.

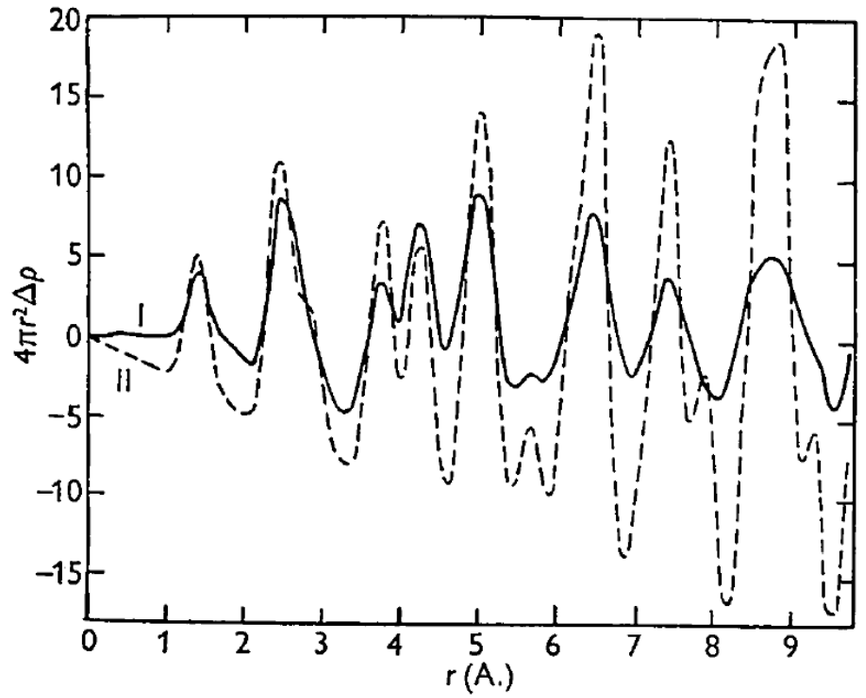
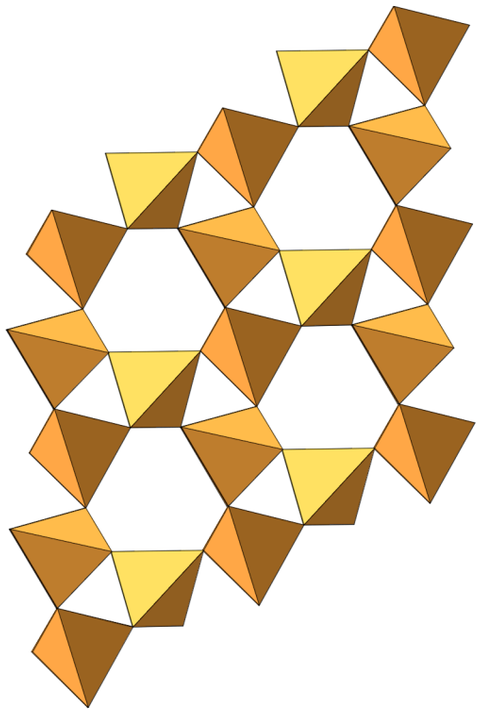


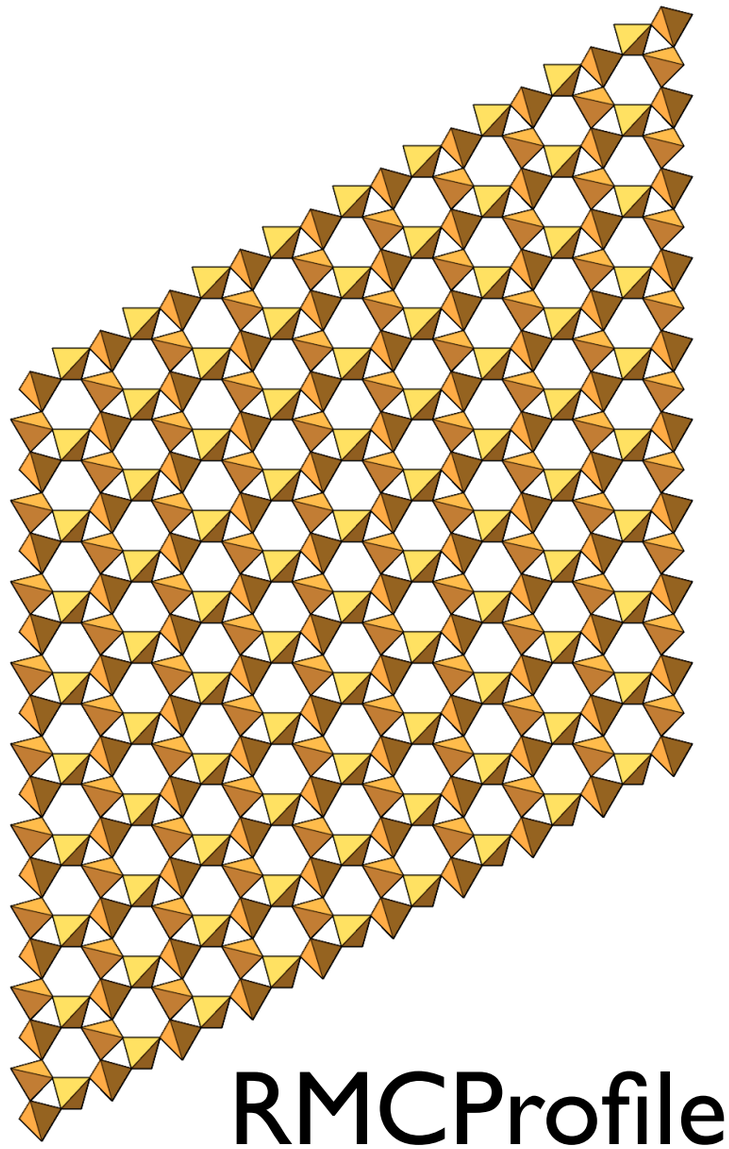
Fig. 6. Curve I, the atomic distribution function obtained after multiplying the corrected intensity curve by $\exp(-0{\cdot}4s^2)$. Curve II, the function which would be given by a single infinite graphite layer under the same conditions.

R E Franklin,
Acta Cryst **3** 107 (1950)

Big box vs small box models

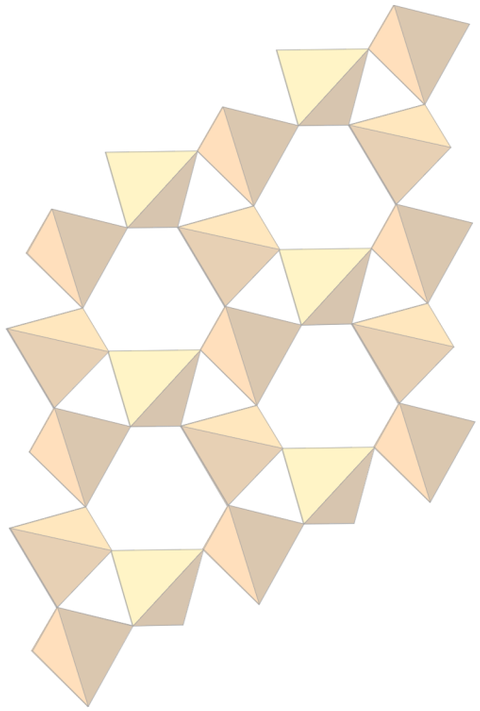


PDFgui
(r-space Reitveld)

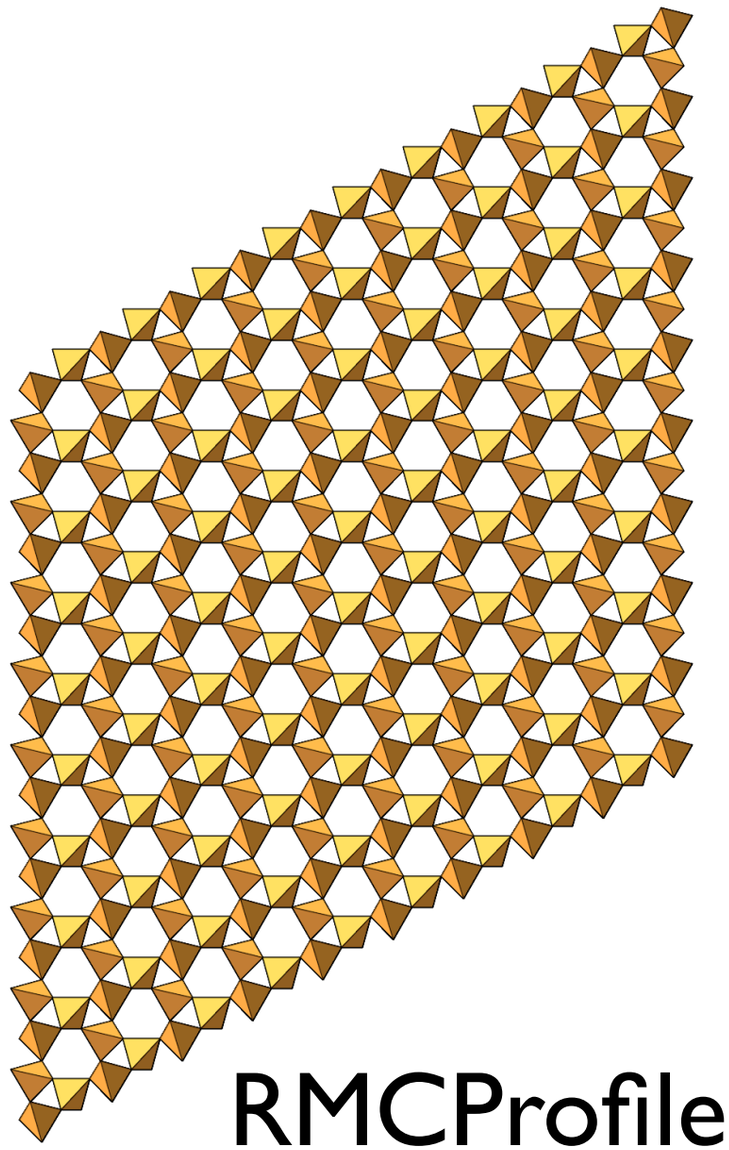


RMCProfile
(Reverse Monte Carlo)

Big box models



PDFgui
(r-space Reitveld)

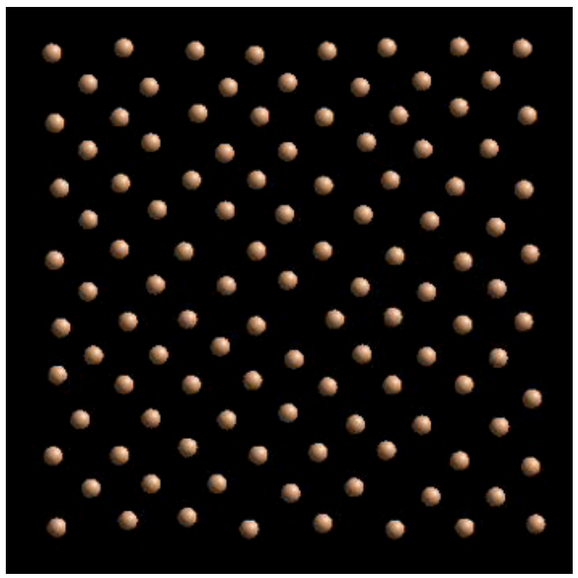


RMCProfile
(Reverse Monte Carlo)

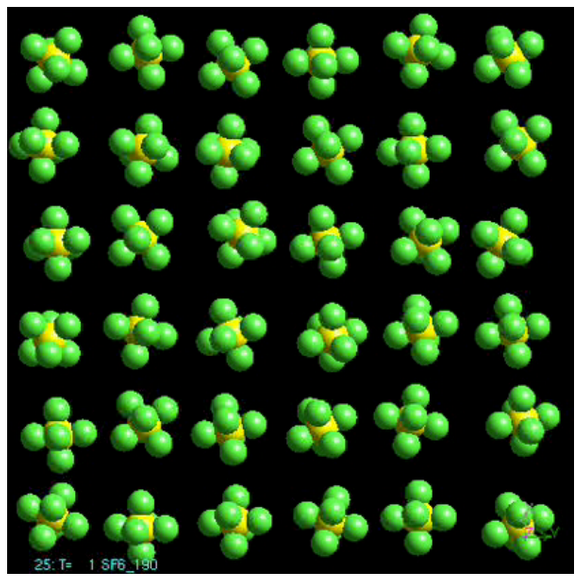
ADD2019, Grenoble

Disordered materials

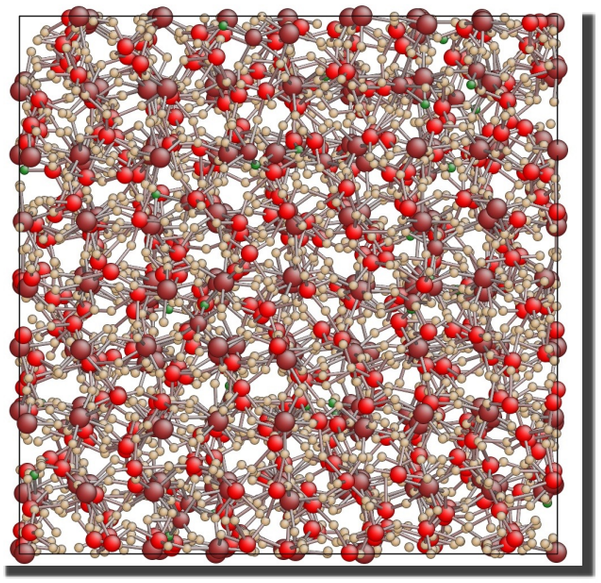
Simple crystals



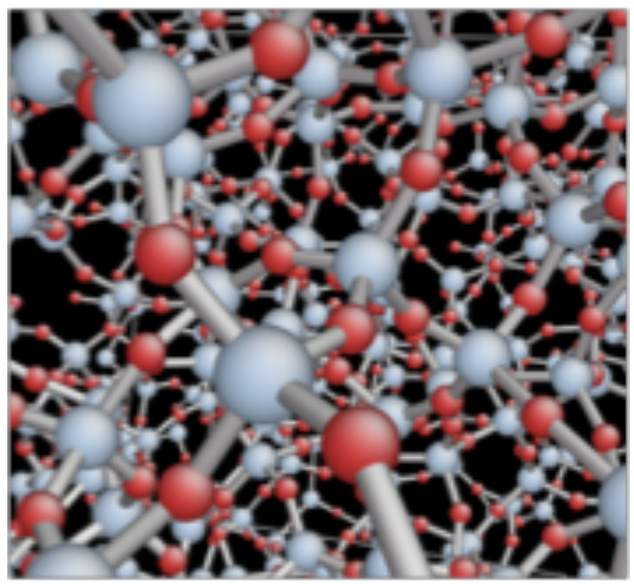
Disordered crystals



Amorphisation



Amorphous



RMCProfile

The RMC Method

Reverse Monte Carlo Simulation: a new technique for the determination of disordered structures

McGreevy R L and Pusztai L, *Molecular Simulation* **1** (1988) 359

We have developed a new technique, based on the standard Monte Carlo simulation method with Markov chain sampling, where a set of three dimensional particle configurations are generated that are consistent with the experimentally measured structure factor, A(Q), and radial distribution function, g(r), of a liquid or other disordered system. Consistency is determined by a standard χ^2 test using the experimental errors. No input potential is required. We present initial results for liquid argon. Since the technique can work directly from the structure factor it promises to be extremely powerful for modelling the structures of glasses or amorphous materials. It also has many other advantages in multicomponent systems and as a tool for experimental data analysis.

Key words: Monte Carlo, structure factor, radial distribution function, liquid, glass.

PACS numbers: 02.50, 61.25, 61.40.

The Reverse Monte Carlo algorithm

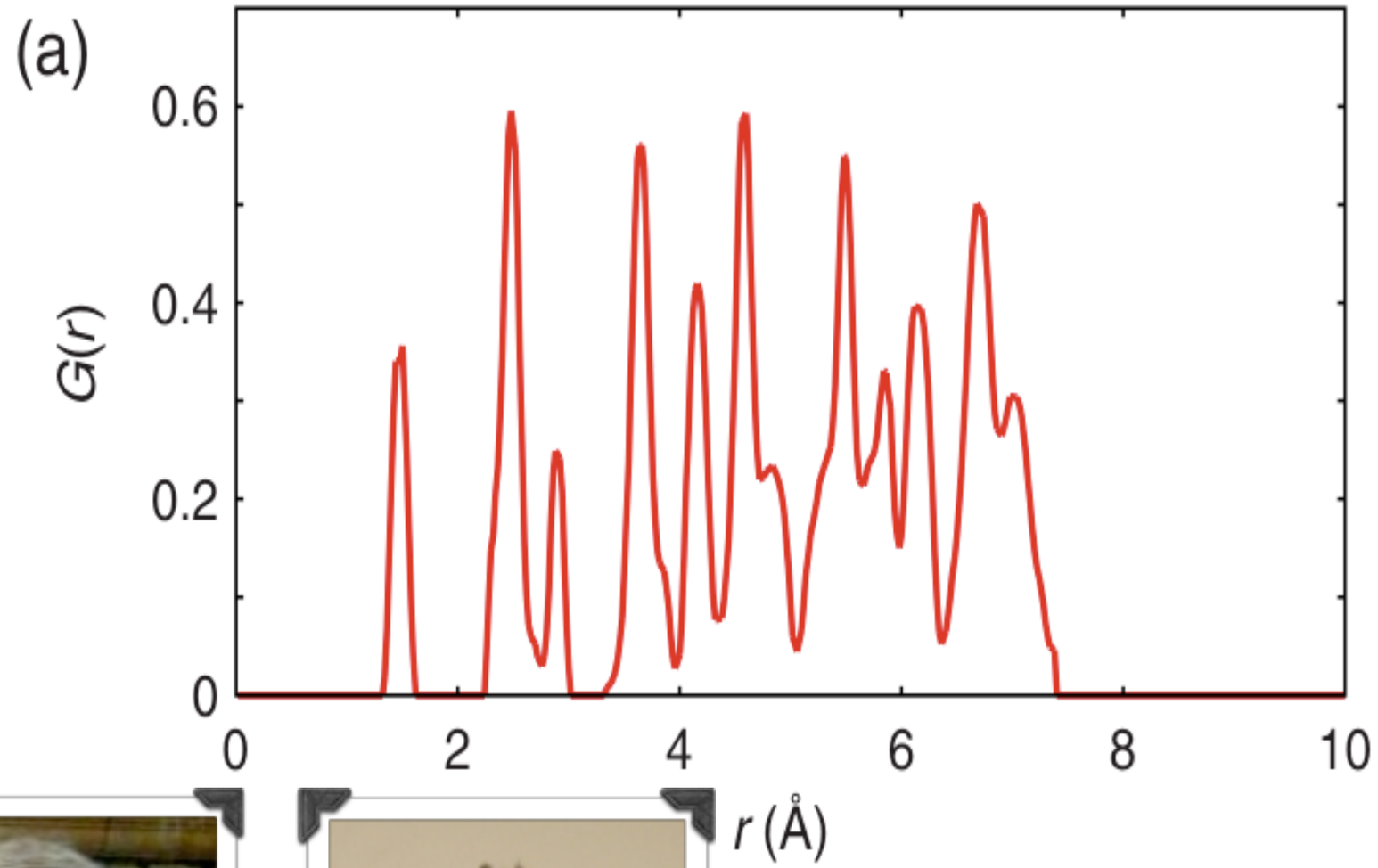
Generate initial configuration

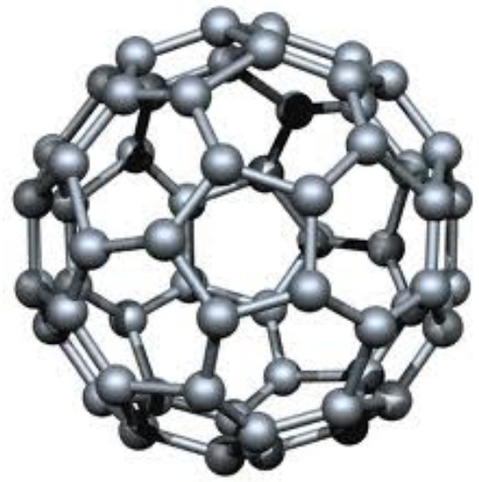
↳ Move a randomly selected atom a random distance

↳ Compute new experimental functions and compare with data

↳ Only reject change if comparison is worse and with some probability

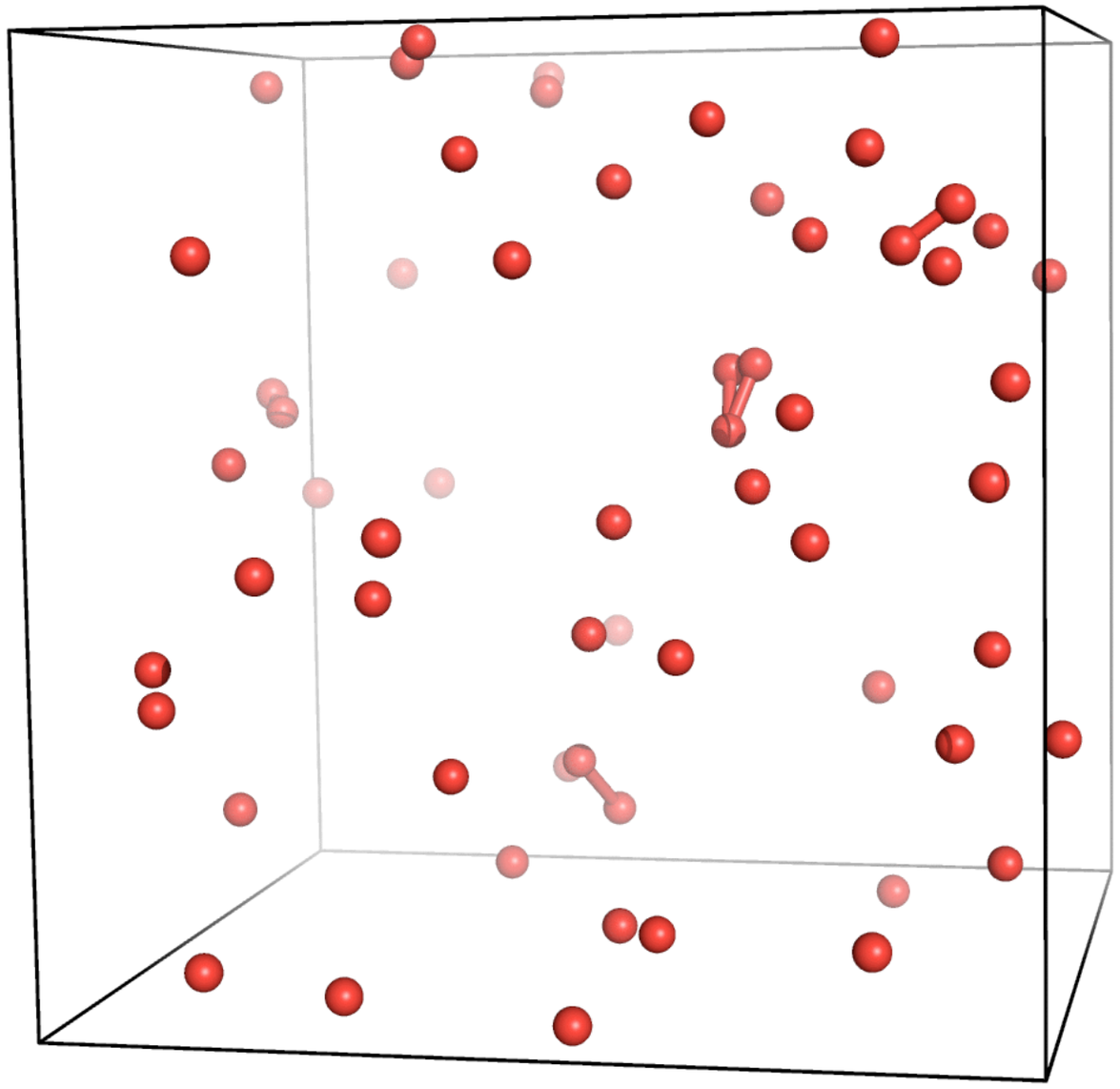
RMC in action: C60





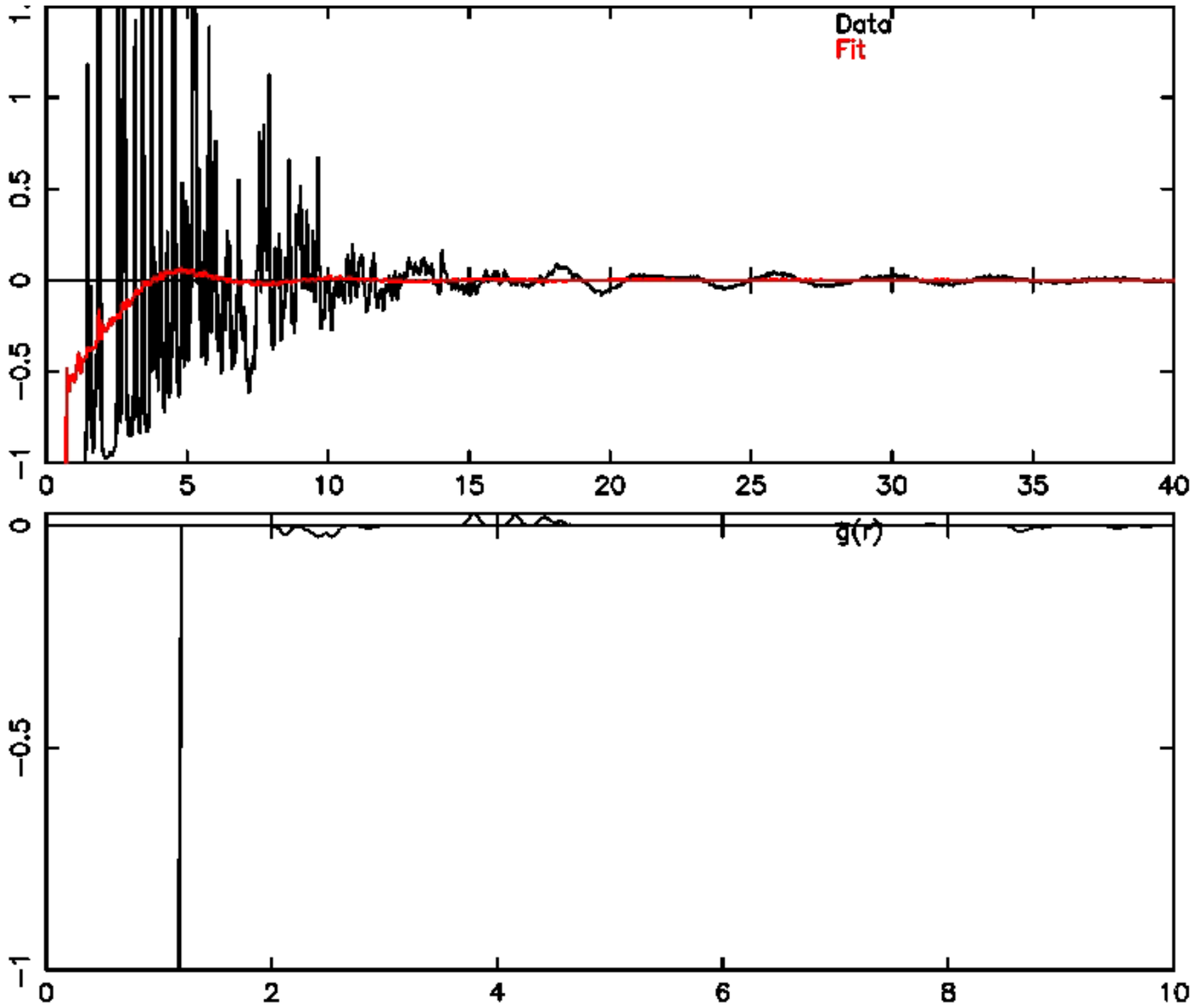
Cliffe M J *et al*
PRL **104** (2010) 1255013

RMC in action: C60



Cliffe M J *et al, PRL* **104** (2010) 1255013

RMC in action



RMCA

J. Phys.: Condens. Matter **2** (1990) 2773–2786. Printed in the UK

Structural disorder in AgBr on the approach to melting

D A Keen†, W Hayes and R L McGreevy
Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

Received 20 October 1989

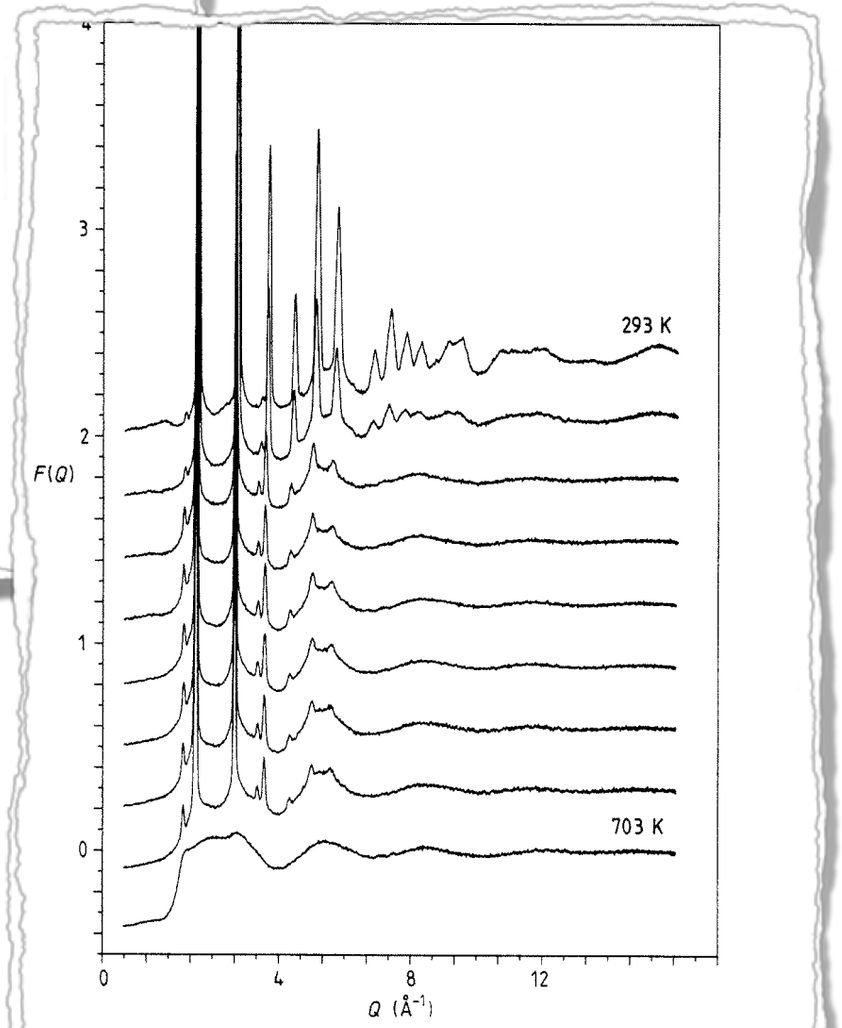
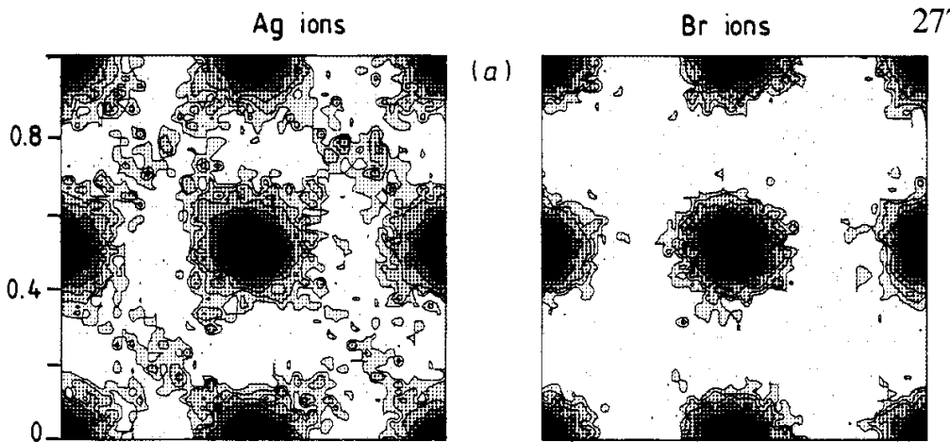
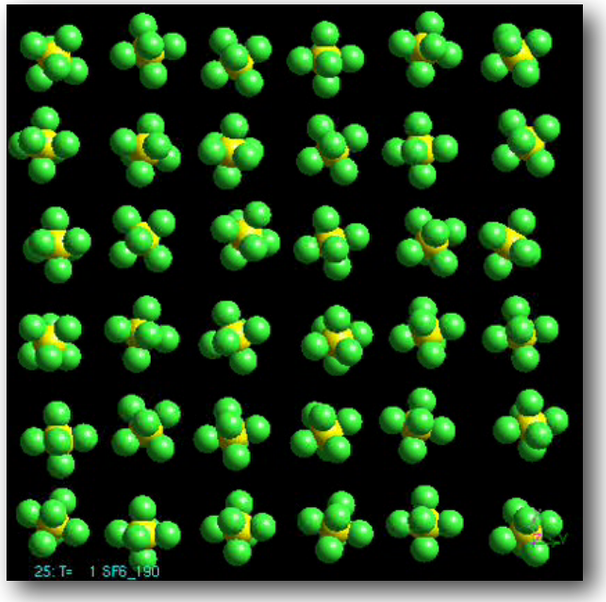


Figure 1. Structure factors of molten AgBr at 703 K and of AgBr powder at 699, 698, 697, 689, 684, 669, 490 and 293 K: each successive temperature has been offset vertically by 0.3. The (111) and (113) Bragg peaks are the first and fourth with increasing Q.



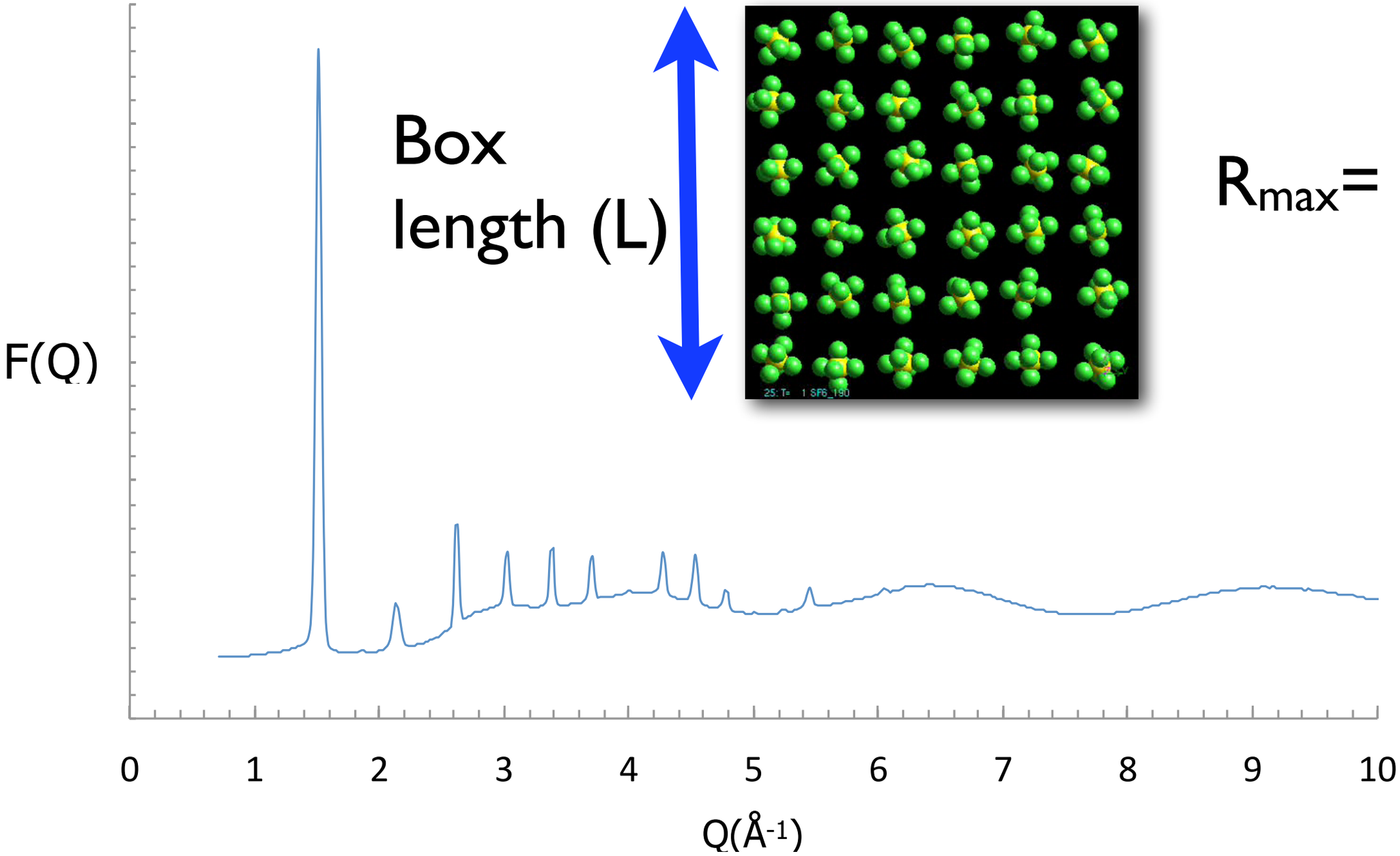
Fitting the Bragg data

Box length (L)



R_{max}= L/2

Fitting the Bragg data



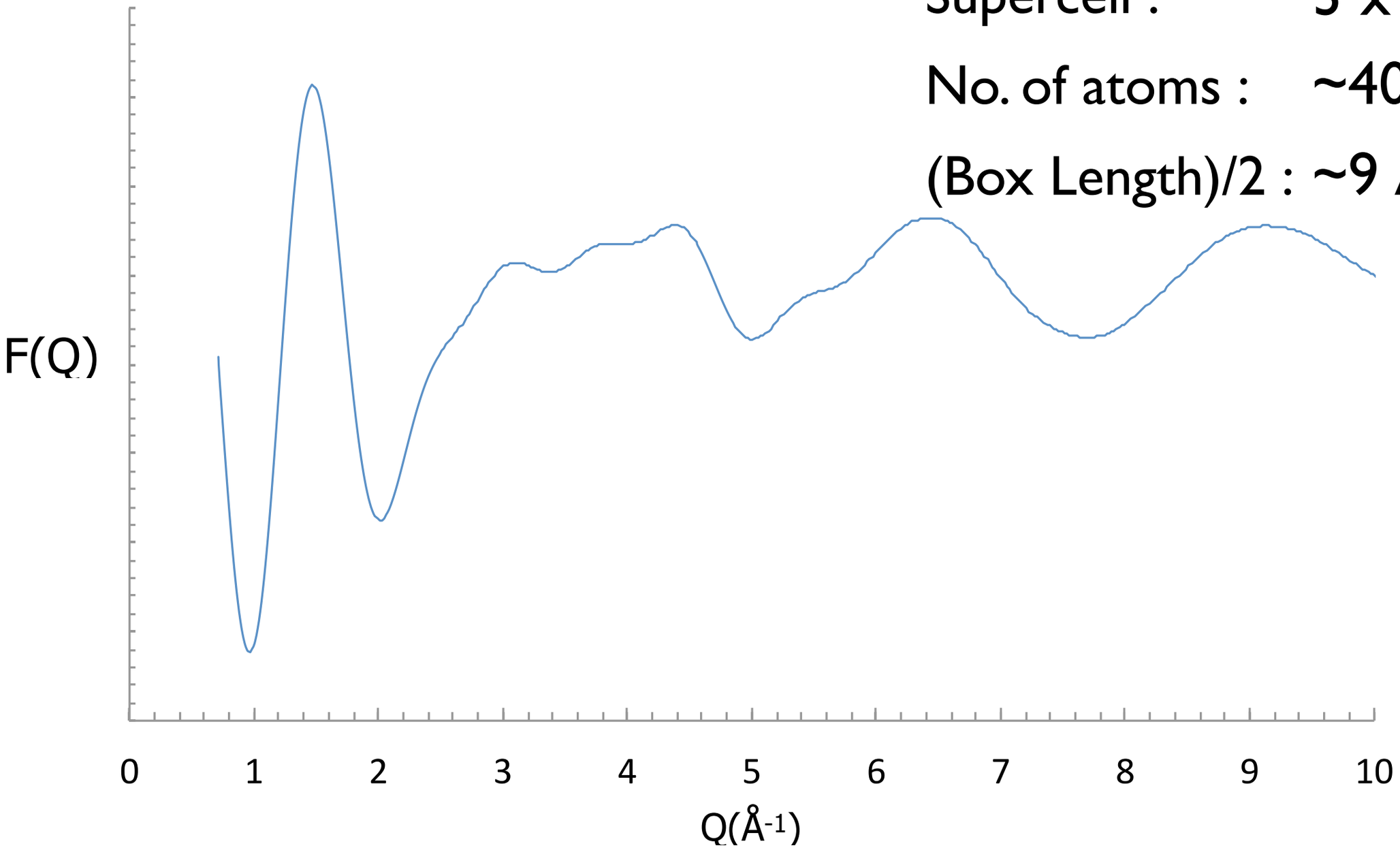
R_{max}= L/2

Fitting the Bragg data

Supercell : 3 x 3 x 3

No. of atoms : ~400

(Box Length)/2 : ~9 Å

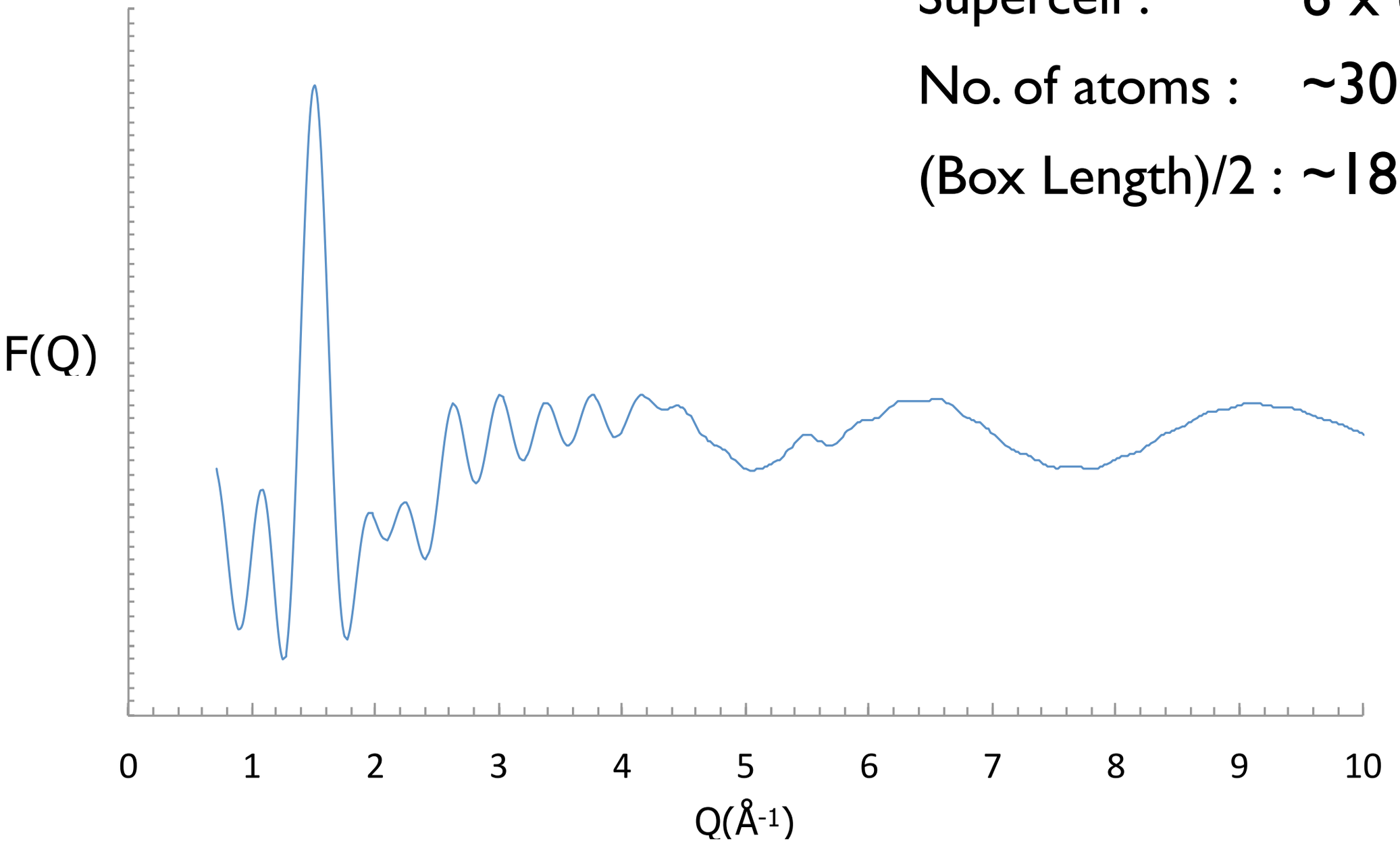


Fitting the Bragg data

Supercell : 6 x 6 x 6

No. of atoms : ~3000

(Box Length)/2 : ~18 Å

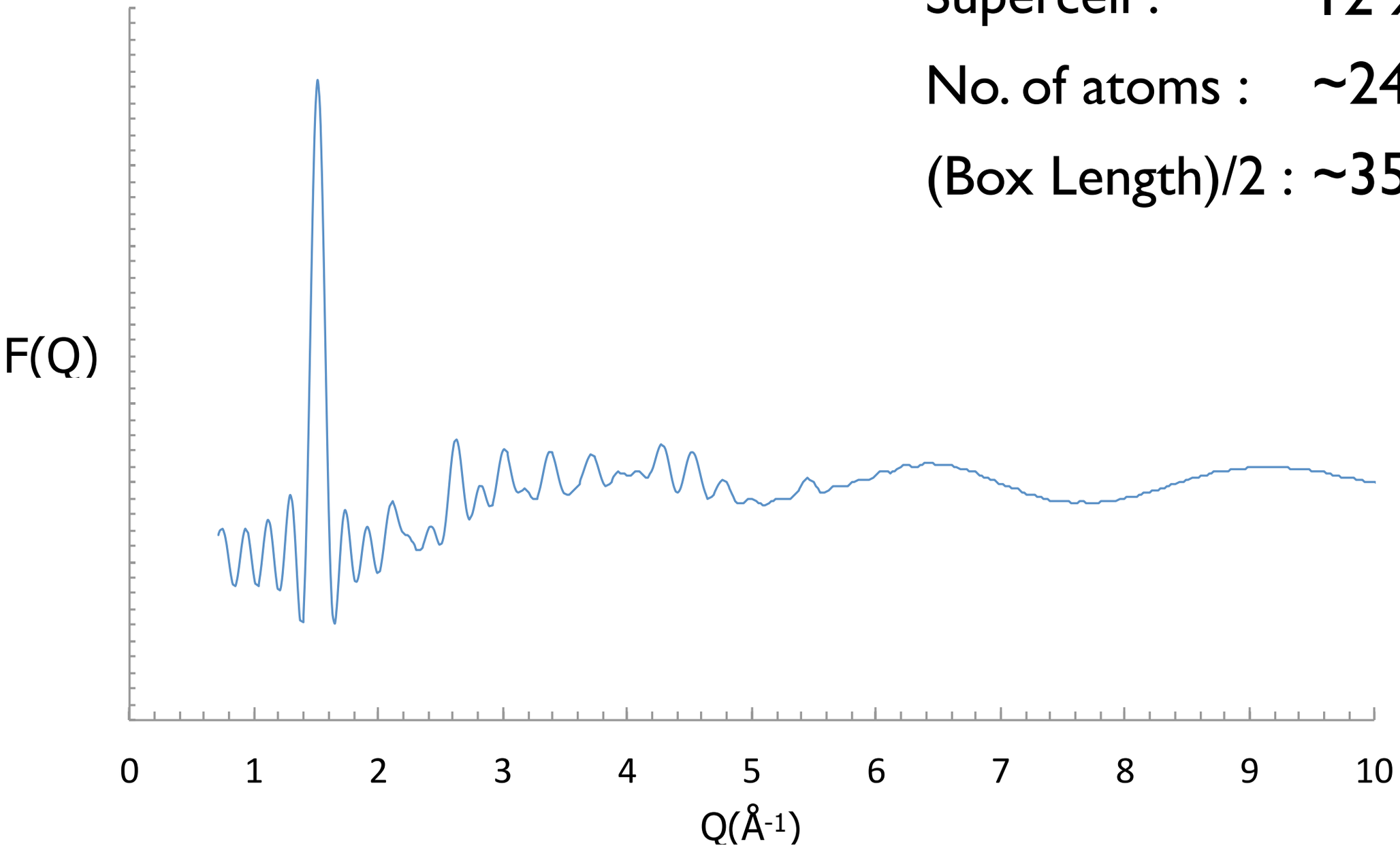


Fitting the Bragg data

Supercell : 12 x 12 x 12

No. of atoms : ~24000

(Box Length)/2 : ~35 Å

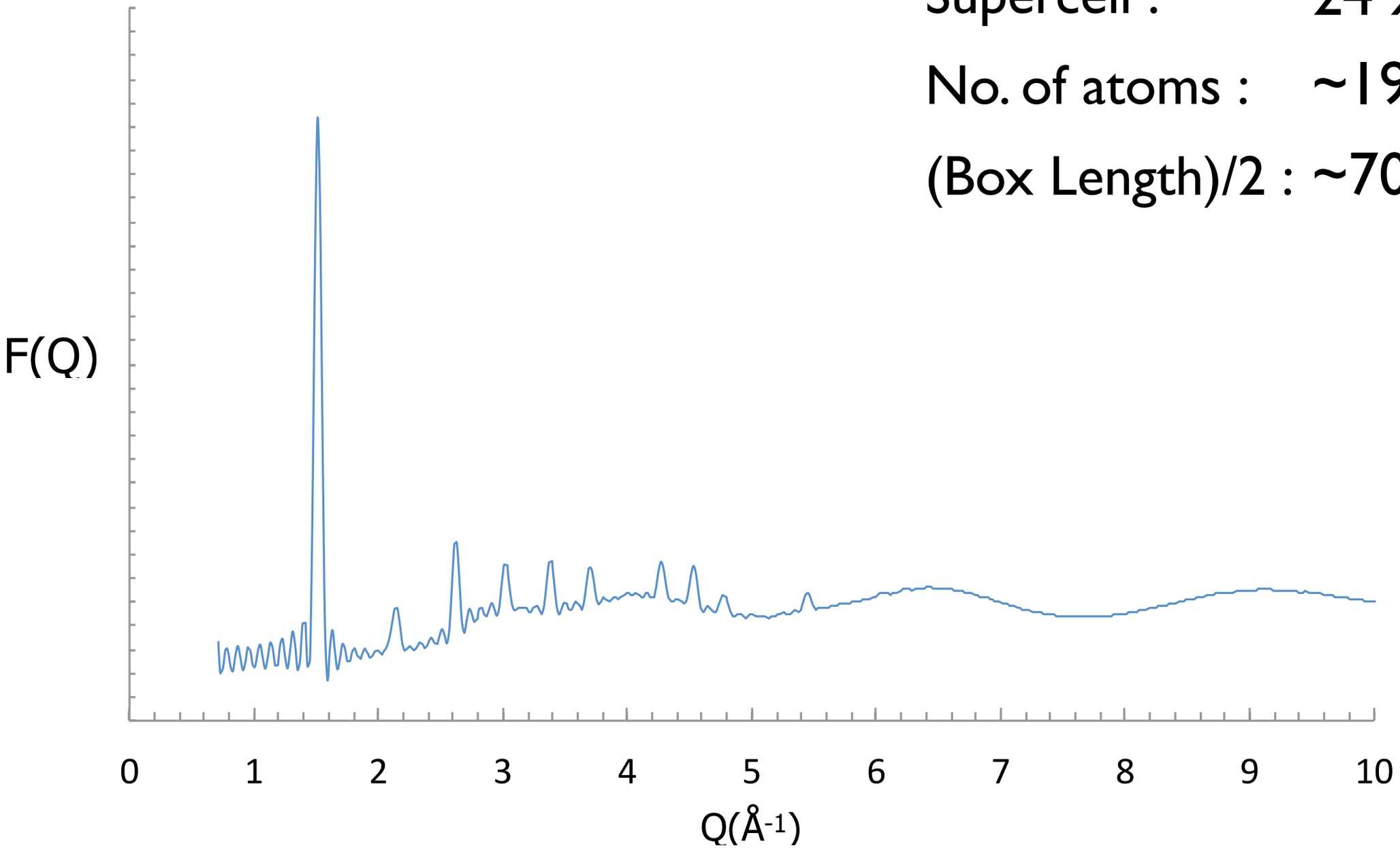


Fitting the Bragg data

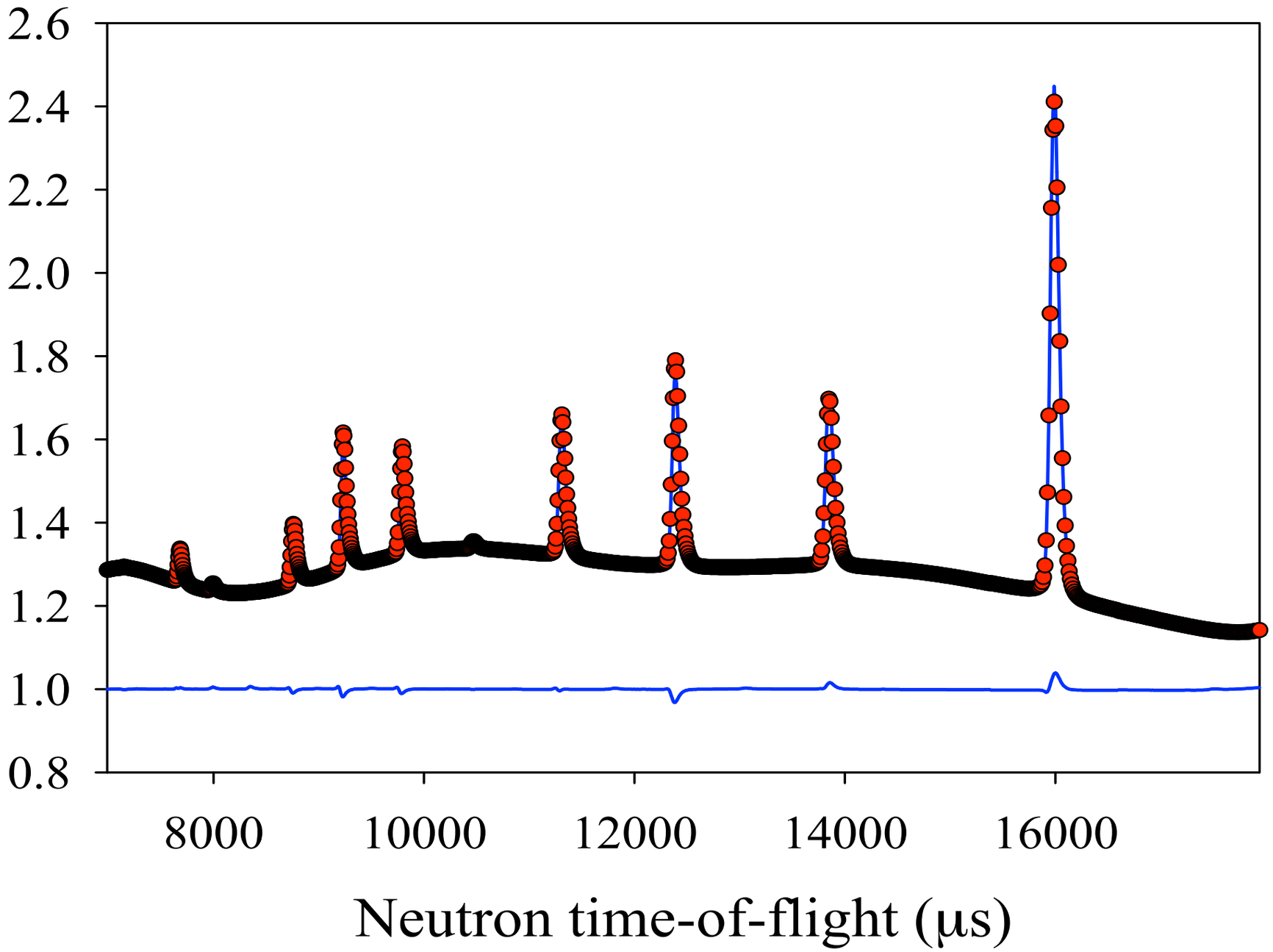
Supercell : 24 x 24 x 24

No. of atoms : ~190000

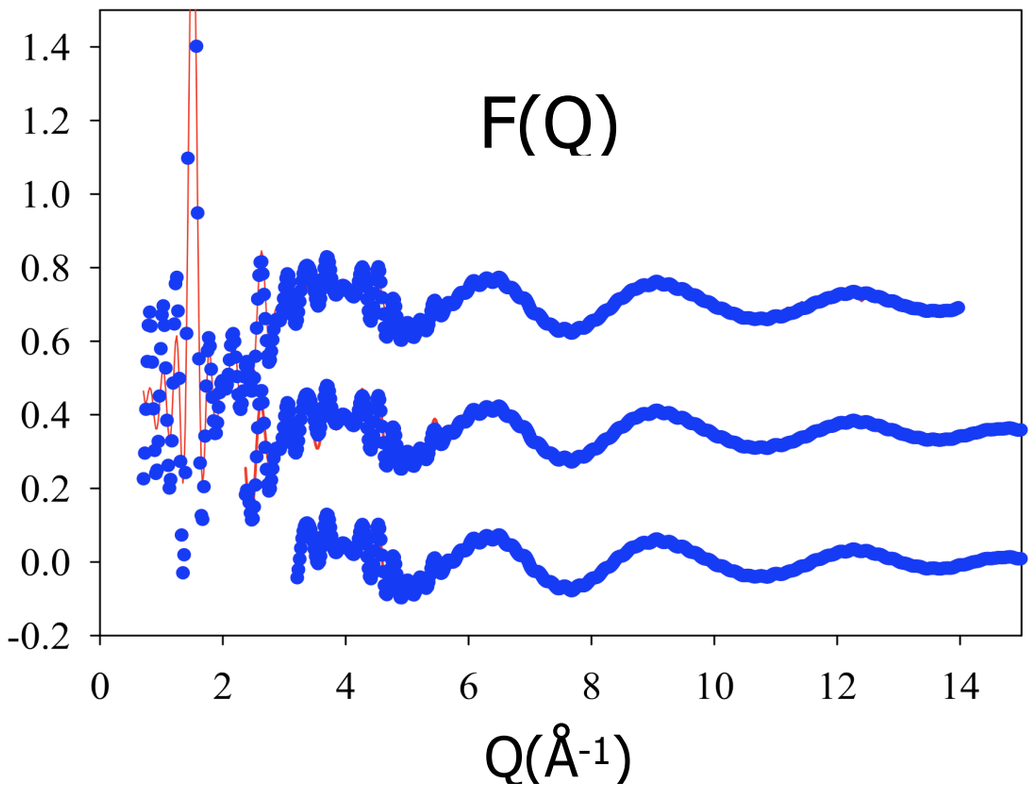
(Box Length)/2 : ~70 Å

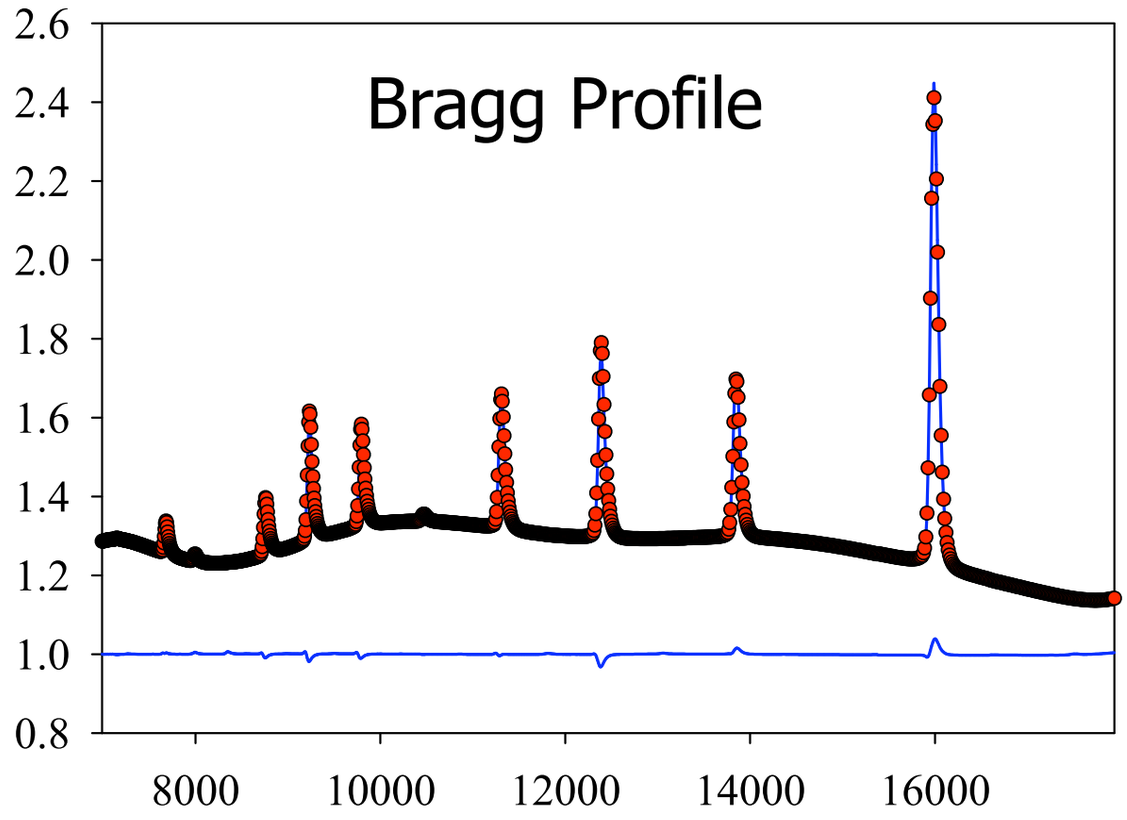


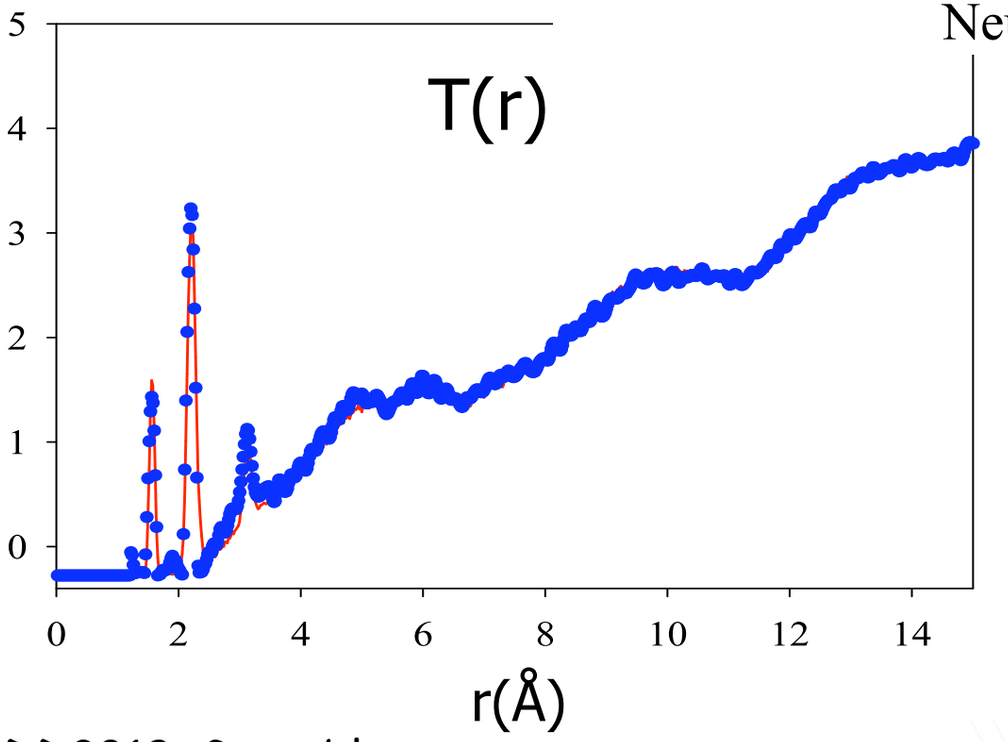
Fitting the Bragg data



RMCProfile: Fits



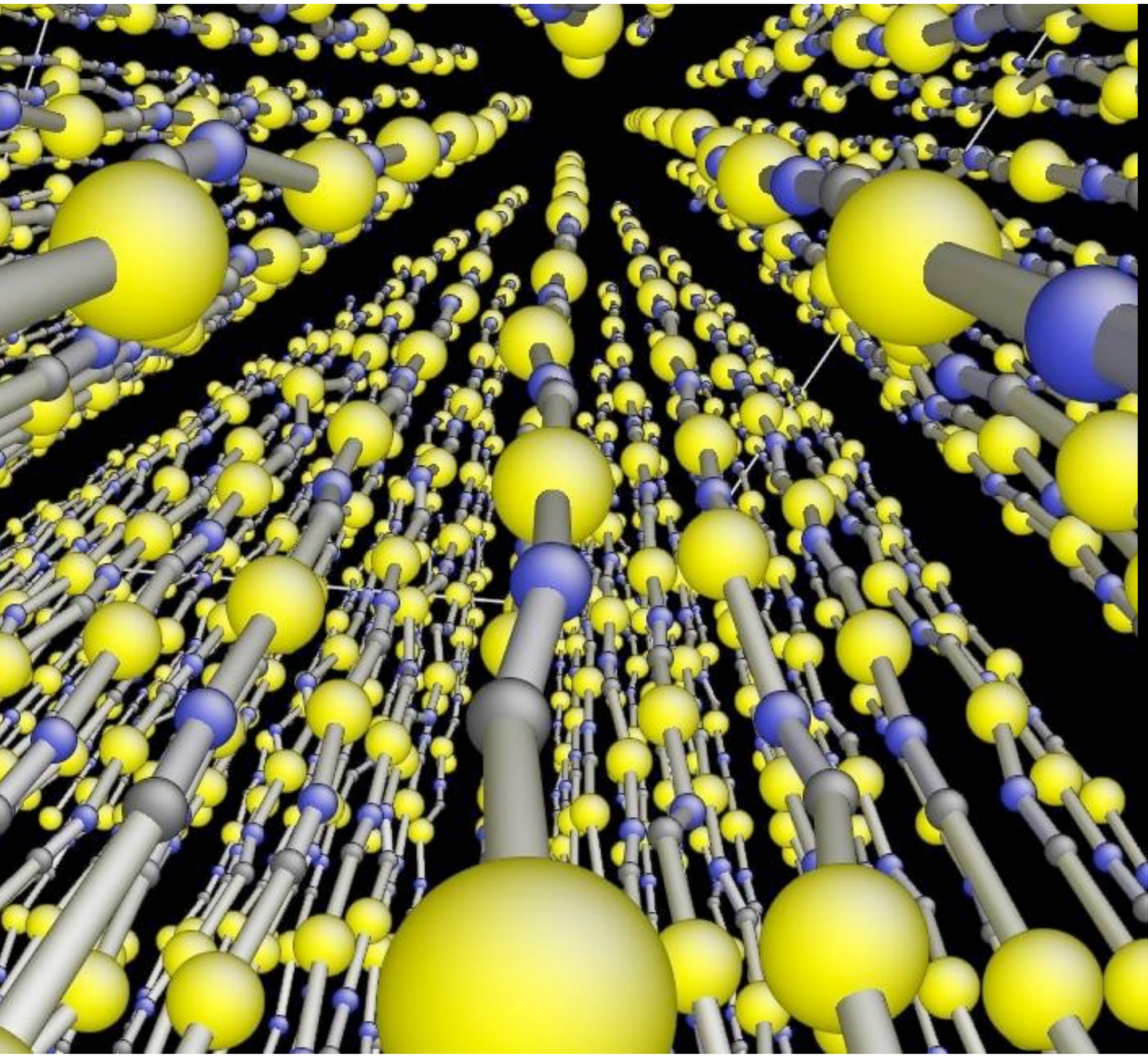


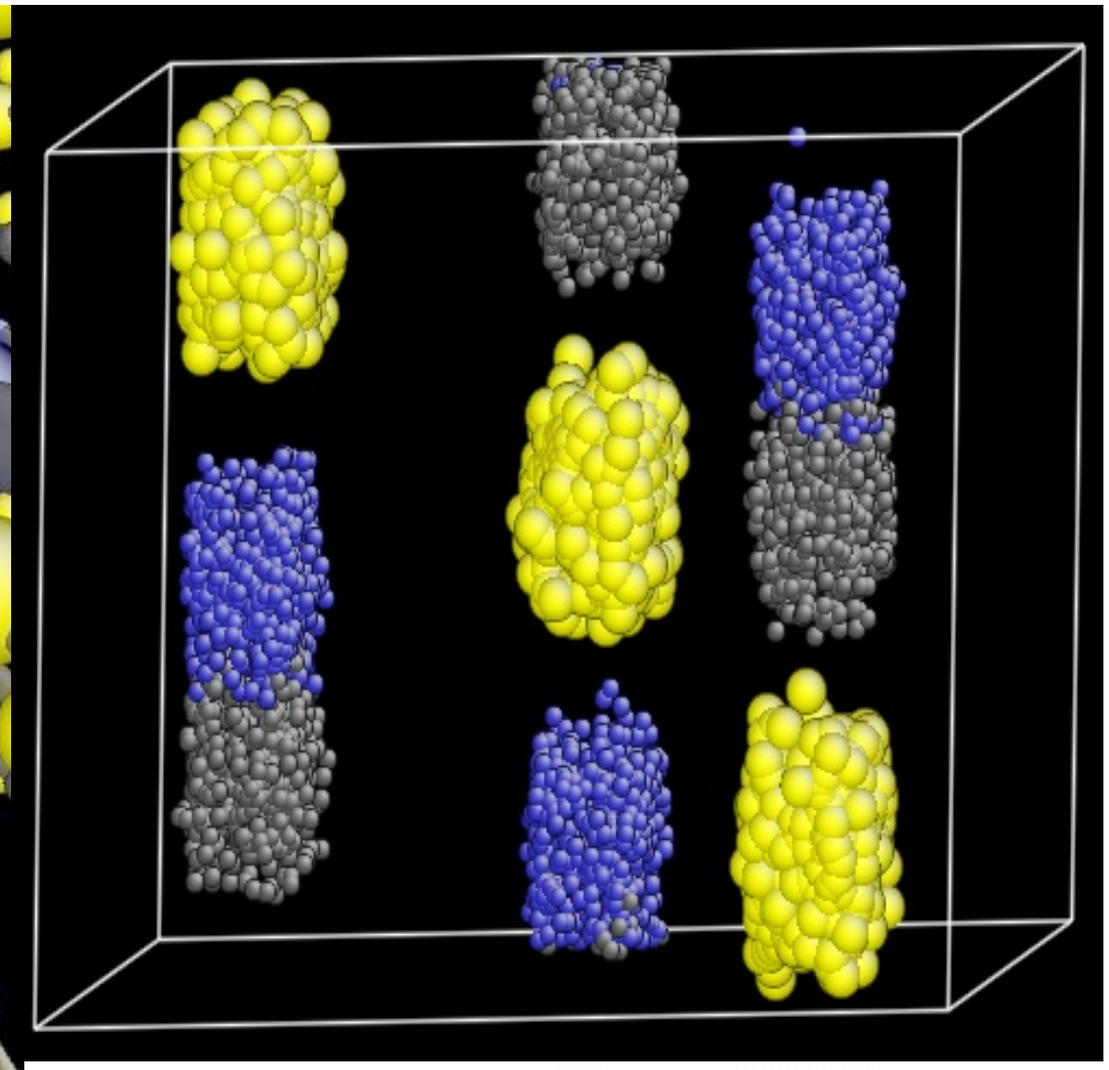


Data

RMC

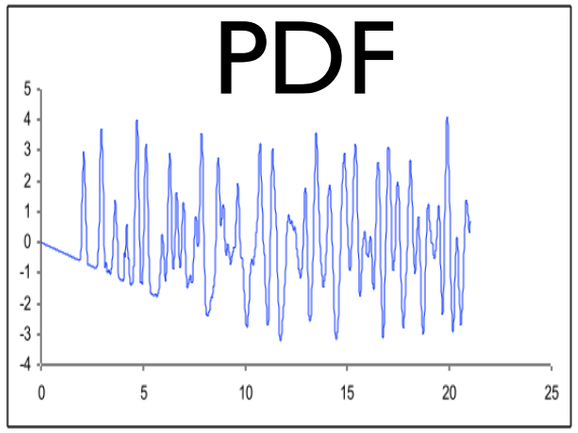
Big box models

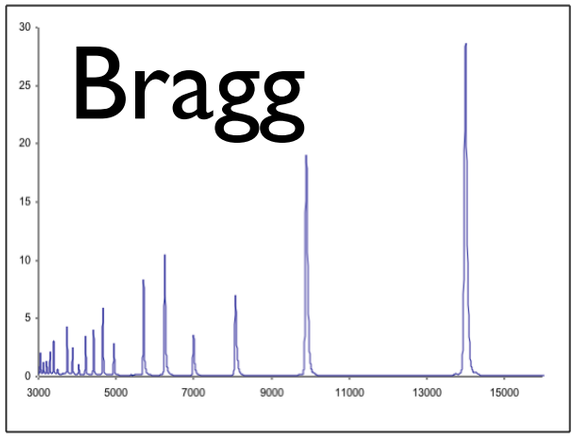


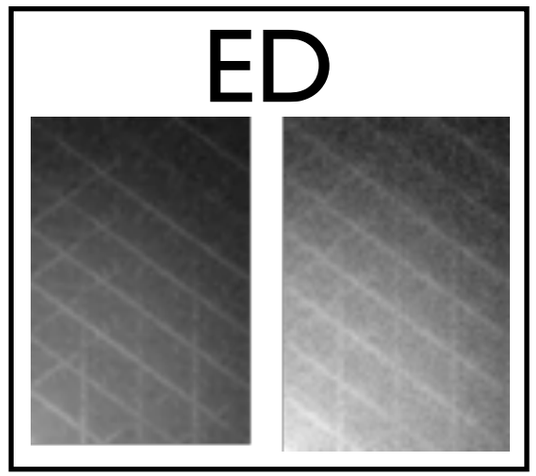


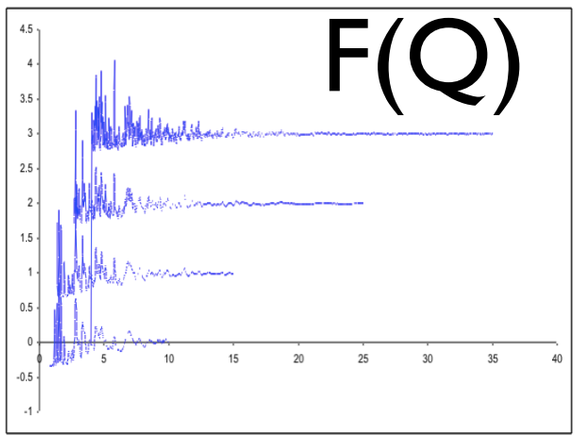
RMCProfile
(Reverse Monte Carlo)

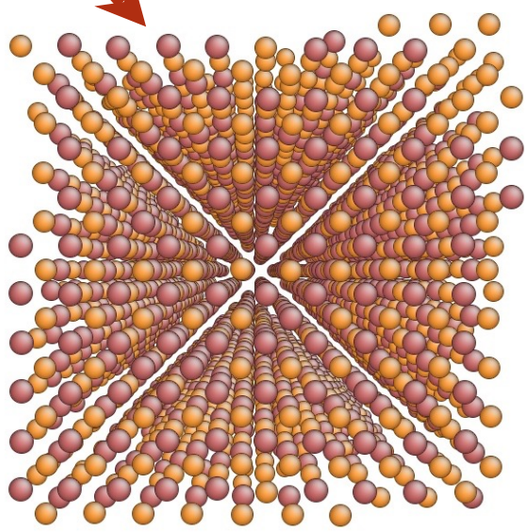
RMC Profile

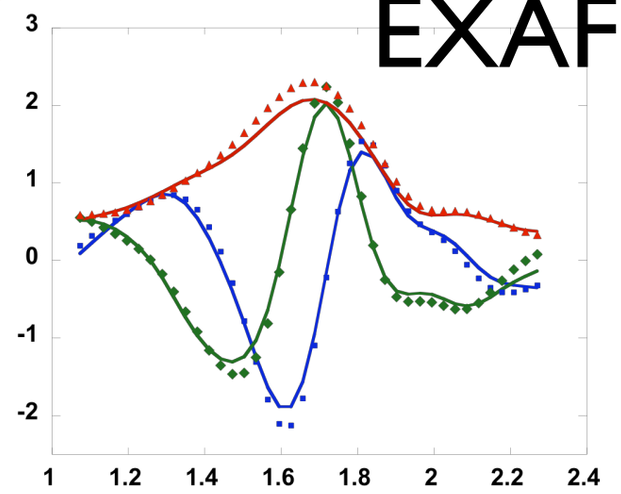


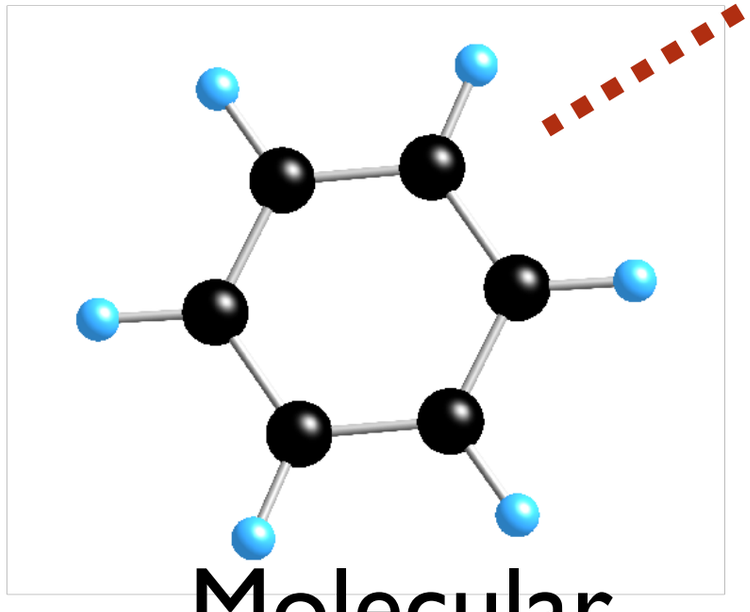




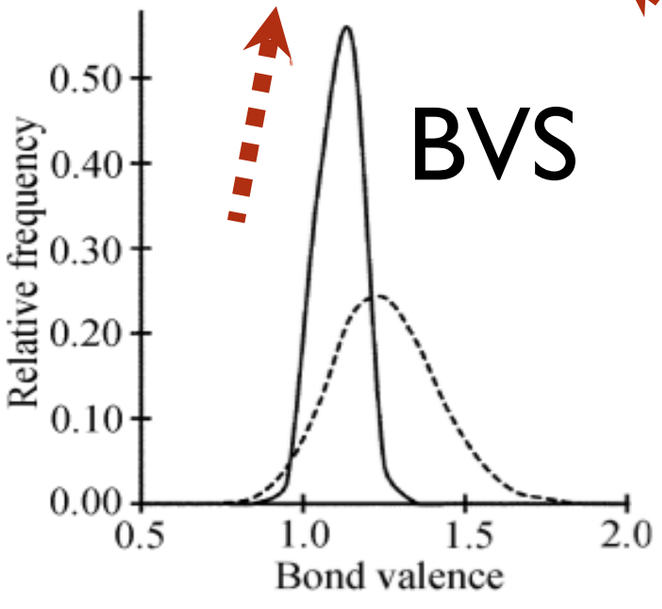


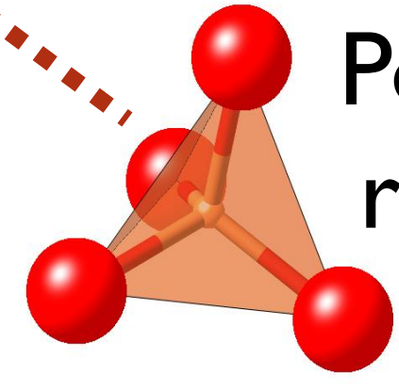






Molecular potentials





Polyhedral restraints

M G Tucker et al, *J. Phys.: Condens. Matter* **19,** 335218 (2007).

Total scattering in action: γ-Ga_2O_3

Playford, H.Y.; Hannon, A. C.; Barney, E. R.;
Walton, R. I. Chem. Eur. J. 2013, 19, 2803

Playford, H.Y.; Hannon, A. C.; Tucker, M. G., Dawson, D. M.; Ashbrook, S. E.;
Kastiban, R. J.; Sloan, J.; Walton, R. I. J. Phys. Chem. C 2014, 118, 16188

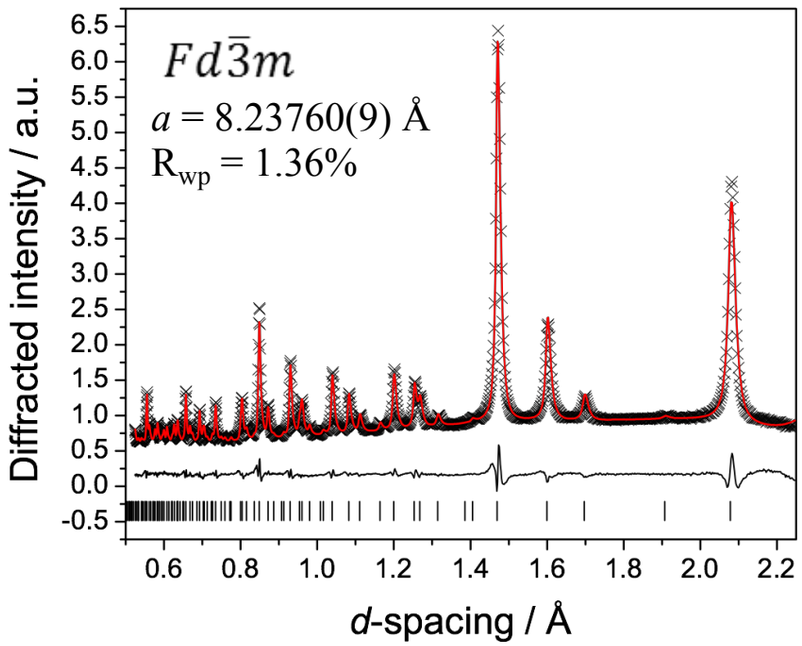
Science & Technology Facilities Council
ISIS

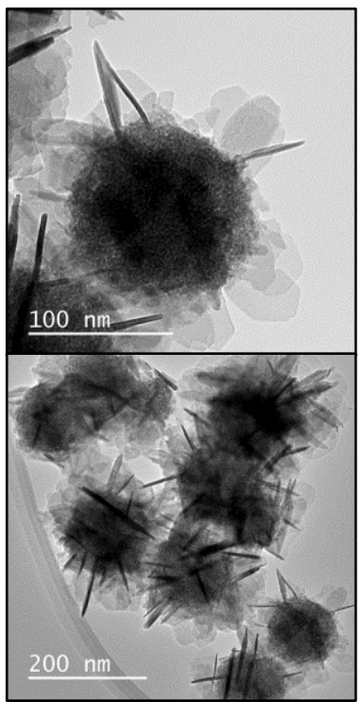
1. Total scattering in action: γ-Ga_2O_3

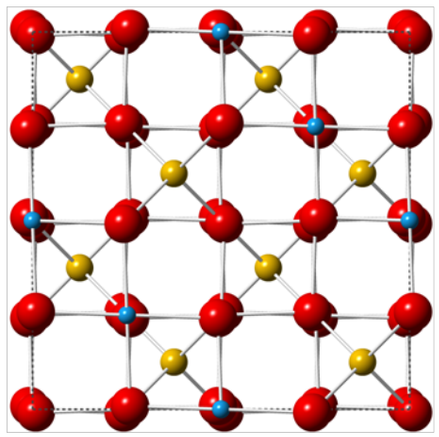
Average structure of γ-Ga_2O_3

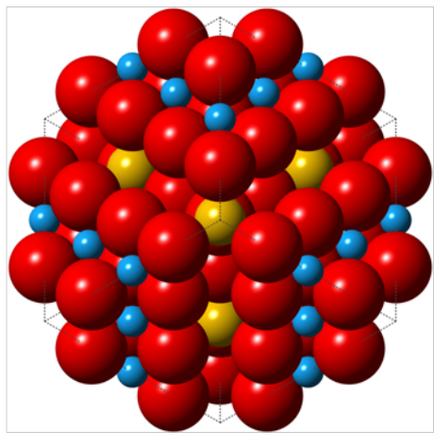
Ga + $HN(CH_2CH_2OH)_2$

Solvothermal synthesis





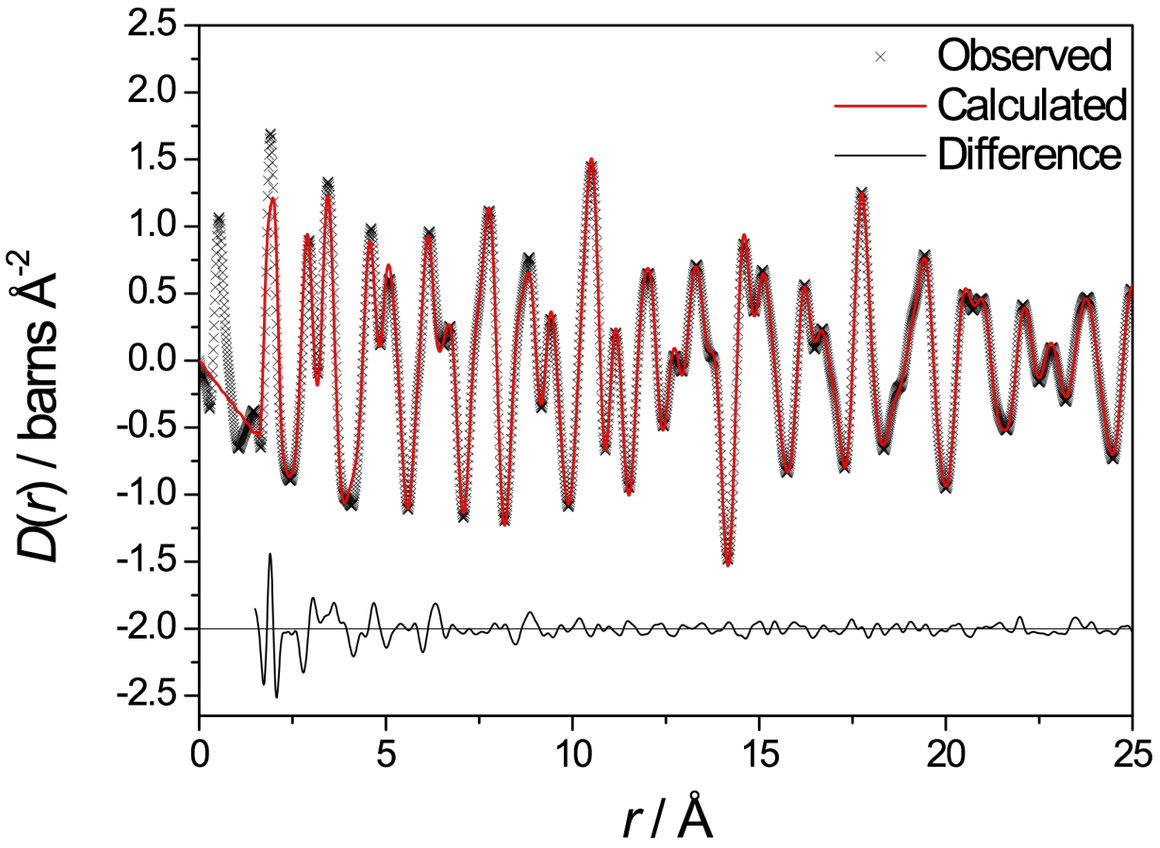


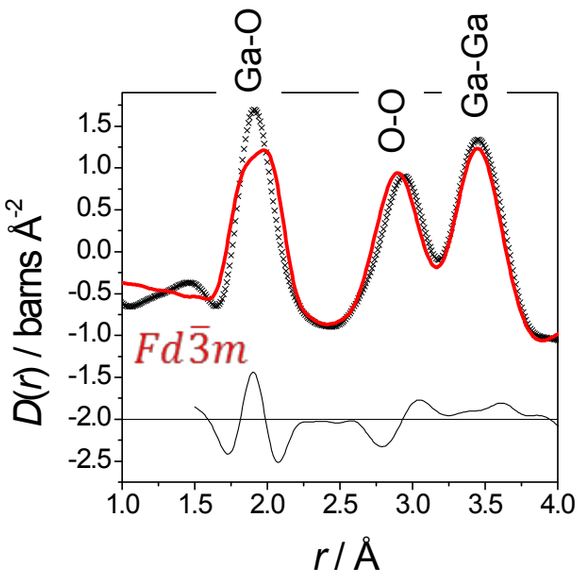


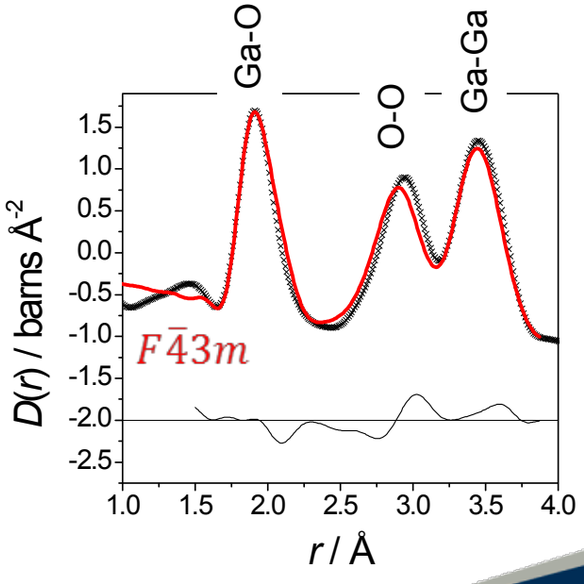
- Potential photocatalyst and catalyst support
- Poorly understood
- Cubic spinel-type structure
- Rietveld refinement reveals four partially occupied Ga sites
- Nanocrystalline

1. Total scattering in action: γ-Ga_2O_3

Small box modelling of γ-Ga_2O_3 (PDFgui)







- 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

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1. Total scattering in action: γ-Ga_2O_3

Big box modelling of γ-Ga_2O_3 (RMCProfile)

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Random starting model:
Ga-Ga < 1Å

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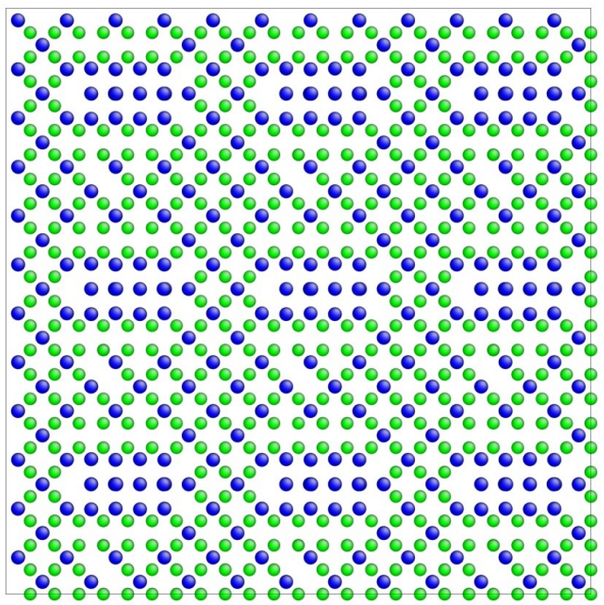
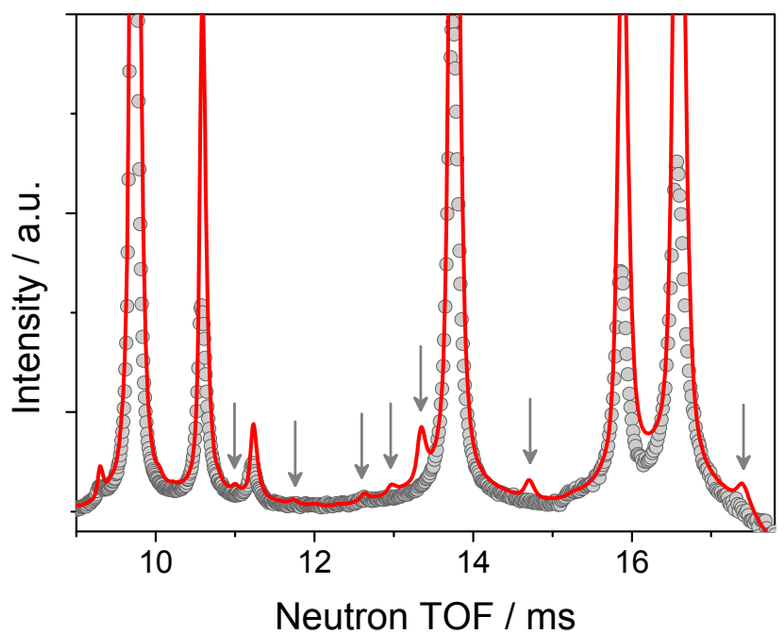


Green = octahedral Ga
Blue = tetrahedral Ga



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↓

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

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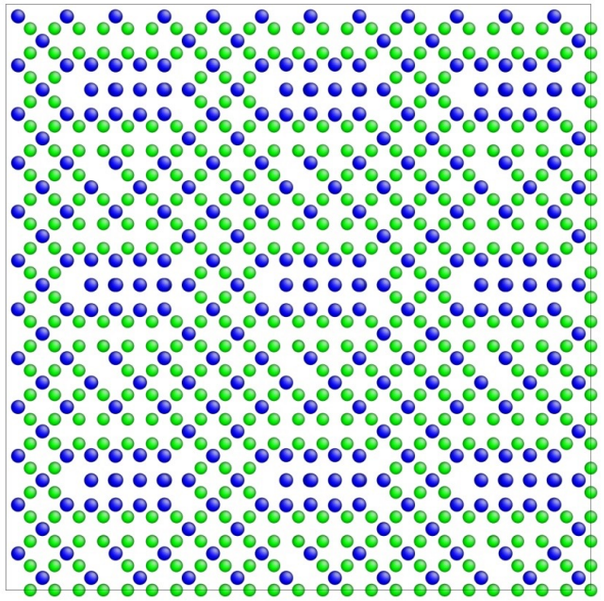

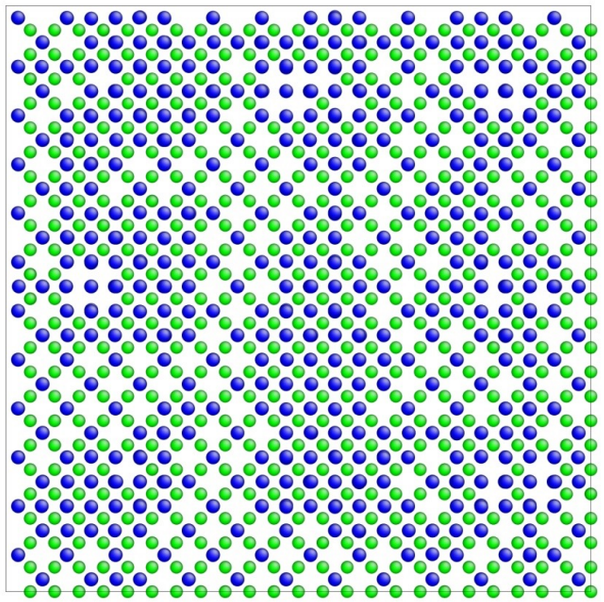

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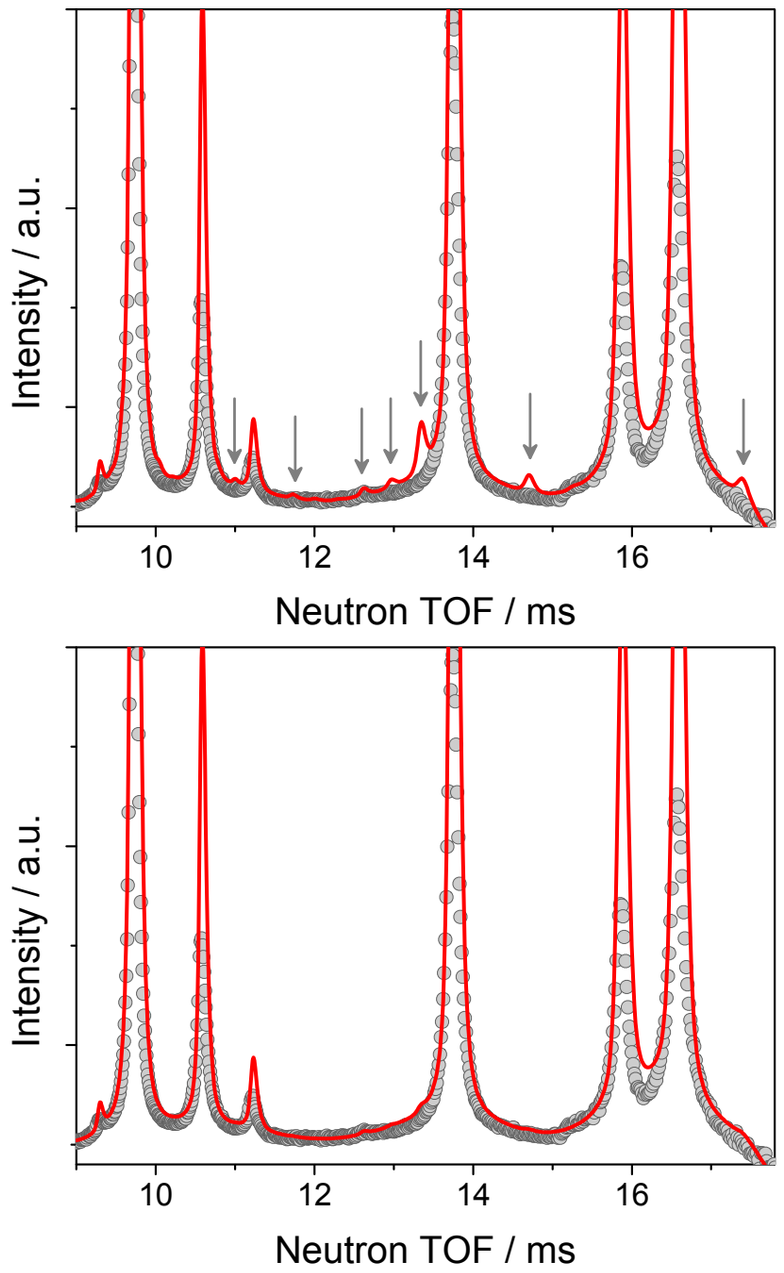

Random starting model:
Ga-Ga < 1Å

↓

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

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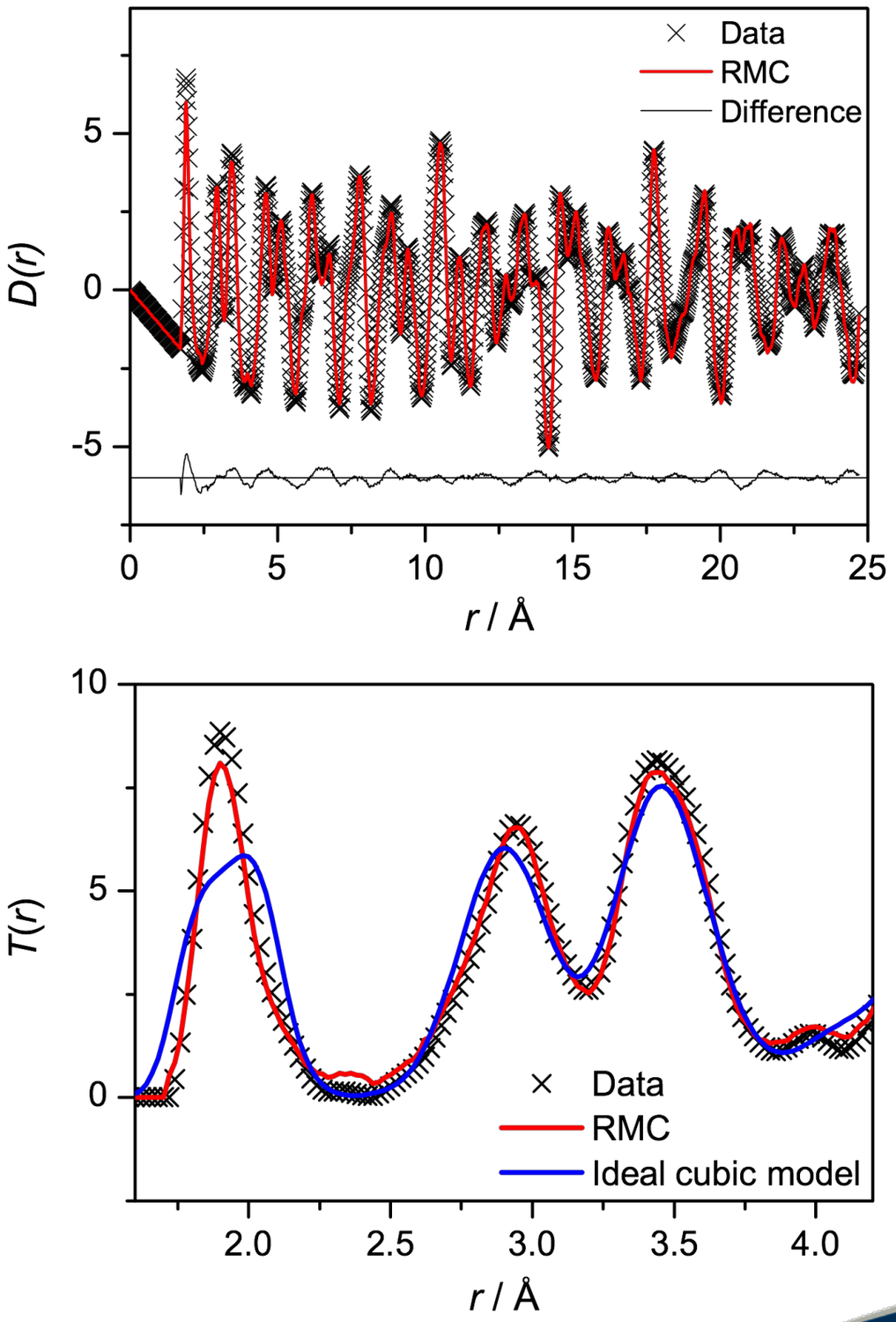
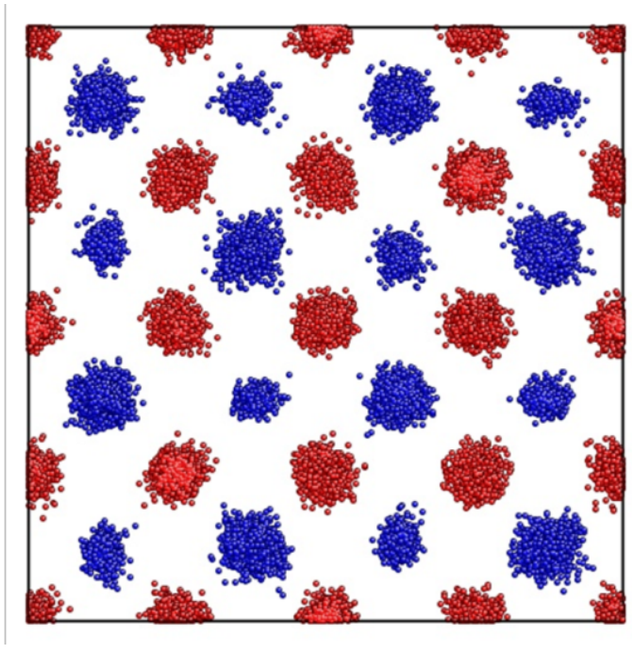
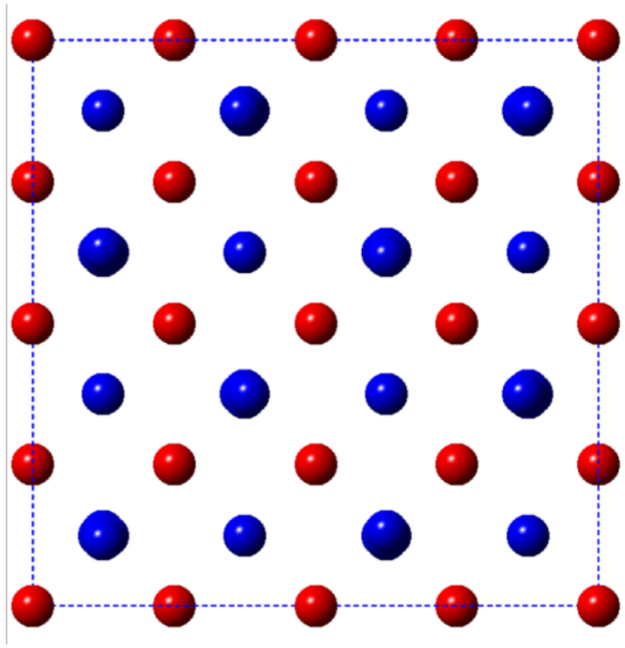


RMC refinement using 6x6x6 supercell
- vastly improved fit to local structure
- maintains correct average



Collapsed RMC box



Unit cell

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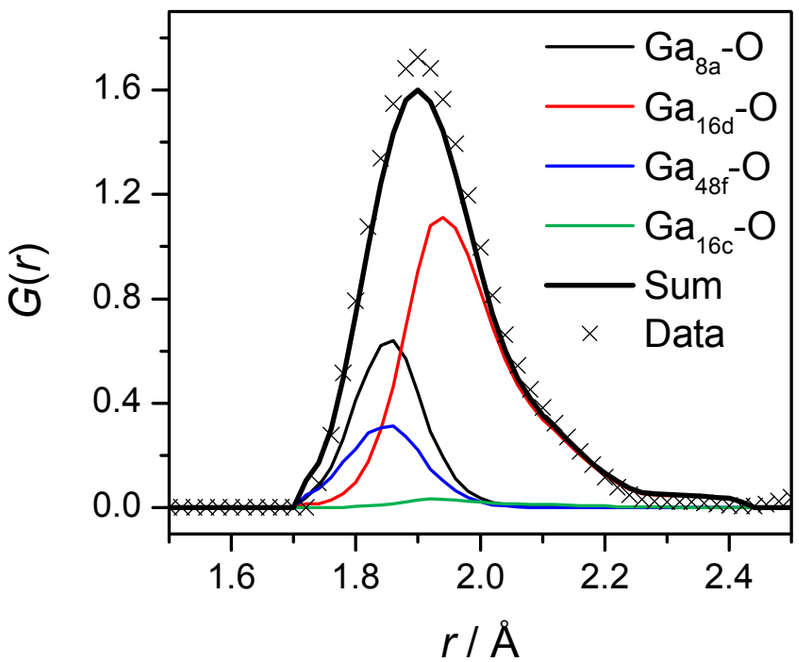
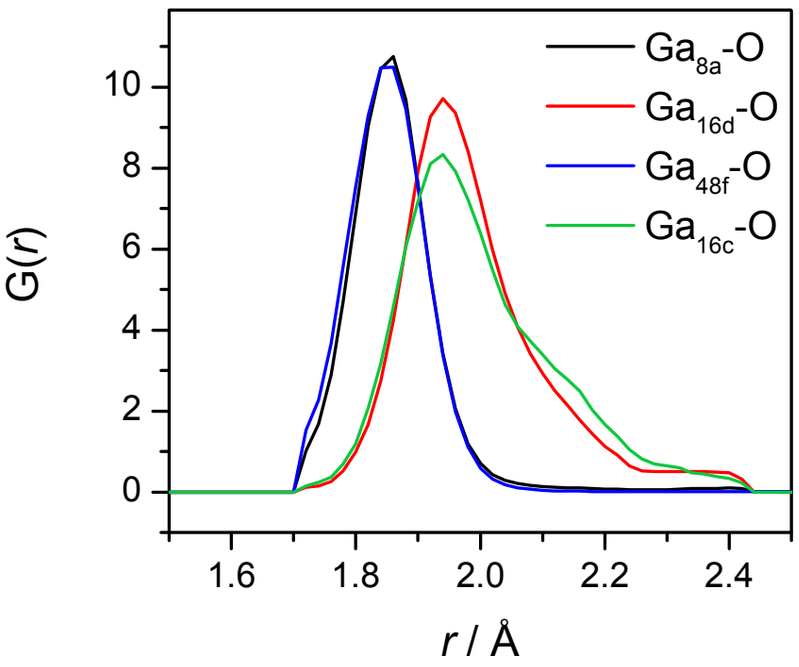
Weighted Ga-O partials



Non-weighted Ga-O partials



RMC provides bond length and angle distributions:

- the O_h sites are highly distorted

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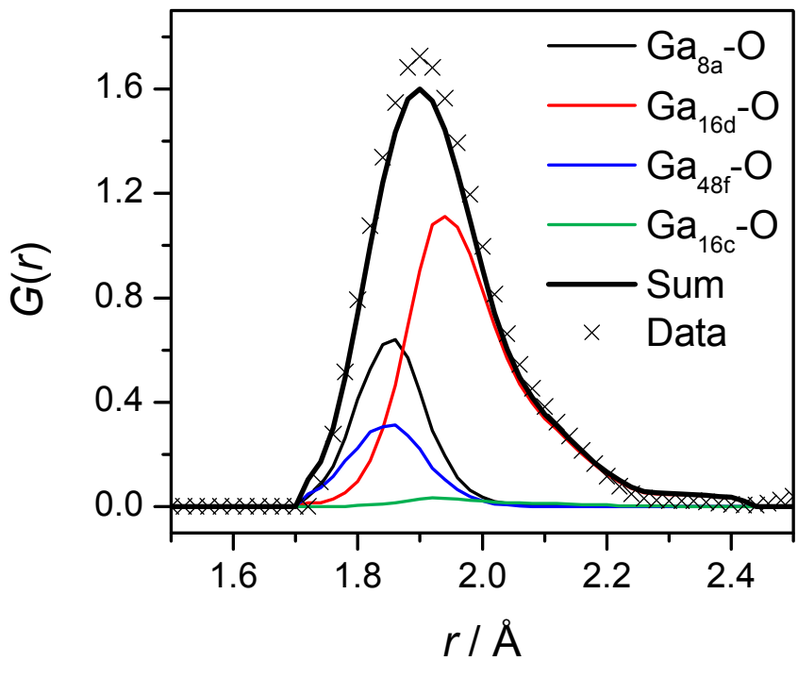

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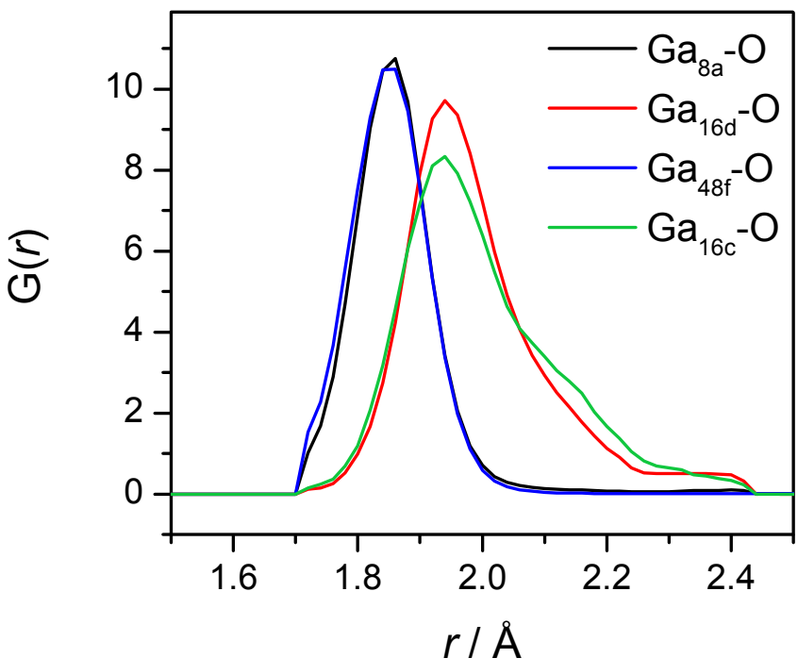
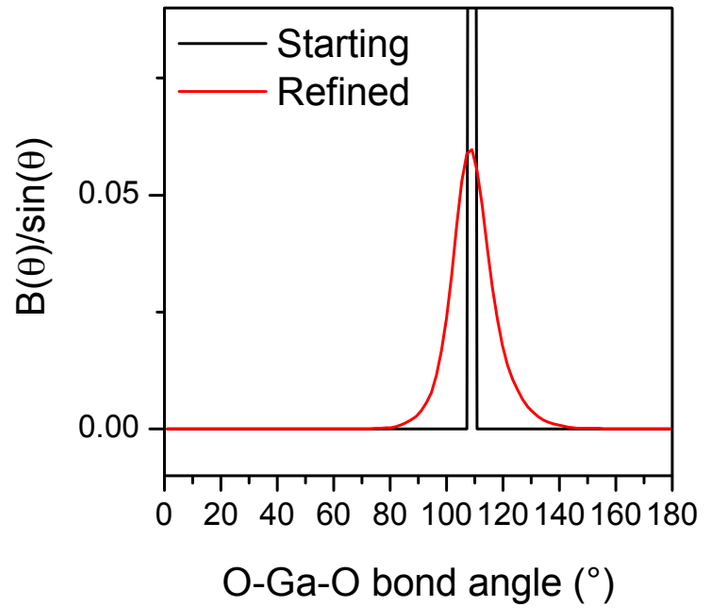


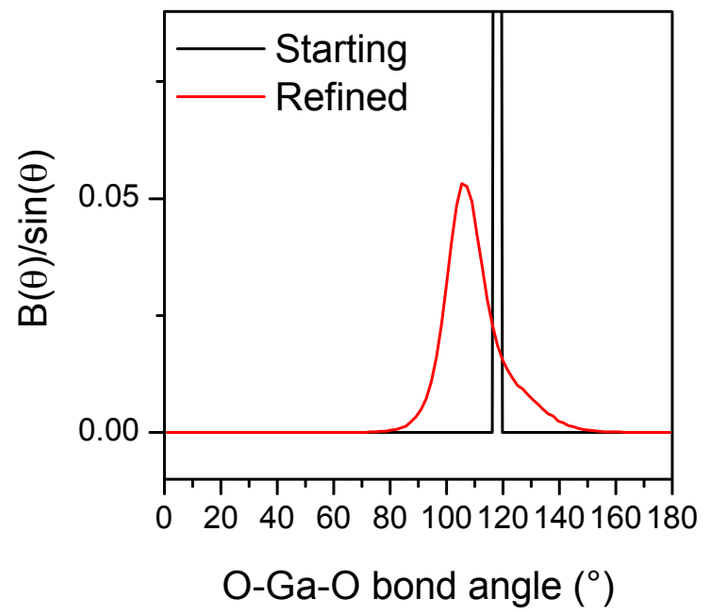
RMC provides bond length and angle distributions:

- 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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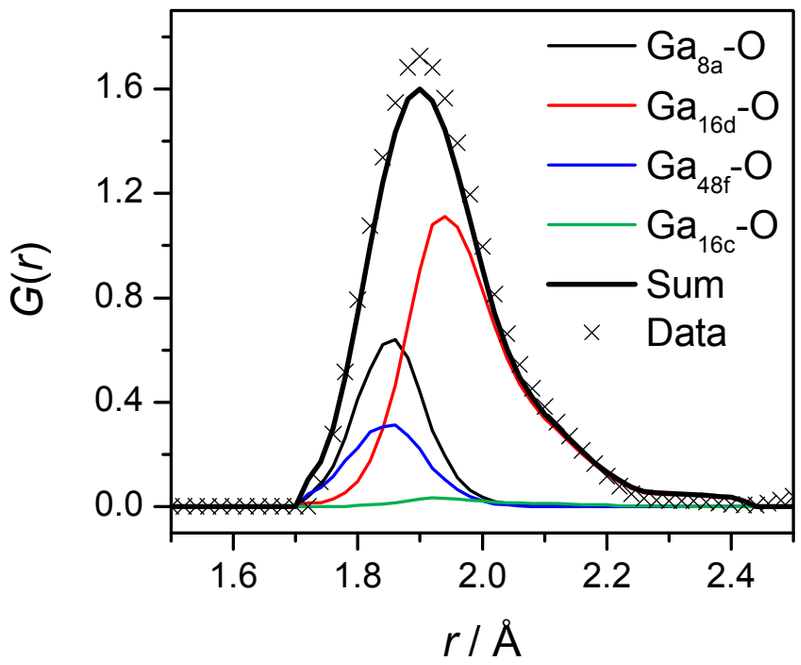
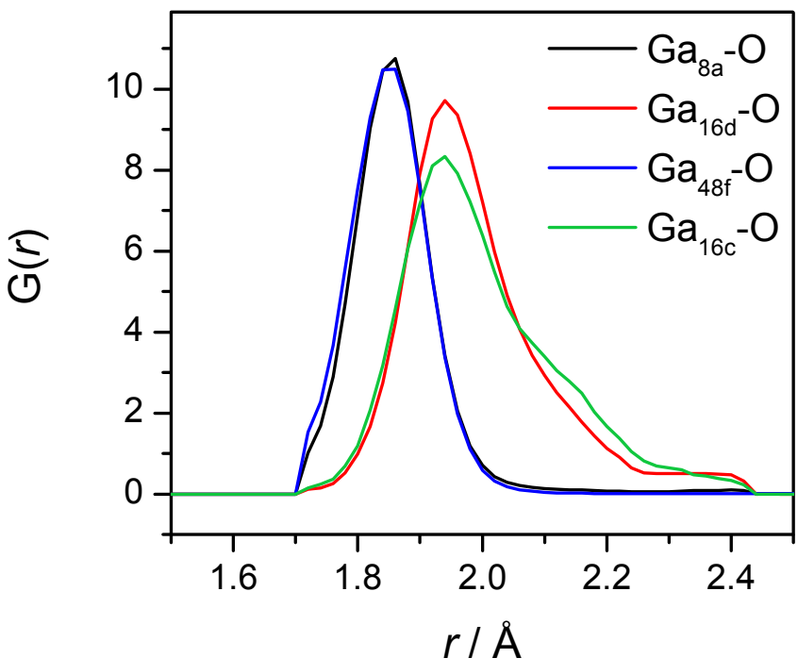


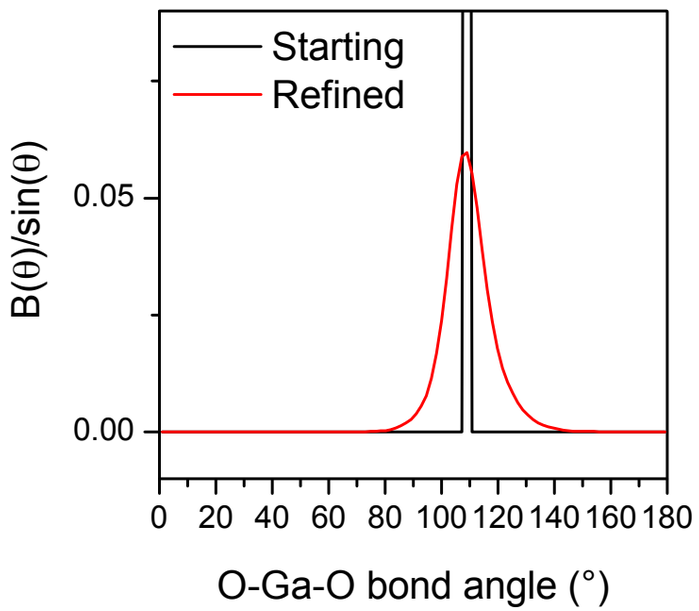
Non-weighted Ga-O partials



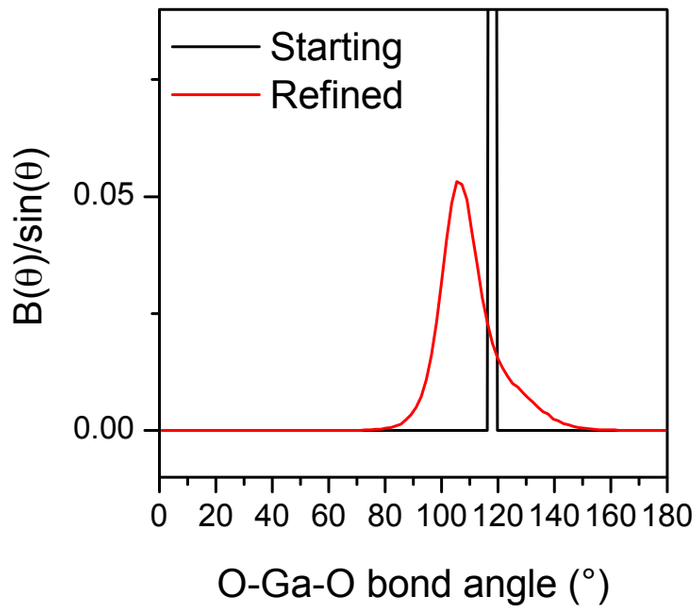
RMC provides bond length and angle distributions:

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

Spinel T_d site



Non-spinel T_d site



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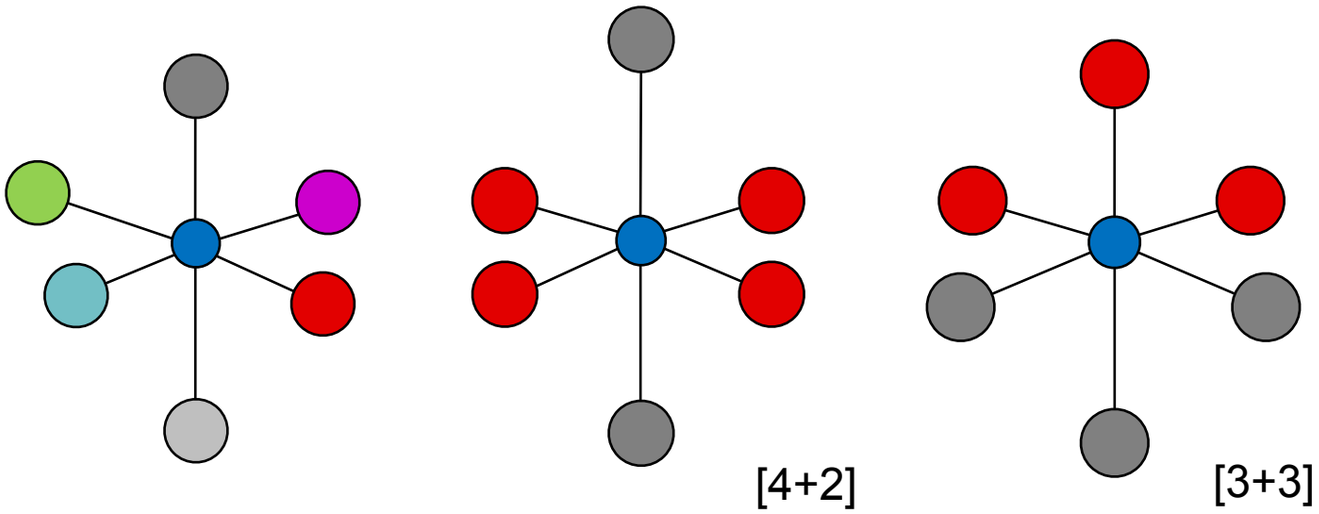

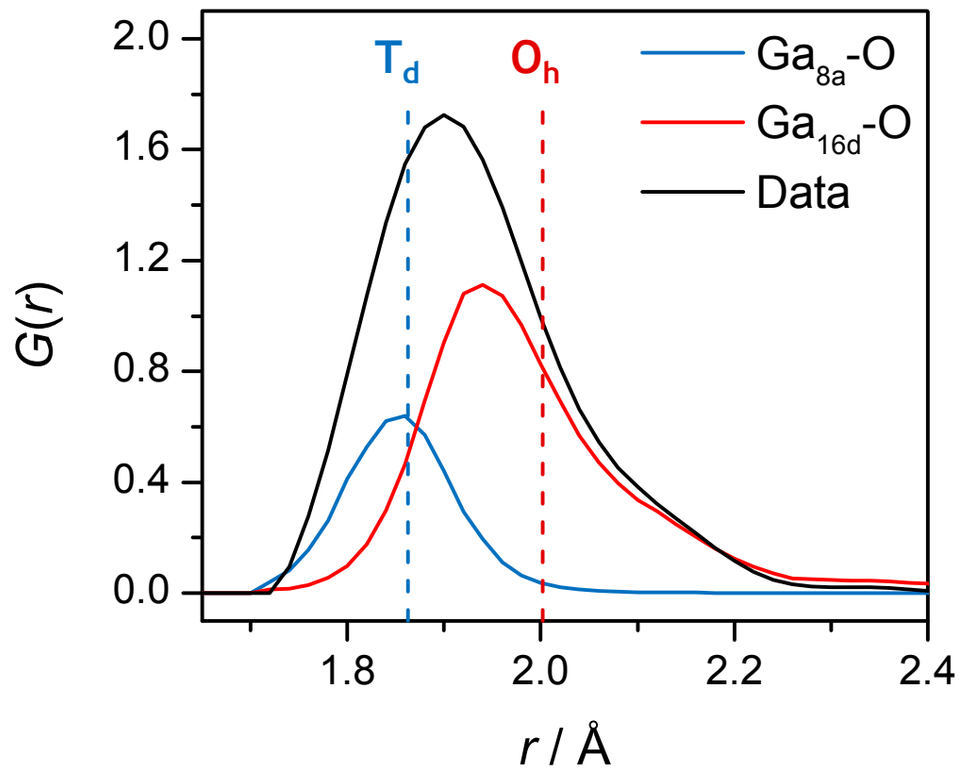

The data clearly show the octahedra are distorted, but what do they actually look like?

- 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

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2. “Secrets” of success

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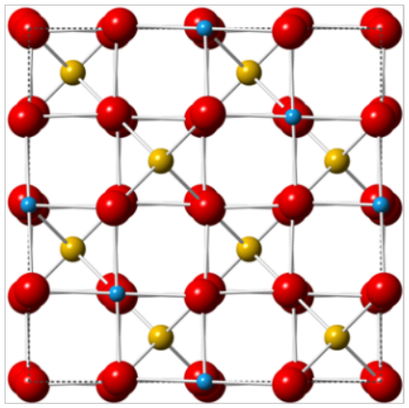


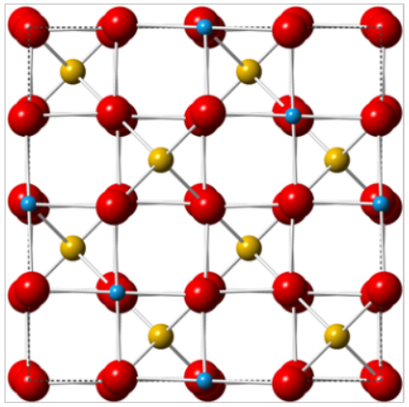
Crystallography

- average structure (symmetry, lattice parameter)
- instrument resolution

↓

Full structural description

2. "Secrets" of success



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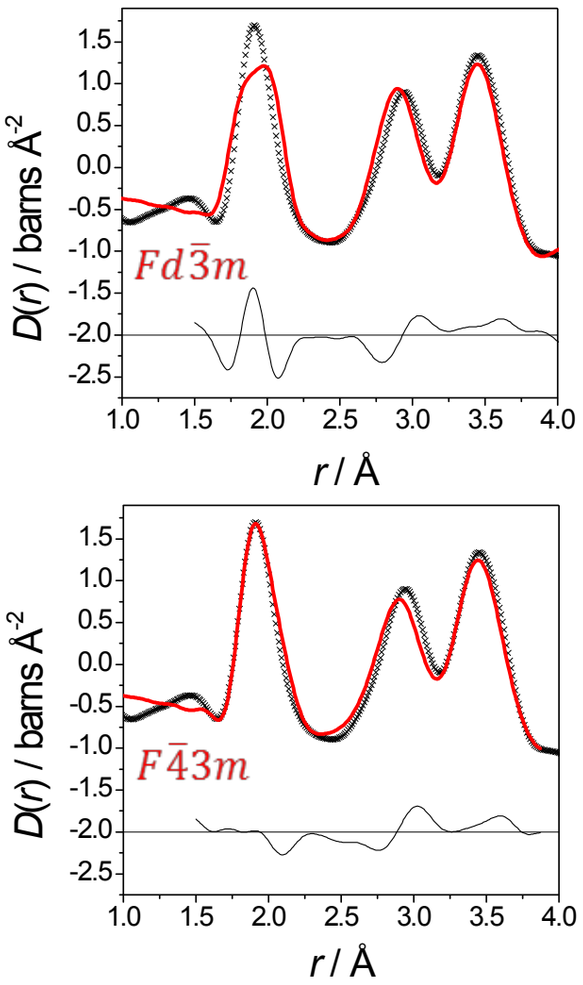

Small-box modelling

- confirmation of mid-range structure
- discrepancies in local structure

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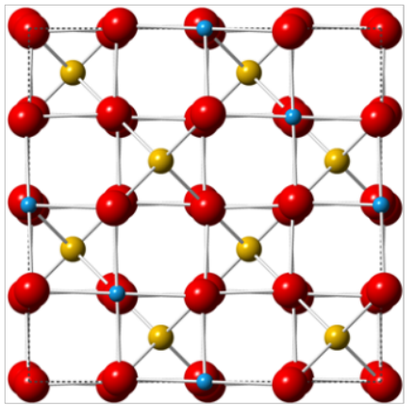

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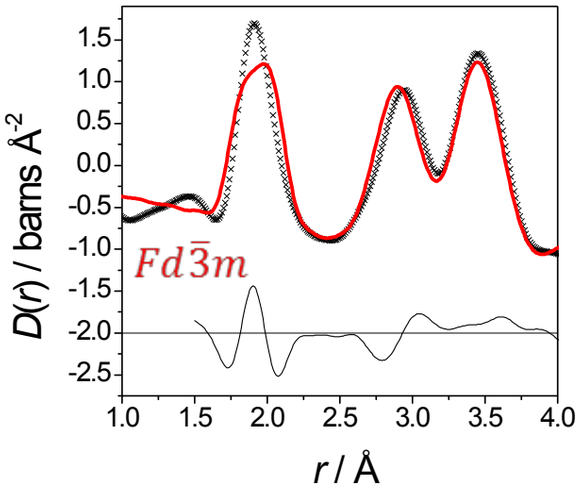
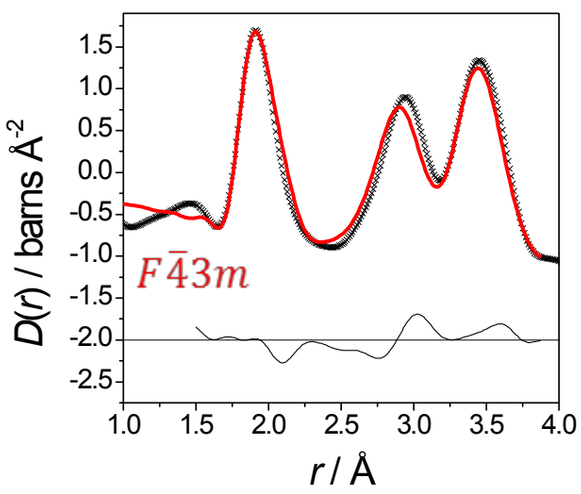
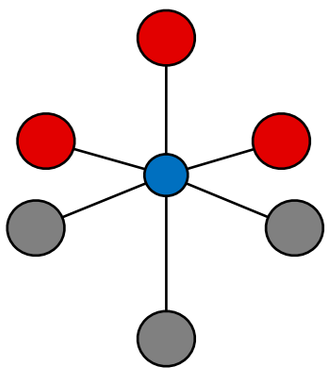


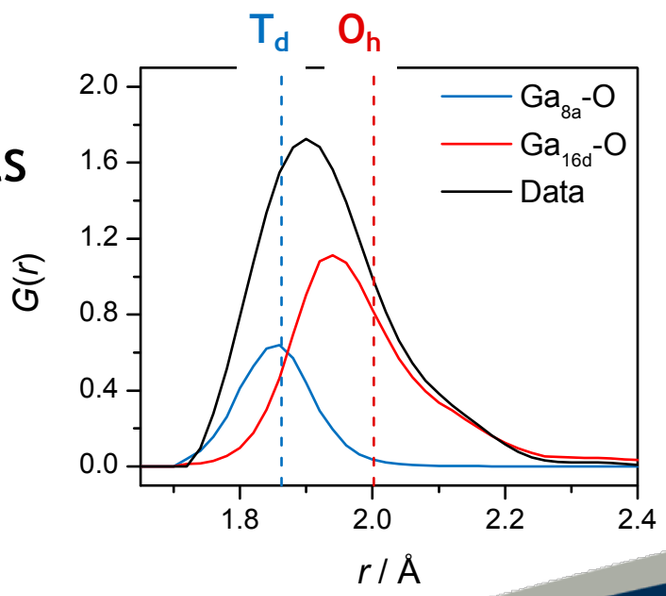




Full structural description

Big-box modelling

- refinement of multiple datasets
- chemically sensible restraints
- explicit atoms and vacancies
- distributions
- one coherent model



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RMCProfile Review

New Insights into Complex Materials Using Reverse Monte Carlo Modeling

Helen Y. Playford,[1] Lewis R. Owen,[2] Igor Levin,[3] and Matt G. Tucker[1,4]

[1]ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire, OX11 0QX, United Kingdom; email: matt.tucker@stfc.ac.uk

[2]Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, CB3 0FS, United Kingdom

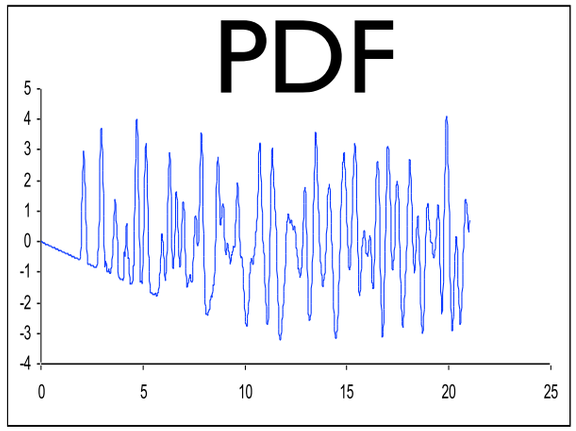
[3]Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

[4]Diamond Light Source, Harwell Oxford, Didcot, Oxfordshire, OX11 0DE, United Kingdom

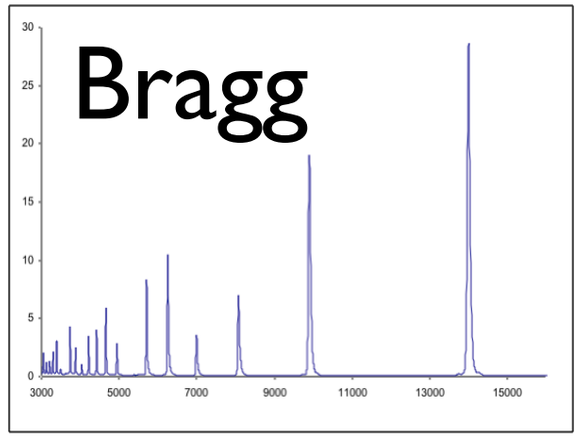
Annual Review Material Research, 2014, 44:429–49

RMC Profile

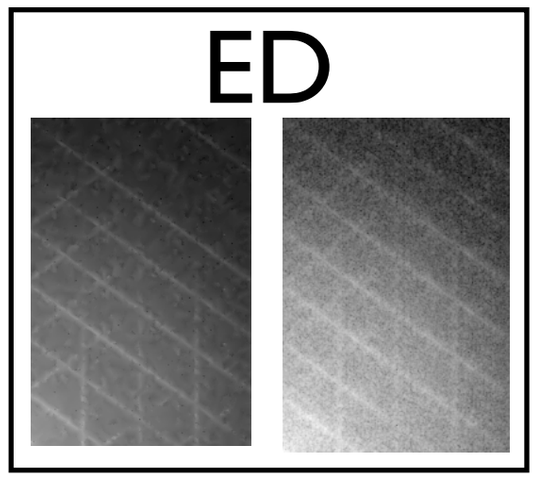
PDF



Bragg



ED



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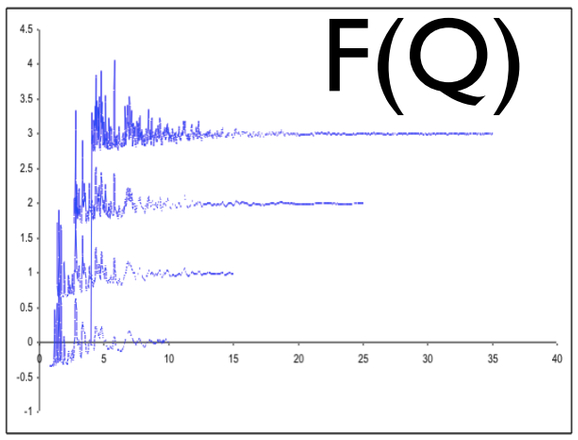
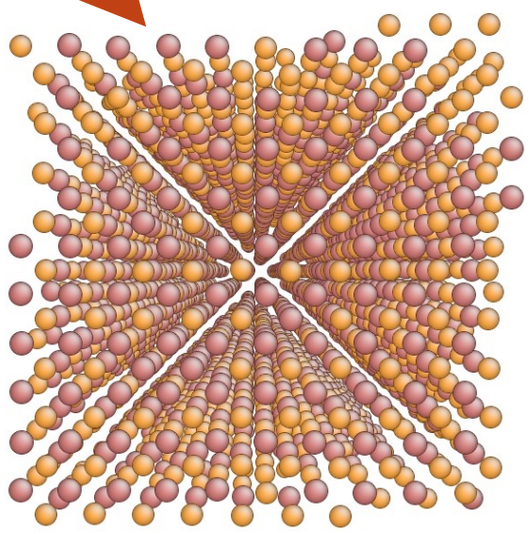
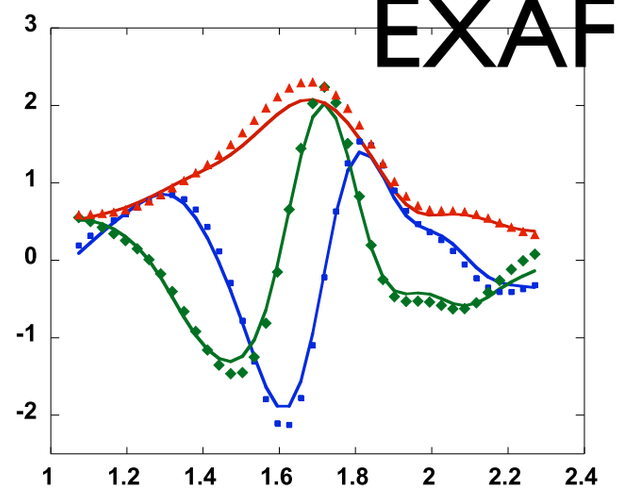
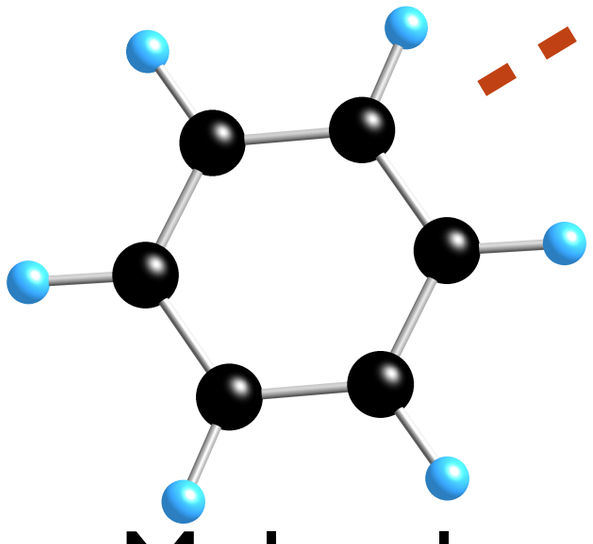




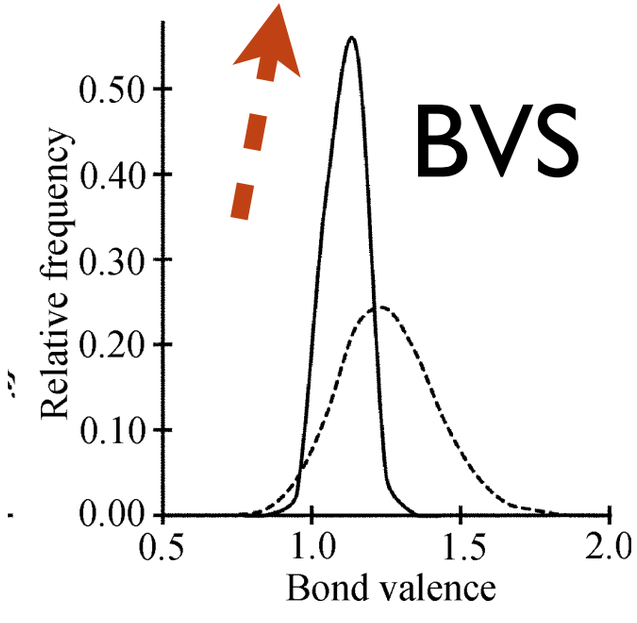
EXAFS

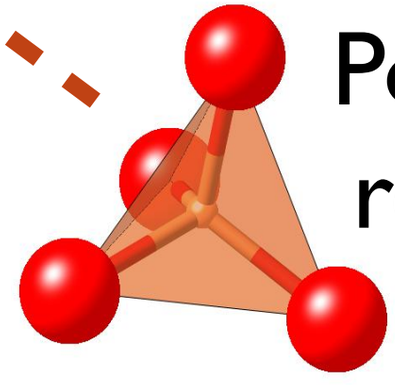




Molecular potentials

BVS





Polyhedral restraints

Big box a Cat’s view

ADD2019, Grenoble

Acknowledgements

Martin Dove (QMUL)

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Andrew Goodwin (Oxford)

Stefan Norberg (Chalmers)

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Wotjek Slawinski (ISIS)

Marshall McDonnell (ORNL)

Yuanpeng Zhang (ORNL/NIST)

www.rmcprofile.org

tuckermg@ornl.gov

helen.playford@stfc.ac.uk