Small box modelling using PDFGui

Emil S. Bozin
Brookhaven National Laboratory

NSLS-II PDF School 2018
Brookhaven National Lab, 17-19 September 2018

September 18, 2018

Outline

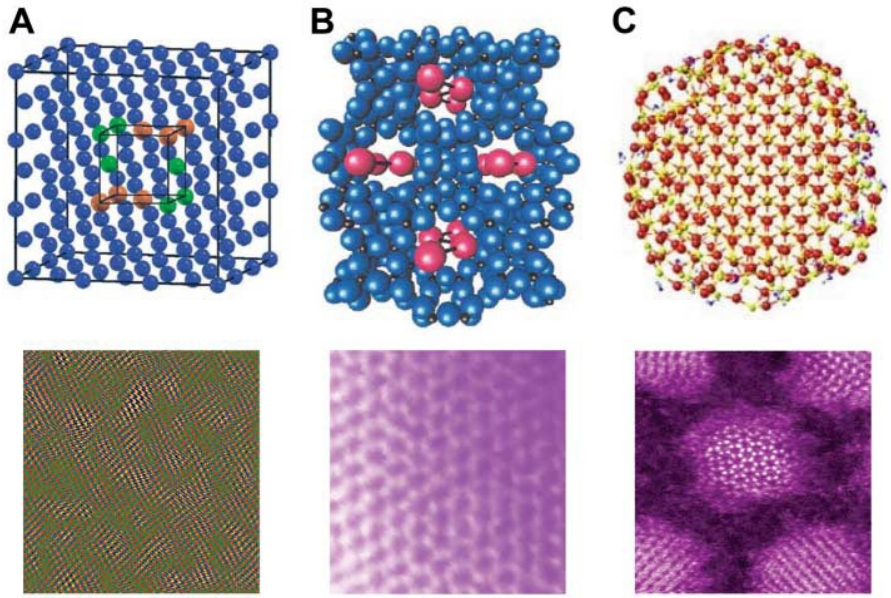
- Introductory notes on PDF approach
- On small box modelling in general and PDFgui in particular
- PDFgui parameters, concepts, and layout
- Agenda for hands-on part and examples to be covered

PDF approach

- Choosing the right tool for the problem

PDF approach

- Non crystalline materials
  (liquids, amorphous solids, polymers)



- Nanoscale materials

- Disordered crystalline systems with nanoscale heterogeneities

S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

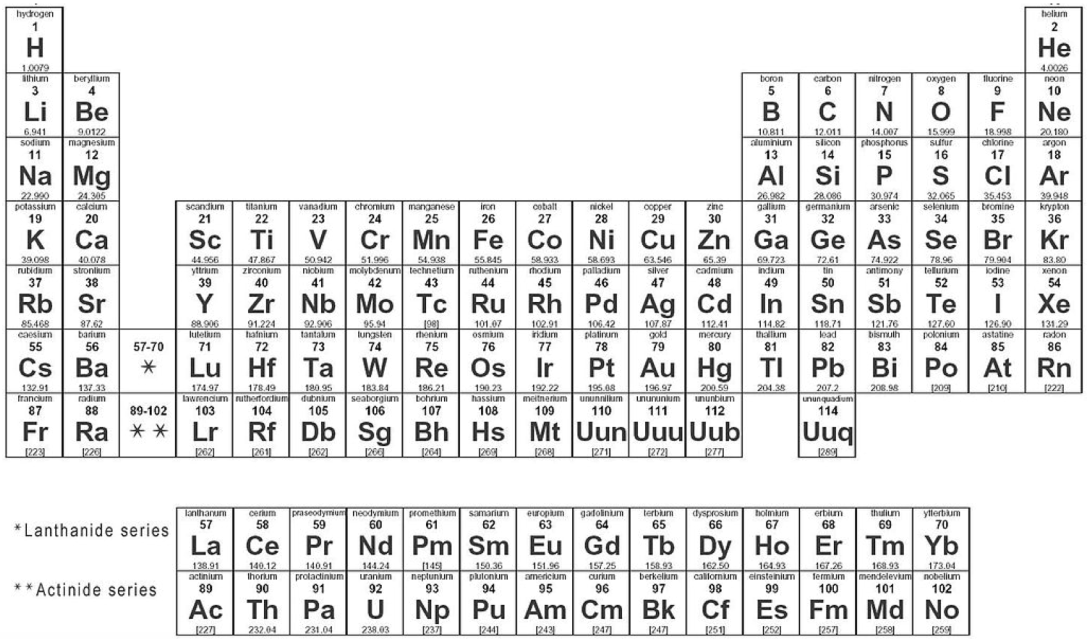
molecule

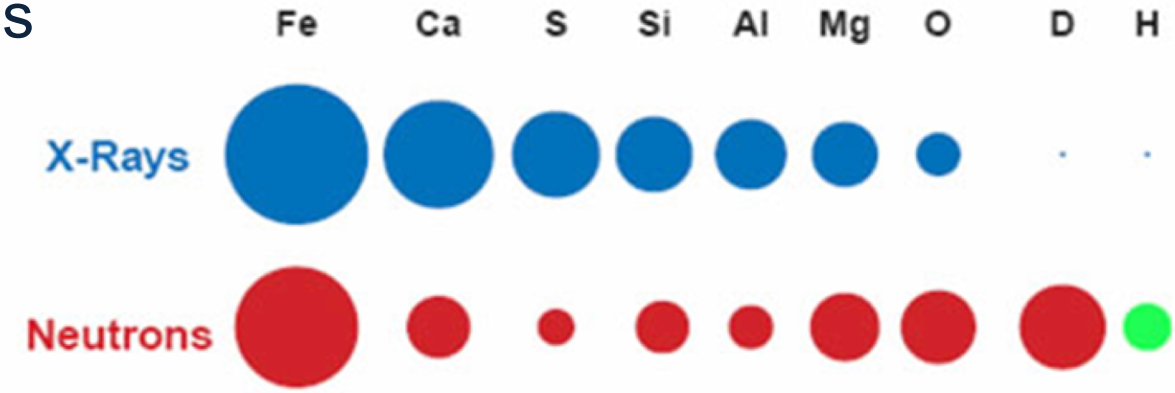
crystal

BROOKHAVEN NATIONAL LABORATORY

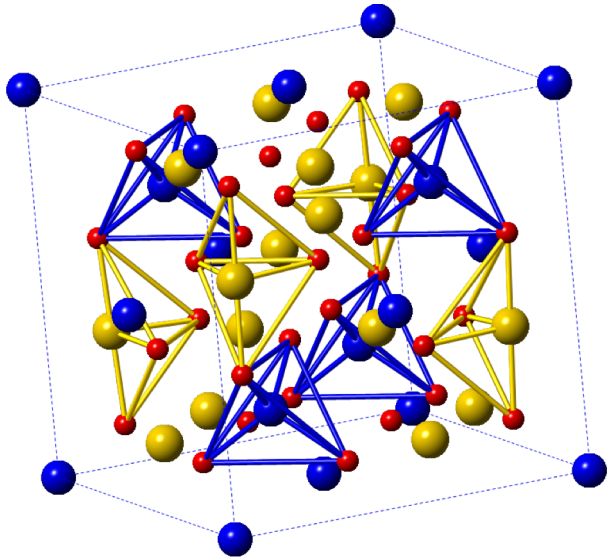
PDF approach

- Considering scattering contrast
- Considering absorption
- Considering isotopes and resonances





PDF recap

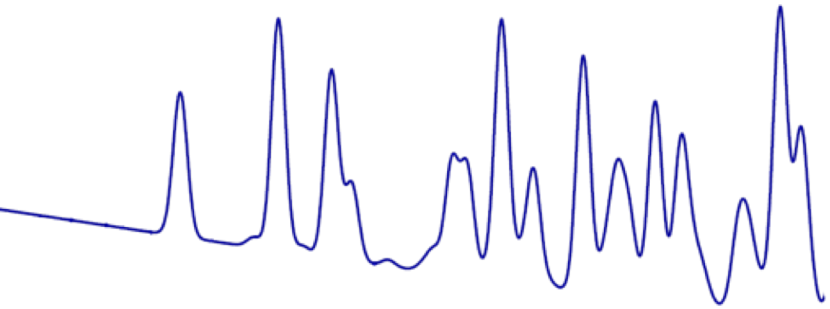


$$I_{tot} = I_{sam} + I_{bgrd}$$

$$I_{sam} = A \cdot P \cdot [C \cdot I_{coh} + I_{inc} + I_{mul}]$$

$$S(Q) = \frac{I_{coh}(Q) - \langle b^2 \rangle + \langle b \rangle^2}{\langle b \rangle^2} \qquad Q = \frac{4\pi \sin\theta}{\lambda}$$

$$G(r) = \frac{2}{\pi} \int_0^\infty Q\,(S(Q) - 1) \sin Qr \, \mathrm{d}Q$$



interatomic distance, r (Å)

Raw data

Data reduction

PDF

Relationship to structure

$$G(r) = \frac{1}{Nr\langle b \rangle^2} \sum_{i \neq j} b_i b_j \, \delta(r - r_{ij}) \; - \; 4\pi r \rho_0$$

NSLS-II National Synchrotron Light Source II

BROOKHAVEN NATIONAL LABORATORY

Atomic PDF skeleton

Relationship to structure

r_{ij} – interatomic distance between atoms *i* and *j*

$$G(r) = \frac{1}{N r \langle b \rangle^2} \sum_{i \neq j} b_i b_j \delta(r - r_{ij}) - 4\pi r \rho_0$$

$\rho_o = N/V$ average number density (number of atoms per unit volume)

r – running variable (distance)

scattering "scale" for pair of atoms *i* and *j* weighted by averaged scattering "strength"

Neutrons: b_{coh}
X-rays: f(Q=0), effectively Z

Experimental setup limitations

$$G(r) = \frac{2}{\pi} \int_{Q_{MIN}}^{Q_{MAX}} Q\,(S(Q) - 1) \sin Qr \, \mathrm{d}Q$$

~~Q_{MAX}~~

~~Q_{MIN}~~

Truncation effects in Fourier transform (termination ripples, limited *r*-resolution)

Small angle scattering information is missing

Ideally one would like to have

- broad Q-range
- good Q-resolution

This is not always essential!

PDFgui – awareness of various effects

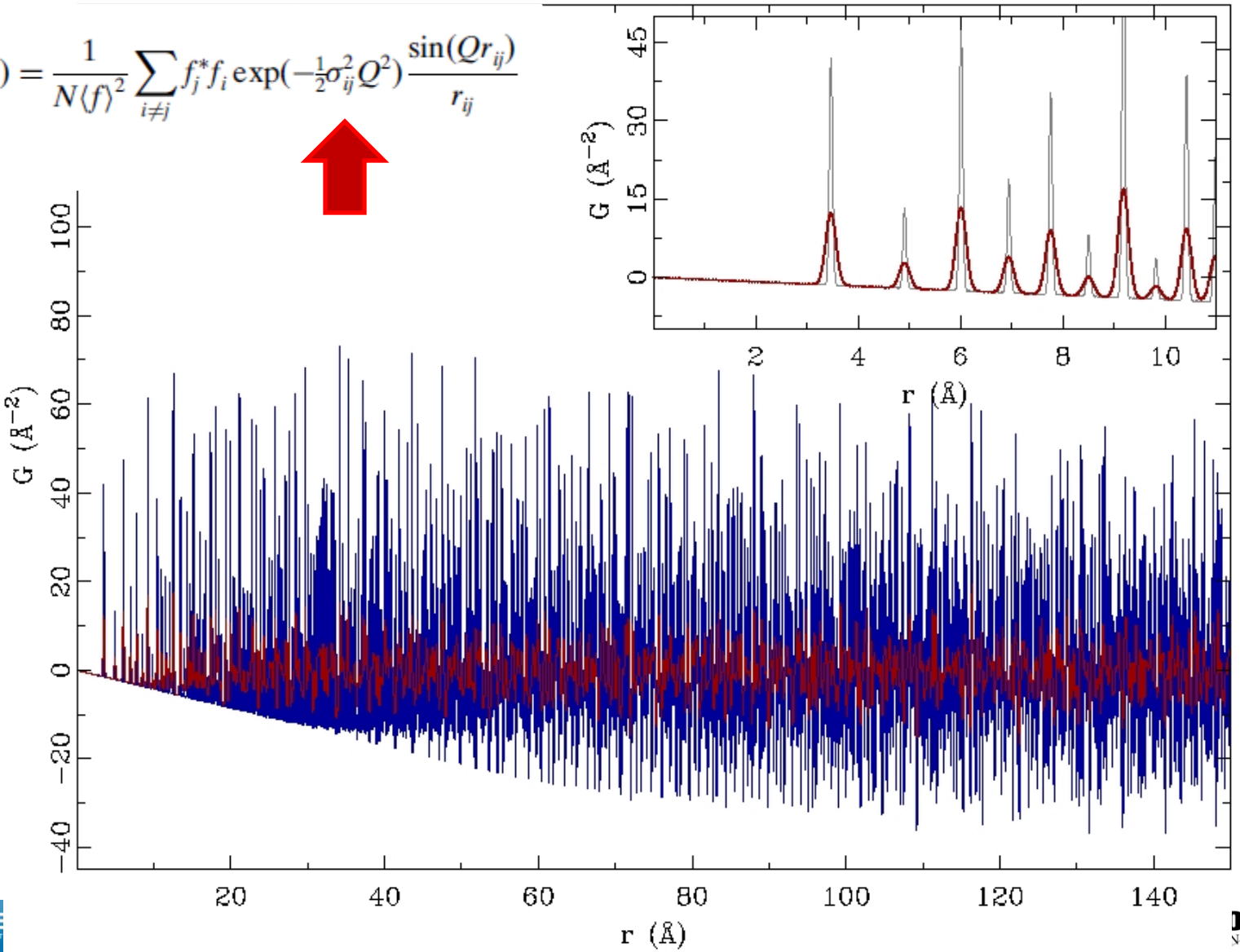
Some effects that should be accounted for

- Thermal broadening
- Correlated motion of nearest neighbours
- Finite Q_{MAX} (truncation)
- Limited Q-space resolution
- Particle size

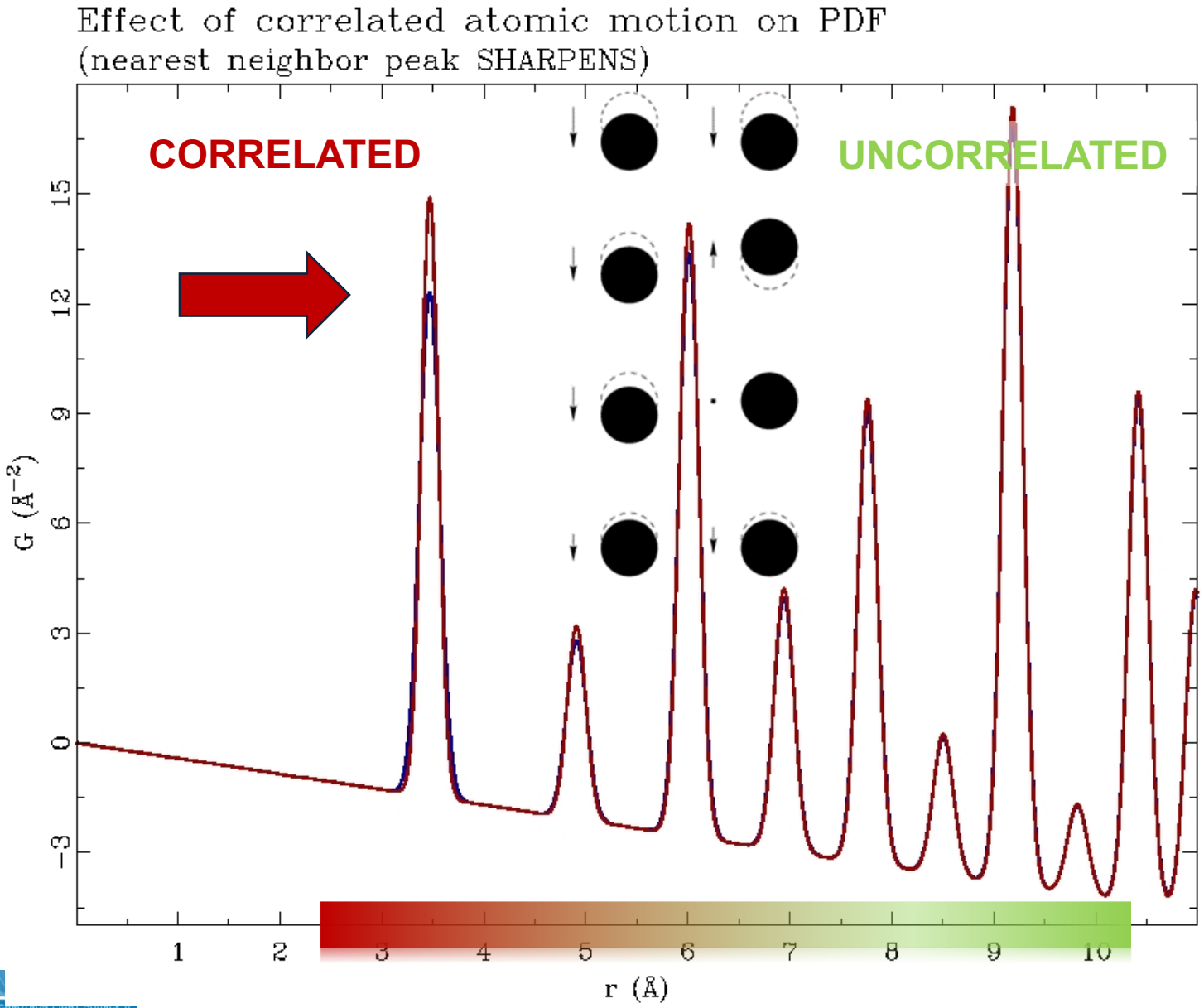
PDF: effect of thermal broadening

Effect of thermal motion U_{iso} on PDF
(thermal displacement parameters)

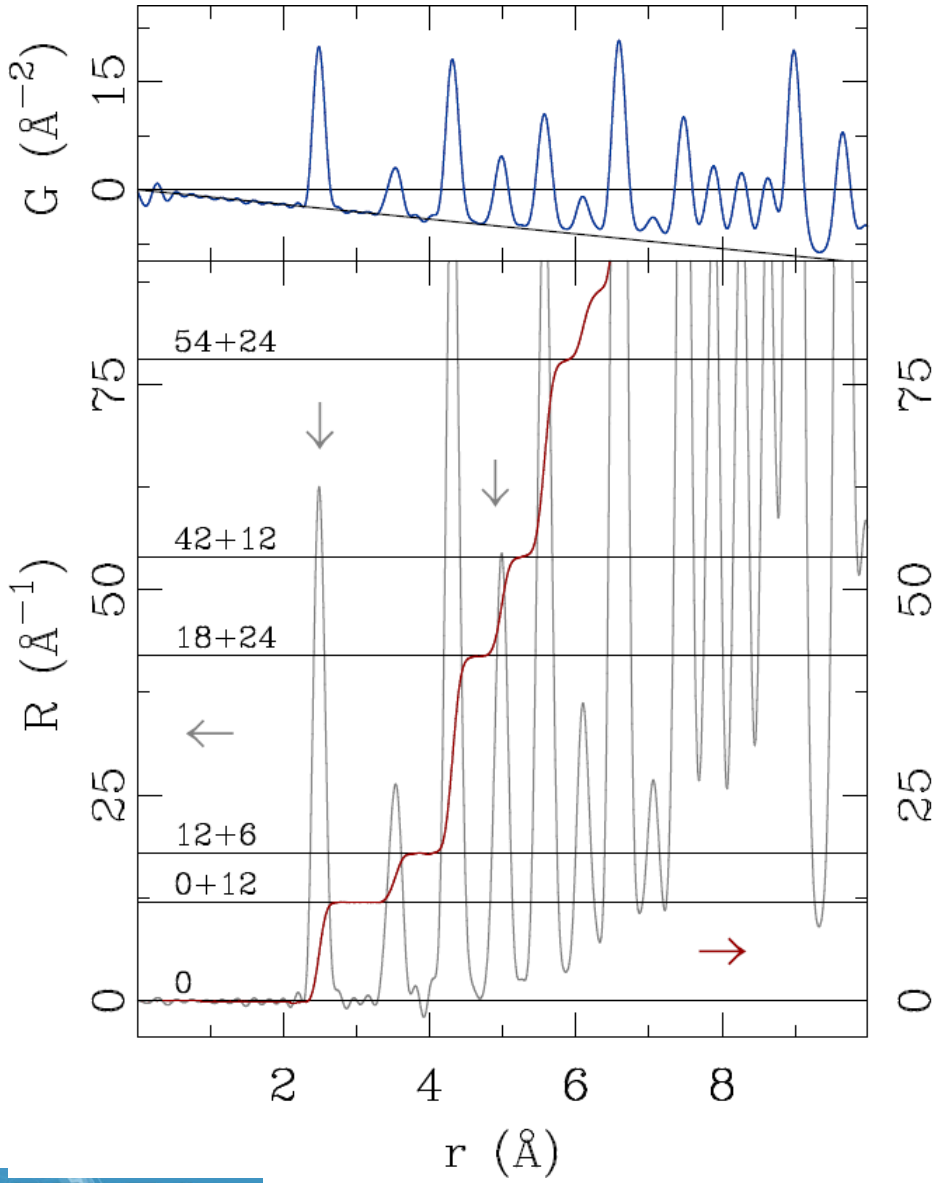
$$F(Q) = \frac{1}{N\langle f\rangle^2}\sum_{i\neq j} f_j^* f_i \exp(-\tfrac{1}{2}\sigma_{ij}^2 Q^2)\frac{\sin(Qr_{ij})}{r_{ij}}$$

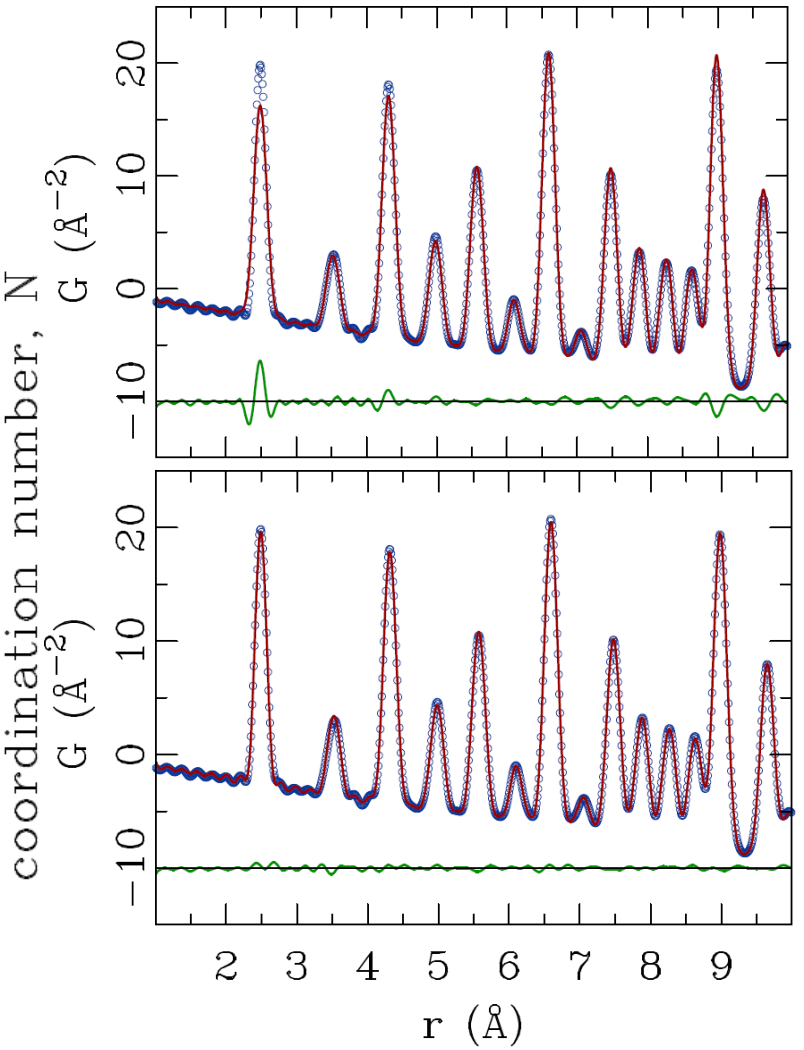


PDF: effect of correlated atomic motion



PDF: effect of correlated atomic motion

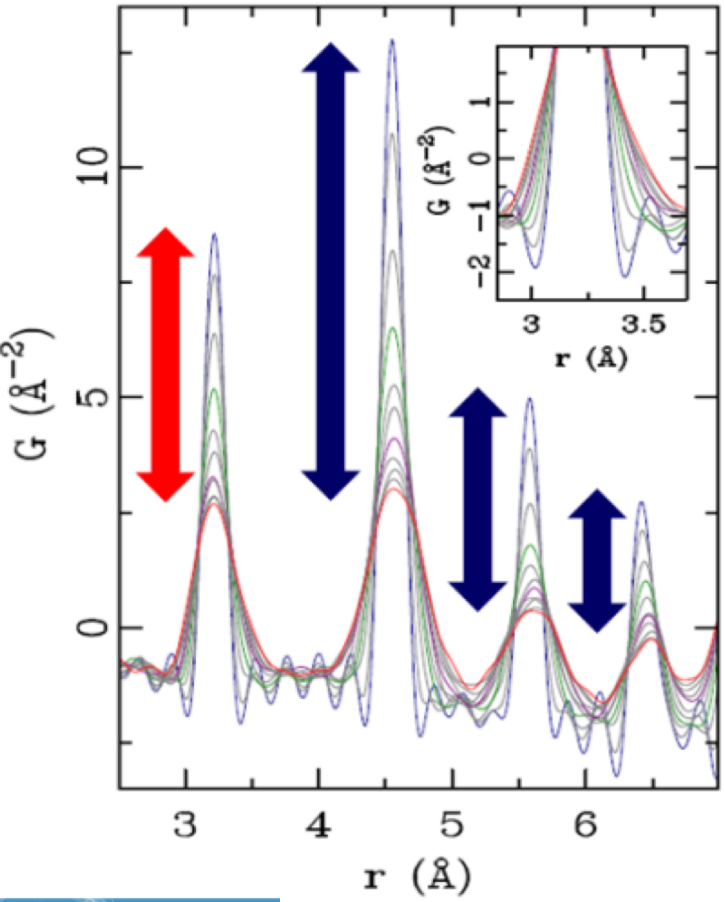




PDF: correlated atomic motion outlaws

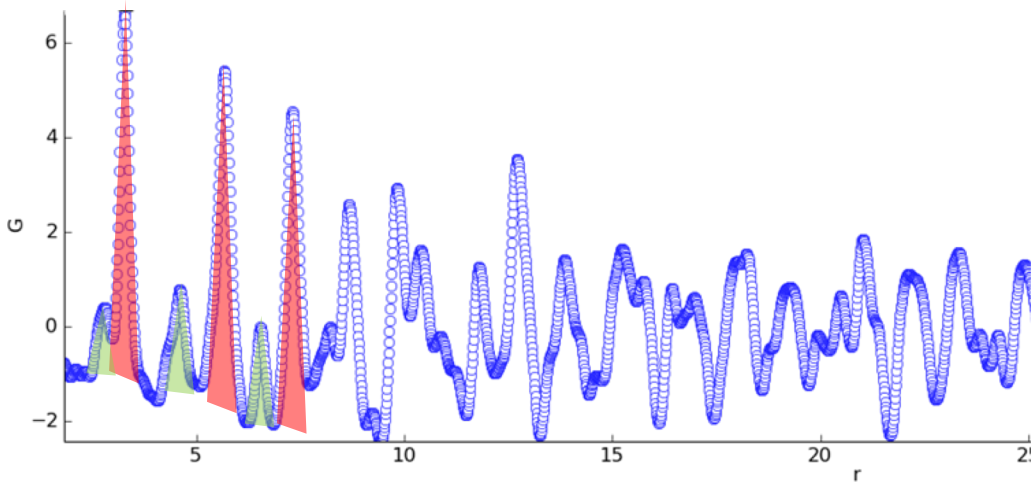
Weak effects
(e.g. PbTe)

break the rule



Strong effects
(e.g. in $CeCoIn_5$)

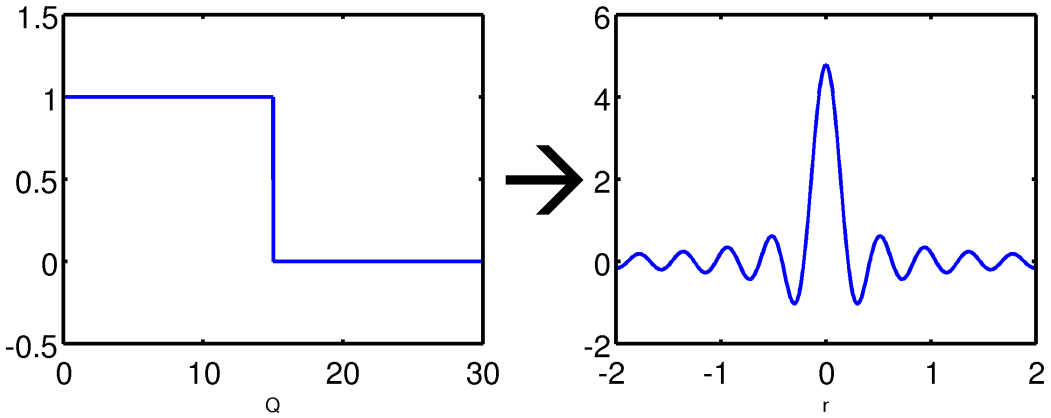
difficult to model



PDF: effect of finite Q_{max} (truncation)

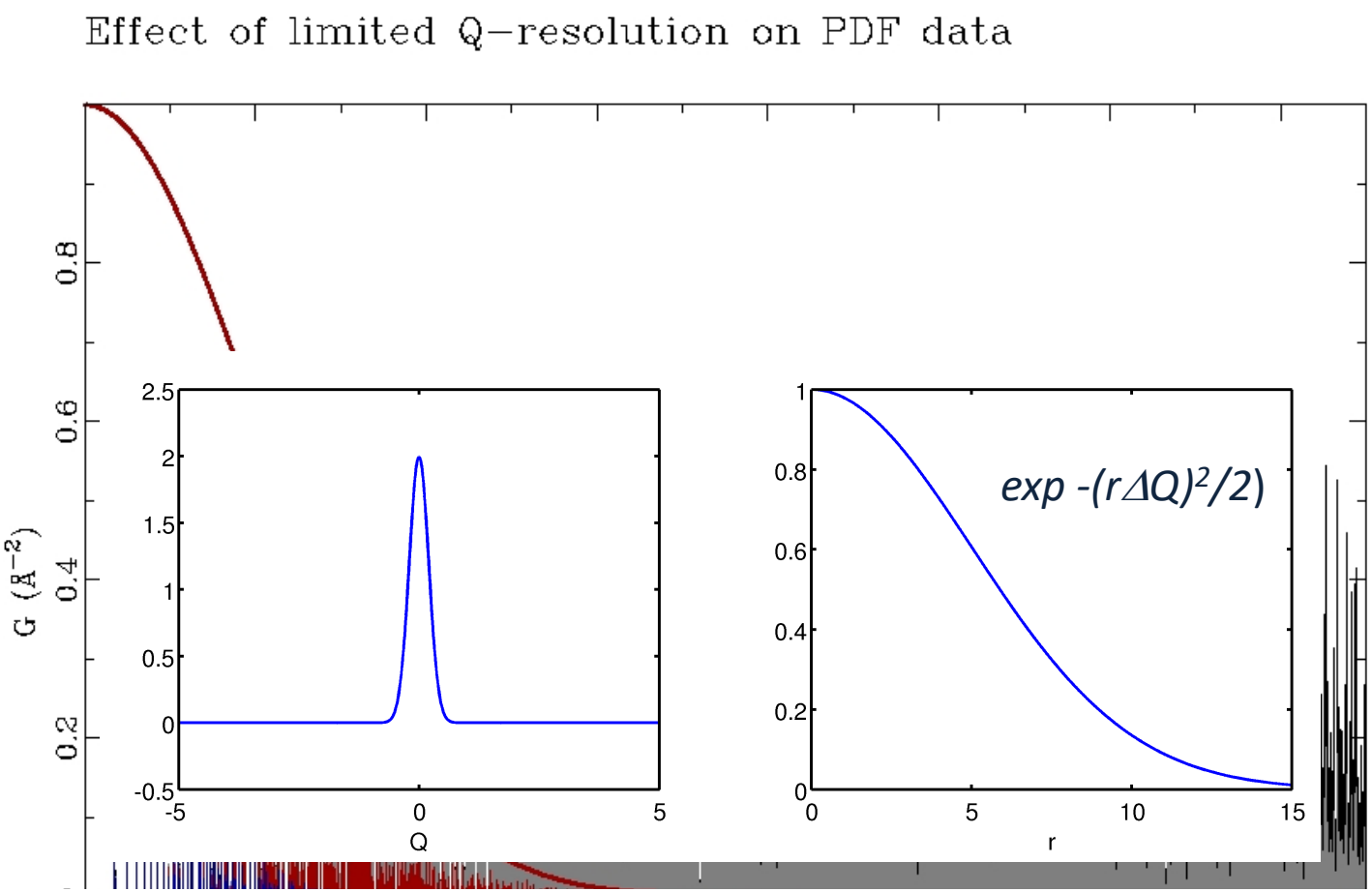
Effects from finite Q-range

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} F(Q) \sin Qr \, \mathrm{d}Q$$



- ideal F(Q) is multiplied by a step function
- G(r) gets convoluted with a sinc function sinc(*r*) = sin(Q_{max} *r*) / *r* → *r*-resolution ≈ π/Q_{max}
- good *r*-resolution of G requires large Q_{max}
  Q = 4π sin θ/λ → best results with TOF neutrons or high-energy x-rays

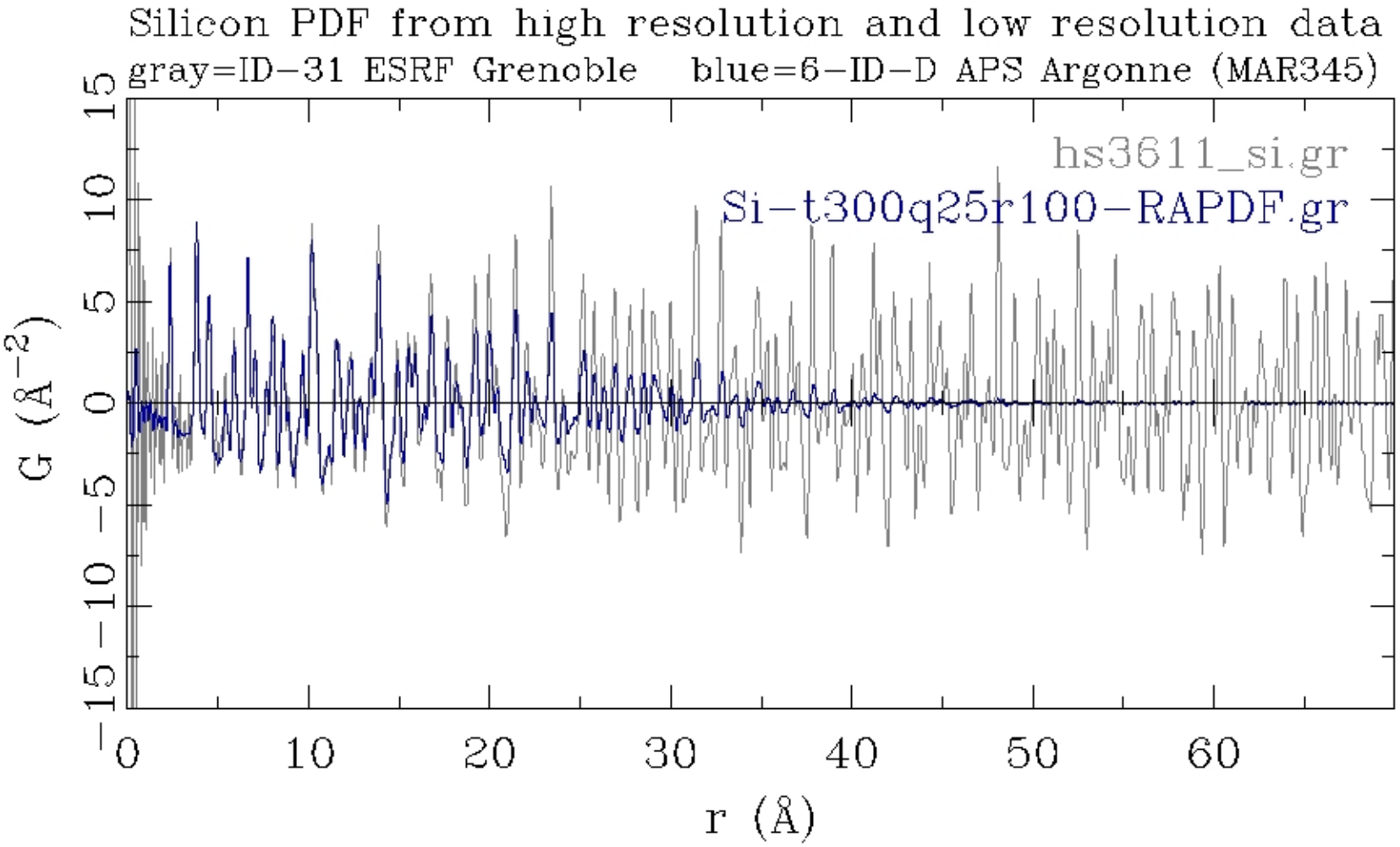
PDF: effect of the Q-space resolution



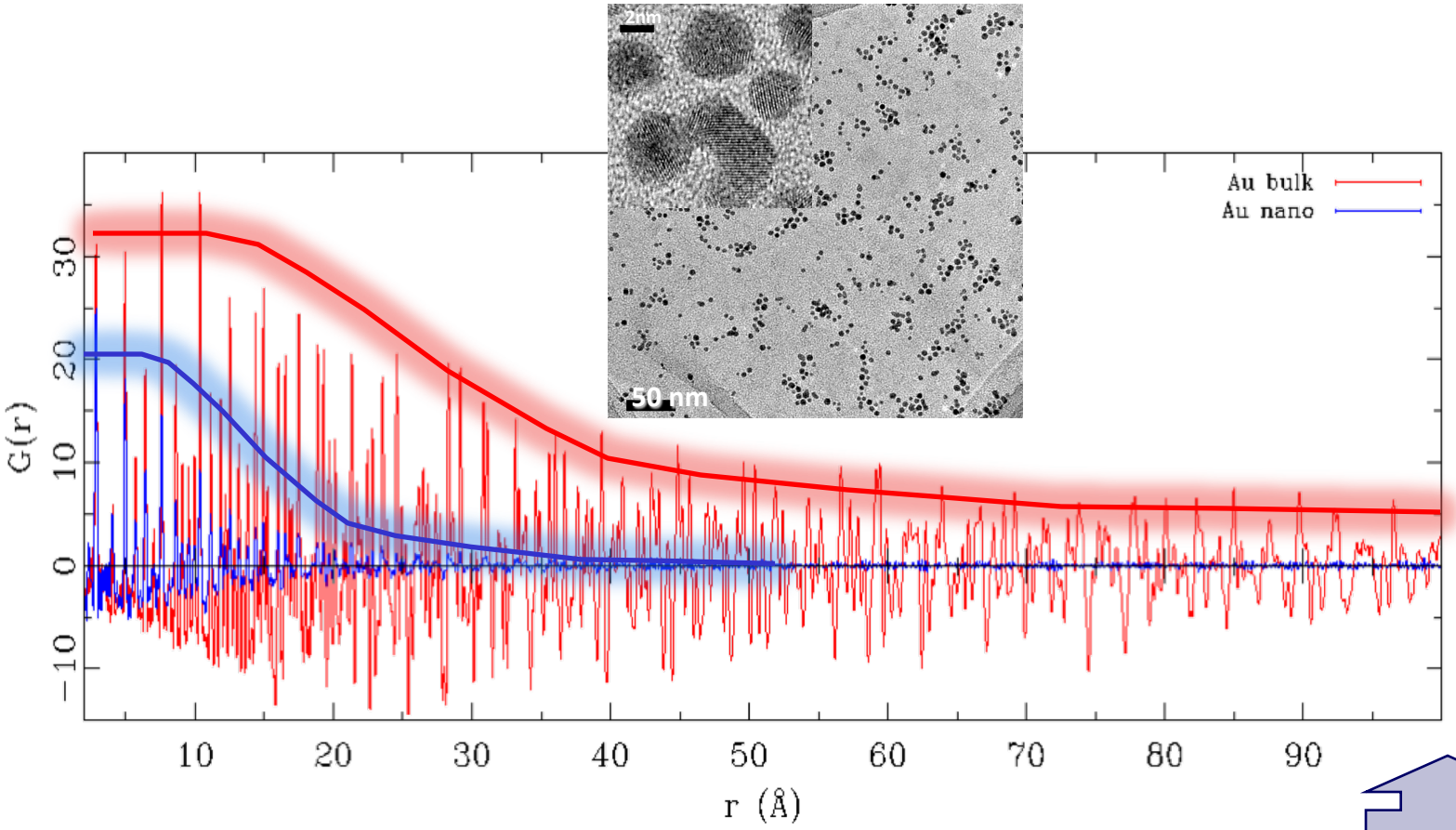
- ideal F(Q) is convoluted by Gaussian to simulate finite Q resolution
- *G(r)* gets multiplied by real-space Gaussian with reciprocal width
- For *G(r)* to have good *r*-range high resolution in *Q* is required

*Q-resolution defines PDF "**field of view**"*

PDF: effect of the Q-space resolution



PDF: effect of the finite particle size – nano vs bulk



Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF.

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

After the PDF experiment …

Now that you have collected your X-ray or neutron data and reduced it to PDF, what is the next step?

- It's time to harvest the information from PDF data, of course!
- Which approach to use depends on the problem at hand
- Good starting point (always) is to observe the PDF data in a model independent way, followed by modelling using the available tools, some of which are presented in this school
- Data inspection could provide valuable clues that would help modelling efforts/strategies tremendously at times

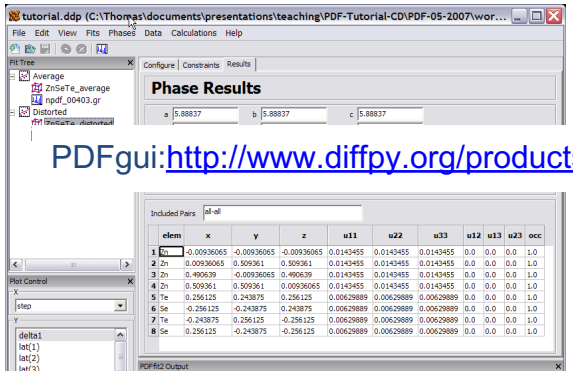
PDF data modeling

Small Models: Least Squares Refinement
Up to several hundreds of atoms
'Rietveld'-type parameters: *lattice parameters, atomic positions, displacement parameters, etc.*
Refinements as function of *r*-range

Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q), G(r)* , Bragg profile
Constraints utilized
Static 3-D model of the structure (a snap-shot)

Multi-level /Complex Modeling
Refine higher level parameters (not each atom)
Example nanoparticle: *diameter, layer spacing, stacking fault probability*
Choose minimization scheme

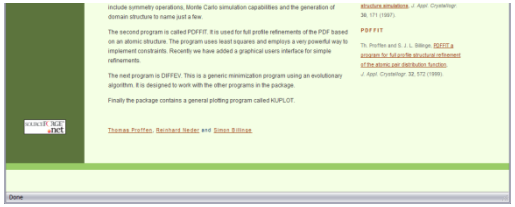
Emerging: *ab initio* and force-field based approaches
Density Functional Theory
Molecular Dynamics



PDFgui:http://www.diffpy.org/products/pdfgui

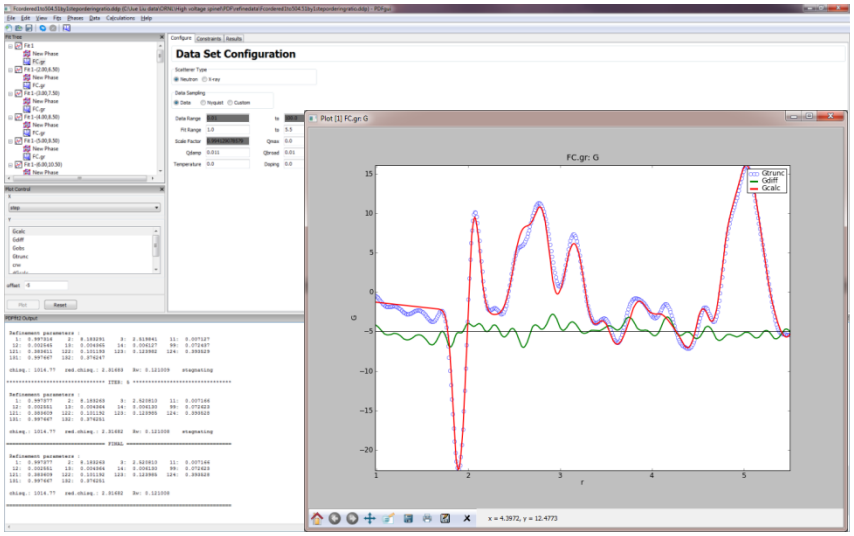
RMCprofile:http://wwwisis2.isis.rl.ac.uk/rmc/
EPSR: www.facebook.com/disord.matt

DIFFEV and DISCUS: http://discus.sourceforge.net
DiffPy-CMI: http://www.diffpy.org/products/diffpycmi



slide courtesy Katharine Page

“Small Box” software comparison

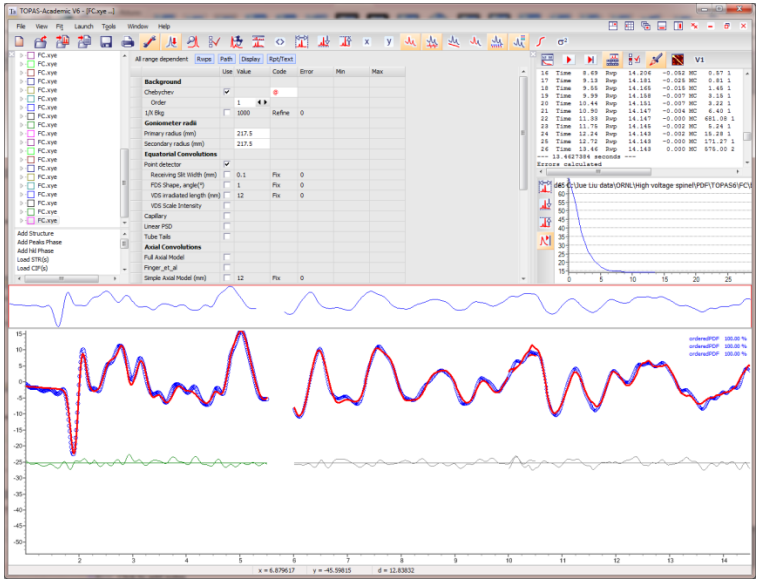


PDFgui http://www.diffpy.org/

- Slow refinement, e.g. for high-*r*
- Cumbersome outputs

\+ Open Source and Free

\+ GUI is Simple and User-friendly



TOPAS PDF

- Commercial
- Steeper learning curve
- Have to write your own macro

\+ Super Fast

\+ Easy manipulation of fitting parameters and plotting

\+ Can easily customize output functions

http://www.topas-academic.net

slide courtesy Katharine Page

Small box PDF modeling approach

- Small box: assumption of periodic boundary conditions (P1)

- Relatively small number of atoms (up to several hundred)

- Built-in symmetry constraints with symmetry equal or usually lower than the average crystal symmetry

- Involves least squares refinement over selected *r*-range (typically up to a few unit cells, translational symmetry not necessarily important as the box size mostly provides “metrics”)

Thigs needed …

- PDF **data** (*sample*.**gr** files) and associated information such as Q_{max} used, range of data, type of radiation, sample chemistry, ...

- In **small box modelling** approach, one typically starts from **a refinement** of a known/suspect structure, (thus reducing the volume of the parameter space as much as possible)
    - High-*r* region ~average structure
    - Low-*r* region ~local structure

  (biased view with bulk materials in mind)

- **Starting structure information**
    - space group and lattice parameters
    - fractional coordinates (asymmetric unit cell) & occupancies
    - having site-multiplicities handy may be helpful for crosschecking (e.g. PDFgui works with symmetrized cells)
    - Having an origin choice handy, if multiple are available, could matter

PDF modeling

- PDF is simulated from a known structure model

$$G_{calc}(r) = \frac{1}{Nr\langle b\rangle^2}\sum_{i\neq j} b_i b_j \frac{1}{\sqrt{2\pi}\sigma_{ij}} \exp\left[-\frac{(r-r_{ij})^2}{2\sigma_{ij}^2}\right] - 4\pi r\rho_0$$

- structure model is parameterized by a set of parameters p_i
- residuum R_w - difference between observed and simulated PDF

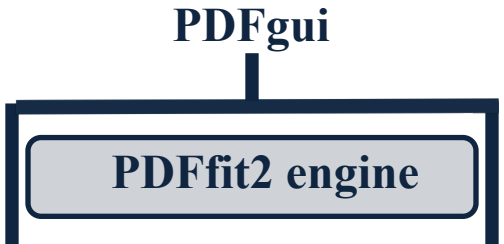
$$R_w(p_1, p_2, \ldots) = \sqrt{\frac{\sum_n \left[G_{obs}(r_n) - G_{calc}(r_n)\right]^2}{\sum_n G_{obs}^2(r_n)}}$$

- least-squares refinement of p_i to minimize R_w
- Effects from setup (such as finite Q-resolution) or sample (correlated NN-motion) accounted for

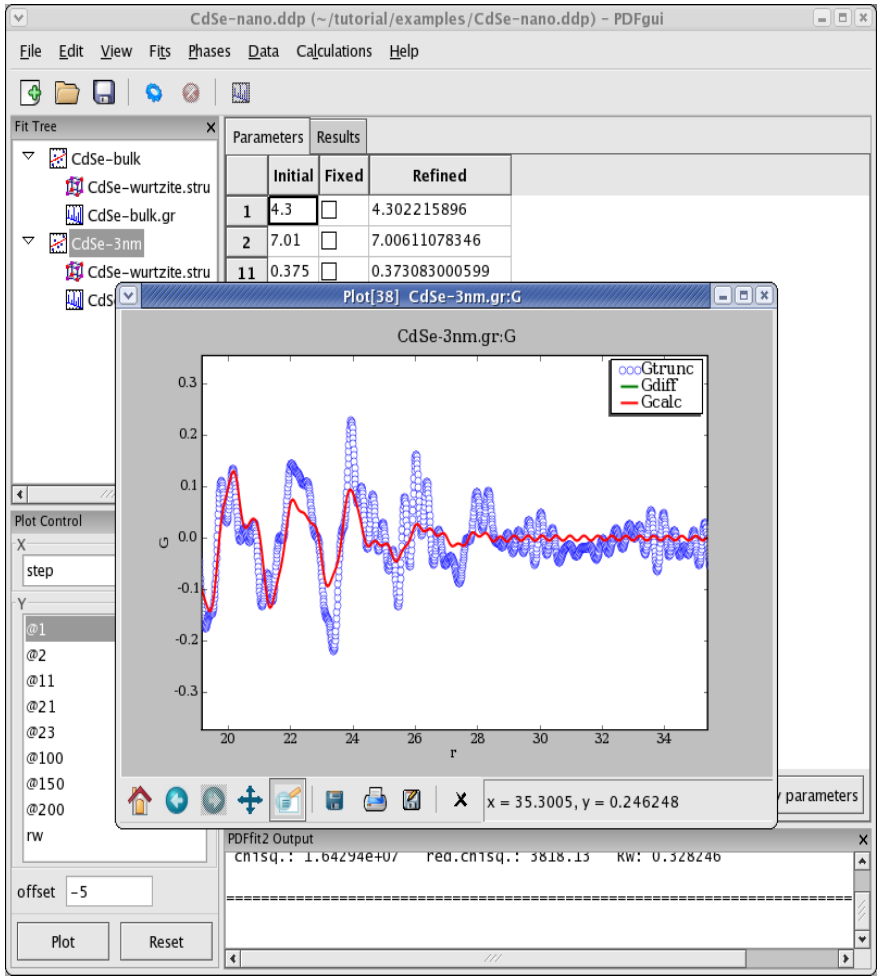
$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}} \qquad \sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

PDFgui overview

- PDFgui is a graphical interface built on the PDFfit2 engine, which is a program as well as a library for real-space refinement of crystal structures based on the atomic pair distribution function (PDF) method.
- PDFgui organizes fits and simplifies many data analysis tasks, such as configuring and plotting multiple fits, adding functionality to script driven PDFfit2.
- PDFfit2 is capable of fitting a theoretical three dimensional structure to atomic pair distribution function data and is well suited for nanoscale investigations.
- The fit system accounts for lattice constants, atomic positions and anisotropic atomic displacement parameters, correlated atomic motion, as well as various experimental factors that may affect the data.
- The atomic positions and thermal coefficients can be constrained to follow symmetry requirements of an arbitrary space group. Limited restraints supported.
- The PDFfit2 engine is written in C++ and accessible via Python, and can also be prompt operated.



PDFgui overview



PDFgui

- GUI interface to PDFfit2 is user friendly modelling environment that **can be used for quick simulations (useful for experiment planning and sensitivity tests)**
- can **organize** multiple related fits in a single project file (.ddp file) easily shareable with colleagues
- powerful **visualization facilities**
  - live plotting of refined PDF profiles
  - parametric plots of variables from multiple fits
  - 3D structure visualization (optional)
- **structure model manipulation**
  - supports xyz, PDF, CIF and PDFfit formats
  - supercell expansion
  - expansion of asymmetric unit
  - generation of symmetry constraints for coordinates and atomic displacement factors, ADPs (“thermals”)
- **wizards** for T-series, doping-series, r-series (smart extraction of meta-data from files)

Easy set up for “on the fly” refinements of incoming data helps making experimental decisions

PDFgui parameters and program structure

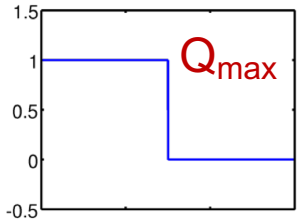
- **PDFgui parameters associated with DATASET**

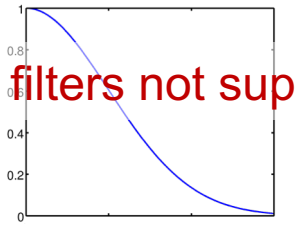
Fit range (r_{MIN}, r_{MAX})
fixed in refinement

user selected refinement *r*-range

Q_{max}
fixed in refinement

upper limit of integration used in Fourier transform
defines r-space resolution, predetermined





Lorch filters not supported

Q_{damp}
refined for calibrant
fixed for sample

Gaussian dampening (due to limited Q-resolution)

Q_{broad}
refined for calibrant
fixed for sample

High-*r* peak broadening (due to increased refined intensity noise at high Q and other sources, only significant r_{MAX} is large

dscale
refined

scale factor associated with dataset

PDFgui parameters and program structure

- **PDFgui parameters associated with PHASE**

pscale refined	phase scale factor NOTE: could be redundant/correlated with dscale
a, b, c, α, β, γ refined	lattice parameters
x[n] y[n] z[n] occ[n] u[*1*..*6*,n] refined (per symmetry)	x-position (fractional coordinates) y-position z-position site occupancy anisotropic displacement parameters U_{ij} [$Å^{-2}$]

NOTE: Refinement parameters can be correlated, particularly when a model is refined over a narrow r-range of data. PDFgui reports on correlations > |0.8|

PDFgui parameters and program structure

- **PDFgui parameters associated with PHASE for correlated atomic motion**

delta1
refined

1/r contribution to peak sharpening [Å^{-1}]

delta2
refined

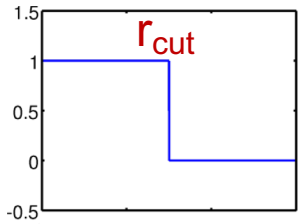
1/r^2 contribution to the peak sharpening [Å^{-2}]

sratio
refined

applied | not applied

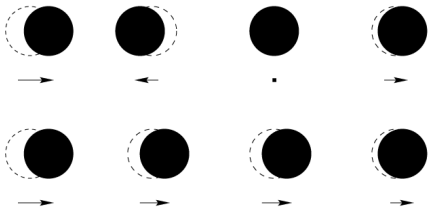
peak width reduction for correlated motion (special cases of rigid structural units)

rcut
constat



radius cuttoff for applying the sratio sharpening factor [Å]

Note: Empirical correlated motion parameters are selected depending on material, they are very strongly correlated and affect other parameters

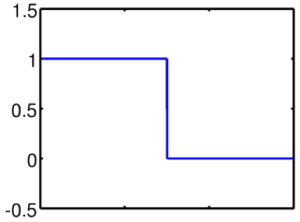


$$\sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

PDFgui parameters for nanoparticles

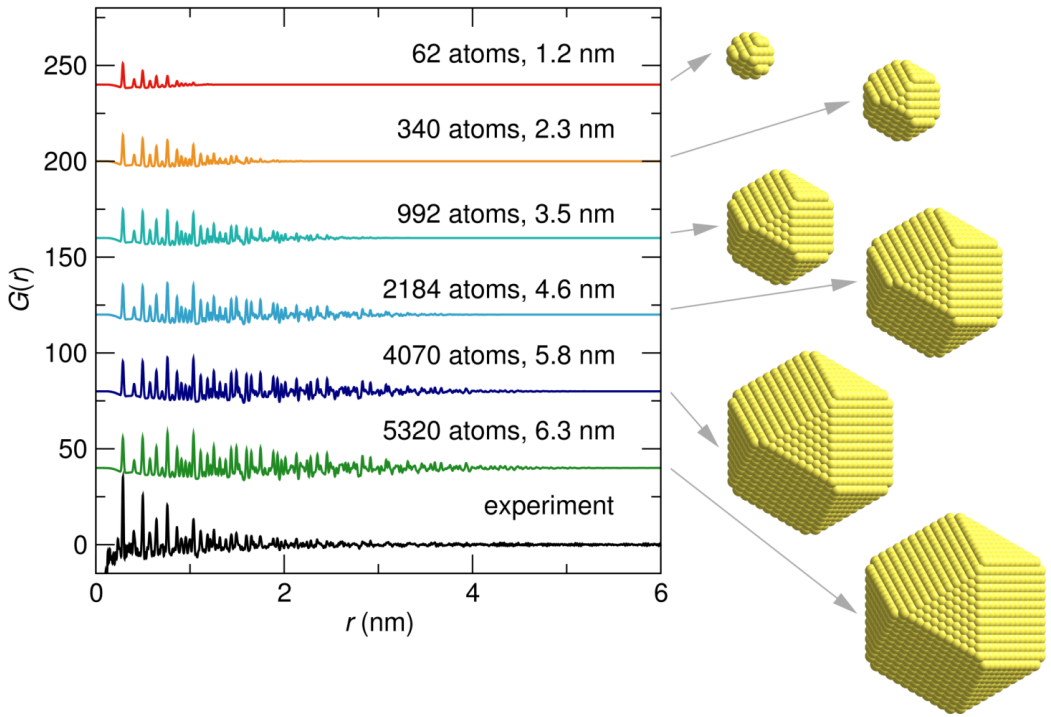
spdiameter
refined

spherical particle diameter for PDF shape damping function [Å]



stepcut
constant

r value above which the PDF is truncated to zero [Å]



PDFgui parameters and program structure

- **PDFgui declarations associated with PHASE**

X declaration	atom type associated with given site (all sites) e.g. Ni/Ta/Ca (label used to read scattering info from lookup tables of b_{coh} and Z).

- **PDFgui declarations associated with DATASET**

Neutron/X-ray declaration	scatterer type (used to determine lookup table)

NOTE: In rare instances one may experience the following

In case of X-ray radiation Z_X is used for element X. If ions present one can change X from original element to a fellow element with adequate electron count.

In case of neutron radiation b_{cohX} is used for element X. Lookup table contains information per natural isotope abundance. If isotope substitution is present, lookup table has to be modified with adequate *b* specified for a dummy element with made-up alphabetical code that will then be declared in the phase using that alphabetical code.

Parameters are assigned using the syntax **@pn**,where **pn** is the parameter number.

For example, @1, @55, @321, etc, numbers do not have to be consecutive.

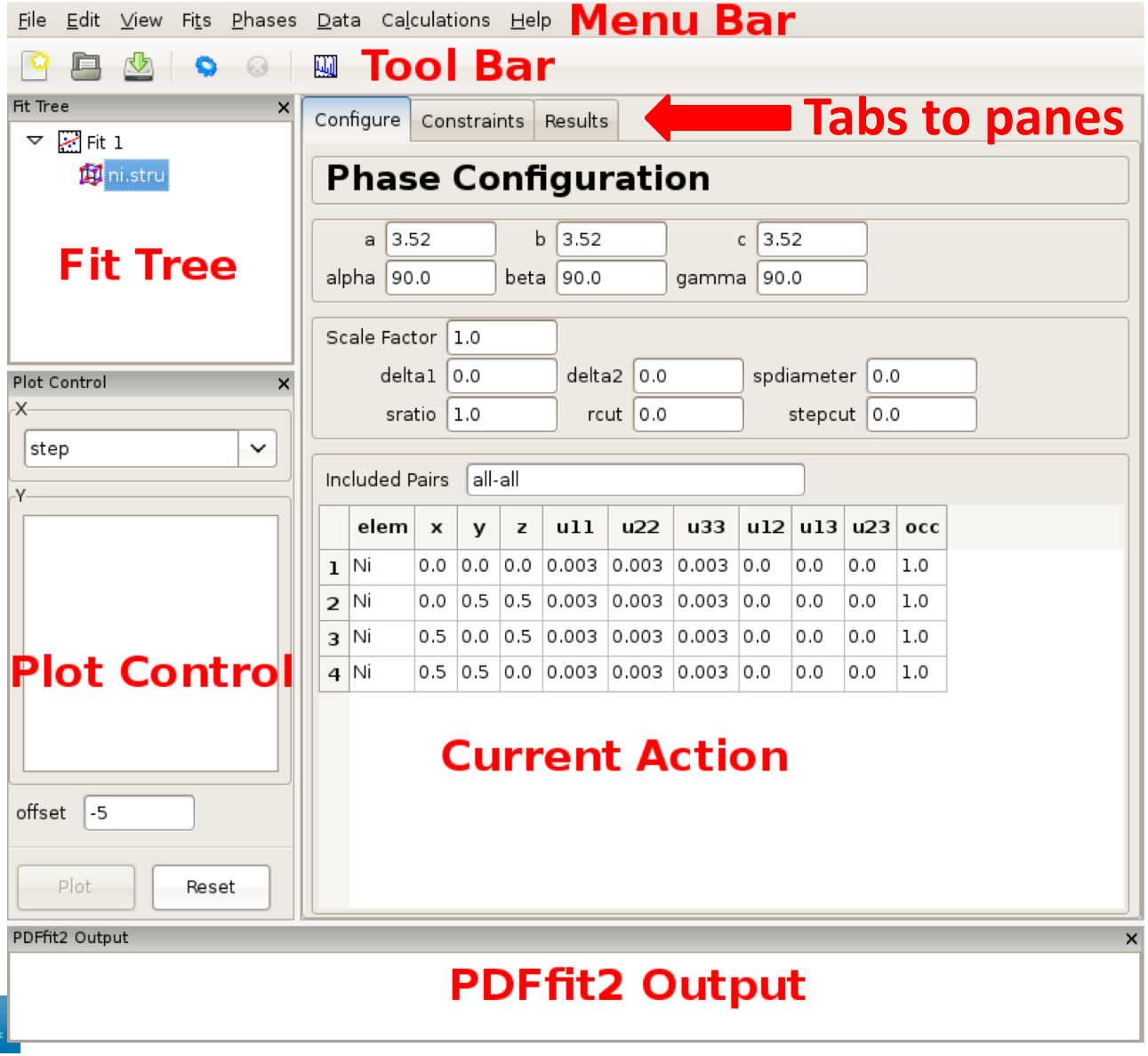
Variables that are assigned the same parameter number will be described by the same parameter.

Caution should be exercised to avoid unintentional assignment of the same parameter number to incompatible variables (variables of different type)

PDFgui: quick start

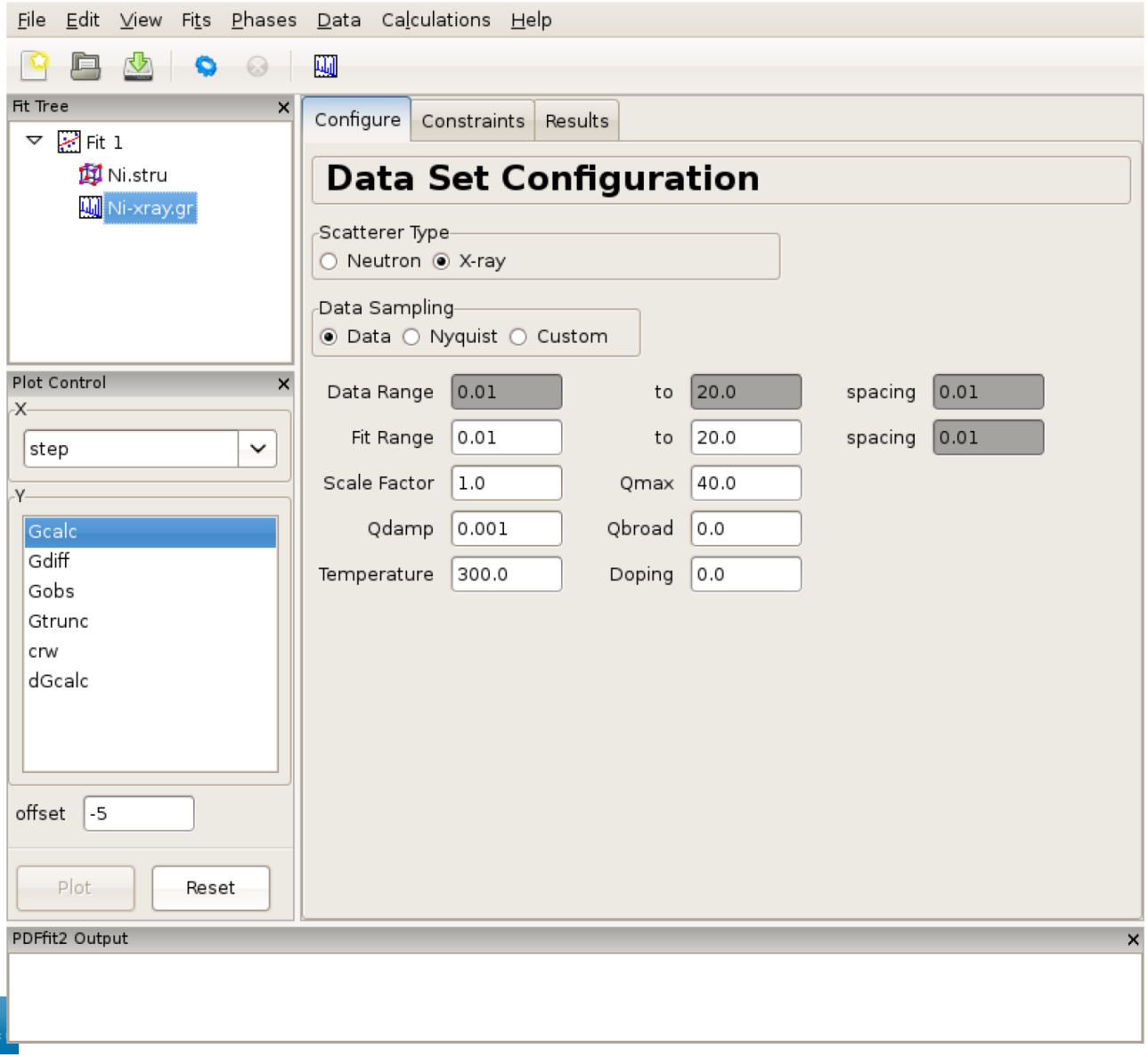
PDFgui: Layout

The layout can be somewhat customized to create comfortable work environment



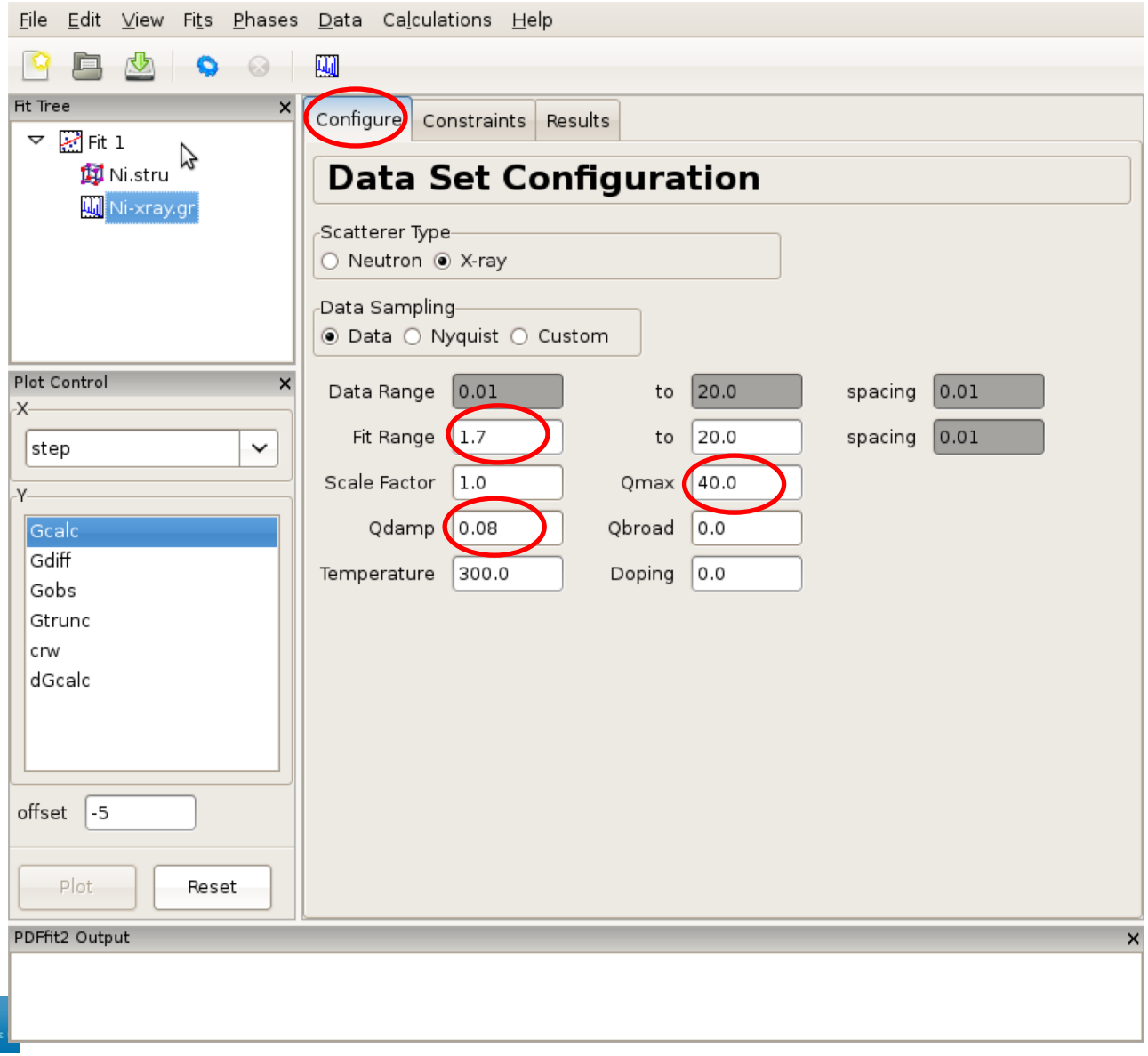
Creating a simple fit using a preexisting struct file

Appearance of a PDFgui window after a PDF dataset is loaded.



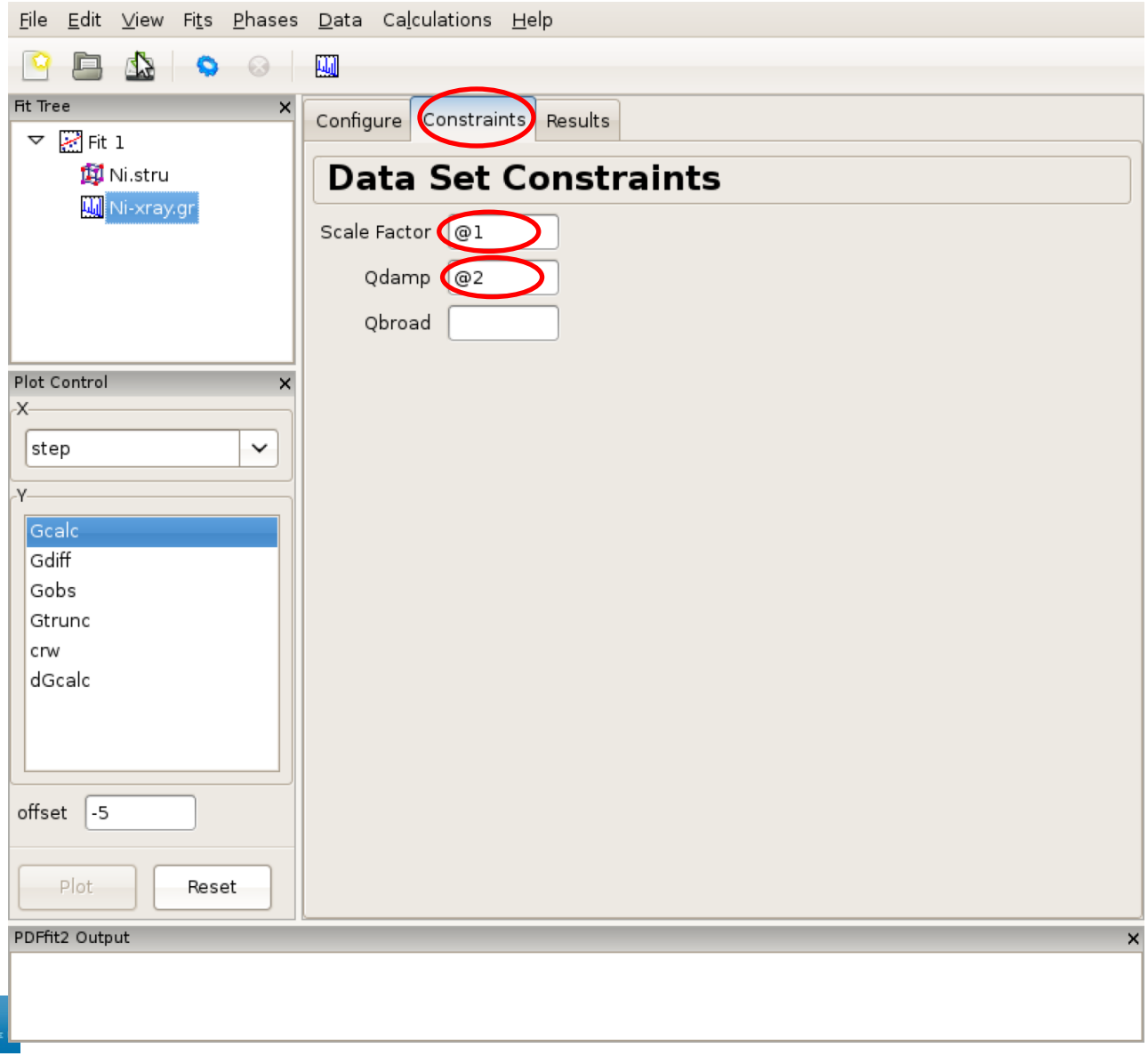
Creating a simple fit using a preexisting struct file

Adjusting data set related configuration.



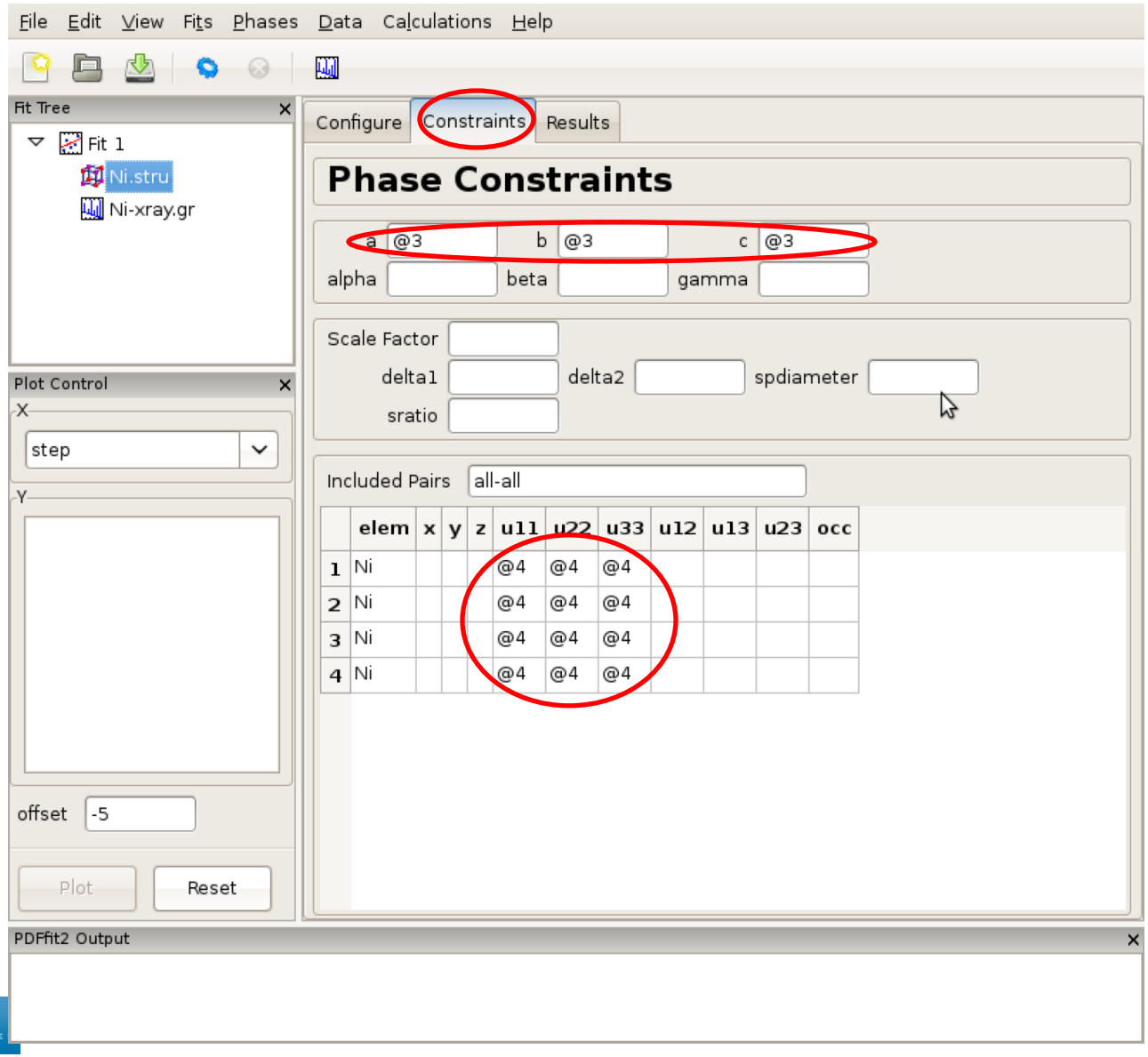
Creating a simple fit using a preexisting struct file

Setting up the refinement parameters and constraints: **experimental parameters**



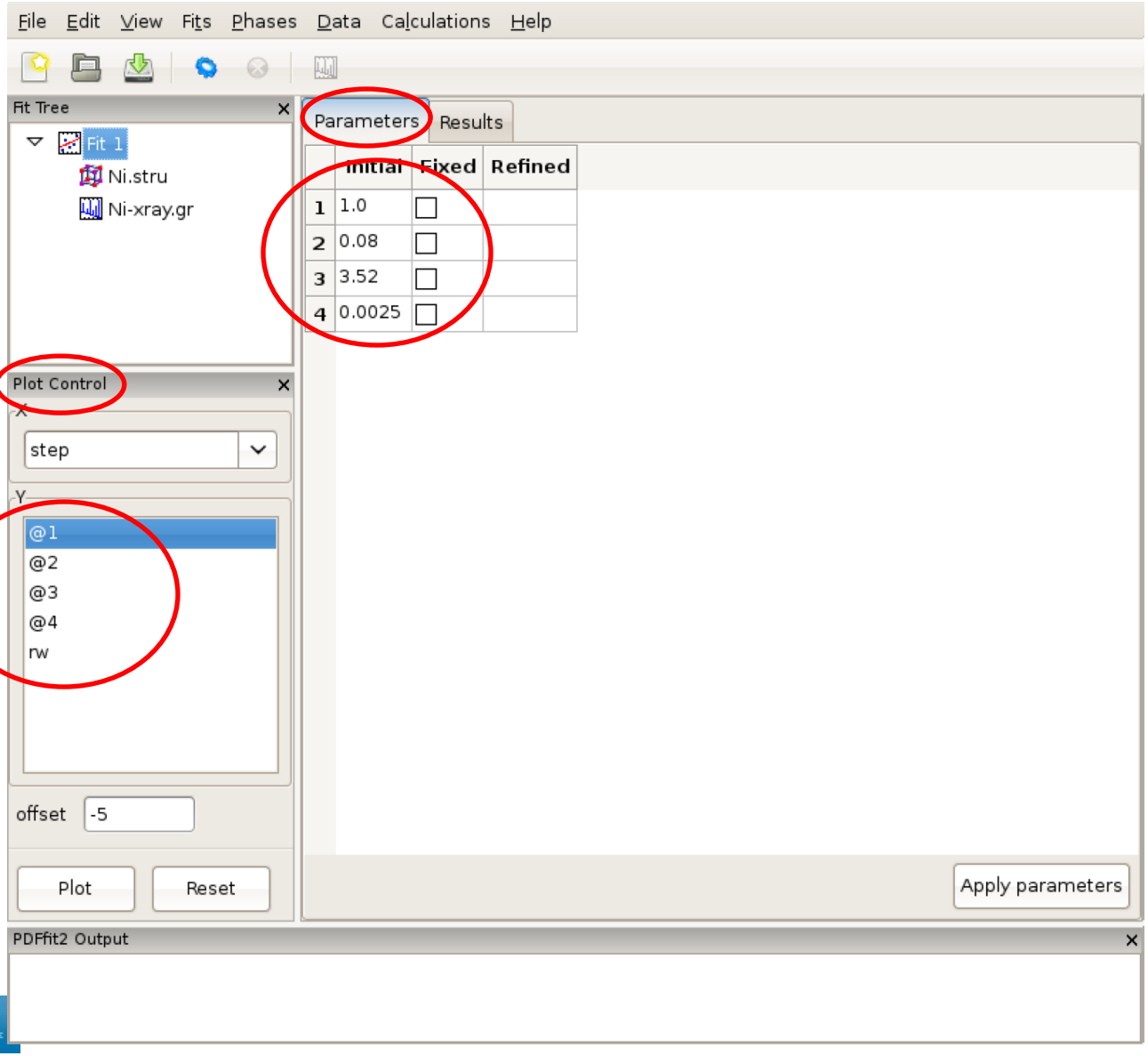
Creating a simple fit using a preexisting structure file

Setting up the refinement parameters and constraints: **model structure**



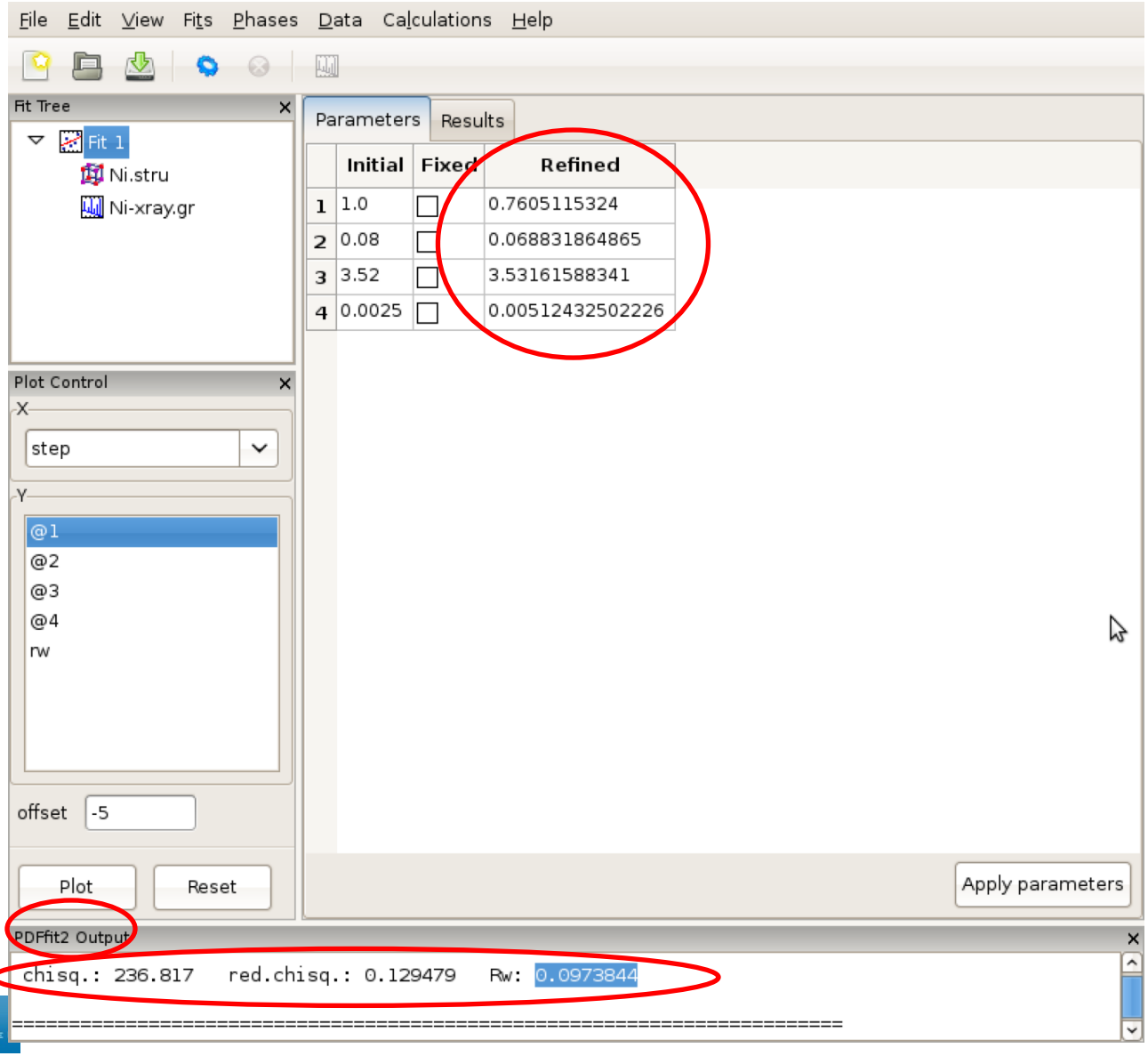
Creating a simple fit using a preexisting struct file

Reviewing the fit parameters and conditions



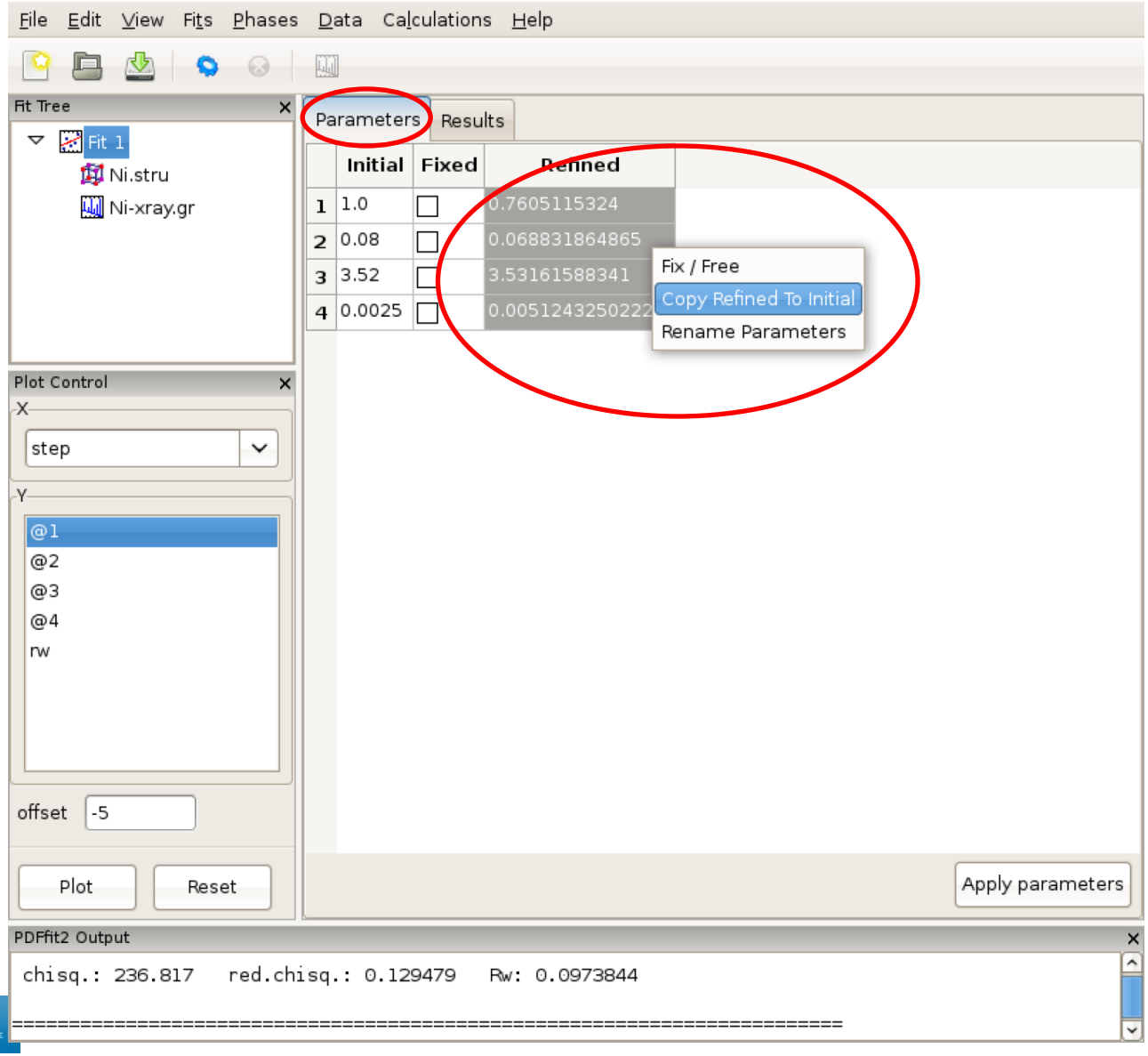
Creating a simple fit using a preexisting struct file

The refinement progress is displayed in the PDFfit2 Output panel.



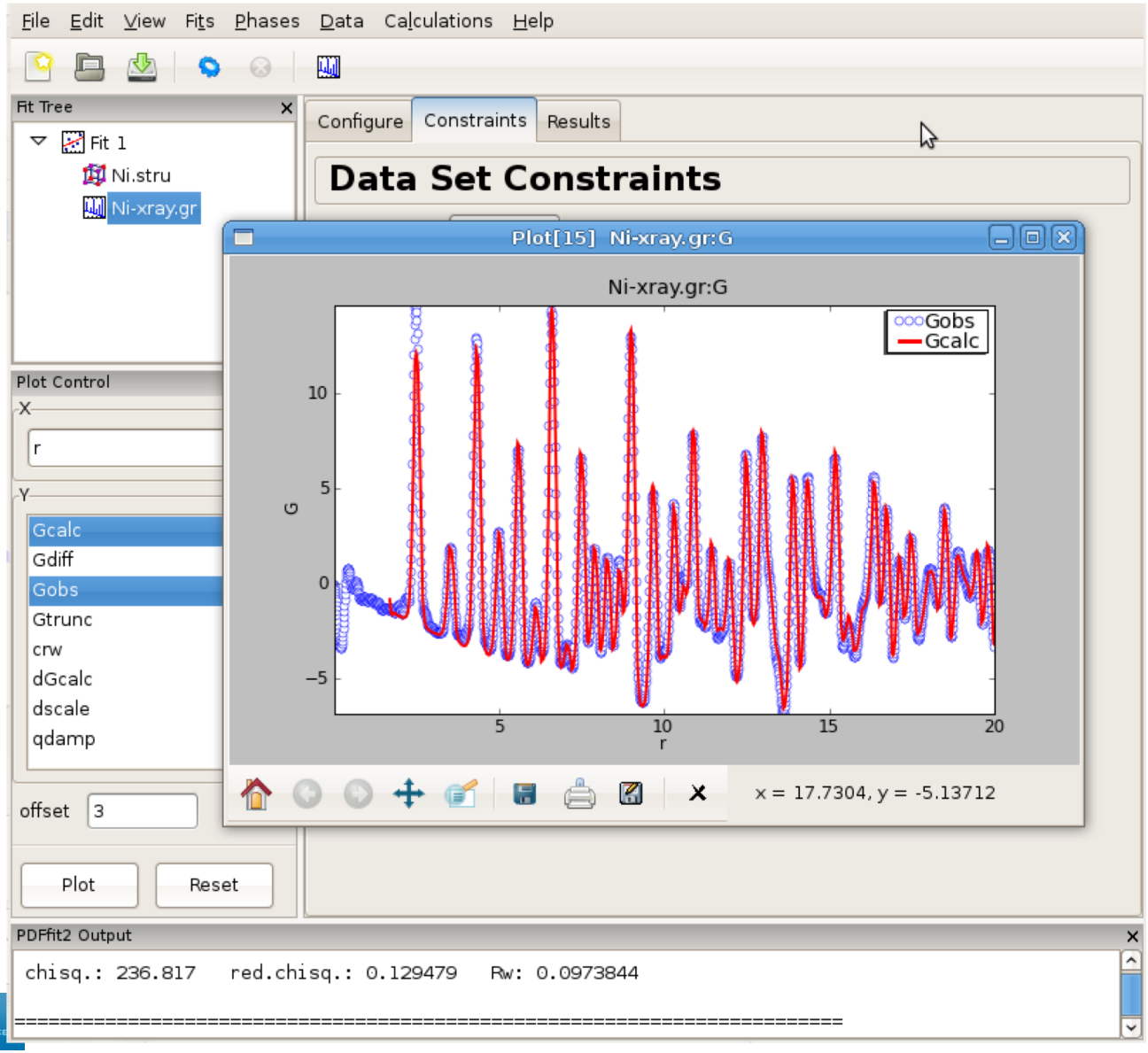
Creating a simple fit using a preexisting struct file

Updating the set of initial values of refined parameters.



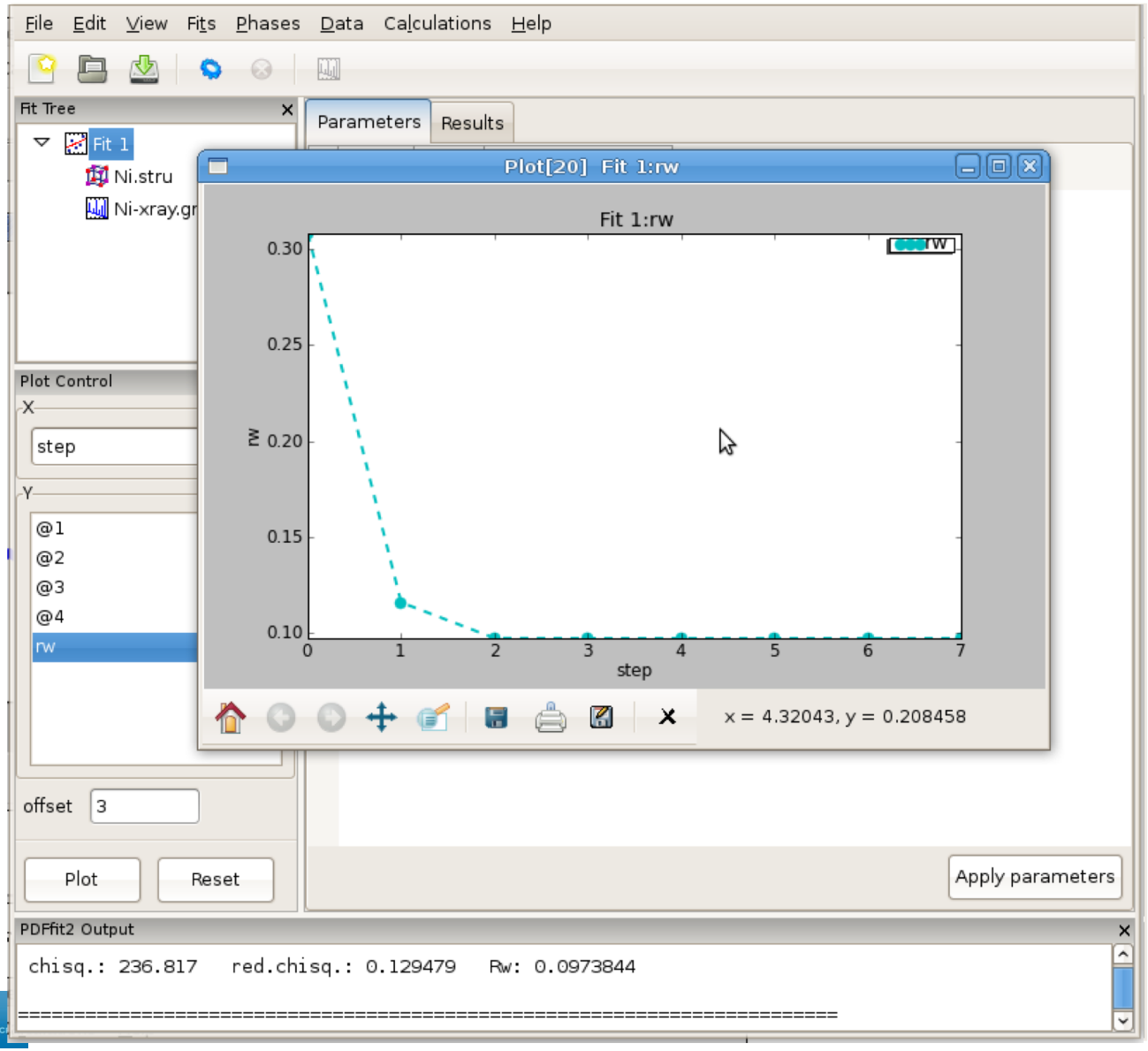
Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a fit.



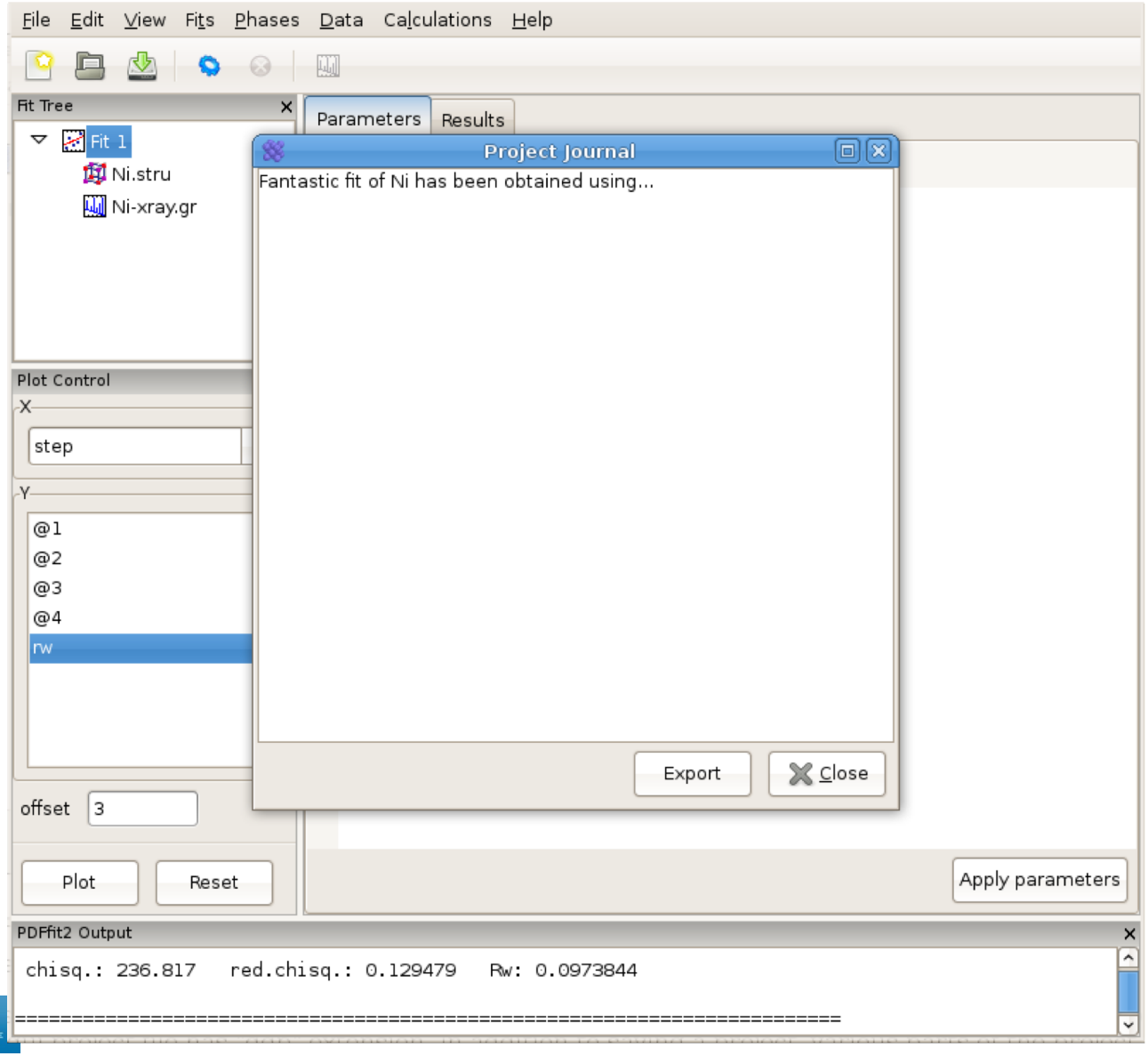
Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a parameter.



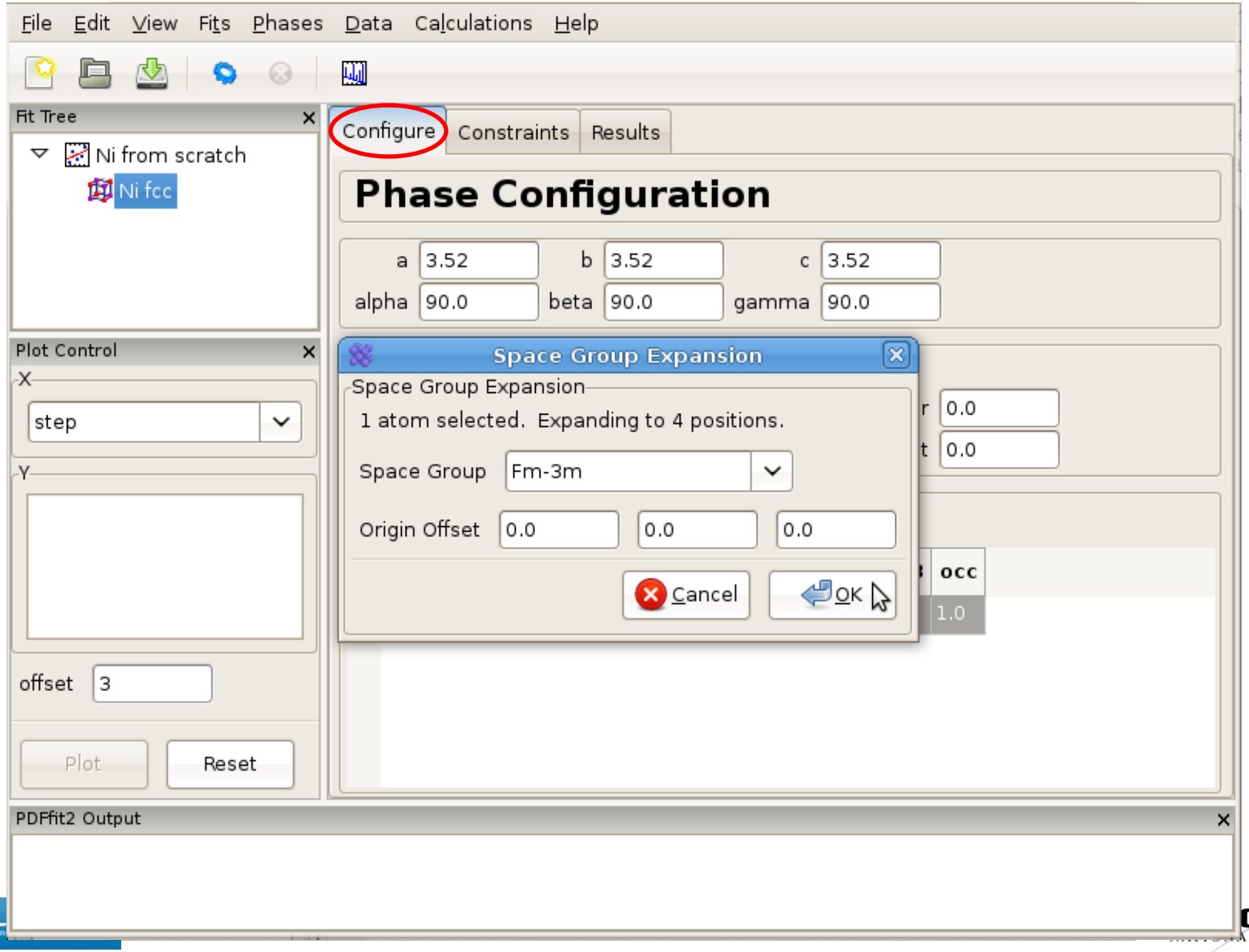
Creating a simple fit using a preexisting struct file

Using “Journal” facility can be a convenient way for taking notes.



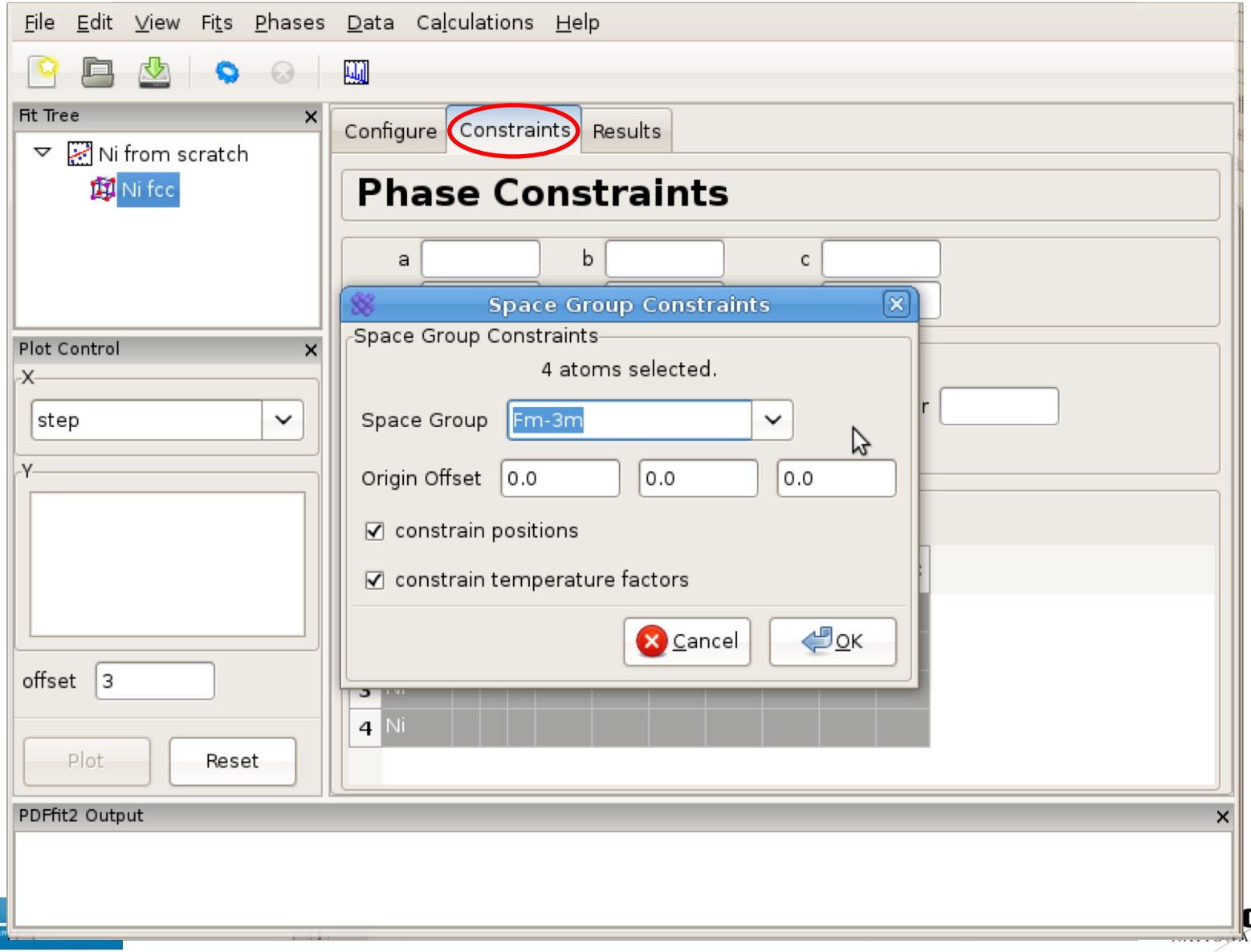
Building structure model using crystal symmetry

Expanding the **unit cell** using space group information.



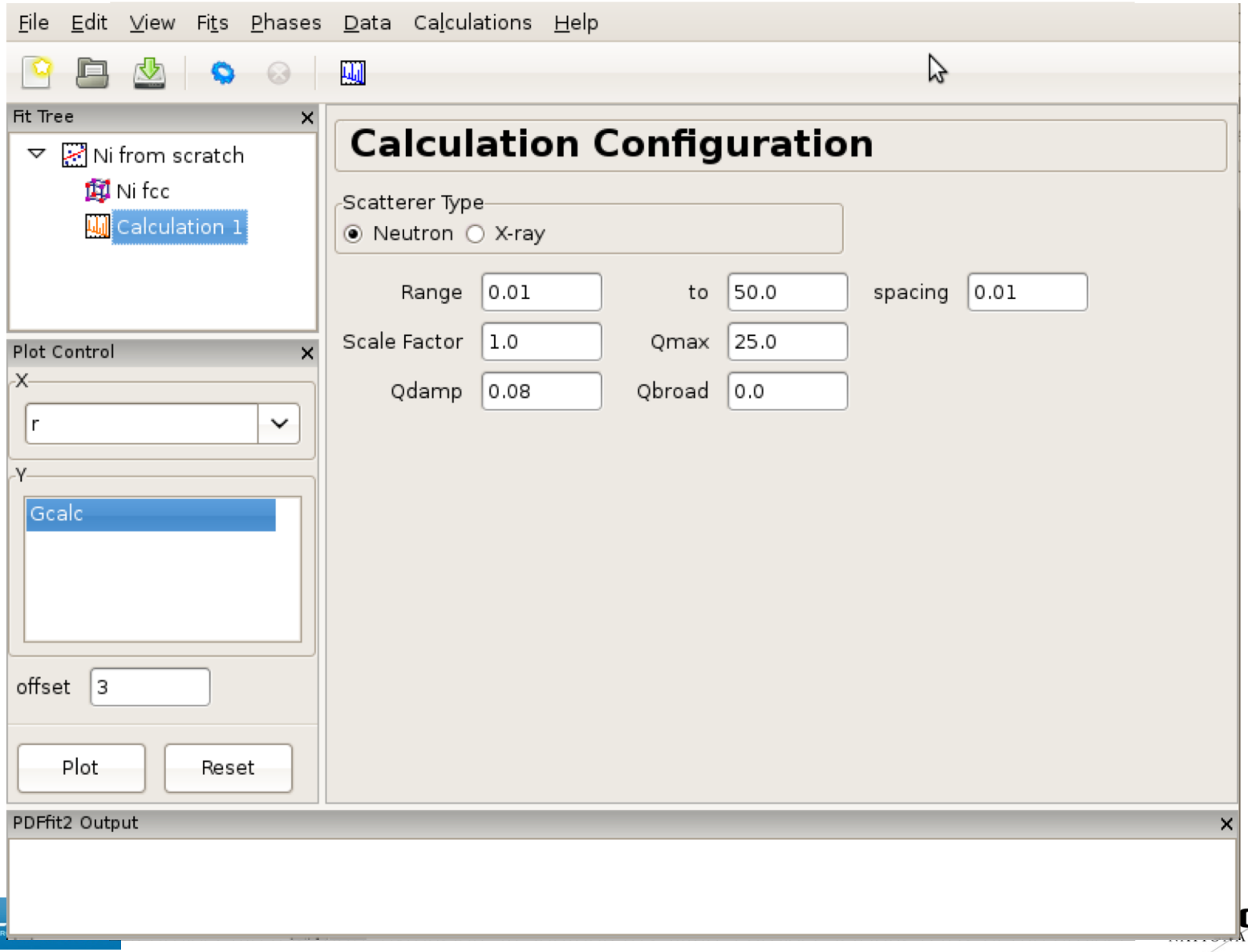
Building structure model using crystal symmetry

Setting up **symmetry constraints** to be used in a refinement.



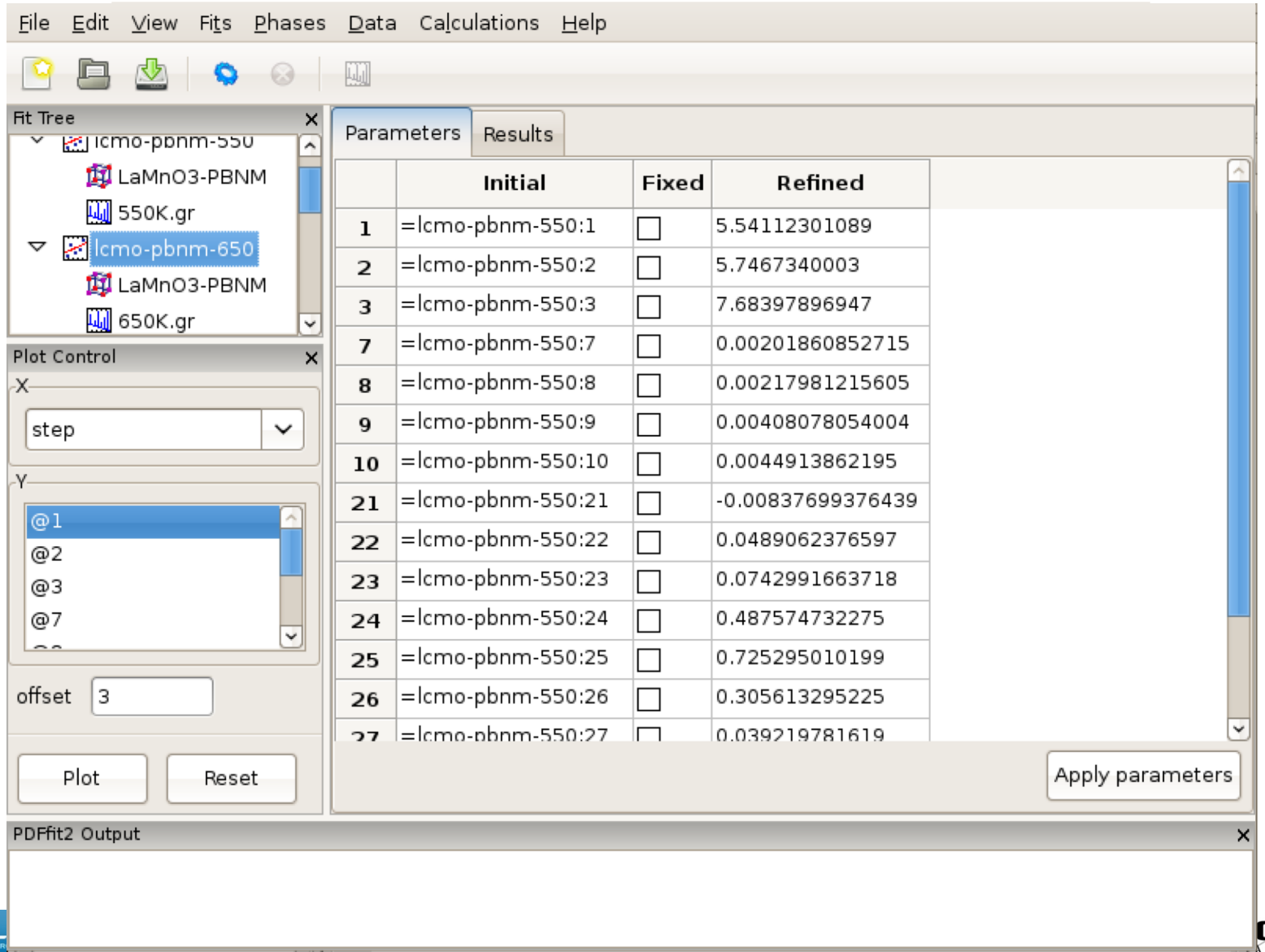
Calculating PDF from a structure

An example of the calculation configuration panel.



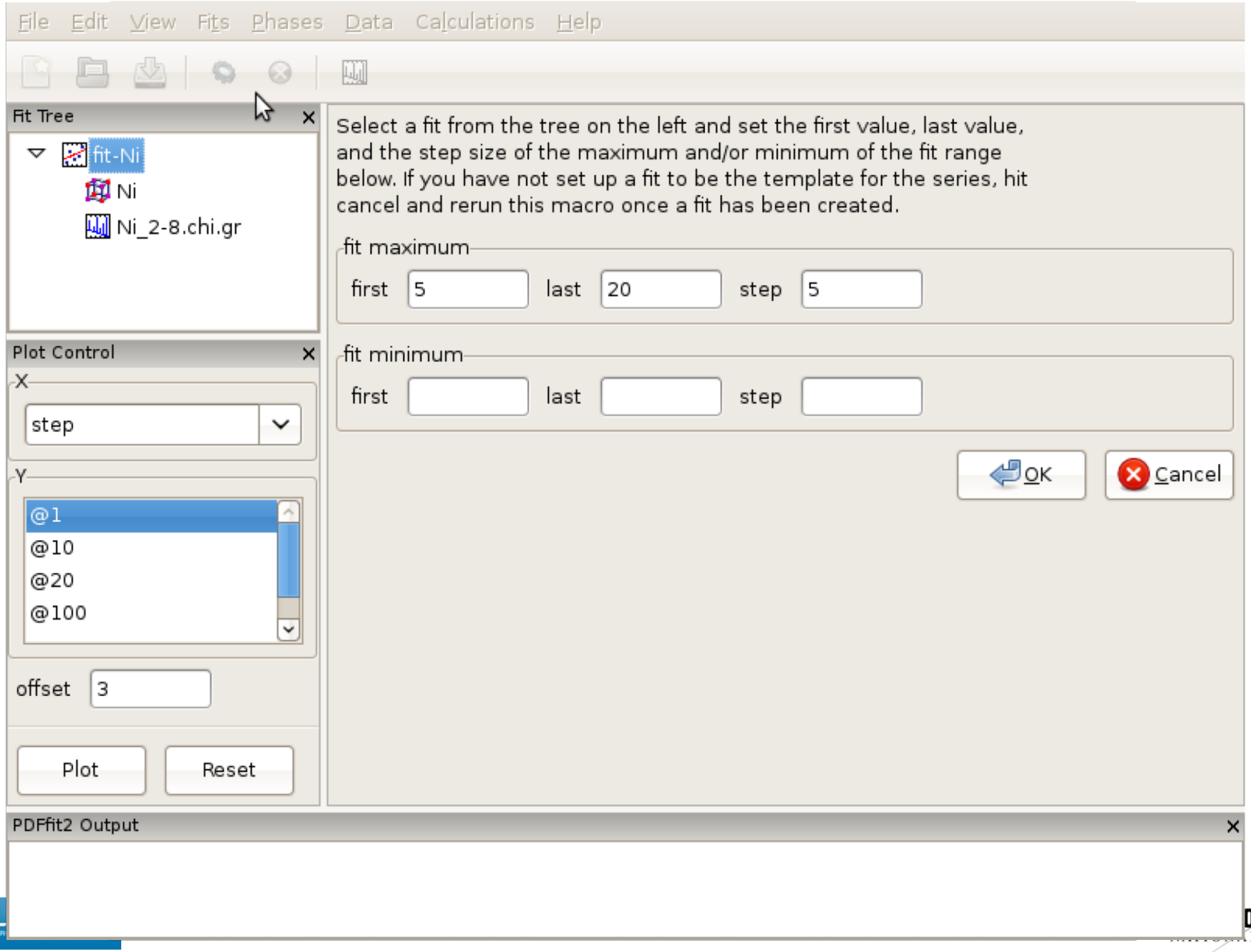
Multistage fitting

Sequential refinement where fits are chronologically linked



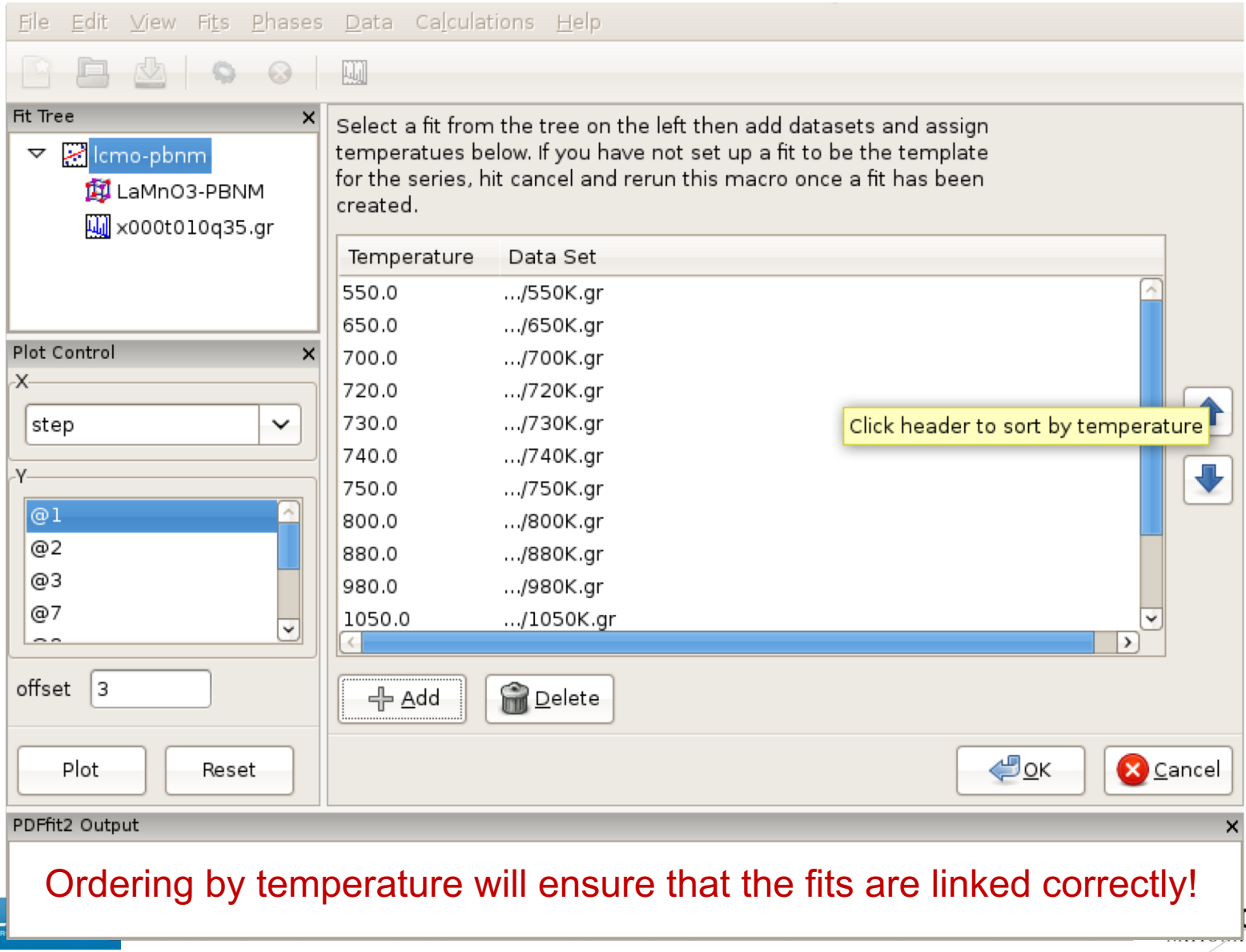
Sequential fitting of incremental r-series

Appearance of the setup panel for specifying an incremental r-series fit conditions.



Sequential fitting of temperature series

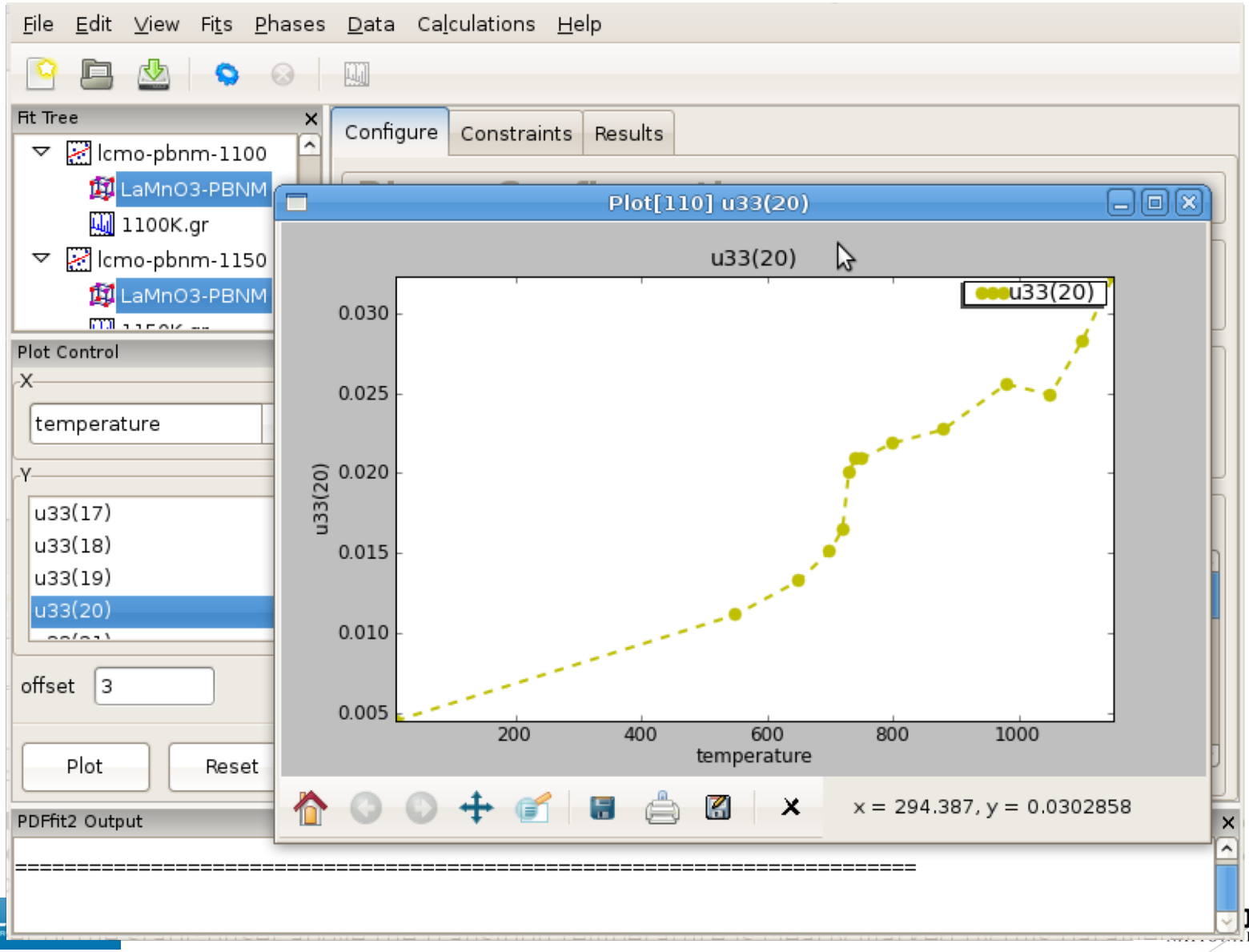
Setting up a T-series sequential refinement for $LaMnO_3$.



Ordering by temperature will ensure that the fits are linked correctly!

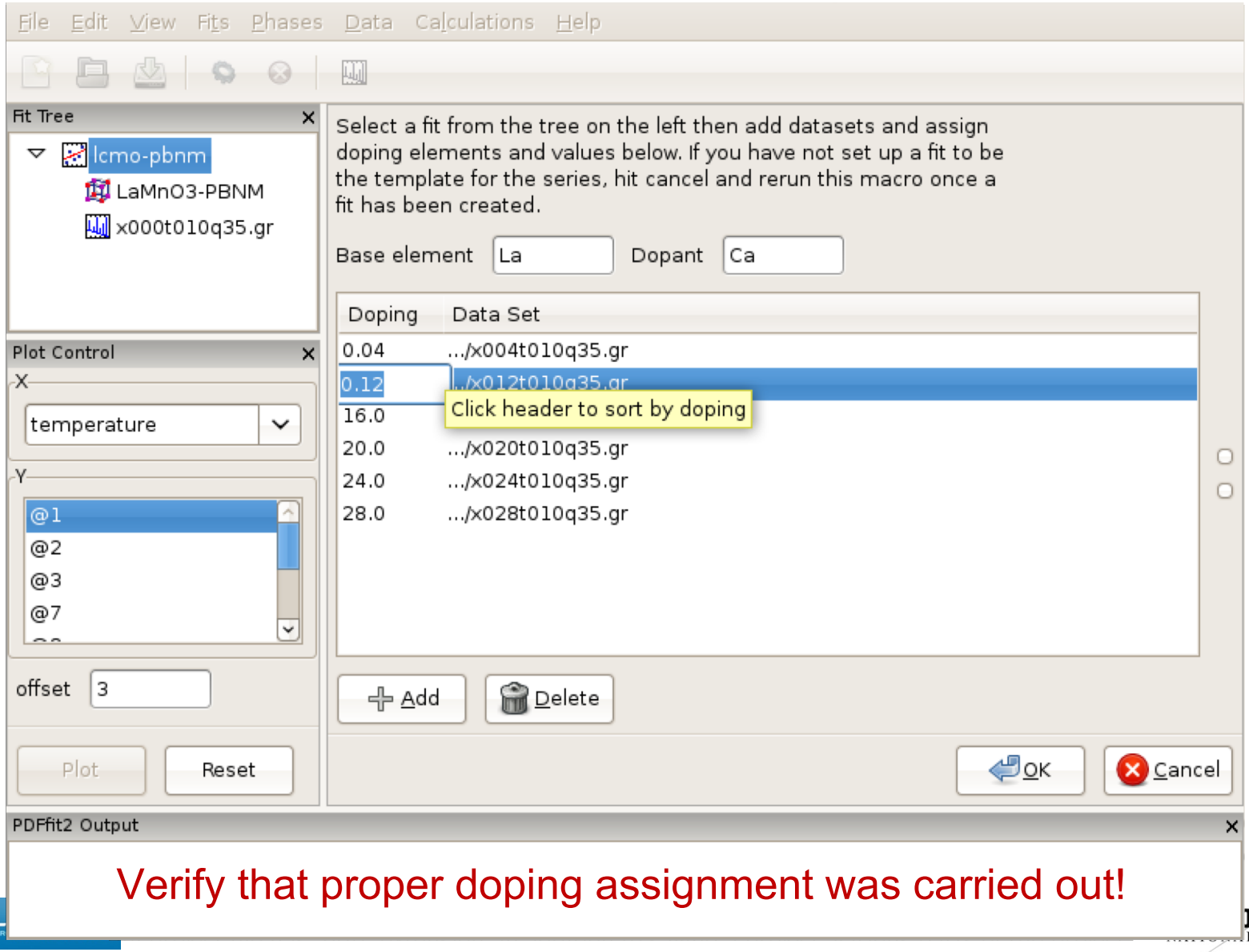
Sequential fitting of temperature series

Displaying refinement results as a function of external parameter: T-series refinement



Sequential fitting of doping series

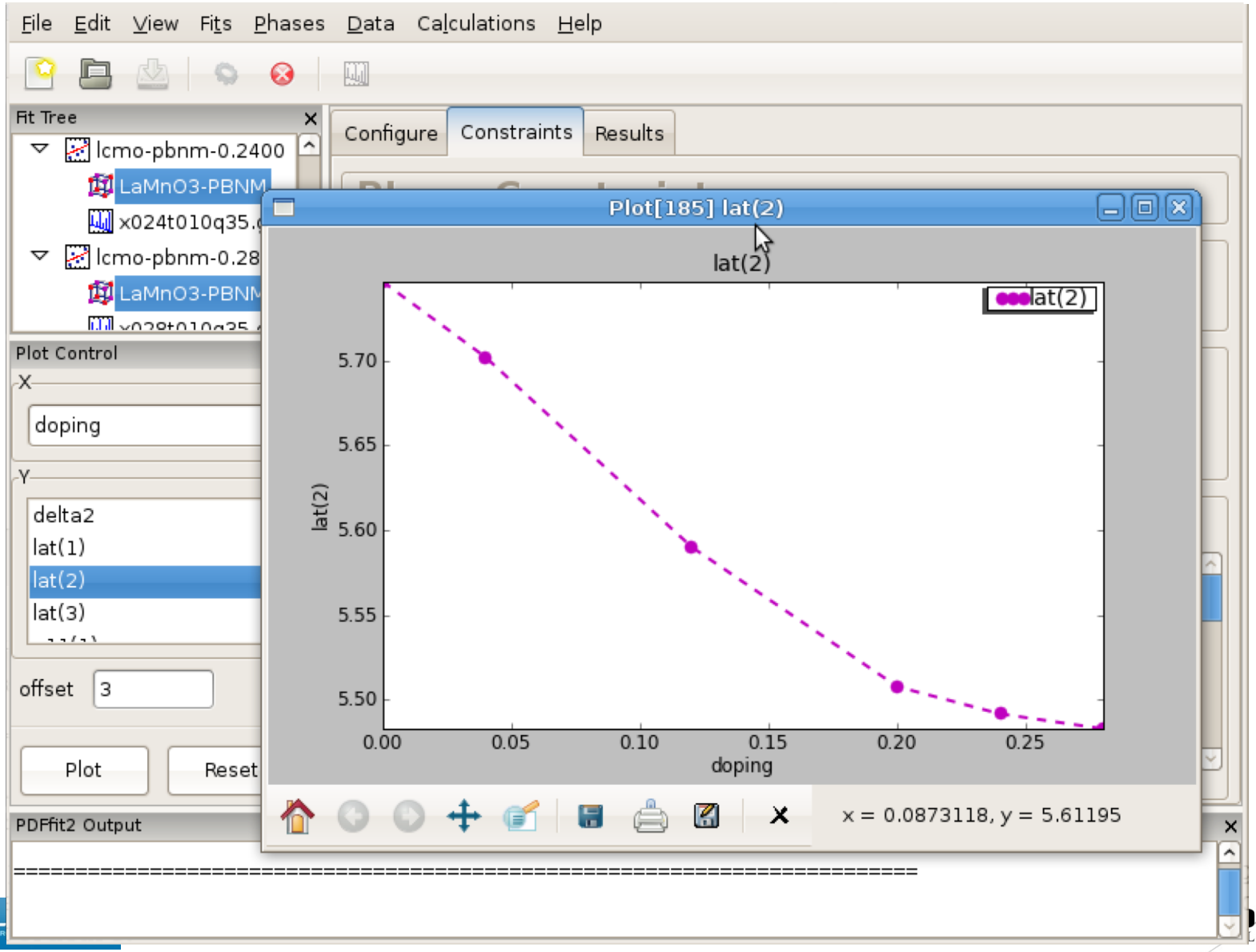
Loading of the Ca-doping data series of $LaMnO_3$ system.



Verify that proper doping assignment was carried out!

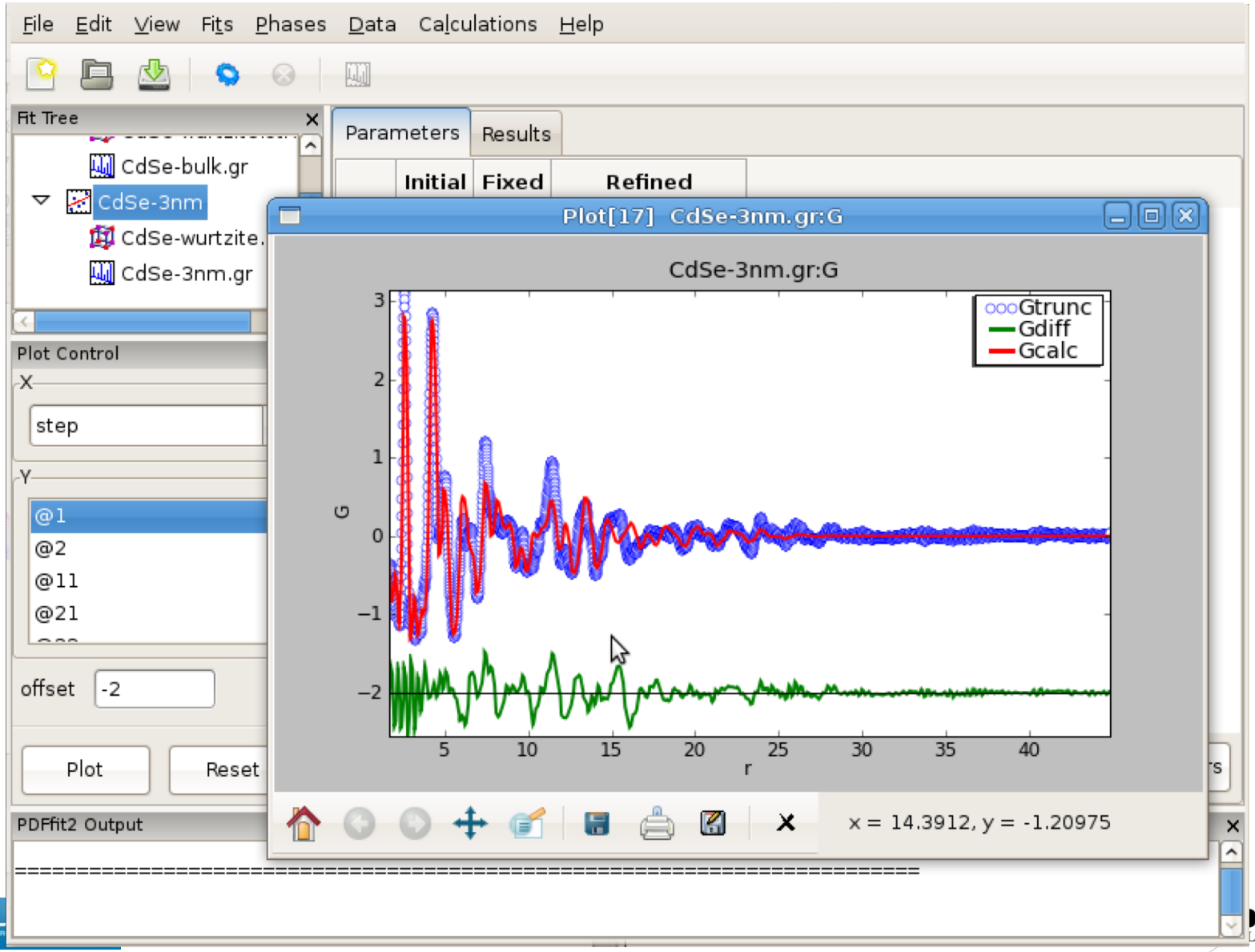
Sequential fitting of doping series

Displaying refinement results as a function of external parameter: doping series



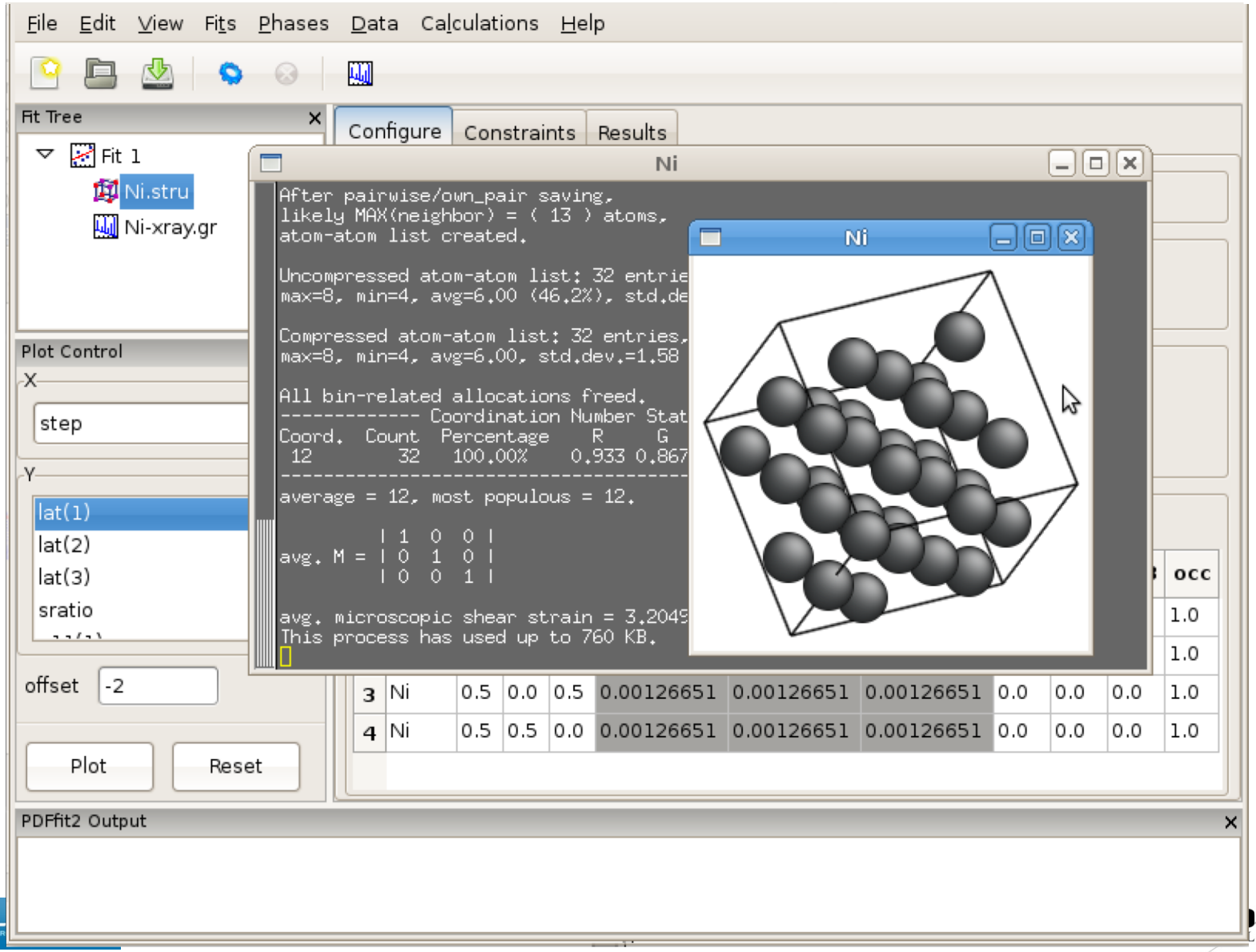
Nanoparticle structure: spherical!

Fitting the structure of a nanoparticle: 3nm CdSe nanoparticle example



Displaying the structure

Using AtomEye functionality for 3D visualization of the initial and refined PDF structures



PDFgui tutorial content & agenda

- Plan is to cover different examples featuring various aspects of PDFgui functionality
- GOALS:
  - becoming familiar and comfortable with the program
  - building up basic expertise and awareness of various PDFgui capabilities
  - Exploring a few more complex examples
- Examples:
  - Simulating PDFs
  - Ni X-ray and neutron data refinement
  - Ni neutron-Xray corefinement
  - Ni/Si mixture refinement; phase analysis
  - Ni T-dependence sequential refinement

  - $LaMnO_3$ at 300 K - complex system
  - $LaMnO_3$ T-dependence sequential refinement
  - $LaMnO_3$ at 800 K r-dependent sequential refinement
  - La_2CuO_4 composition/doping-dependence sequential refinement