Introduction to small box modelling and PDFgui

Phil Chater, Crystallography Science Group Leader, Diamond Light Source

PolyU Synchrotron Radiation Summer School

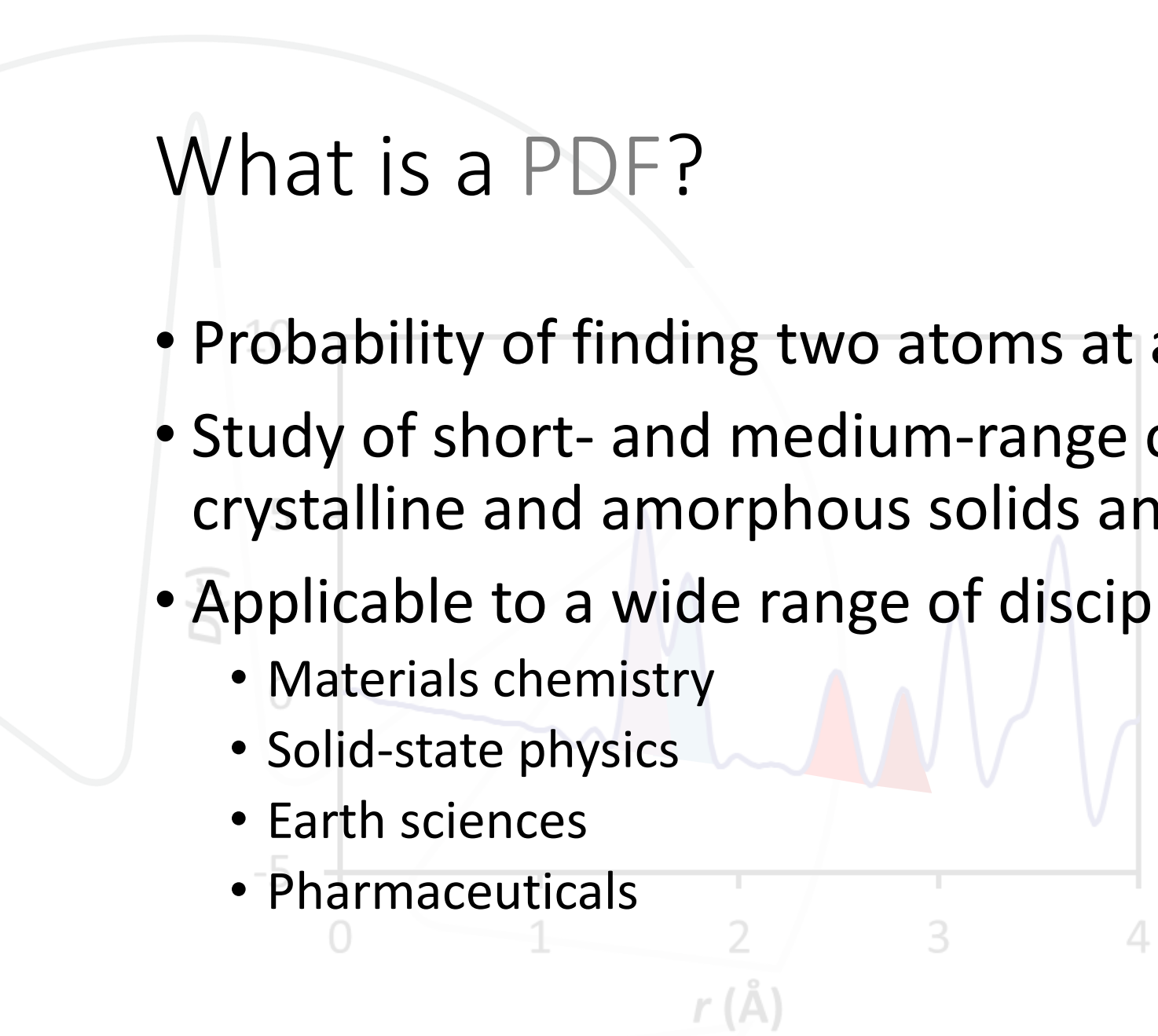
19th June 2024

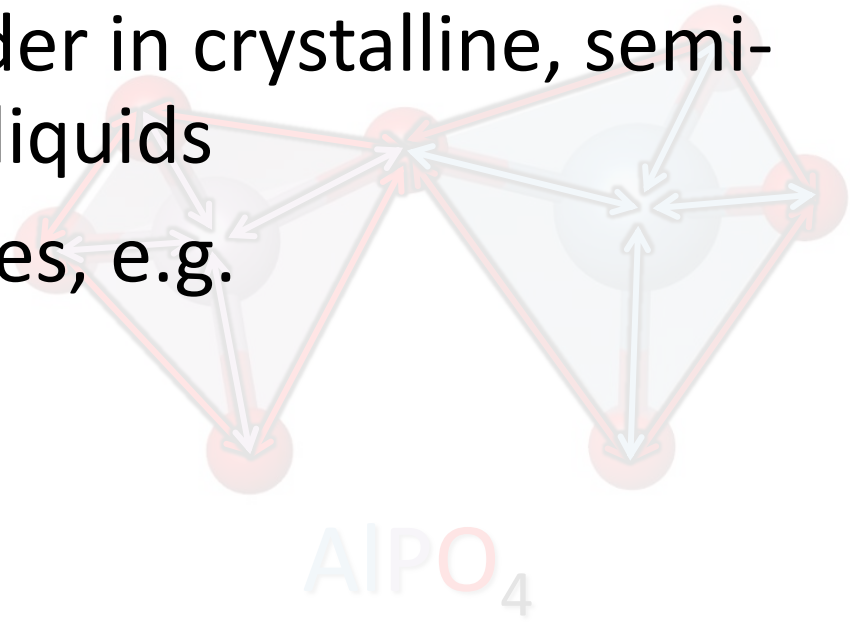
Short (re)introduction to PDF

diamond

What is a PDF?

- Probability of finding two atoms at a given separation, *r*
- Study of short- and medium-range order in crystalline, semi-crystalline and amorphous solids and liquids
- Applicable to a wide range of disciplines, e.g.
  - Materials chemistry
  - Solid-state physics
  - Earth sciences
  - Pharmaceuticals

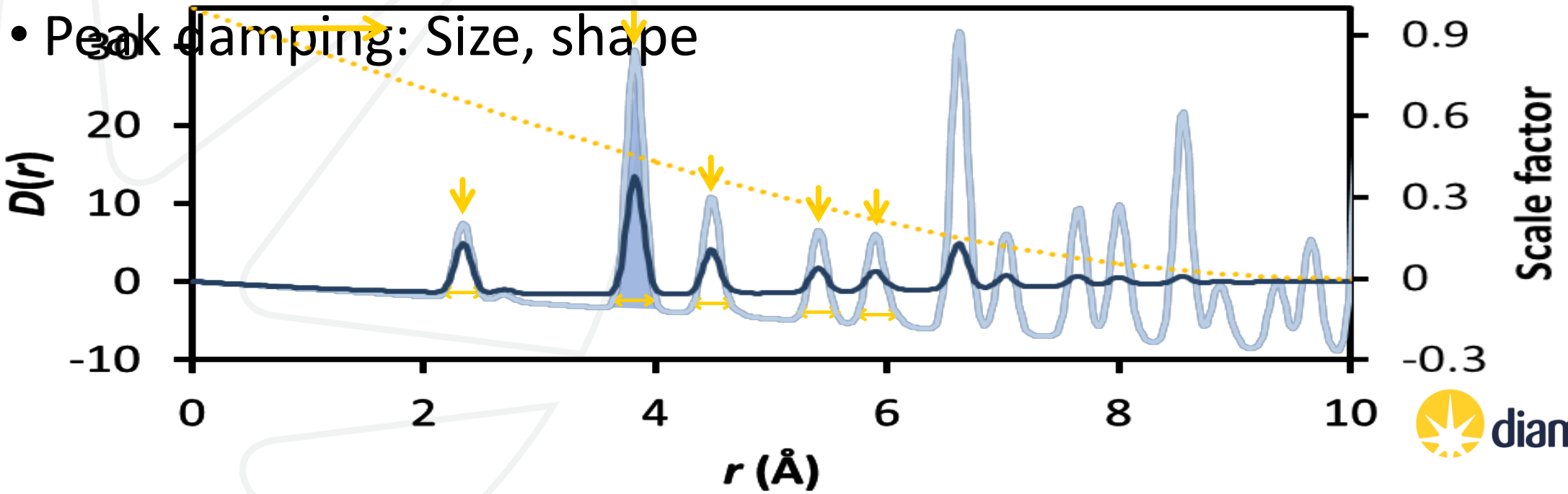




diamond

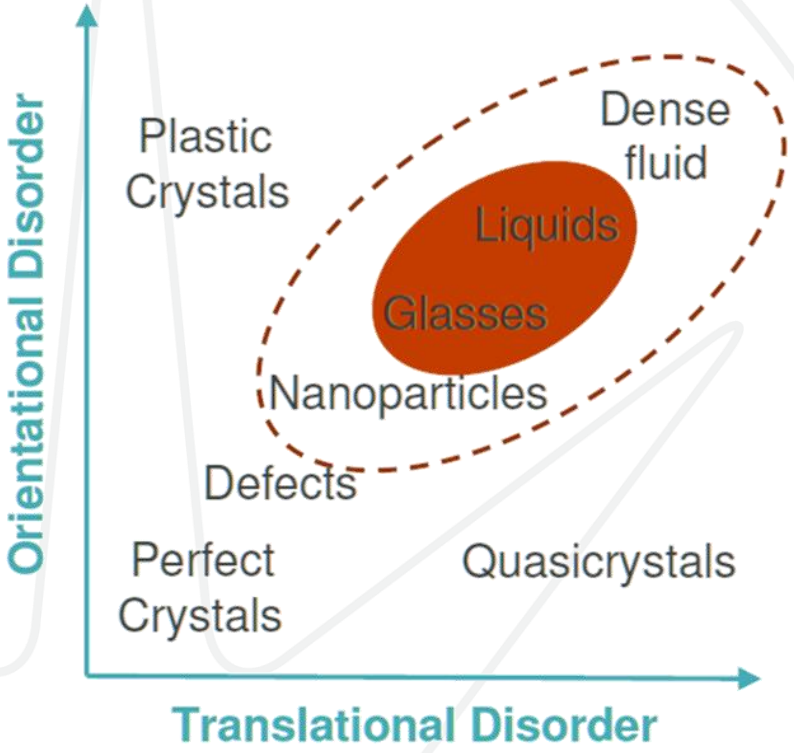
What is a PDF?

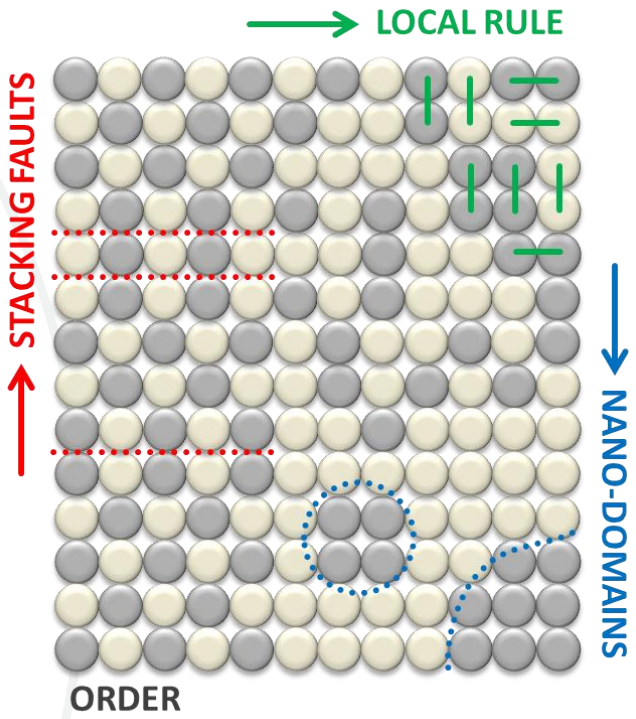
- Peak positions: Bond lengths, geometry, unit cell
- Peak widths: Vibrations, phonons, disorder
- Peak areas: Coordination number, occupancies
- Peak damping: Size, shape

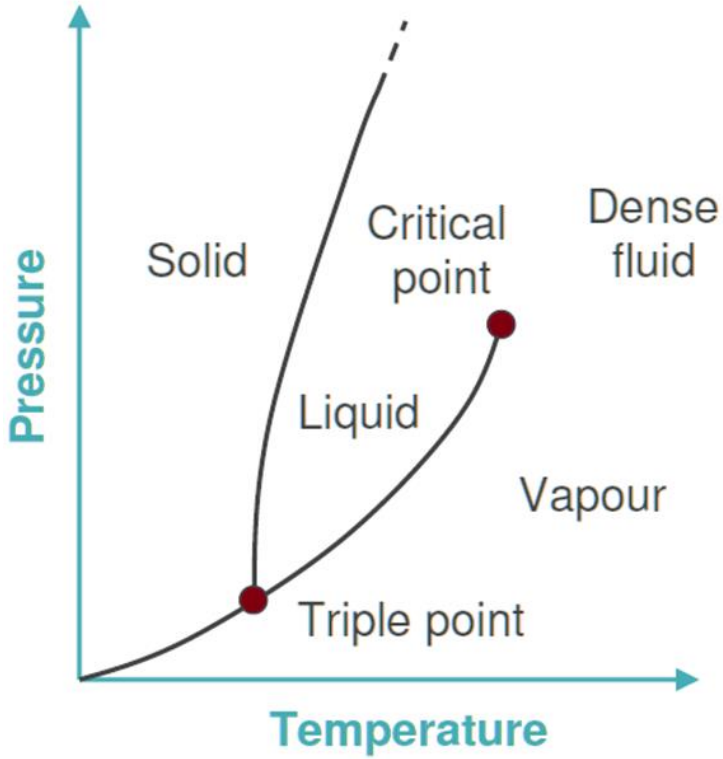


diamond

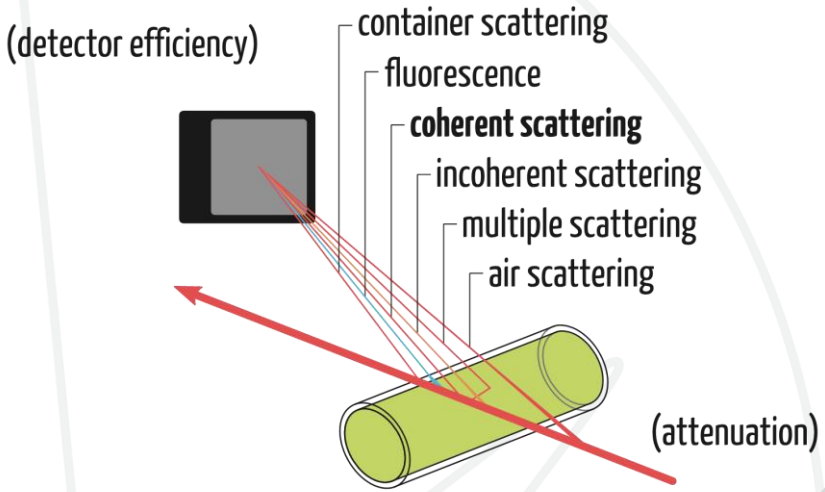
Why are total scattering and PDF useful?

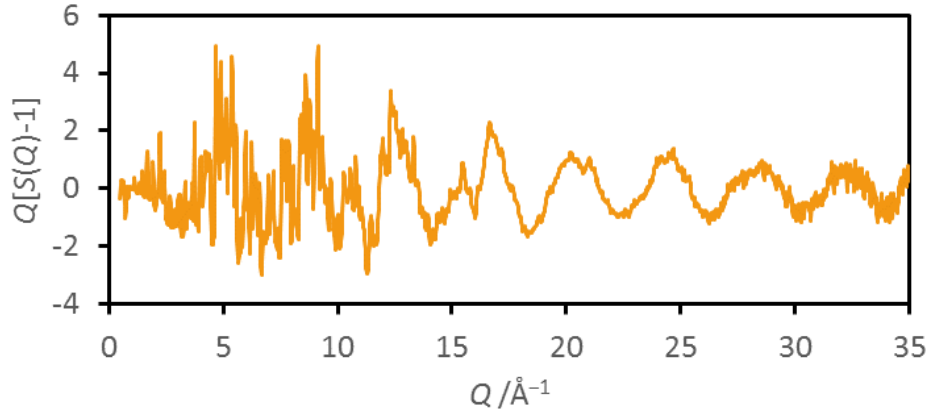




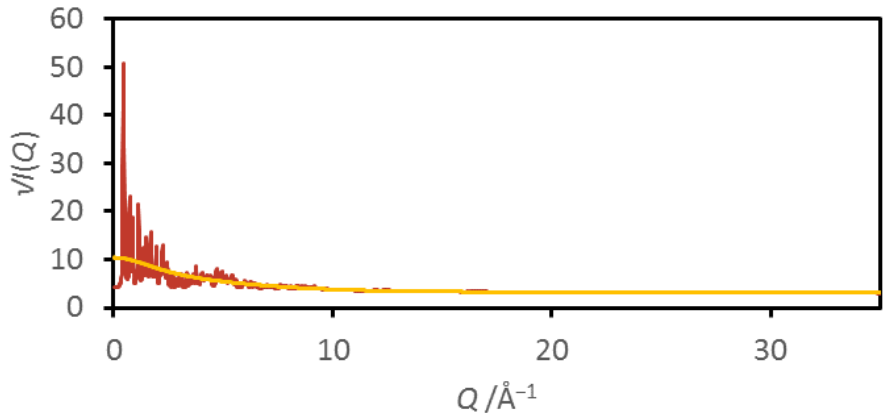


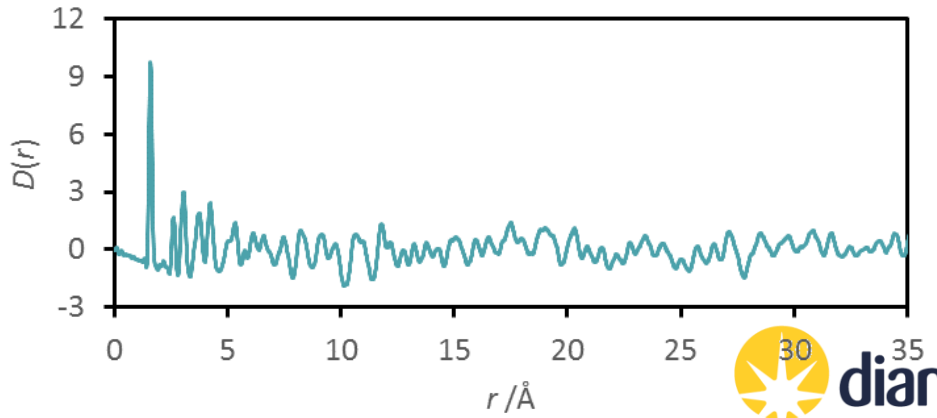
How do you get a PDF?





$$D(r) = \frac{2}{\mu}\int Q[S(Q)-1]\sin(Qr).dQ$$

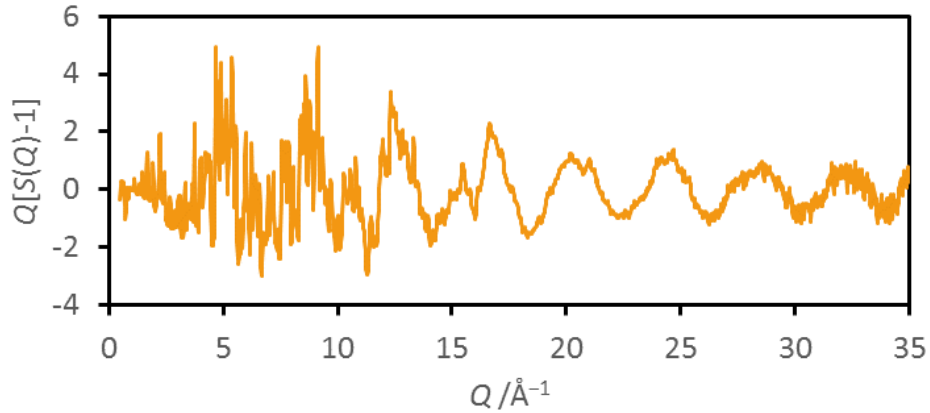




diamond

How do you get a PDF?

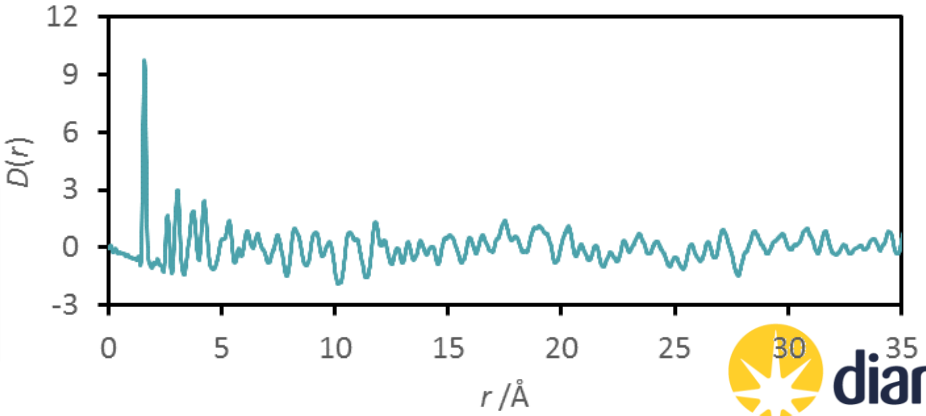
$$I(q) = \sum_{i=1}^{N}\sum_{j=1}^{N} f_i(q) f_j(q) \frac{\sin(qr_{ij})}{qr_{ij}}$$



$$D(r) = \frac{2}{\mu}\int Q[S(Q) - 1]\sin(Qr).dQ$$

$$D(r) = 4\pi r[\rho(r) - \rho_0]$$

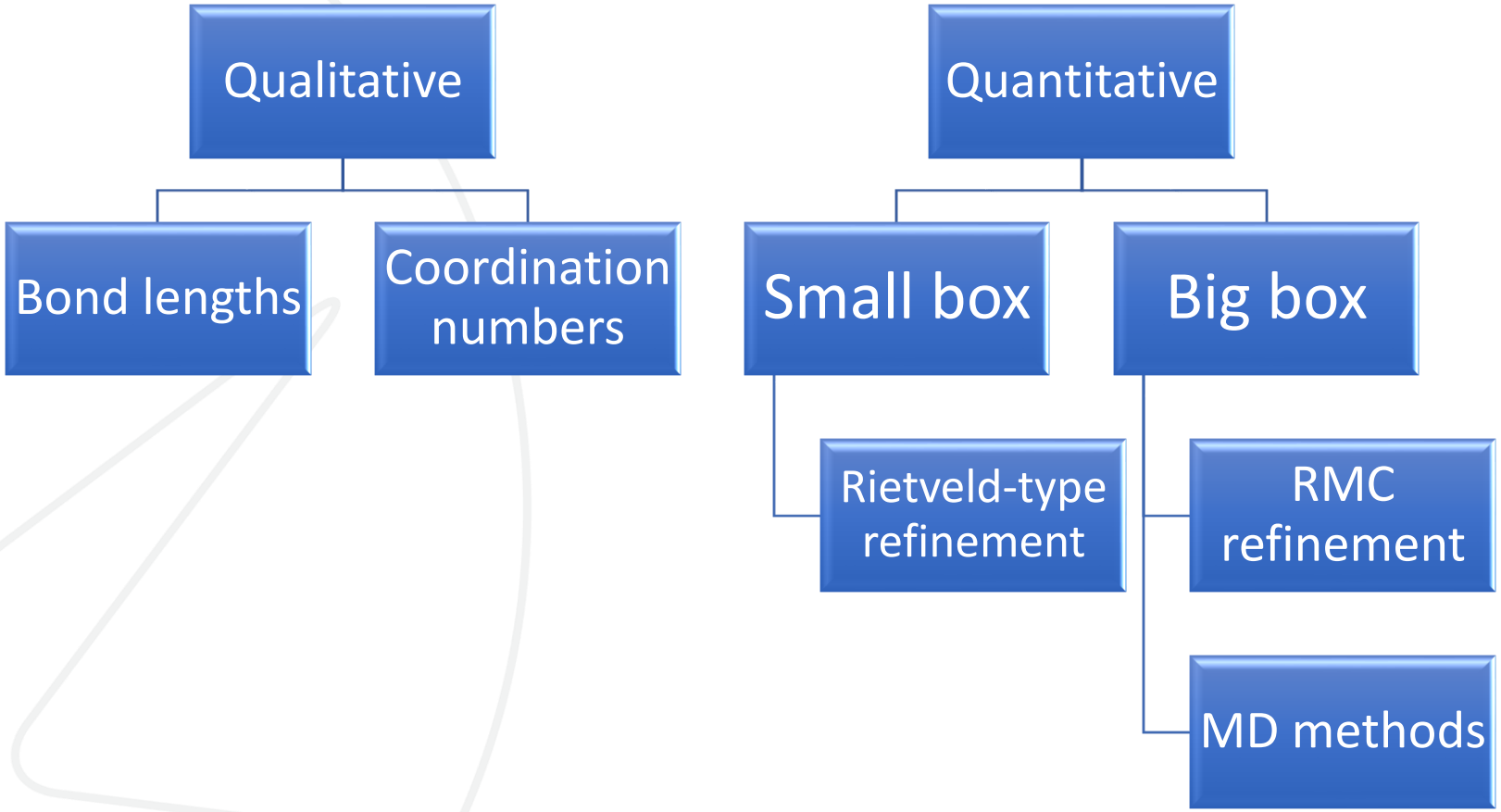
$$D(r) = 4\pi r\rho_0 \sum_{i,j=1}^{n} c_i c_j b_i b_j \left[\frac{n_{ij}(r)}{4\pi r^2 \mathrm{d}r\rho_i} - 1\right]$$



diamond

PDF analysis

PDF analysis



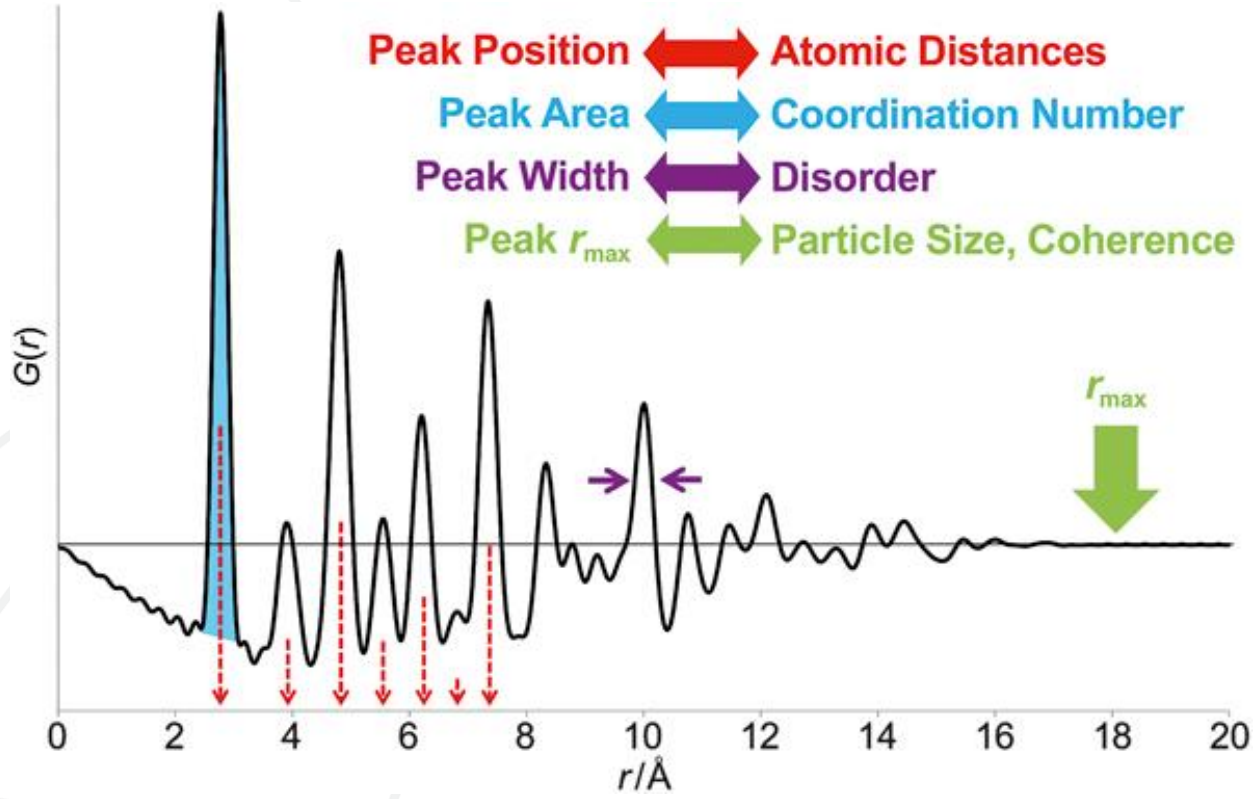
Outline

1. Model-independent analyses
    - Visual analysis of the PDF
    - Peak-picking and trends
    - Principal component analysis / NMF

2. Real-space refinement methods using PDFgui
    - Introduction and basics
    - Calculated PDFs and partial PDFs

Model-independent analyses

What can we learn from looking at the PDF?



Chapman, K. E., *MRS Bull.* **41**, 231 (2016).

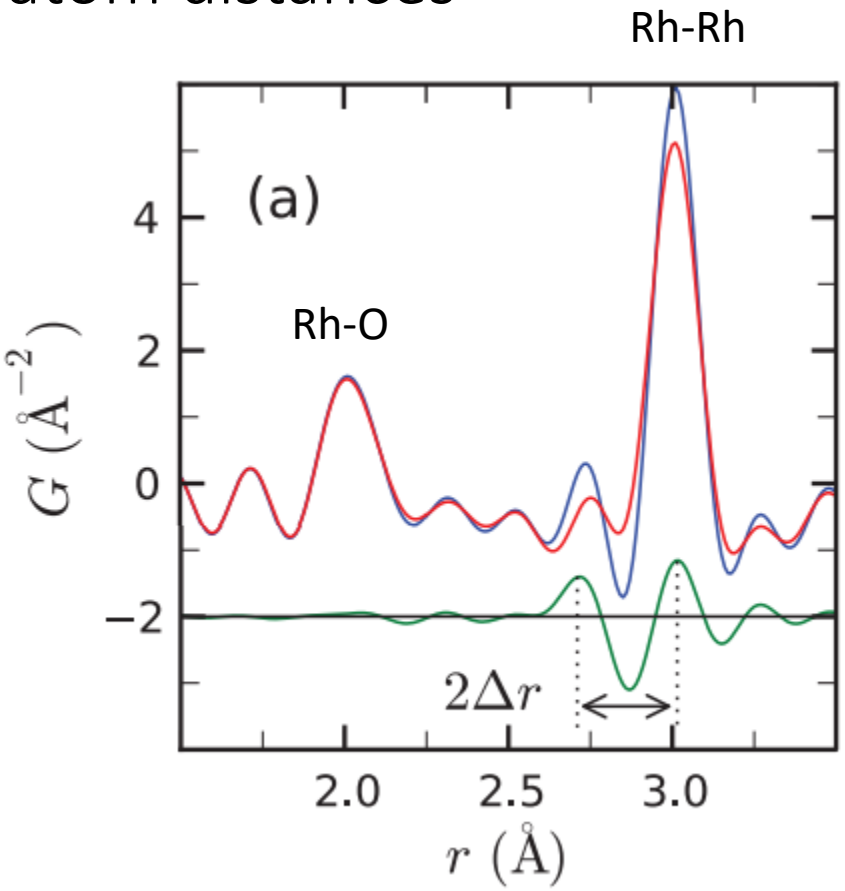
diamond

Model-independent info | Peak-picking

- Peak positions ⟷ atom-atom distances

e.g. $LiRh_2O_4$
Red = High temperature cubic
Blue = low temperature orthorhombic

Rh-Rh peak splits
→ Peak presence at 2.7 Å indicative of Rh-Rh dimers

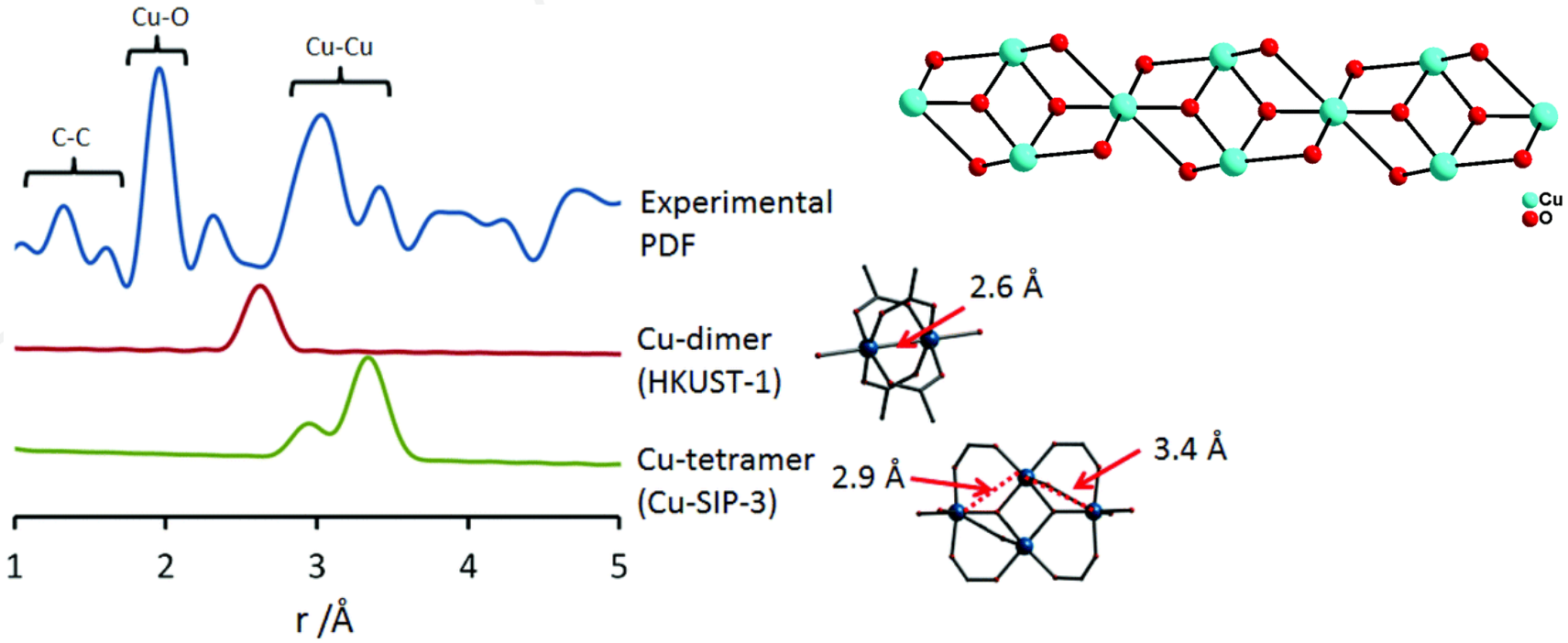


PHYSICAL REVIEW B 88, 174114 (2013)

diamond

Model-independent info | Peak-picking

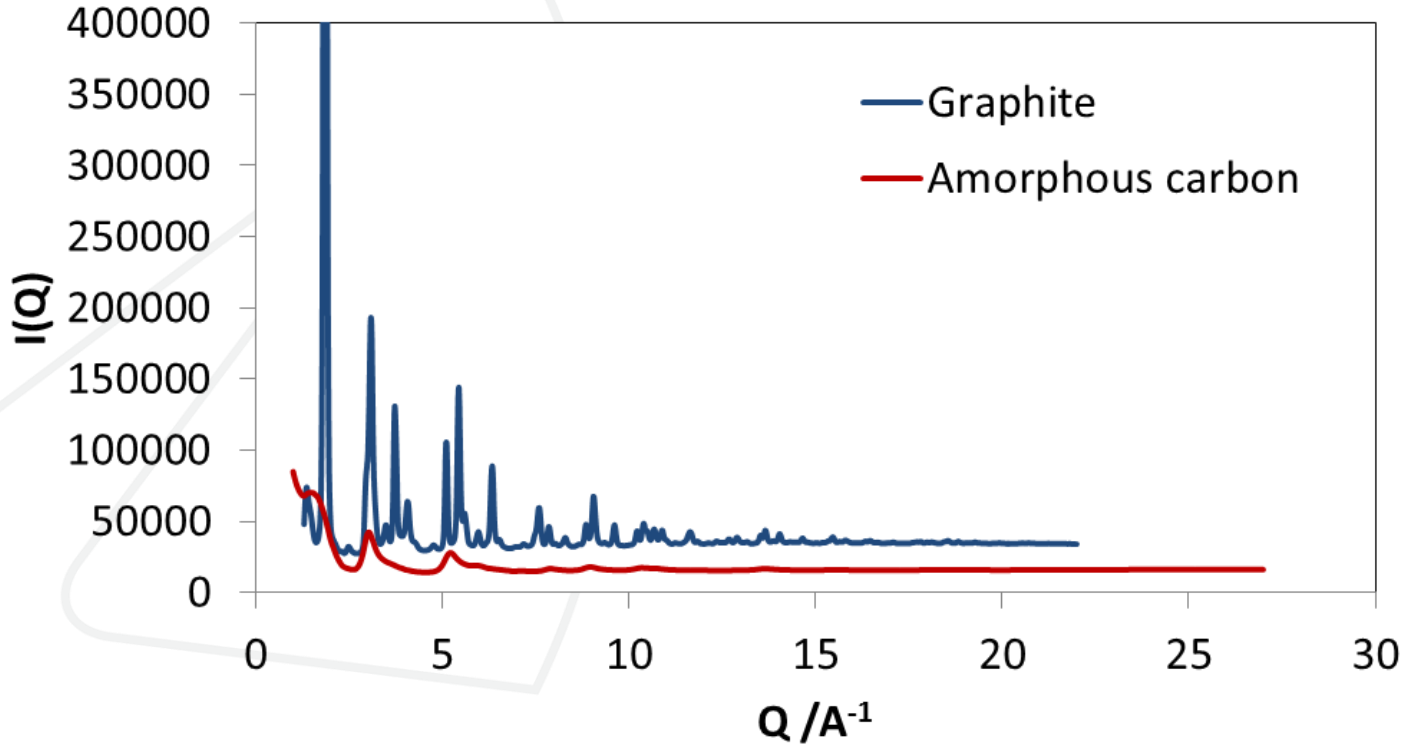
- Peak positions ↔ atomic positions
- Obtain the Cu-Cu connectivity in unknown metal-organic framework
- Constrain the structure solution from powder diffraction



Mohideen, M. I. et al, *Dalton Trans.*, **43**, 10438-10442 (2014)

Model-independent info | Peak-picking

- Peak positions ↔ atom-atom distances
- e.g. amorphous carbon: graphene-like distances, no interlayer distances

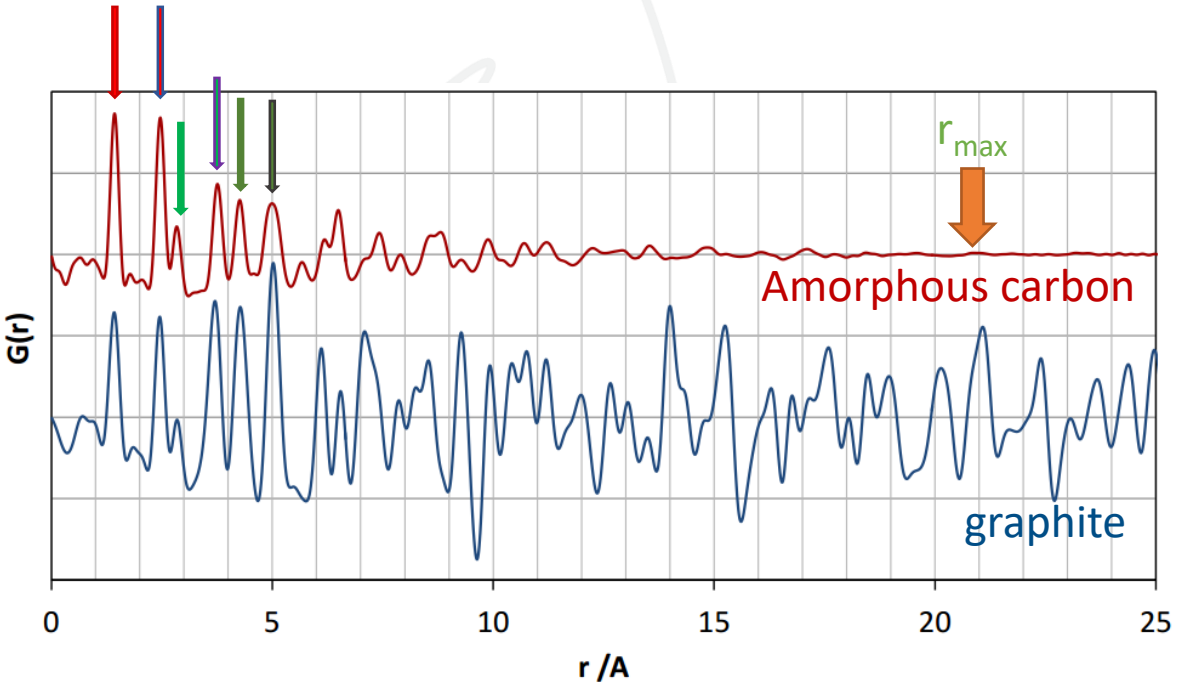


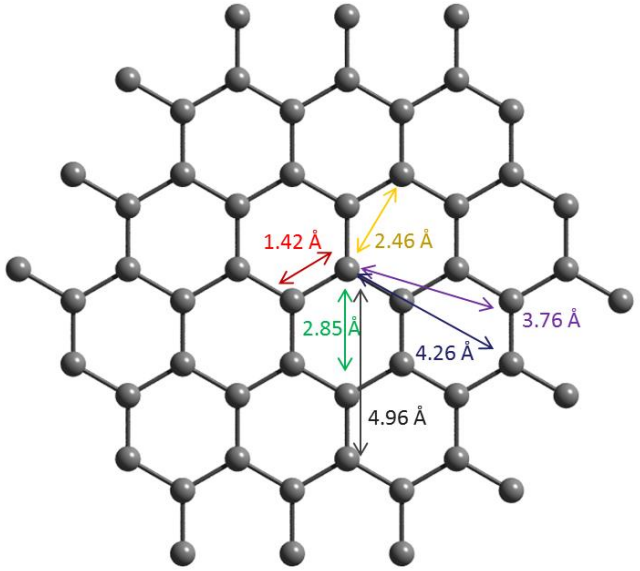
Straford, J. M., *Chem Comm*, **52**, 12430 (2016)

diamond

Model-independent info | Peak-picking

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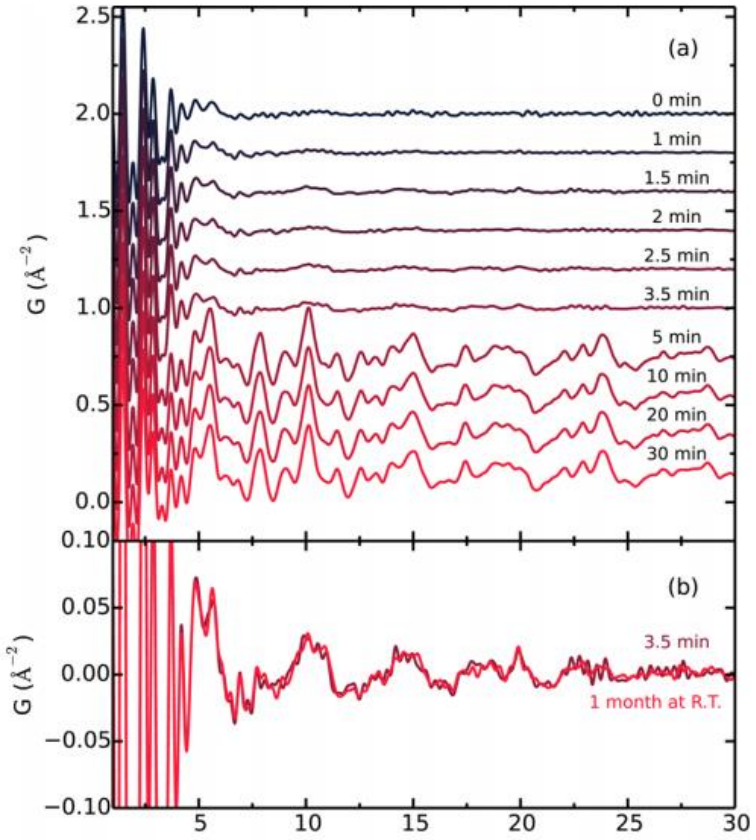


Straford, J. M., *Chem Comm*, **52**, 12430 (2016)

diamond

Model-independent info | R_{max}

- $R_{max} \leftrightarrow$ particle size or coherence
- Crystallisation processes result in increase in R_{max}



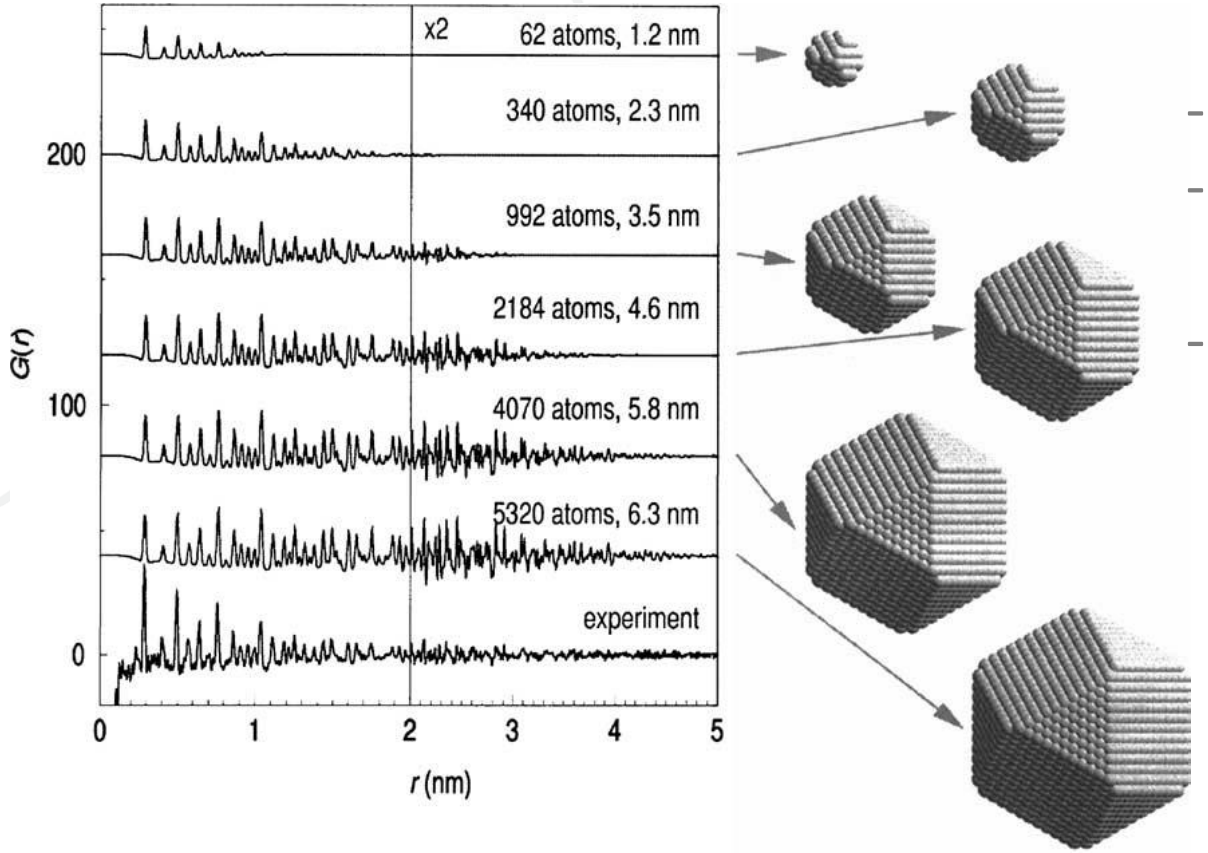
- a-Flowlac after aging for different lengths of time

Maxwell et al., *Cryst. Growth Des*. **16**, 210–220 (2015)

diamond

Model-independent info | R_{max}

- $R_{max} \leftrightarrow$ particle size or coherence
- Attenuation of PDF due to finite particle size



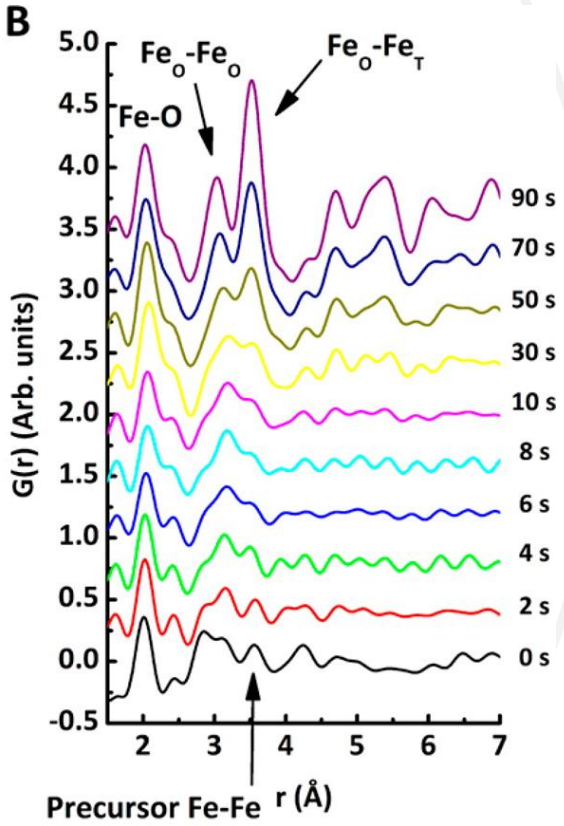
- Gold nanoparticles
- Au-S and thiol cap layer @ 2.4 Å
- Comparison to simulated G(r) for nanoparticles

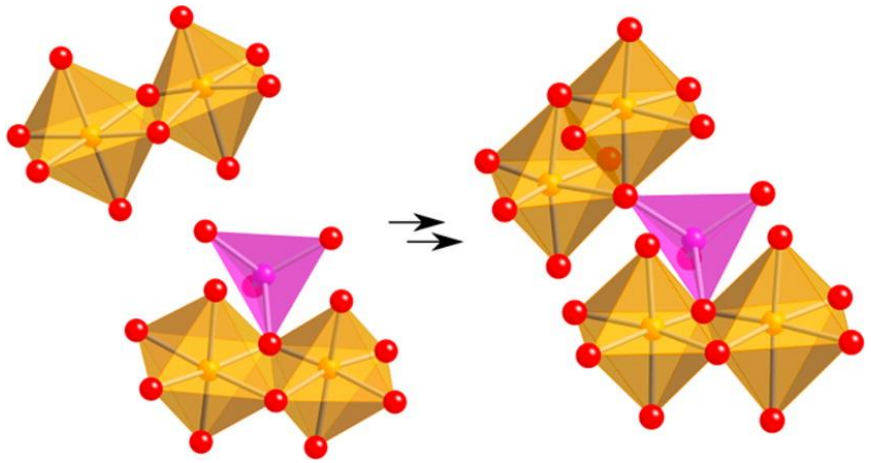
Page, K. et al, *Chem. Phys. Lett.*, **393**, 385 (2004)

diamond

Model-independent info | Peak-picking

- Peak position ↔ atomic positions
- Compare to expected bond-lengths from crystal structures
- e.g. hydrothermal synthesis of nanoparticles of γ-Fe_2O_3





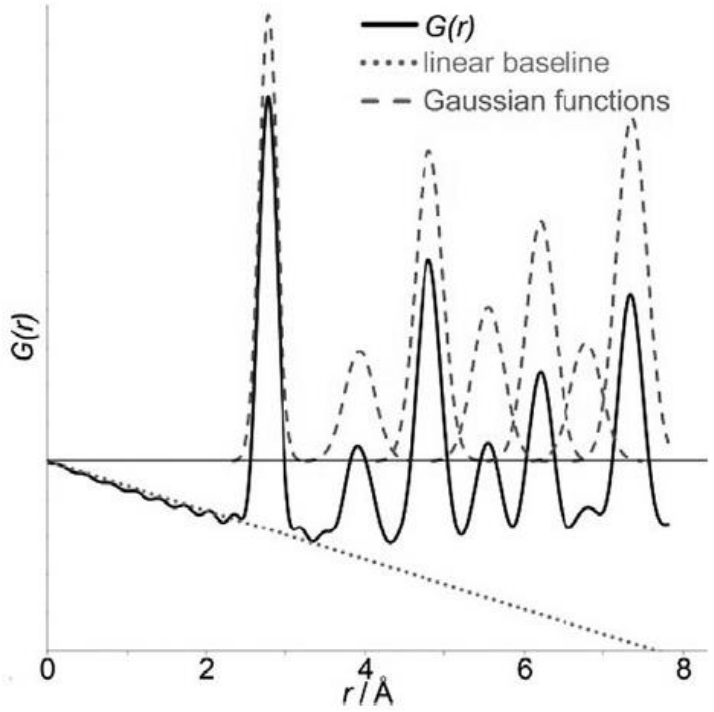
1. Growth of Fe_o-Fe_o
2. Growth of Fe_o-Fe_T
   → implies condensation of clusters along corner-sharing tetrahedral units

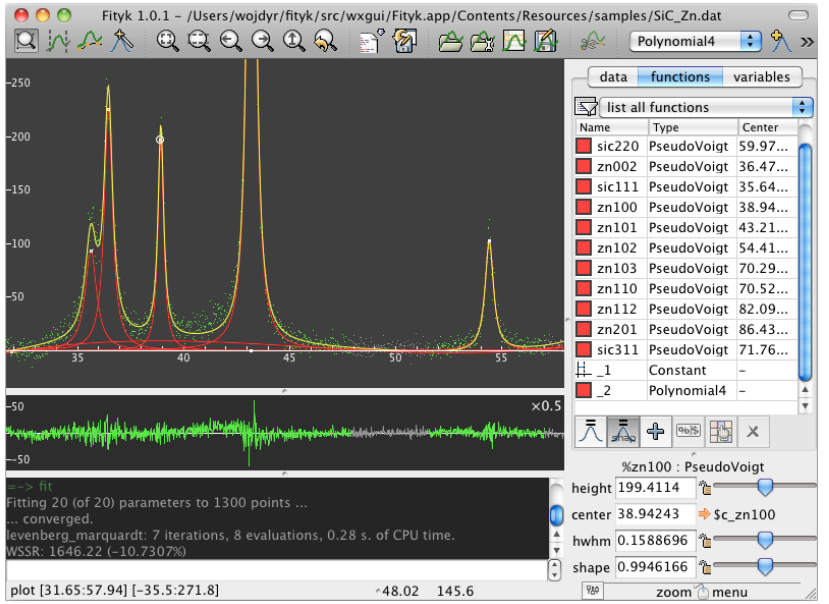
Jensen, K. M. Ø, *ACS Nano*, 8, *10*, 10704 (2014)

diamond

Model-independent info | Peak-picking

- Fit a linear baseline of -4πrρ (ρ = density of the sample)
- Fit Gaussian peak shapes to the peaks
- Extract position, width, area, etc.
- Note: useful for low-r, difficult at high-r - many overlapping peaks



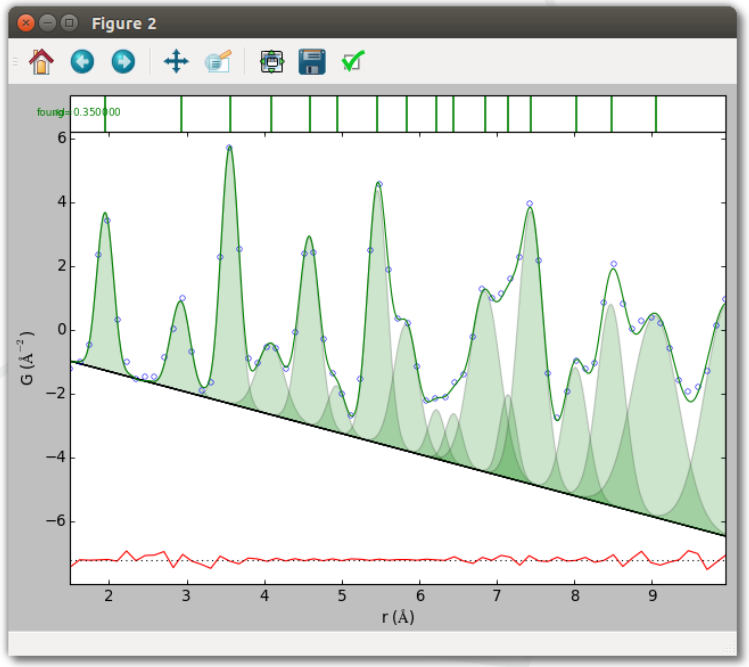


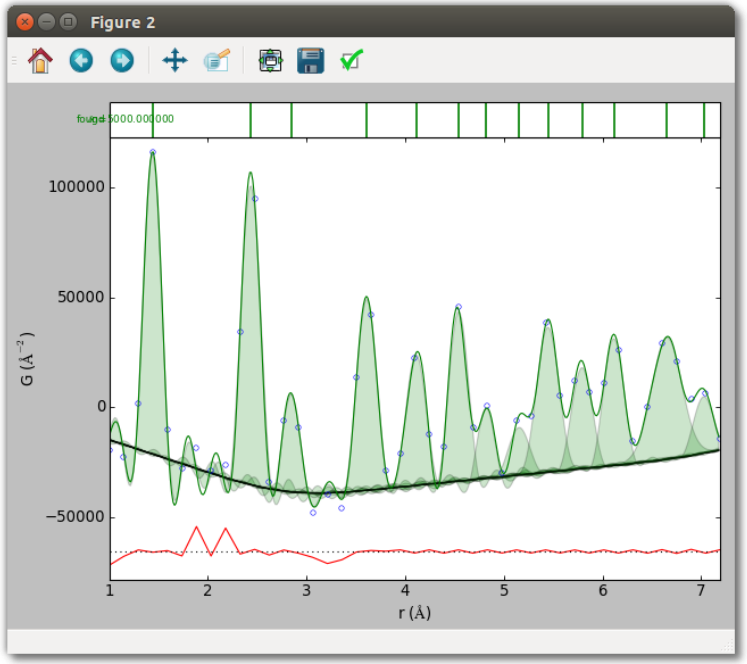
http://fityk.nieto.pl/

diamond

Model-independent info | Peak-picking

- SrMise is a package for ‘unbiased’ peak extraction from PDF data
- Automatically estimates whether the addition of a peak is justified
- Termination effects are accounted for

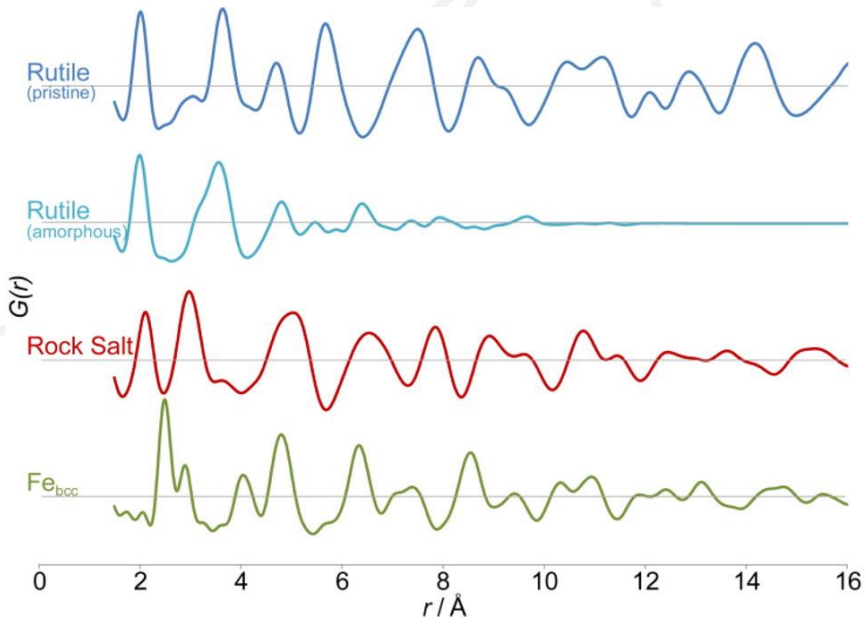


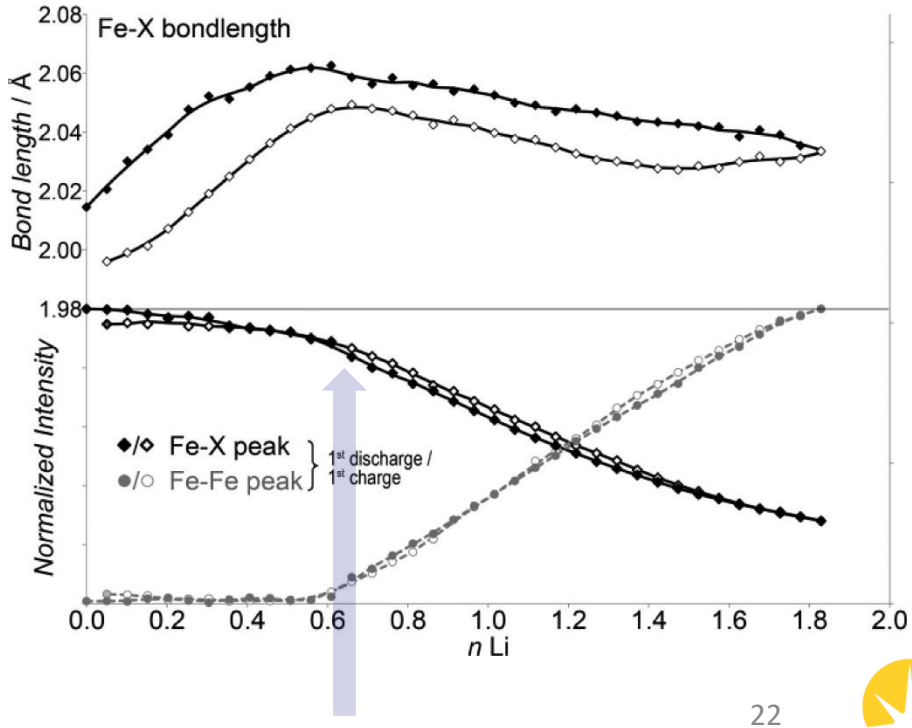


https://www.diffpy.org/diffpy.srmise/

Model-independent info | Peak-picking

- Peak position ↔ atomic positions
- Compare to expected bond-lengths from crystal structures
- e.g. FeOF as a lithium-ion battery anode
- $FeOF + 3Li^+ + 3e^- \rightarrow LiF + Li_2O + Fe$





Fe-metal formation

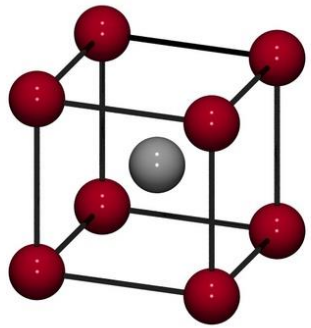
Wiaderek, K. M., et al, *JACS*, 135, 4070 (2013)

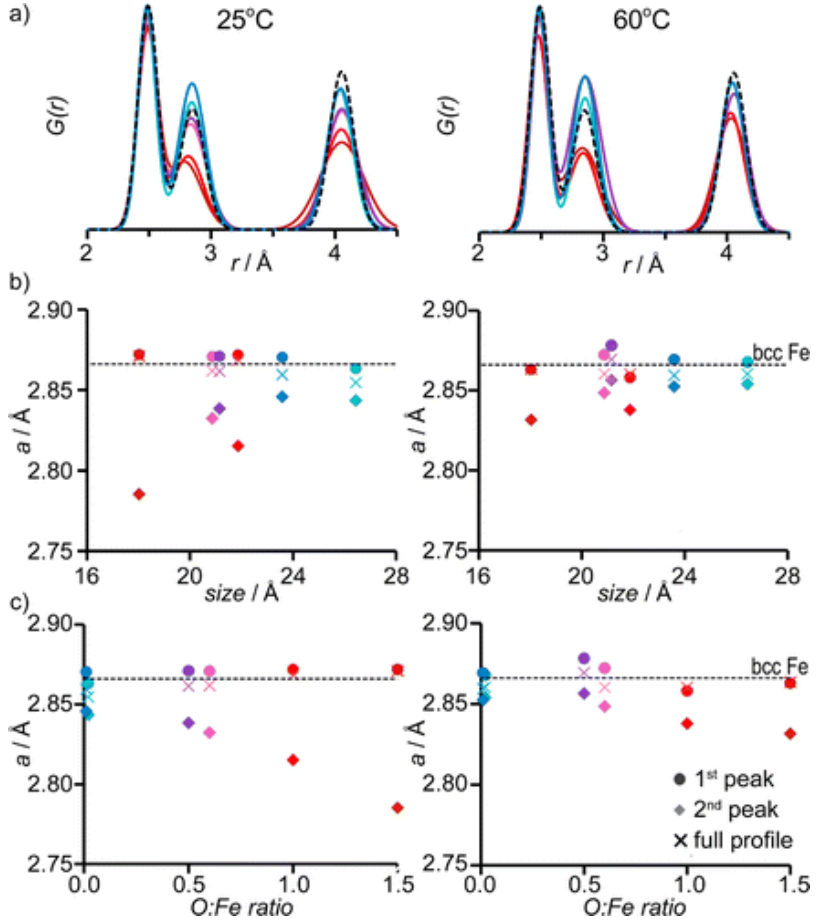
diamond

Model-independent info | Peak area

- Peak area gives information about coordination number

- Lithiated FeF_x forming bcc Fe
- Reduced intensity of the second peak (along the unit cell edge) used to quantify **defect concentration**
- Note that these effects must be decoupled from instrumental dampening and spherical particle dampening of G(r)



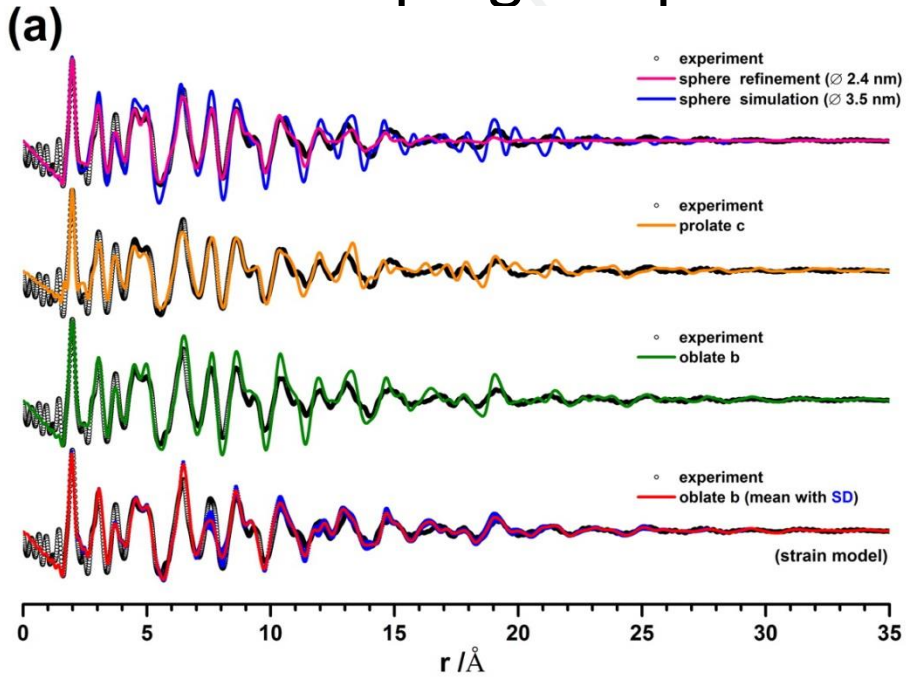


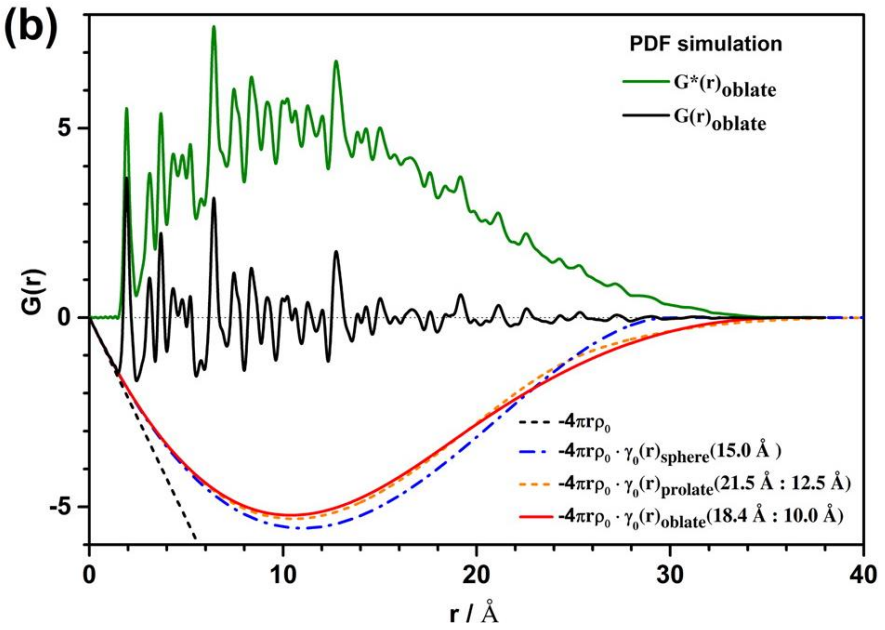
Wiaderek, K. M., *JACS*, 136, 6211 (2014)

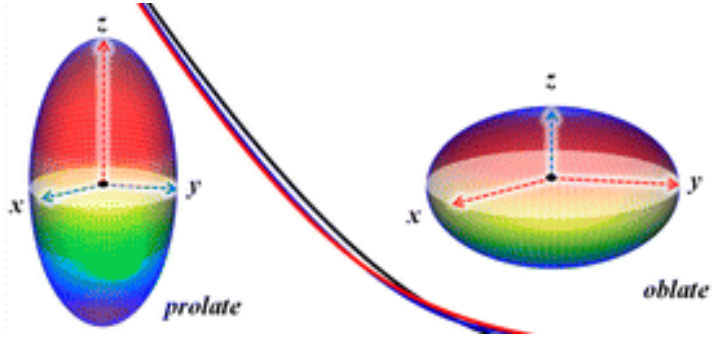
diamond

Model-independent info | Peak damping

- Peak-damping ↔ particle shape information





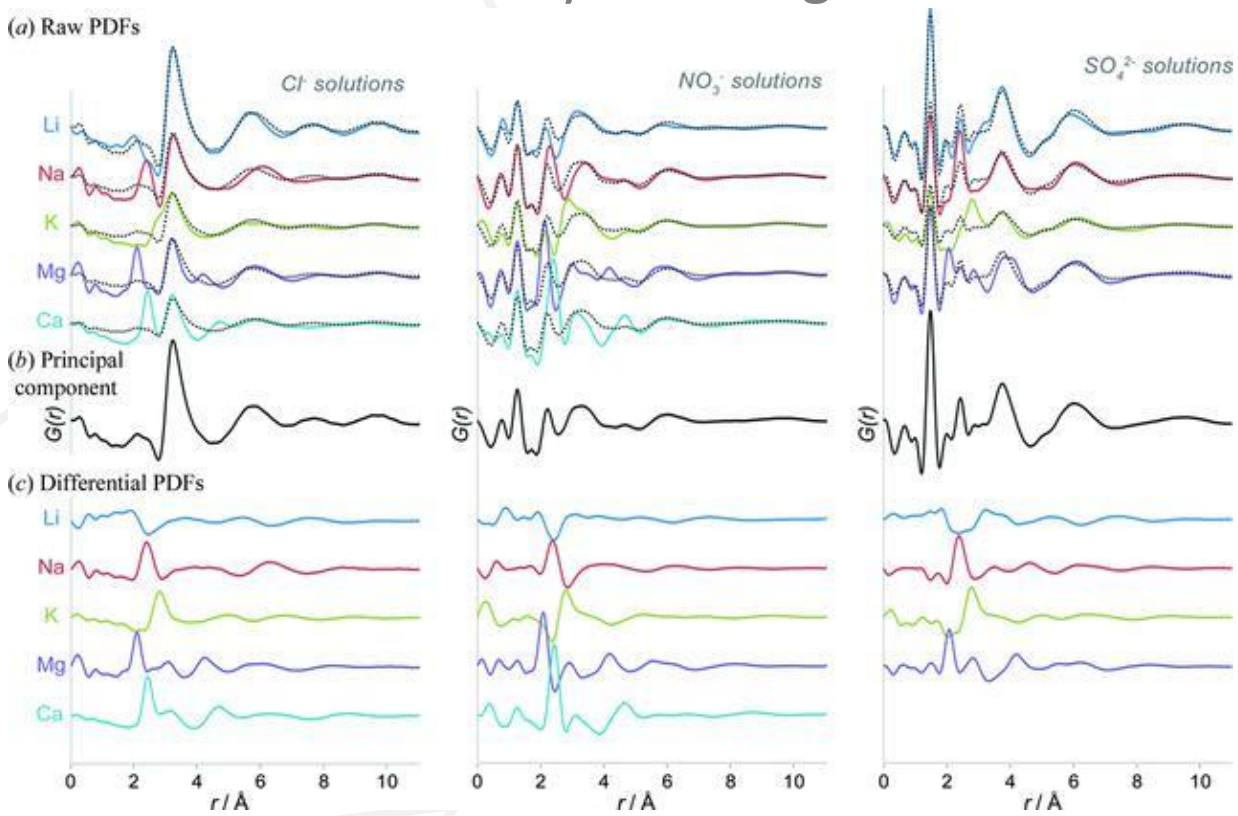


Hua, X. et al., *JACS*, **137**, 13612 (2015)

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Model-independent info | PCA/NMF

- Principal component analysis / NMF separates common atom-atom correlations from a series of solutions
- Not suitable for some systems e.g. solid-solutions



Collect data on a series of samples

↓

Find principal component

↓

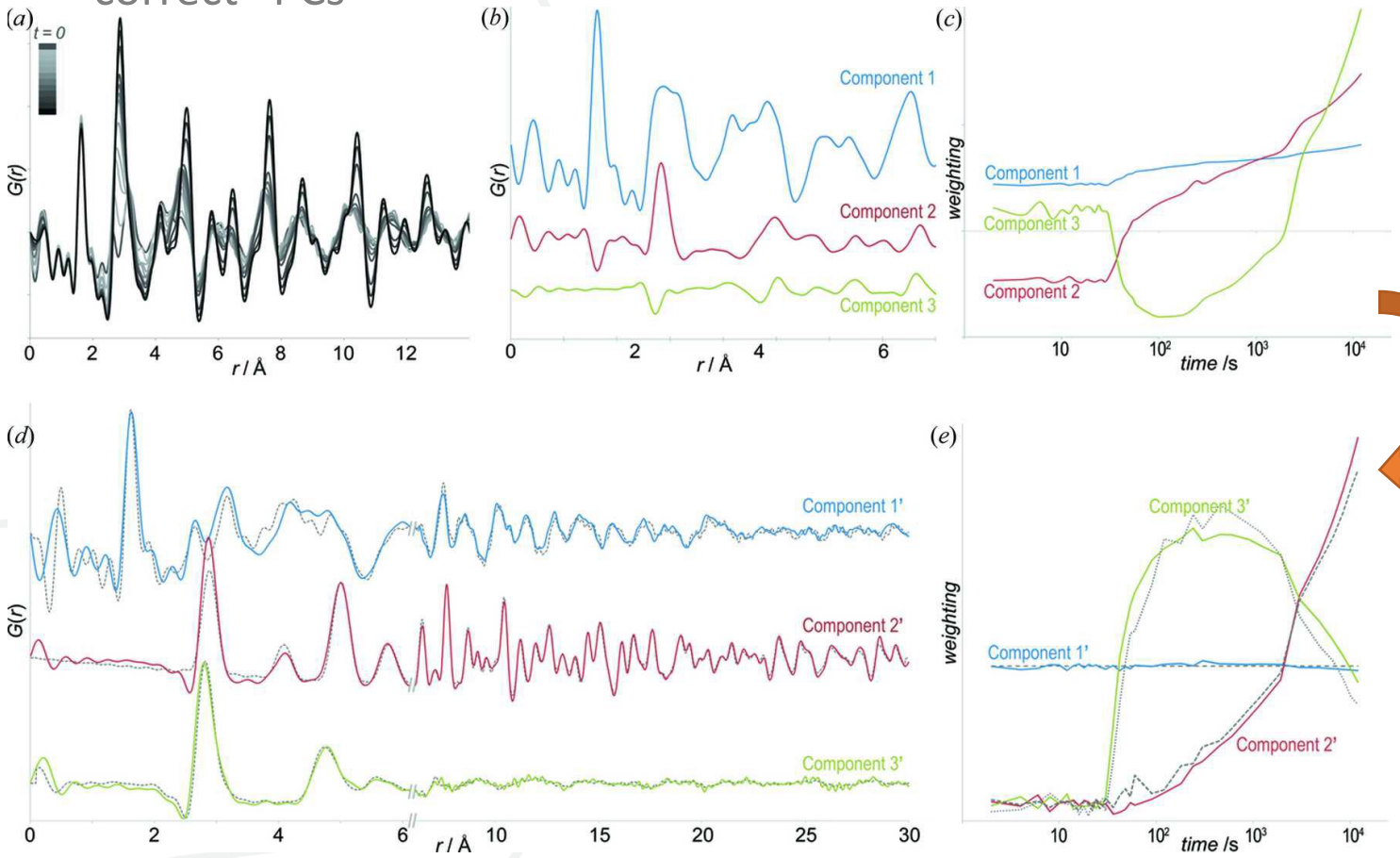
Use differential approach to obtain counter ion information

Chapman, K. W. et al, *J Appl. Cryst.*, **48**, 1619 (2015)

diamond

Model-independent info | PCA/NMF

- Note that the raw PC can be linear combinations of actual PCs
- Use physical constraints (e.g. peaks +ve above baseline for X-ray) to obtain the "correct" PCs



- Sum 1 + 3
- invert component 3

Chapman, K. W. et al, *J Appl. Cryst.*, **48**, 1619 (2015)

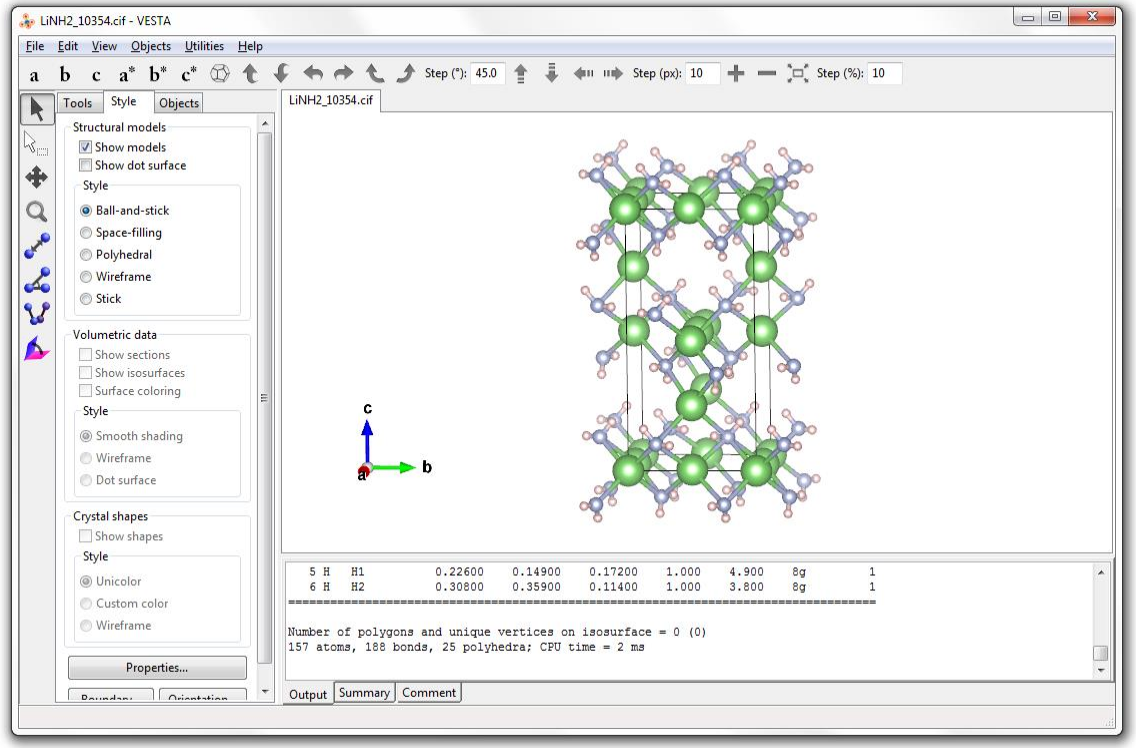
diamond

Creating and querying models with VESTA

diamond

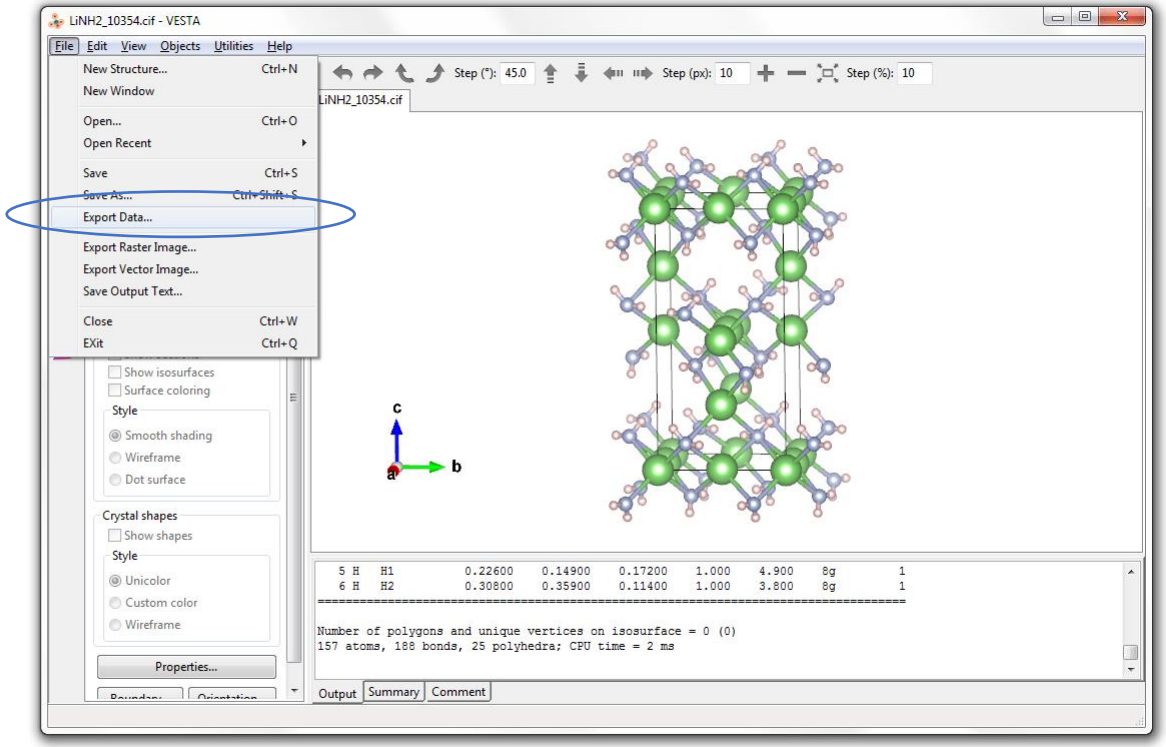
VESTA | Structure viewer

- Visualisation for Electronic and STructural Analysis
- http://jp-minerals.org/vesta/en/
- Flexible and free 3D structure viewer



VESTA | Robust structure (.cif) reader

- Read a structure (.cif) into VESTA and check it looks sensible
- Export the structure from VESTA to a new .cif, and most programs will read it correctly (e.g. TOPAS, PDFgui)



diamond

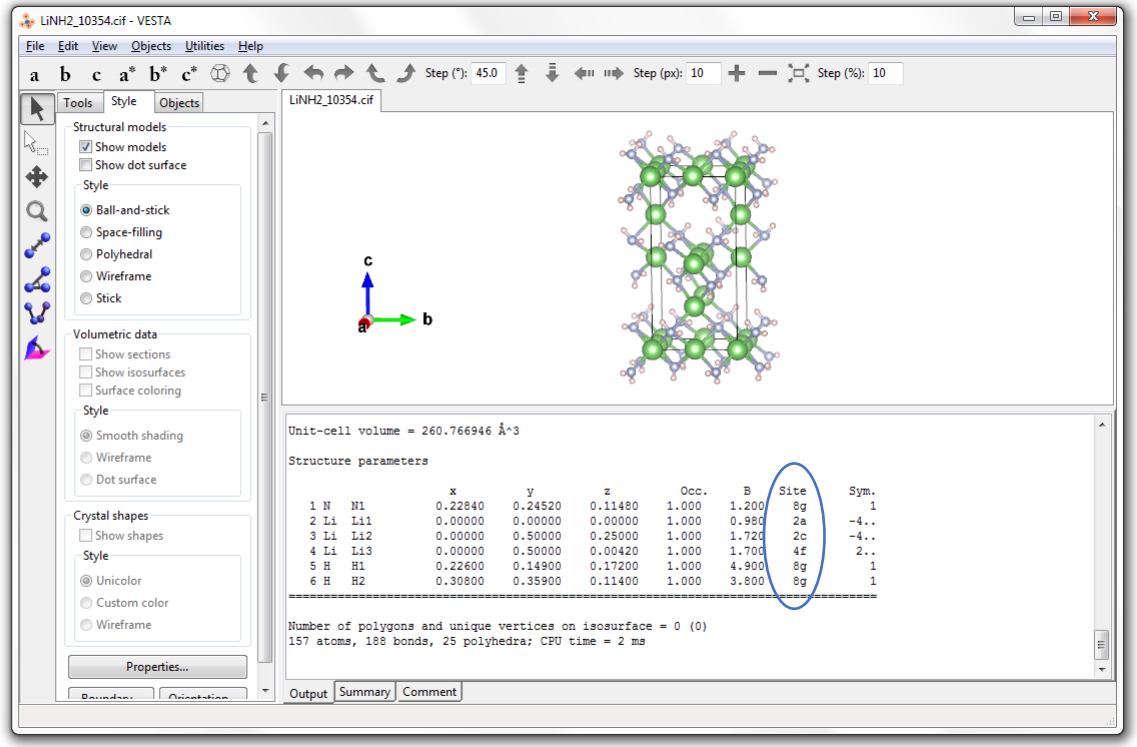
…an aside on .cif files

- Crystallographic Information Framework file format
- Most common format for inorganic and small molecule structures
- Available from various free and paid-for sources



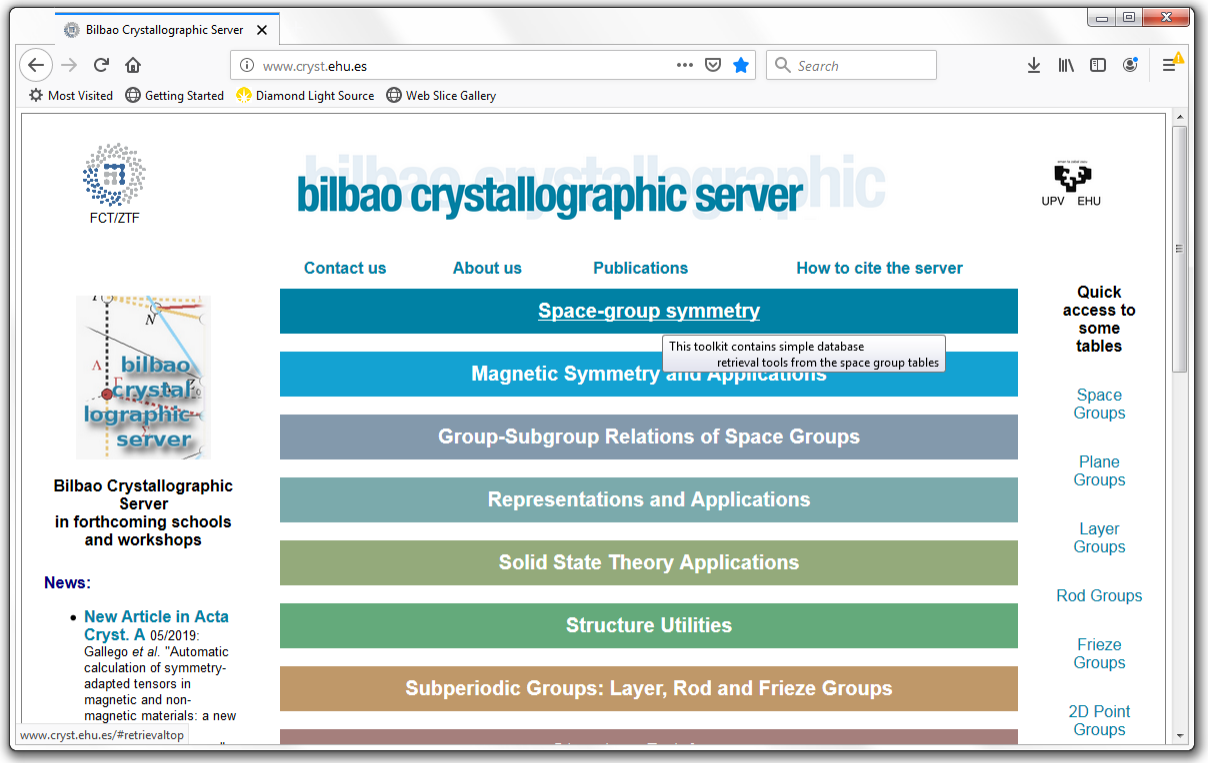
VESTA | Crystal symmetry helper

- When reading in the structure, it will tell you the Wyckoff position of each site



VESTA | Crystal symmetry helper

- Go to the Bilbao Crystallographic Server

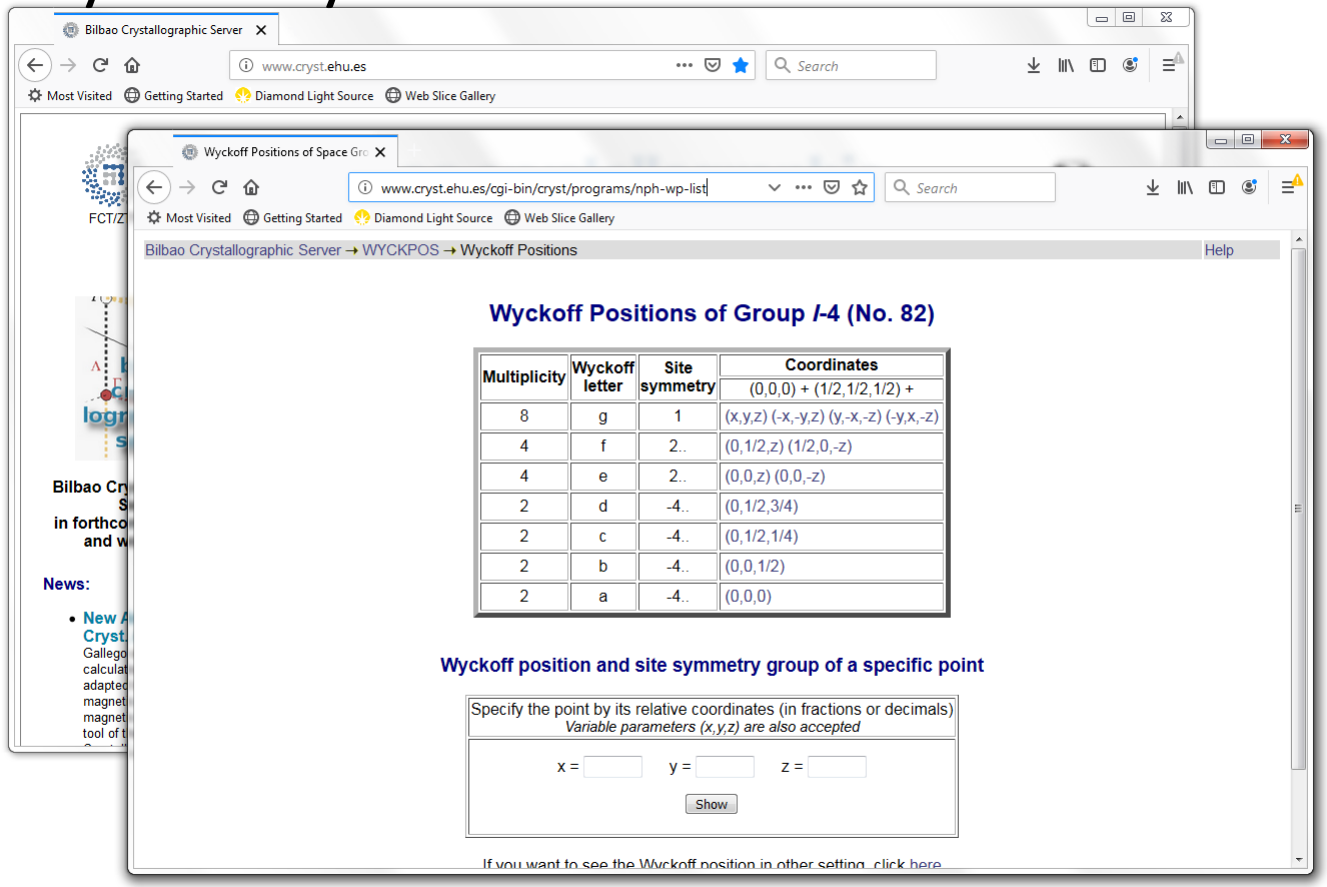


http://www.cryst.ehu.es/

diamond

VESTA | Crystal symmetry helper

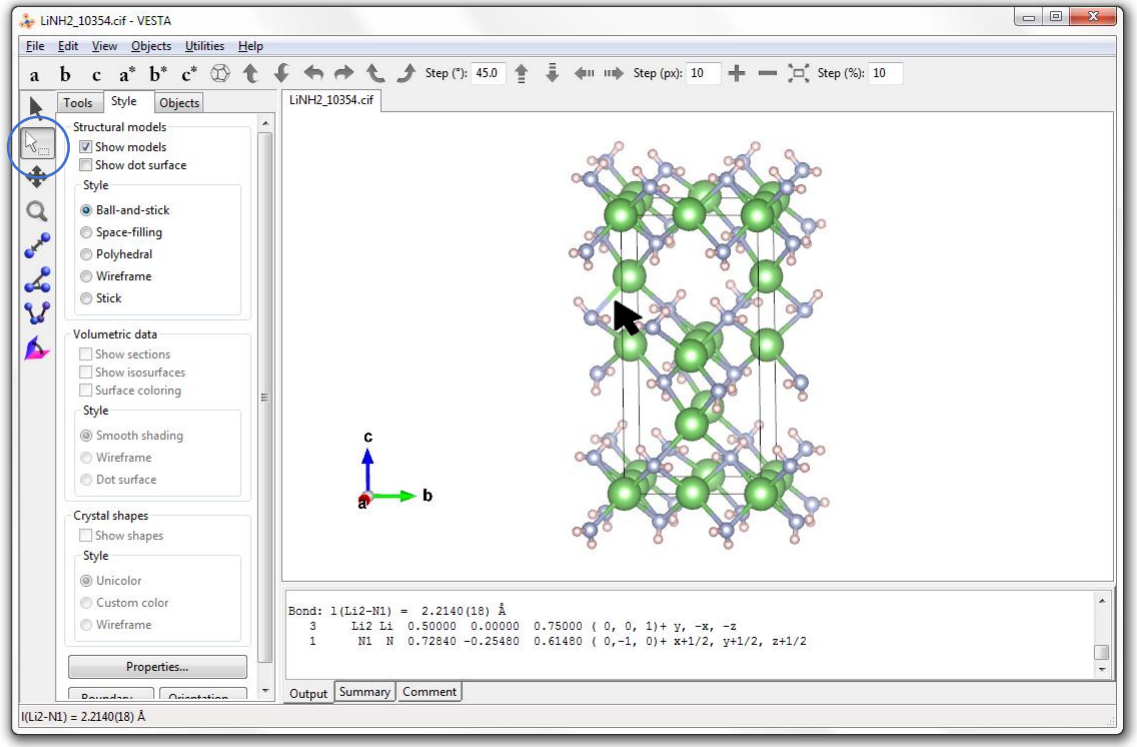
- Go to the Bilbao Crystallographic Server
- Look up to symmetry rules for each site



http://www.cryst.ehu.es/

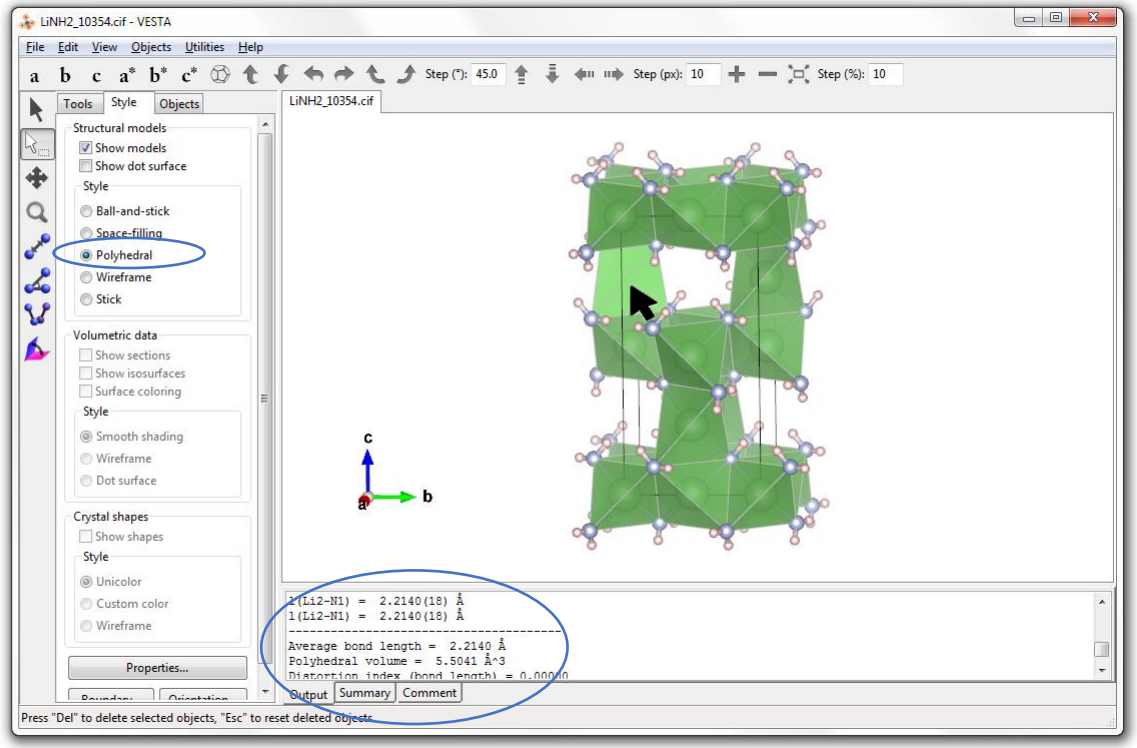
VESTA | Bond lengths

- Select a bond to see its length (with errors)



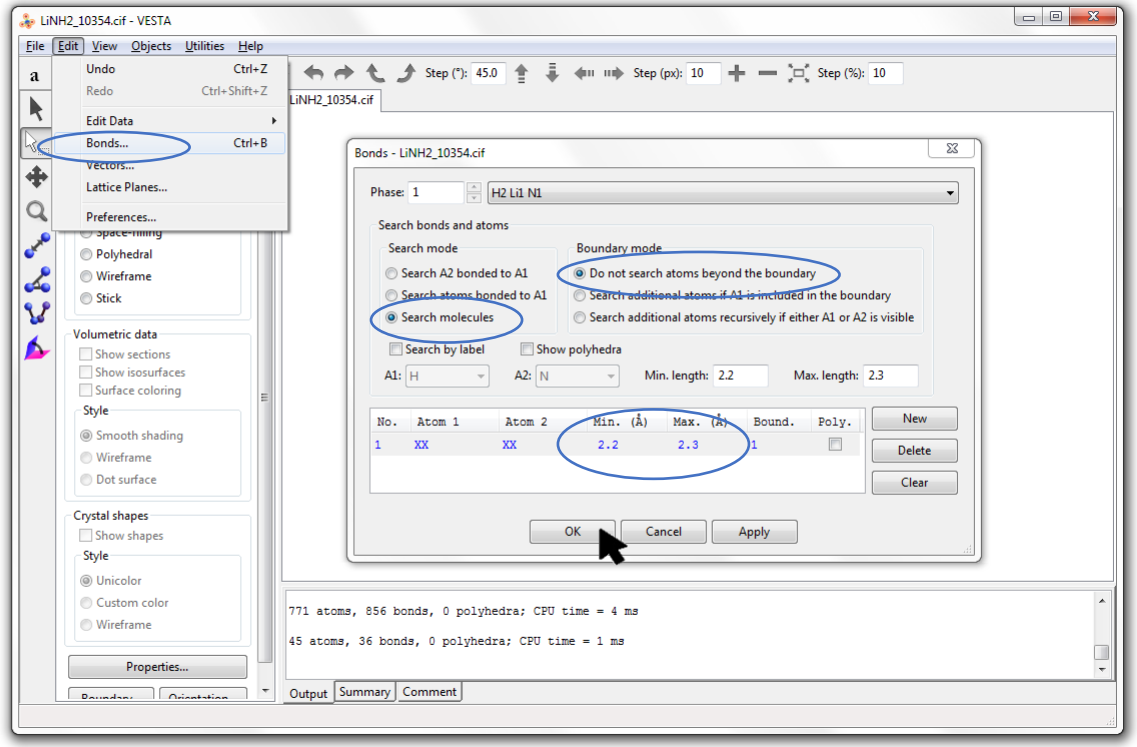
VESTA | Bond lengths

- Select a bond to see its length (with errors)
- If polyhedra are selected, it will tell you all of the bond lengths and details



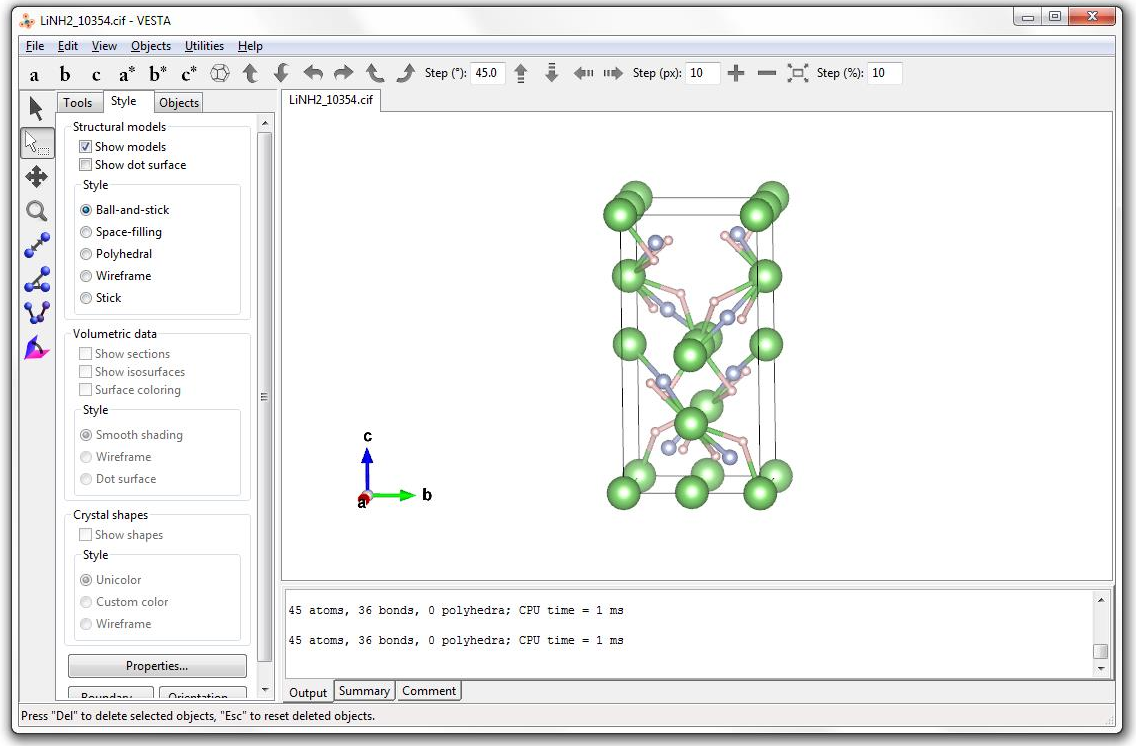
VESTA | Bond lengths

- If you want to know what bonds are present for a given r range, you can edit the displayed bonds
- e.g. all bonds between 2.2 and 2.3 Å



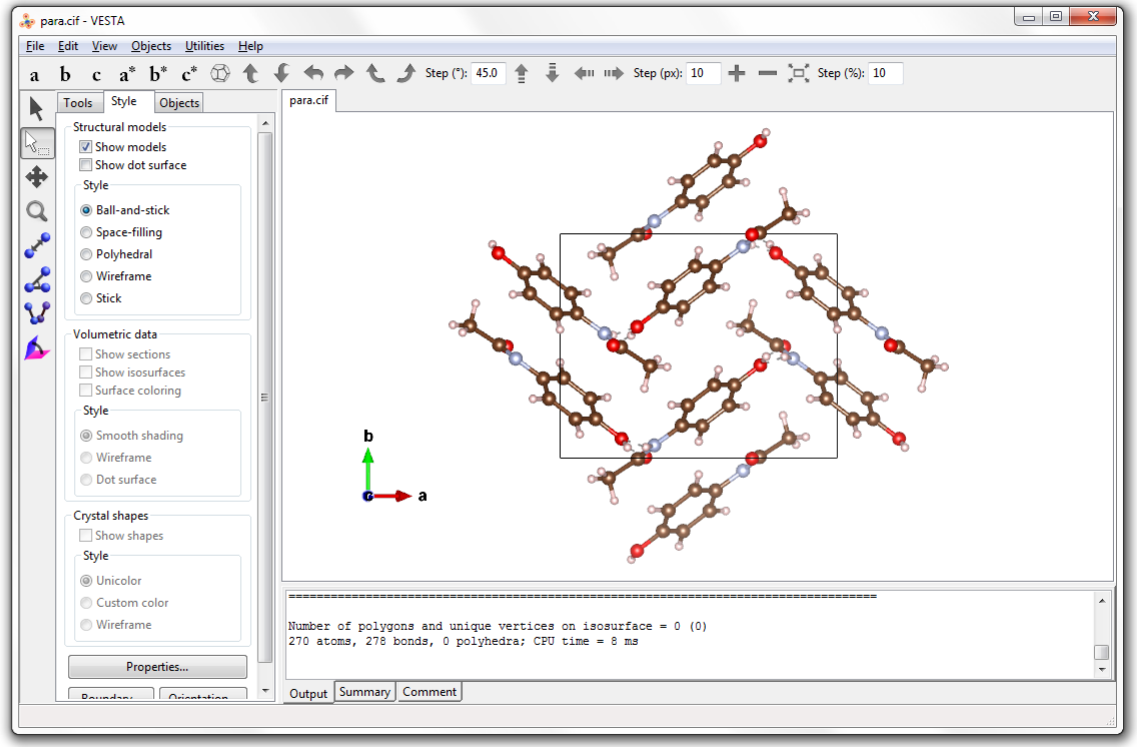
VESTA | Bond lengths

- If you want to know what bonds are present for a given r range, you can edit the displayed bonds
- e.g. all bonds between 2.2 and 2.3 Å



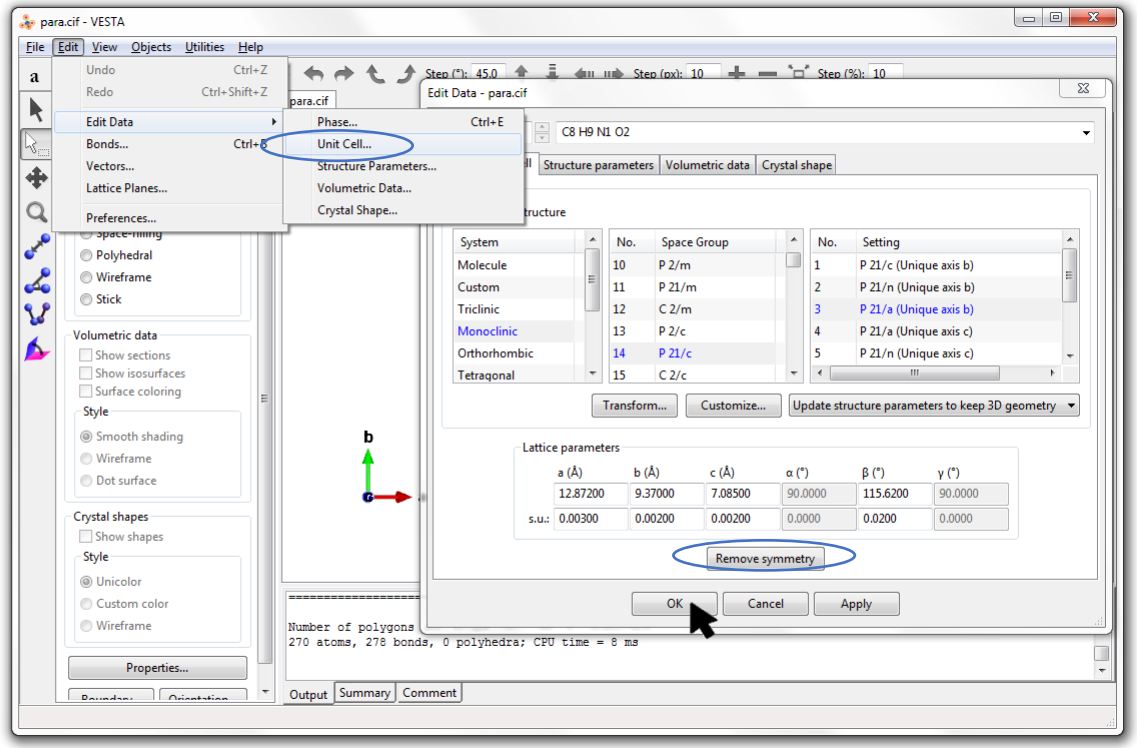
VESTA | Creating models

- For PDF data you may want to model part of a structure e.g. one molecule in isolation



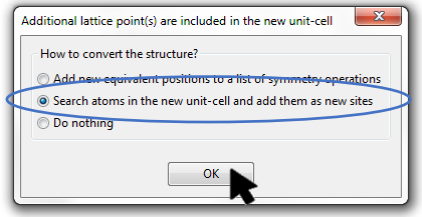
VESTA | Creating models

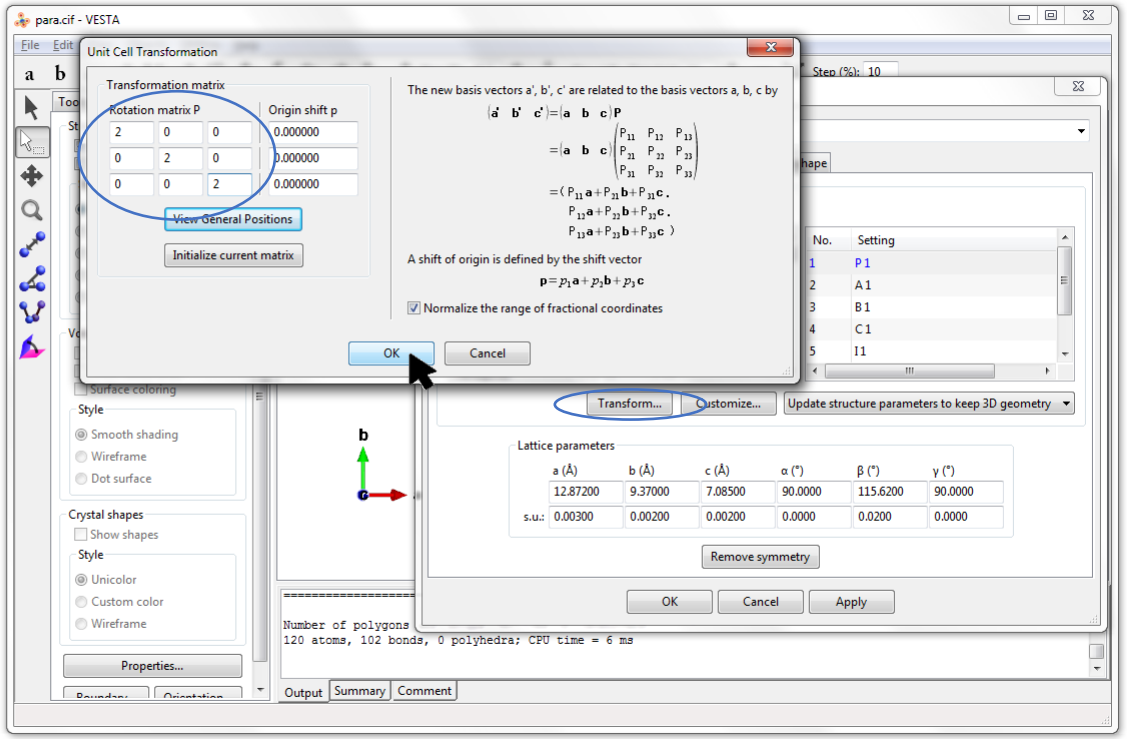
- 1. Remove symmetry



VESTA | Creating models

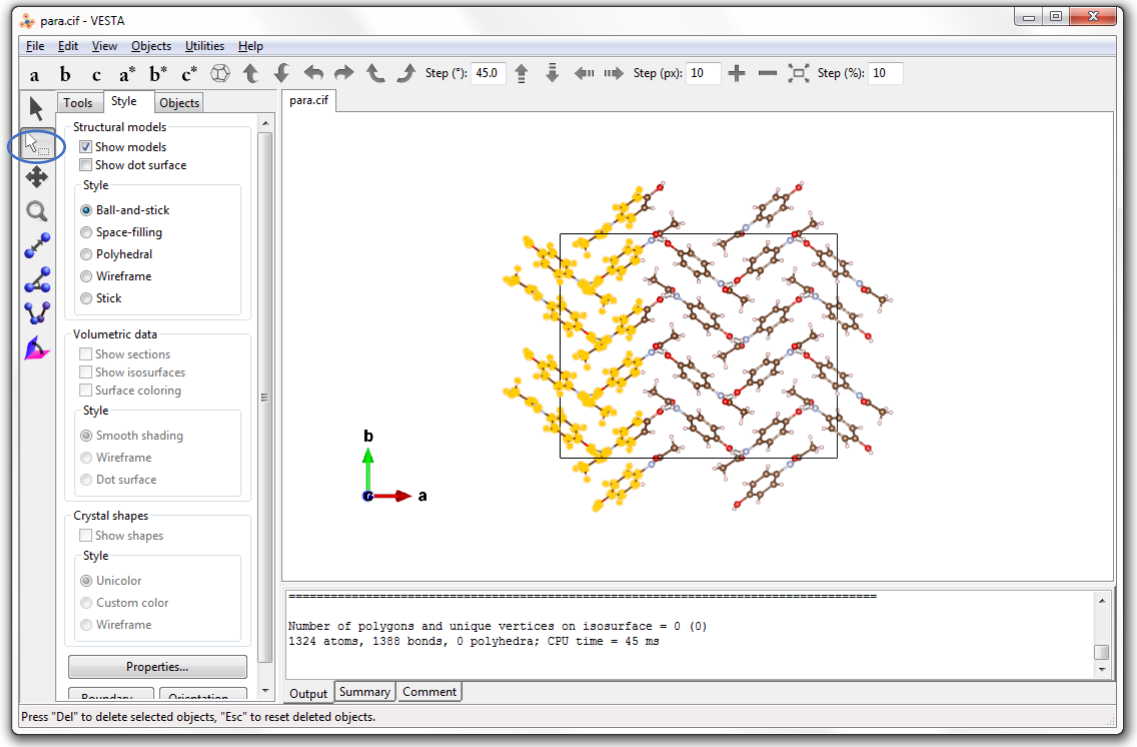
- 1. Remove symmetry
- 2. Create a supercell, e.g. 2×2×2





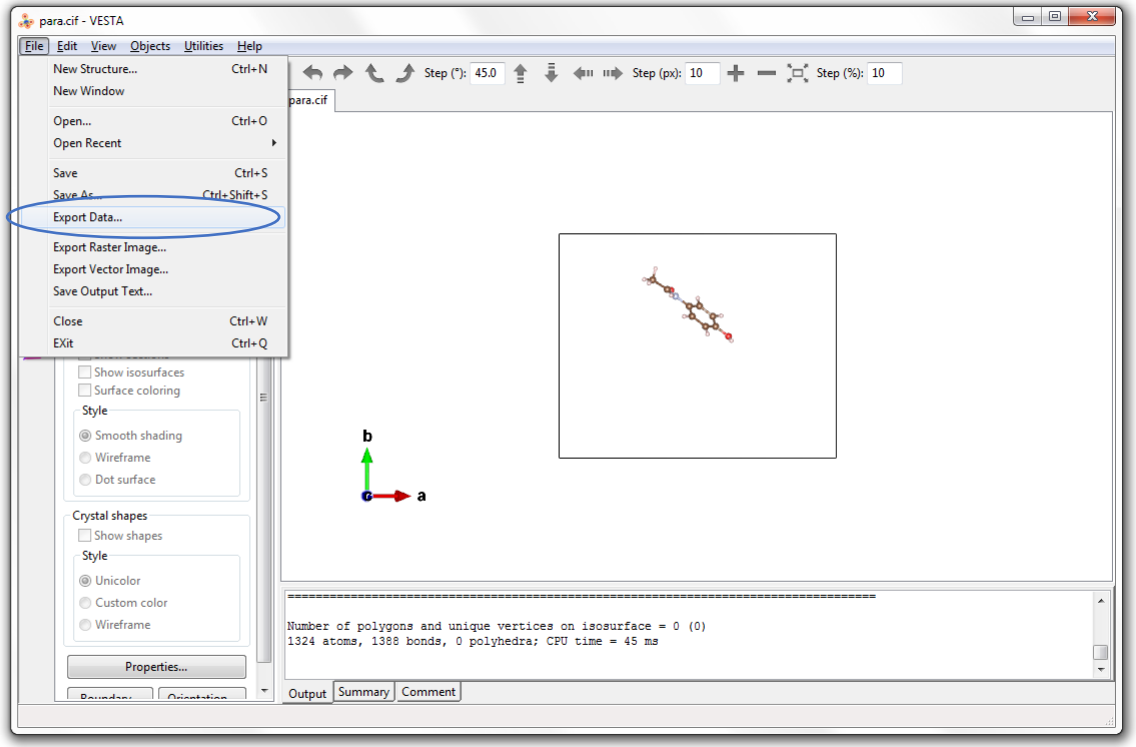
VESTA | Creating models

- 1. Remove symmetry
- 2. Create a supercell, e.g. 2×2×2
- 3. Select and delete atoms that you don’t want



VESTA | Creating models

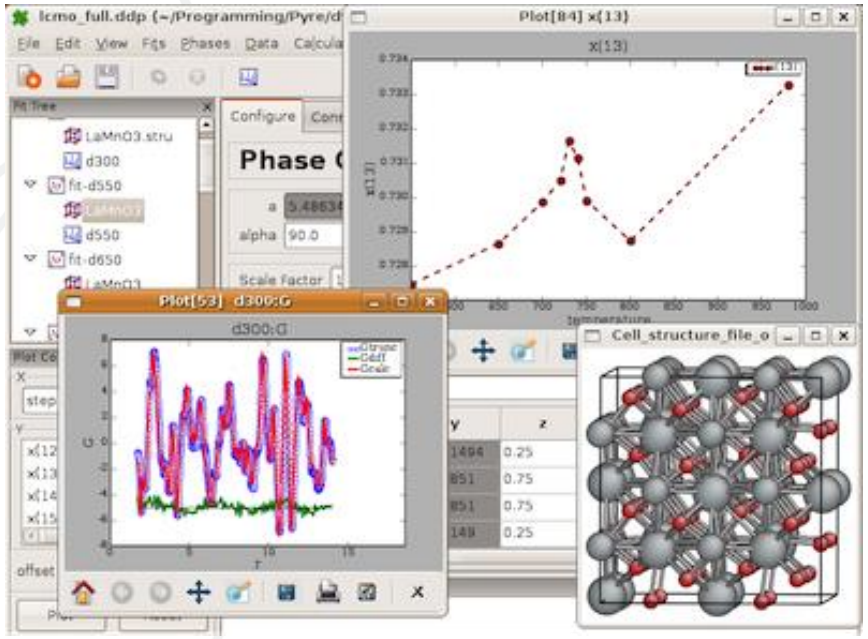
- 4. Export to .xtl format to just export the visible atoms
- 5. Open the .xtl format file in VESTA
- 6. Export to .cif format to use in other software



Real-space refinement methods using PDFgui

PDFgui

- A graphical interface for the full-profile fitting of the atomic pair distribution function
- Available at http://www.diffpy.org/products/pdfgui.html



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PDFgui

- PDFgui can calculate and refine model systems (< 1000) atoms.
  - full-profile least squares approach
  - minimises the difference between the observed PDF and the PDF calculated from a model by refining set parameters

$$\Phi = \sum_{i=1}^{n} w_i (G(r)_i^{obs} - G(r)_i^{calc})^2$$

  - A residual factor can be determined using:

$$R_w = \left\{ \frac{\sum w_i (G_i^{exp} - G_i^{calc})^2}{\sum w_i (G_i^{exp})^2} \right\}$$

lower residual = better fit of model to data

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Data set parameters:

Set (or calibrated) parameters:

Refinement range

Q_{max}: data range used for the Fourier transform step → G(r)

Q_{damp}: instrument resolution Gaussian dampening envelope ($Å^{-1}$)

Q_{broad}: Peak broadening due to increased noise at high Q

Refineable parameters: dscale: data set scale parameter

Model parameters:

Refined parameters:

pscale: scale factor *(do not refine this **and** dscale!)*

lattice parameters: a, b, c, α, β, γ

For each atom:

fractional coordinates, x, y, x

occupancy

Atomic displacement parameters

Possible to refine these parameters within the symmetry of the crystal structure if required

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Peak width parameters:

Nearest neighbour peaks are sharpened due to correlated motion:

$$\sigma_{ij} = \sigma_{ij}' \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r^2{}_{ij}} - Q^2{}_{broad} r^2{}_{ij}}$$

Refined parameters

delta1: 1/r contribution to peak sharpening (high temperature)

delta2: $1/r^2$ contribution to the peak sharpening (low temperature)

Sratio: peak width reduction for correlated motion, to a radius of rcut

Size parameters:

Refined parameters

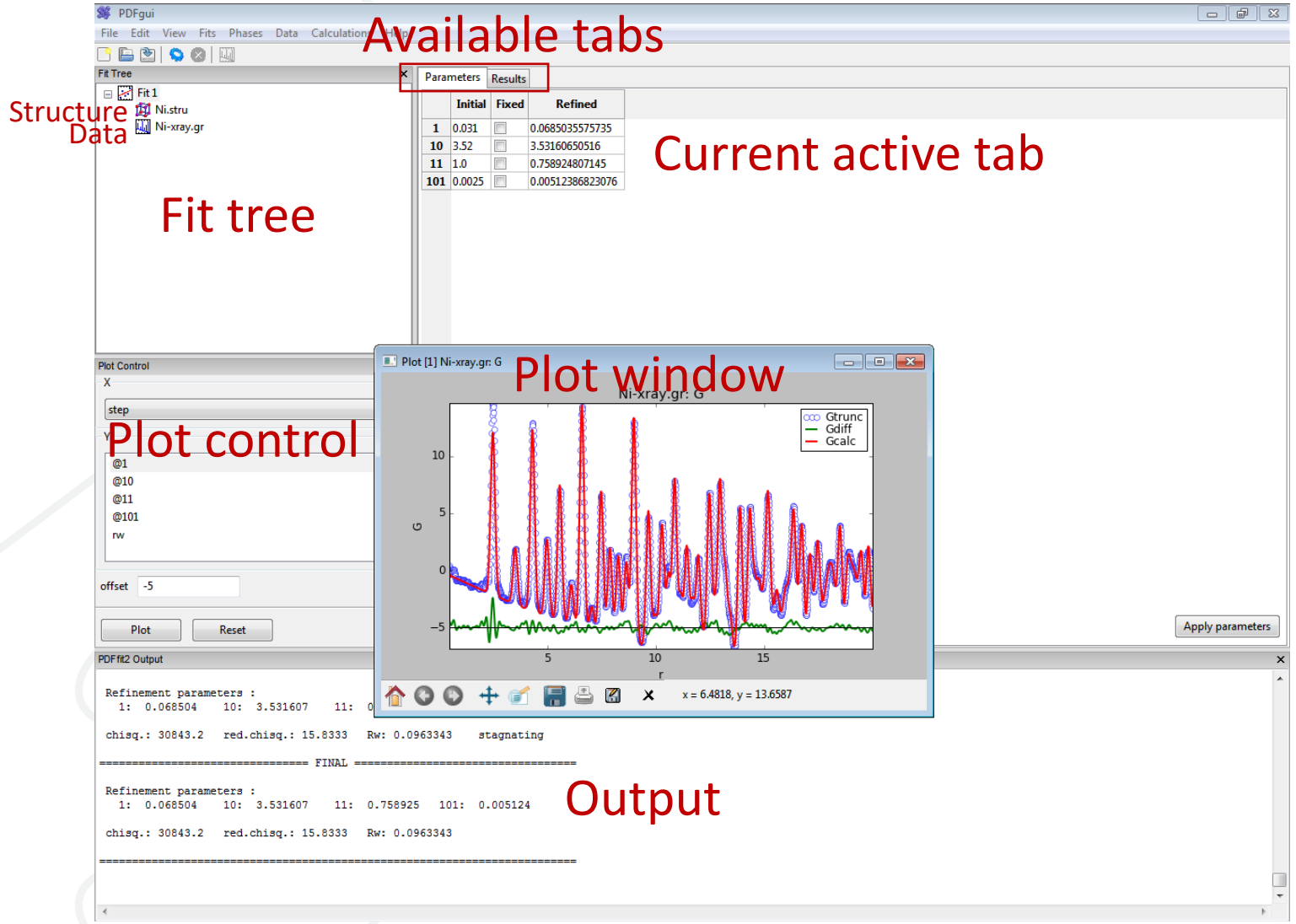
spdiameter: particle diameter for PDF shape damping function

stepcut: r-value above which the PDF is truncated to zero

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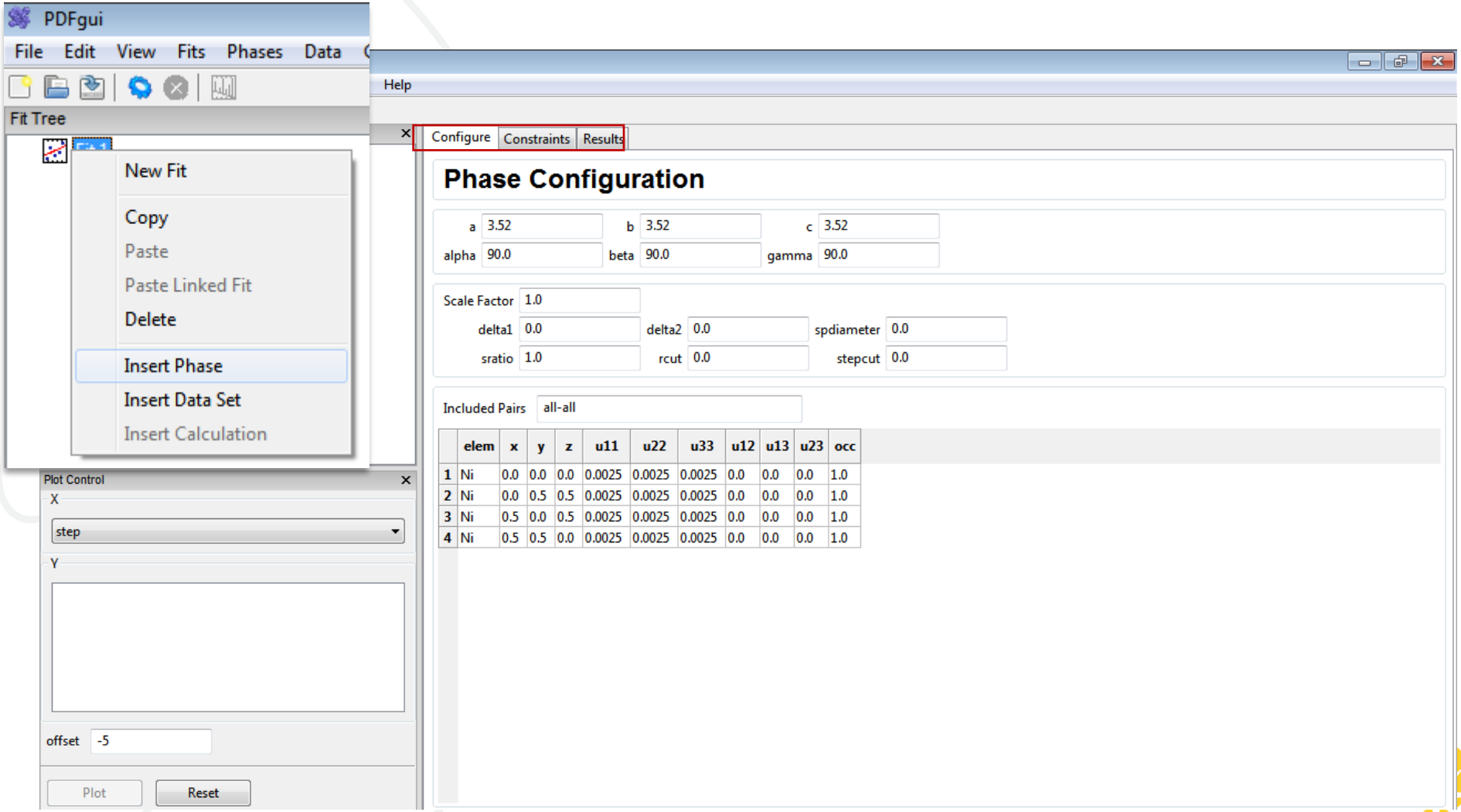
Using PDFgui

- Available at http://www.diffpy.org/products/pdfgui.html



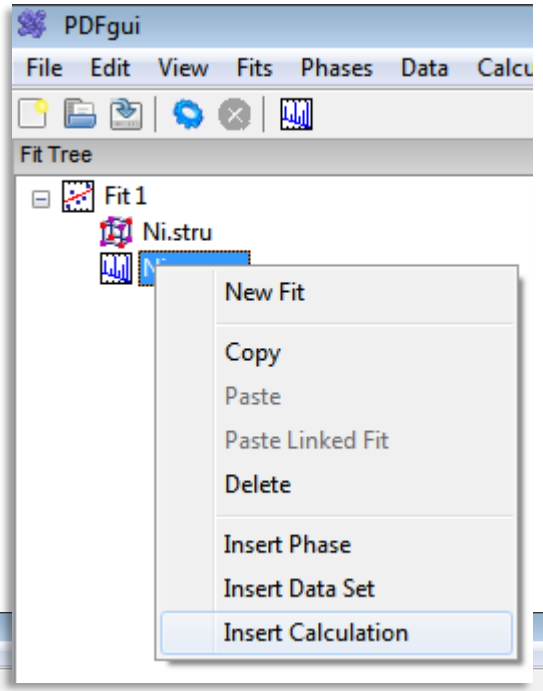
Using PDFgui to calculate a PDF

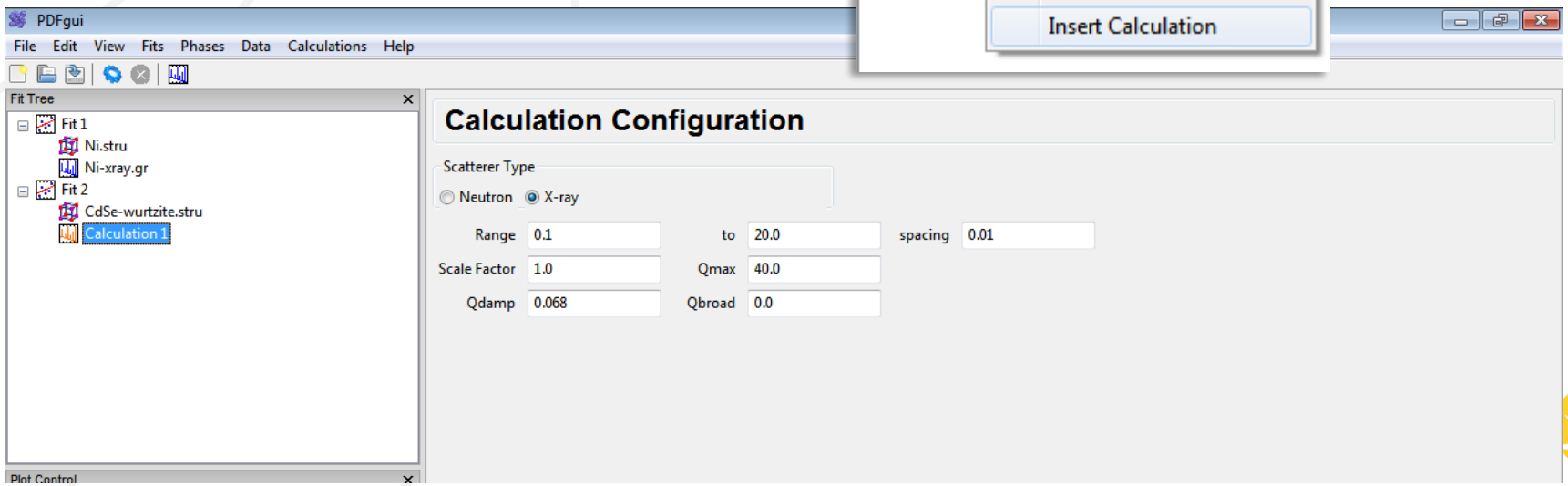
- Structures can be added from a .cif file, or from input by hand



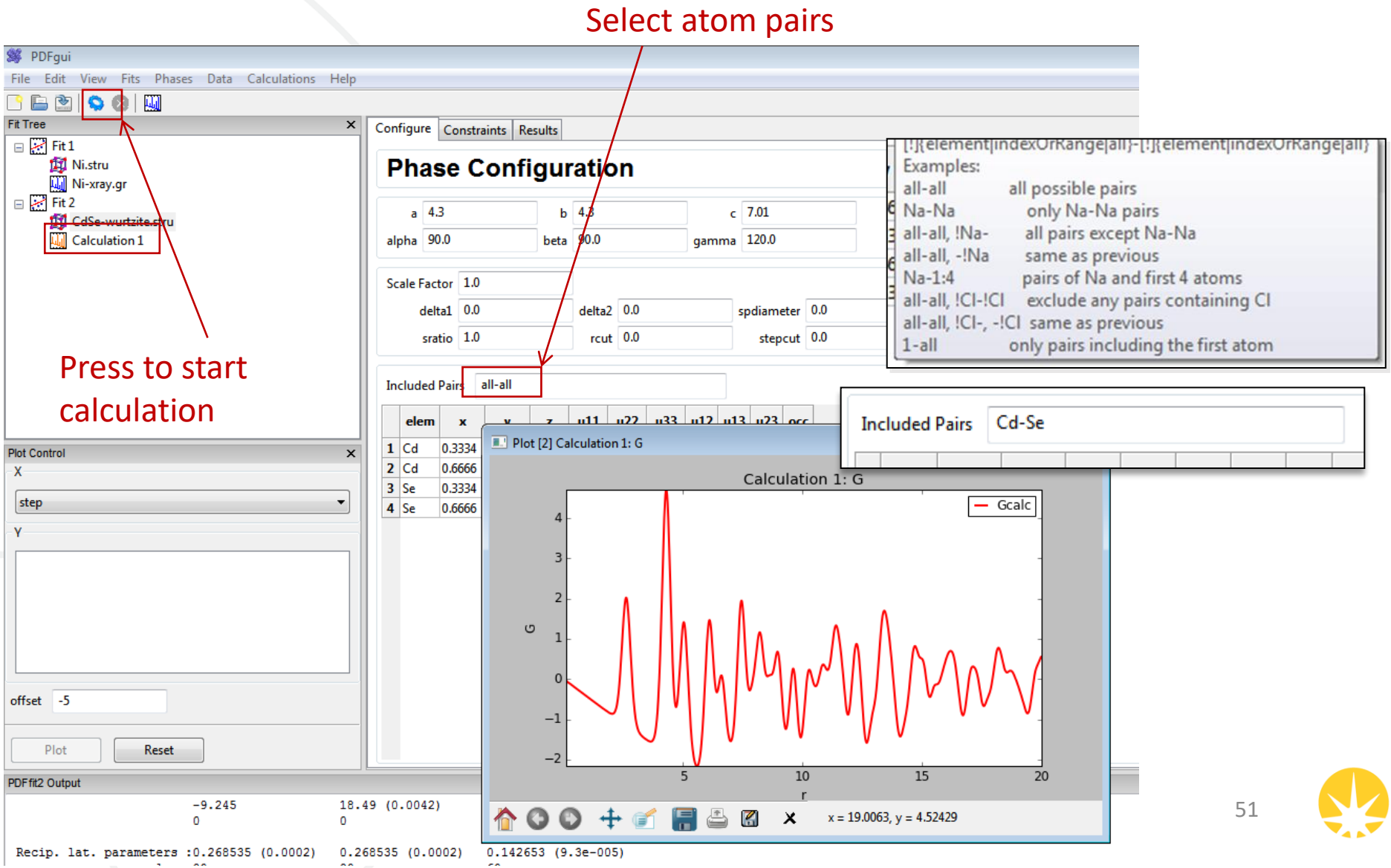
Using PDFgui to calculate a PDF

1. Right click on fit → insert calculation
2. Add calculation configuration parameters





Using PDFgui to calculate a PDF



Using PDFgui to calculate a PDF

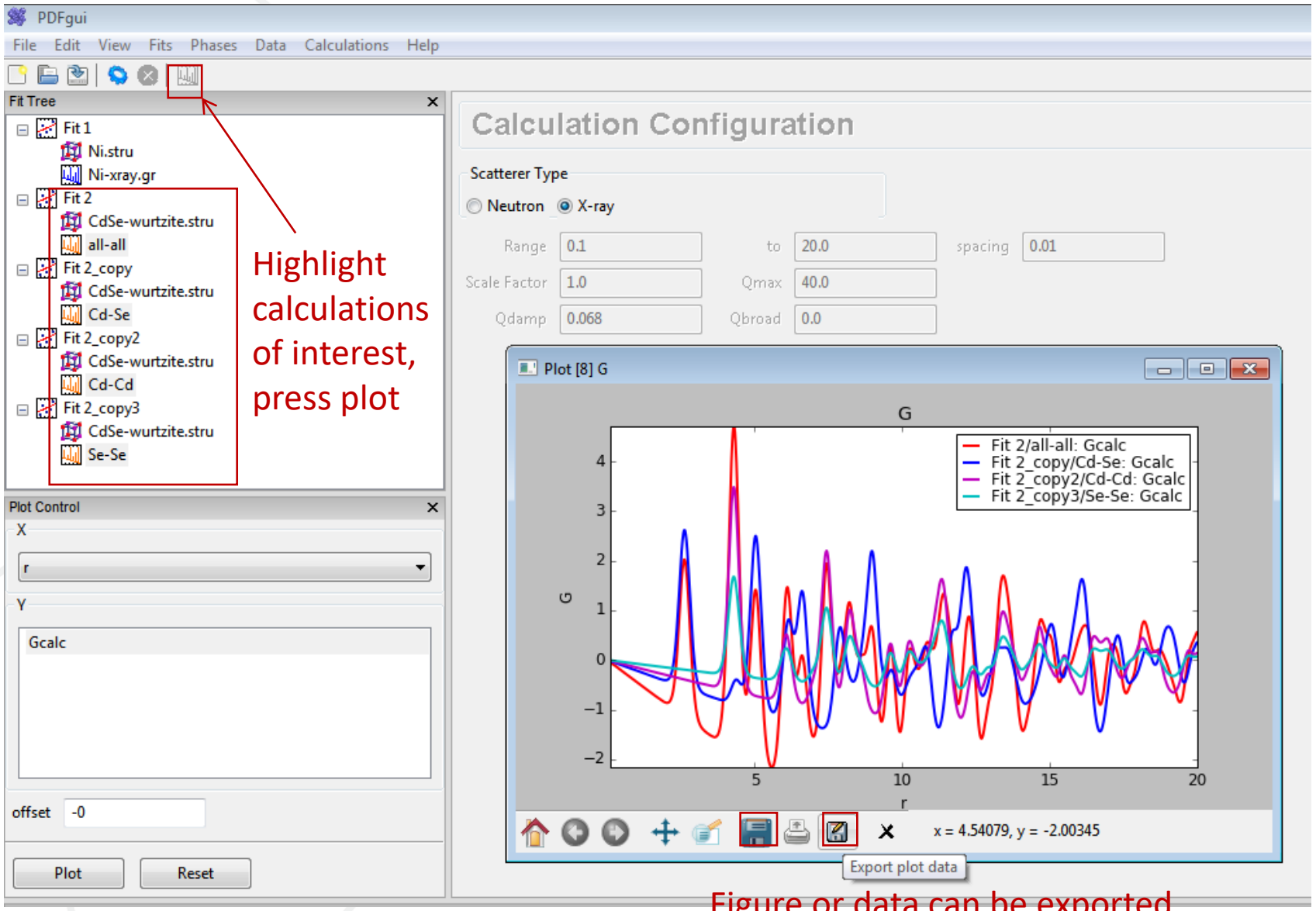
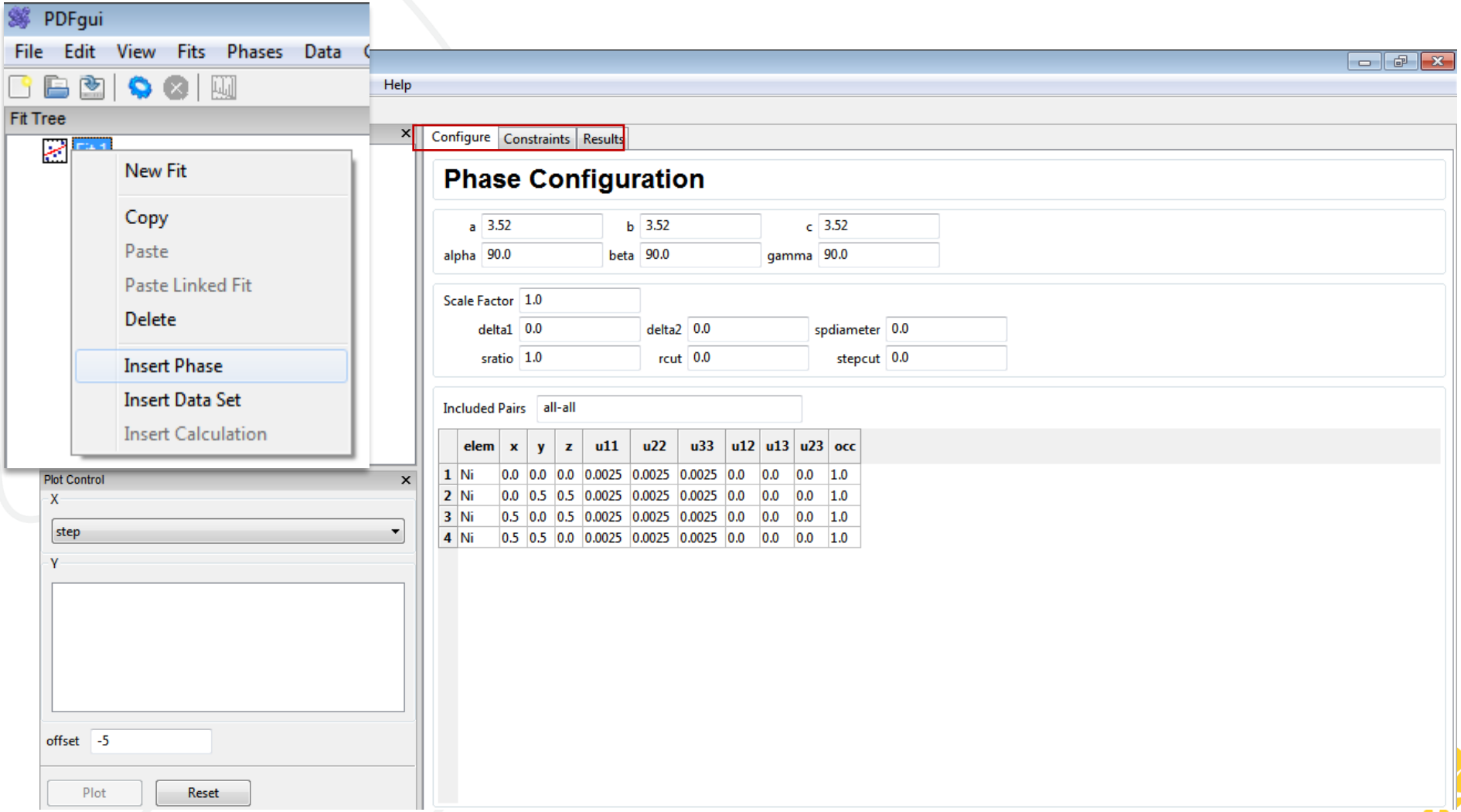


Figure or data can be exported

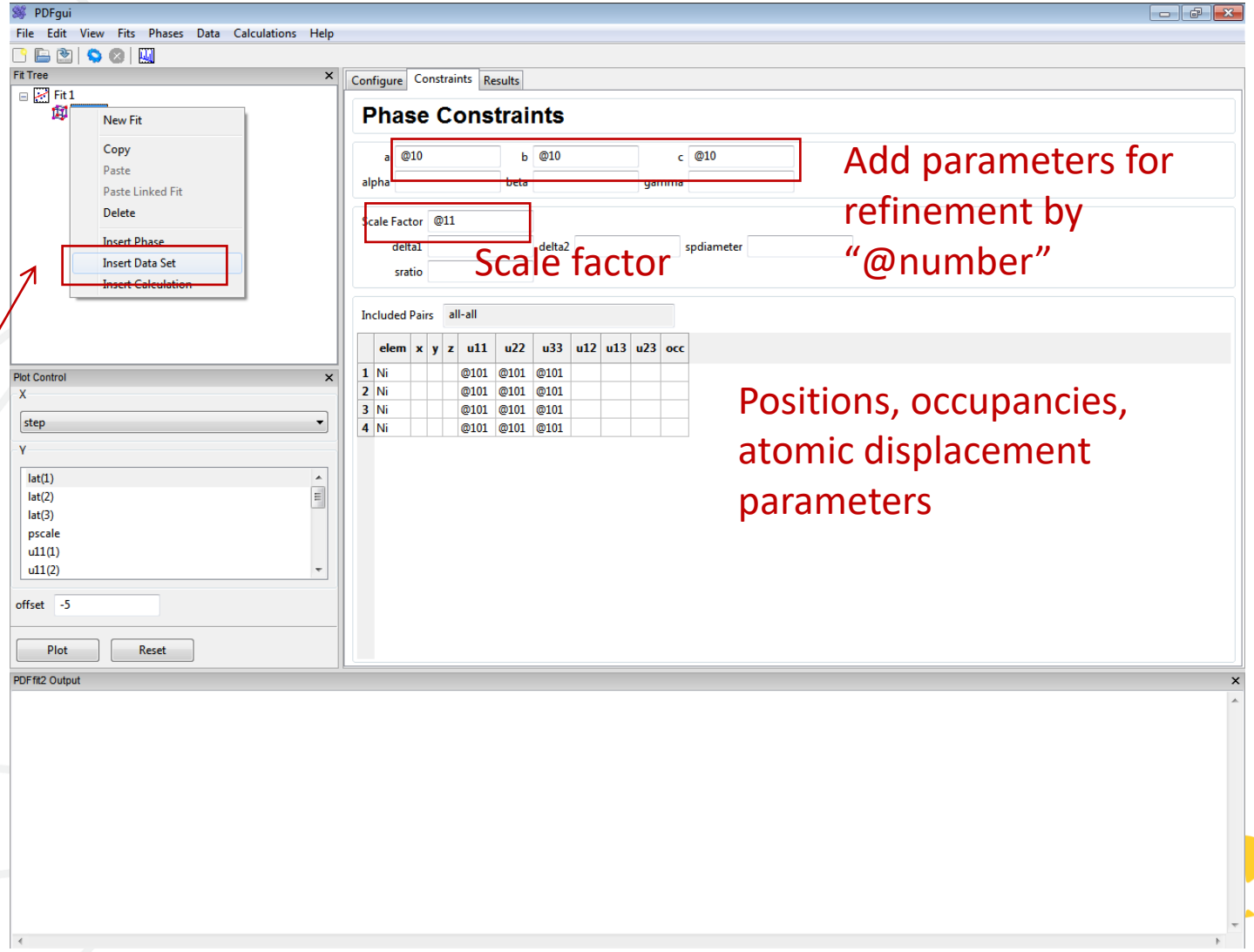
Using PDFgui for a refinement

- Structures can be added from a .cif file, or from input by hand



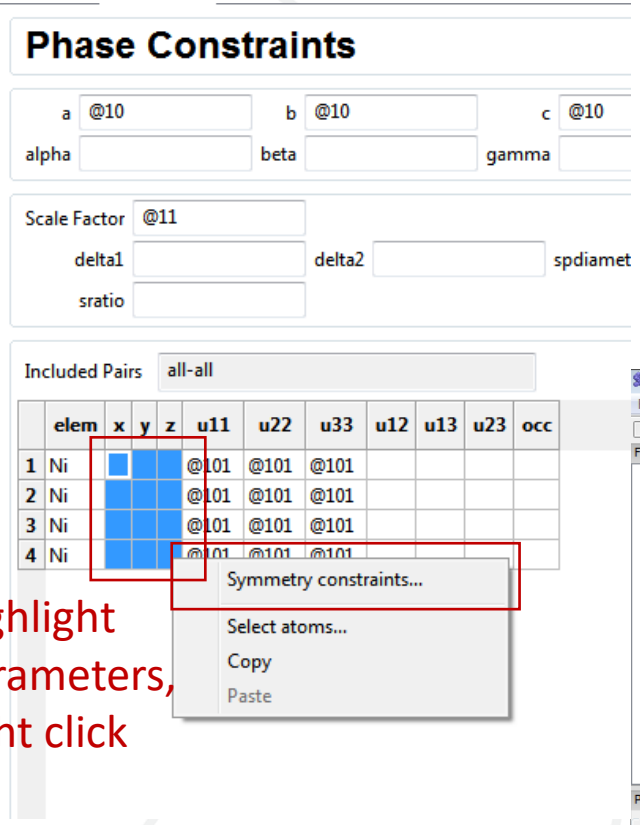
Using PDFgui for a refinement

- Add parameters for refinement using “@number”

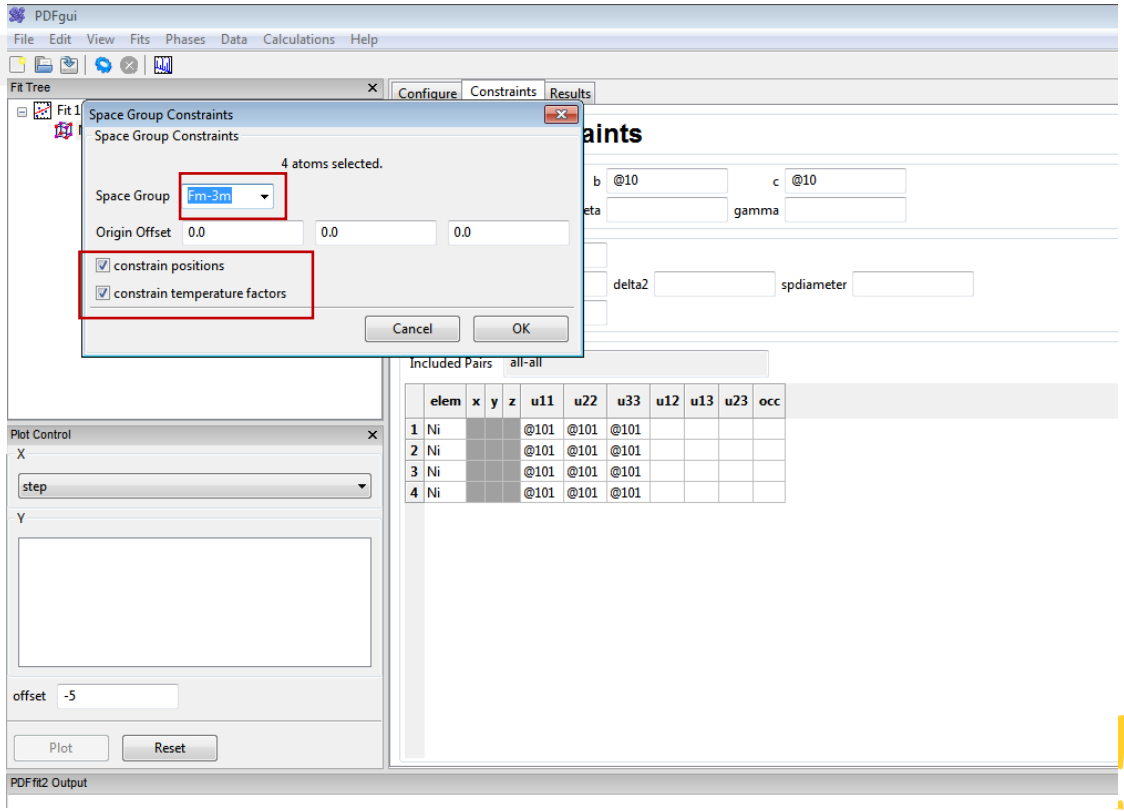


Right click → insert data set (can add multiple, e.g. X-ray and neutron)

Using PDFgui for a refinement



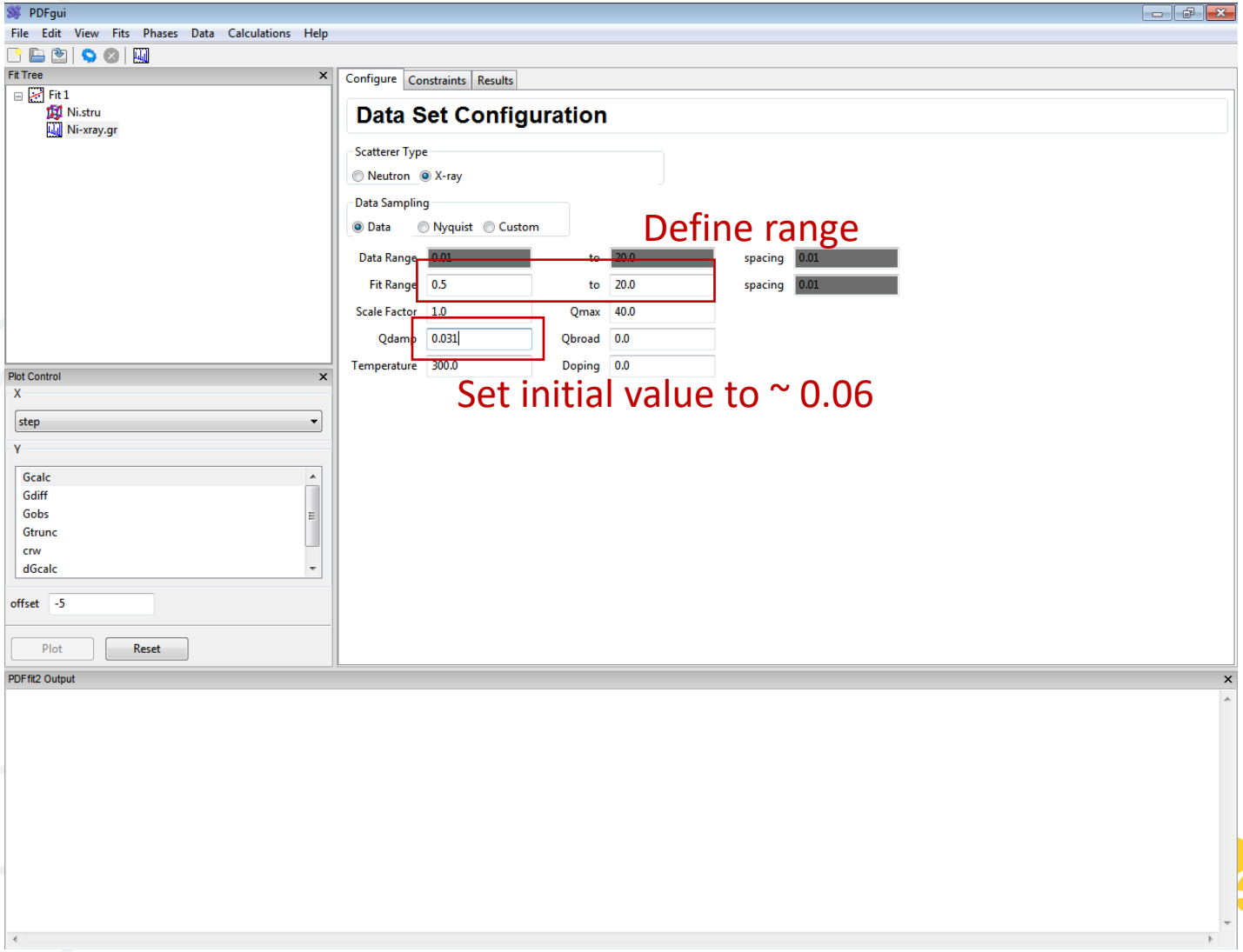
Highlight parameters, right click



Thermal parameters and temperature factors can be constrained by the space group

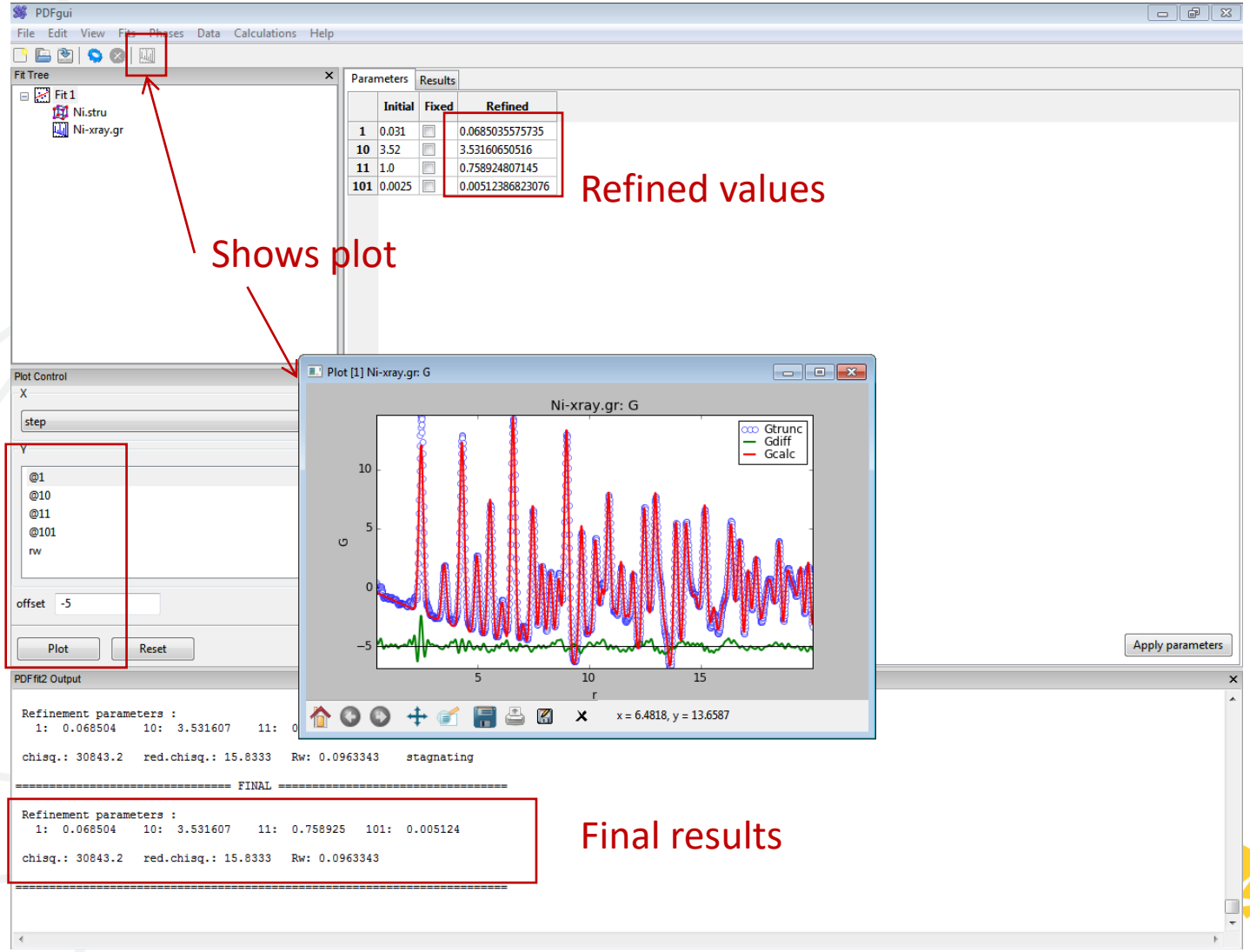
Using PDFgui for a refinement

- Data Set configuration: set range, and Q_{damp}



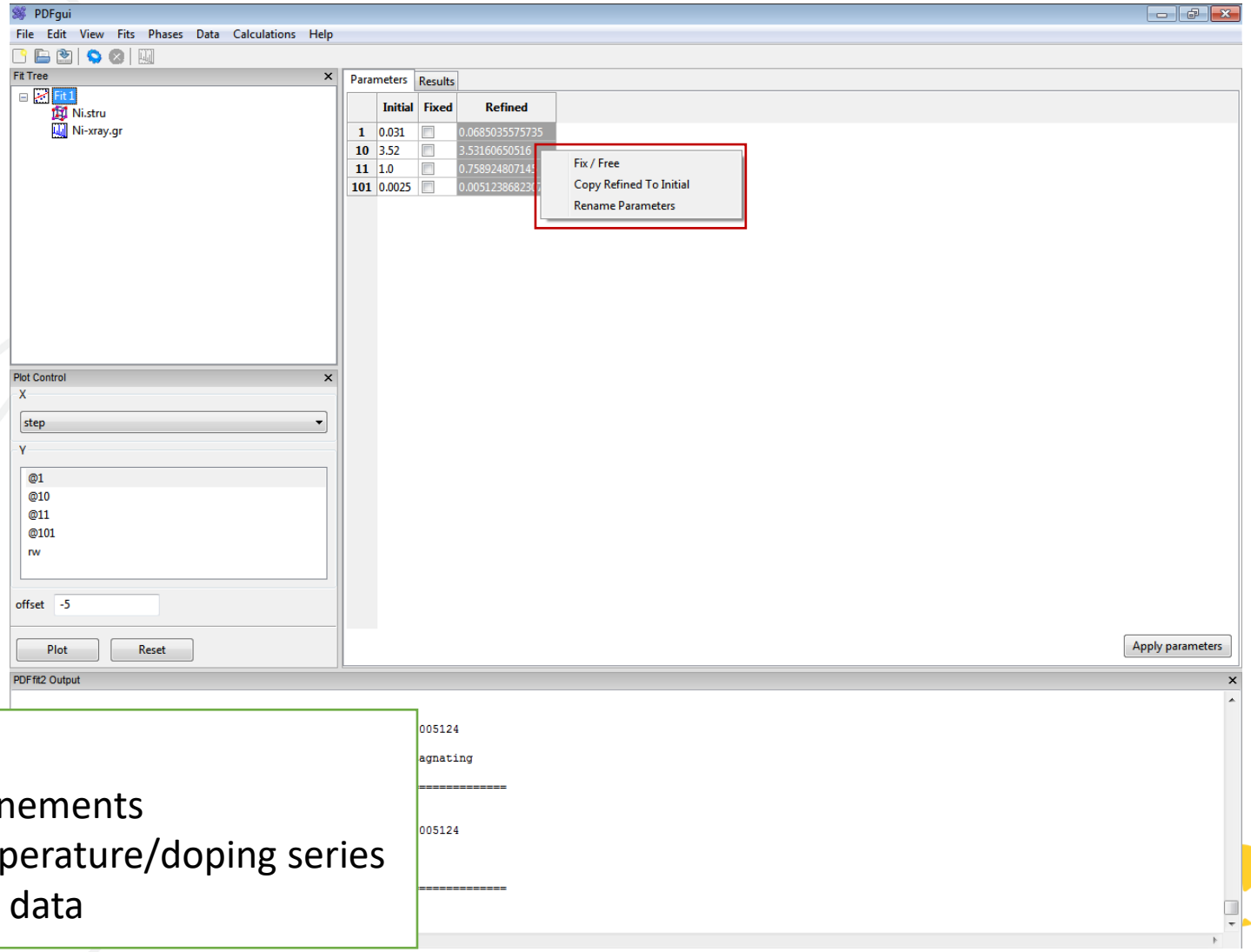
Using PDFgui for a refinement

- PDFGui can calculate and refine model systems (< 1000) atoms.



Using PDFgui for a refinement

- Highlight the refined values → right click → copy refined to initial



Also possible:

- Multiphase refinements
- Macros for temperature/doping series
- X-ray + neutron data

A generic PDFgui refinement recipe

1. Unit cell and pscale
2. Atomic displacement parameters

(2a Q_{damp} for CeO_2 or Ni standard **only –** instrument resolution)

3. delta1 / delta2 / sratio – one only
4. Atomic positions
5. spdiameter (if nanoparticle)

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THINGS TO ADD

Types of refinement
Unit cell
Extended unit cell / alternative symmetry
Box-car refinement

Conclusions

1. Model-independent analyses
   - Peak position ↔ atom-atom distance
   - Peak-picking, trends and observations can give information about processes
   - Differential PDF analysis increases sensitivity to particular species
   - Principal component analysis and NMF can help identify phases in the system
2. Creating and interrogating simple models
   - VESTA is a free and useful tool
3. Using real-space refinement methods (PDFGui)
   - Extract structural information from fit (refinement)
   - Compare different models to the data
   - Calculate model PDFs for pairs of atoms

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