PDFgui – a small box modelling platform for nanoscale structure analysis

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EPN campus, Grenoble, 17-22 March 2019

March 18, 2019

A reflection on PDFgui usage

Use the checkboxes to remove individual items from this Citation Report

or restrict to items published between 1900 and 2019 Go

☐ 1. PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals

By: Farrow, C. L.; Juhas, P.; Liu, J. W.; et al.
Conference: 3rd Workshop on Reverse Monte Carlo Methods Location: Budapest, HUNGARY Date: SEP 28-30, 2006
JOURNAL OF PHYSICS-CONDENSED MATTER Volume: 19 Issue: 33 Article Number: 335219 Published: AUG 22 2007

☐ 2. PDFgetX3: a rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions

By: Juhas, P.; Davis, T.; Farrow, C. L.; et al.
JOURNAL OF APPLIED CRYSTALLOGRAPHY Volume: 46 Pages: 560-566 Part: 2 Published: APR 2013

	2015	2016	2017	2018	2019	Total	Average Citations per Year
	200	217	198	268	43	1506	125.50
1.	83	93	81	119	14	723	55.62
2.	42	50	57	68	15	267	38.14

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

ADD 2019

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PDF approach

- Choosing the right tool for the problem

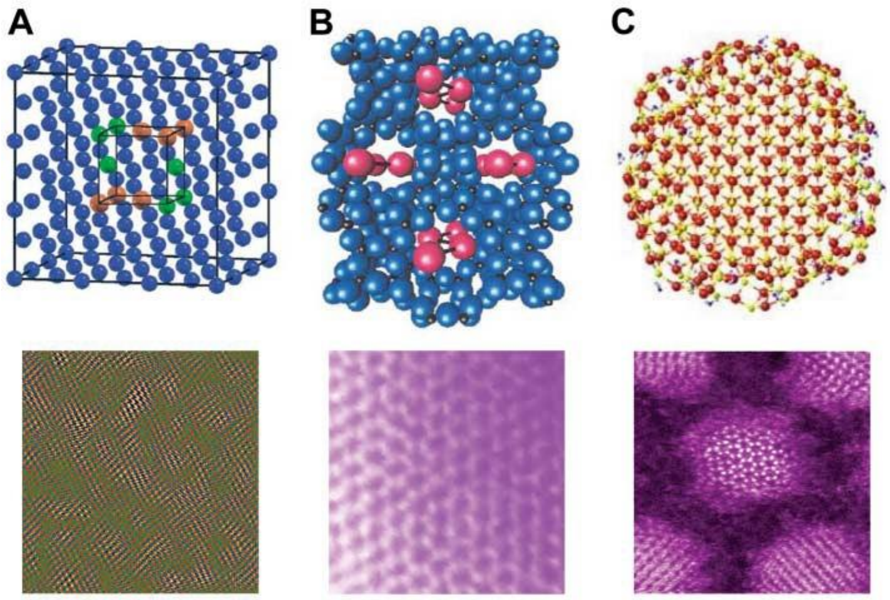
PDF approach

- Non crystalline materials

(liquids, amorphous solids, polymers)

- Nanoscale materials

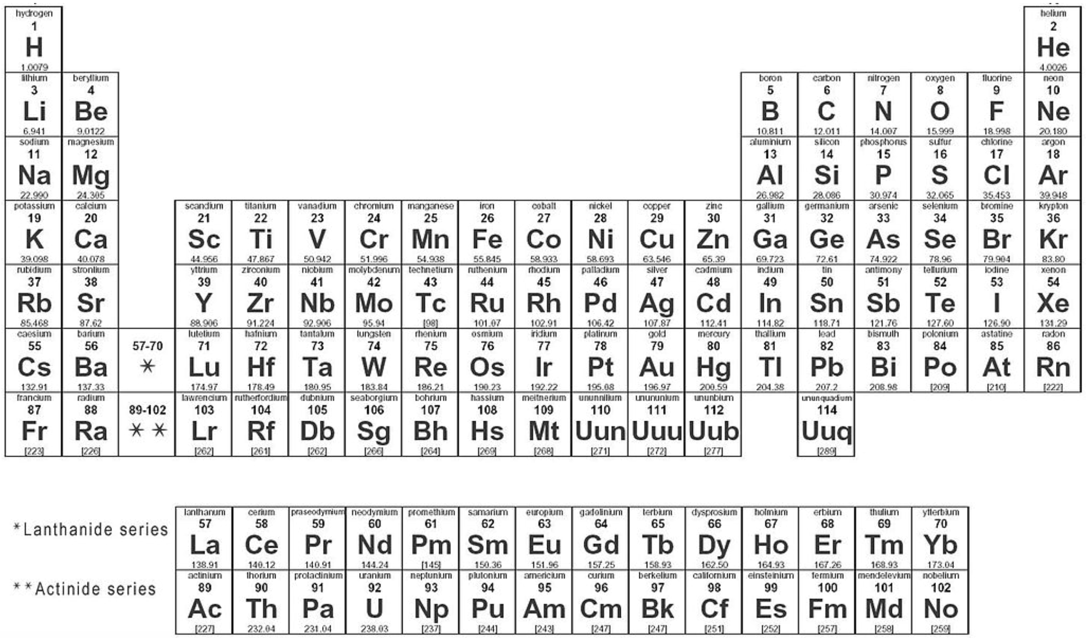
- Disordered crystalline systems with nanoscale heterogeneities

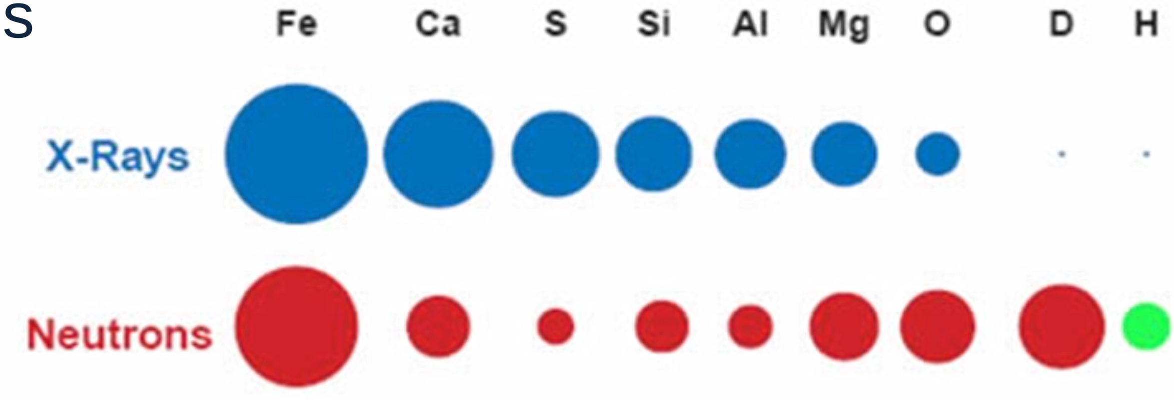


S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

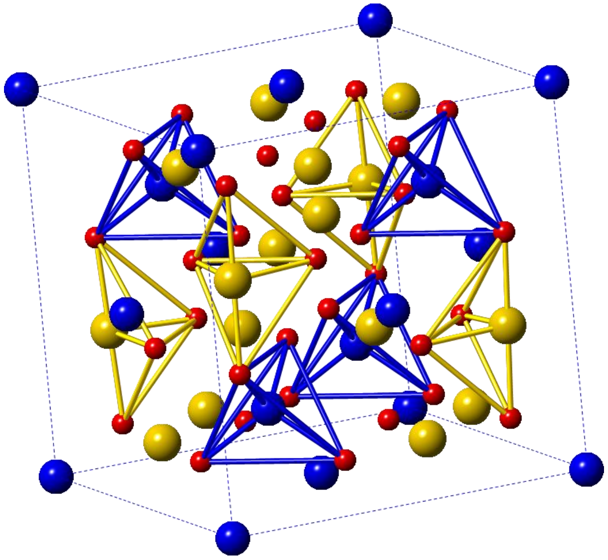
PDF approach

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





PDF recap

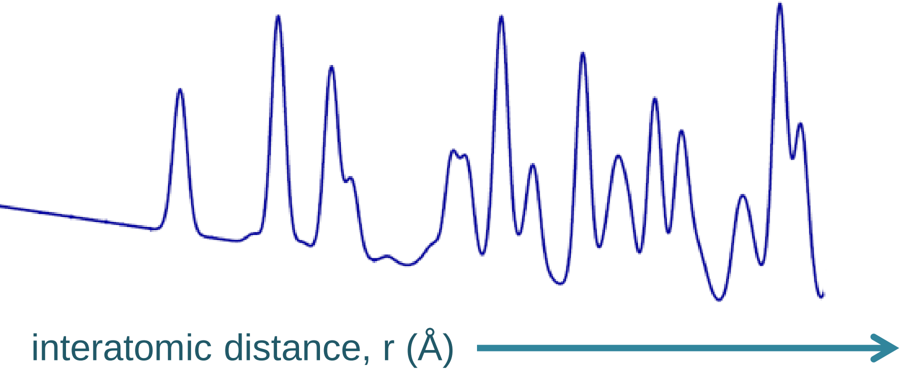


$$I_{tot} = I_{sam} + I_{bgrd}$$

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

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

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



Raw data

Data reduction

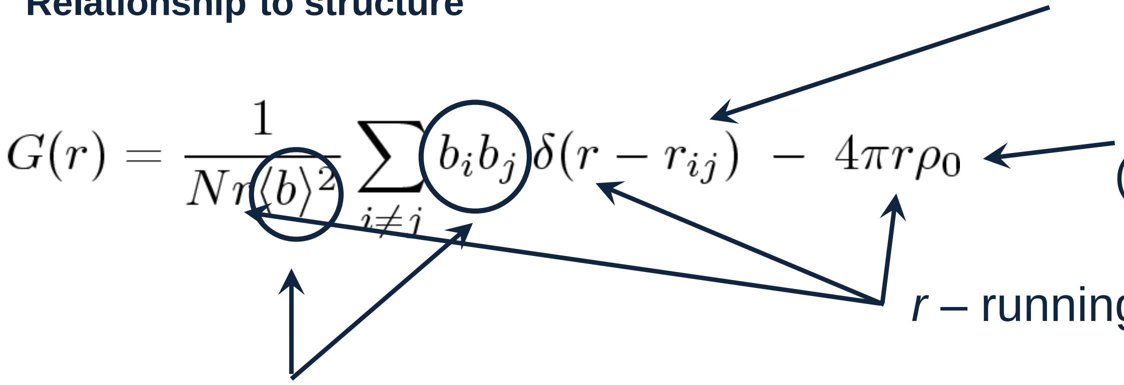
PDF

Relationship to structure

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

Atomic PDF skeleton

Relationship to structure



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

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

$\rho_o=N/V$ 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

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

$$G(r)=\frac{2}{\pi}\int_{\cancel{0}\;Q_{MIN}}^{\cancel{\infty}\;Q_{MAX}}Q\,(S(Q)-1)\sin Qr\,\mathrm{d}Q$$

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

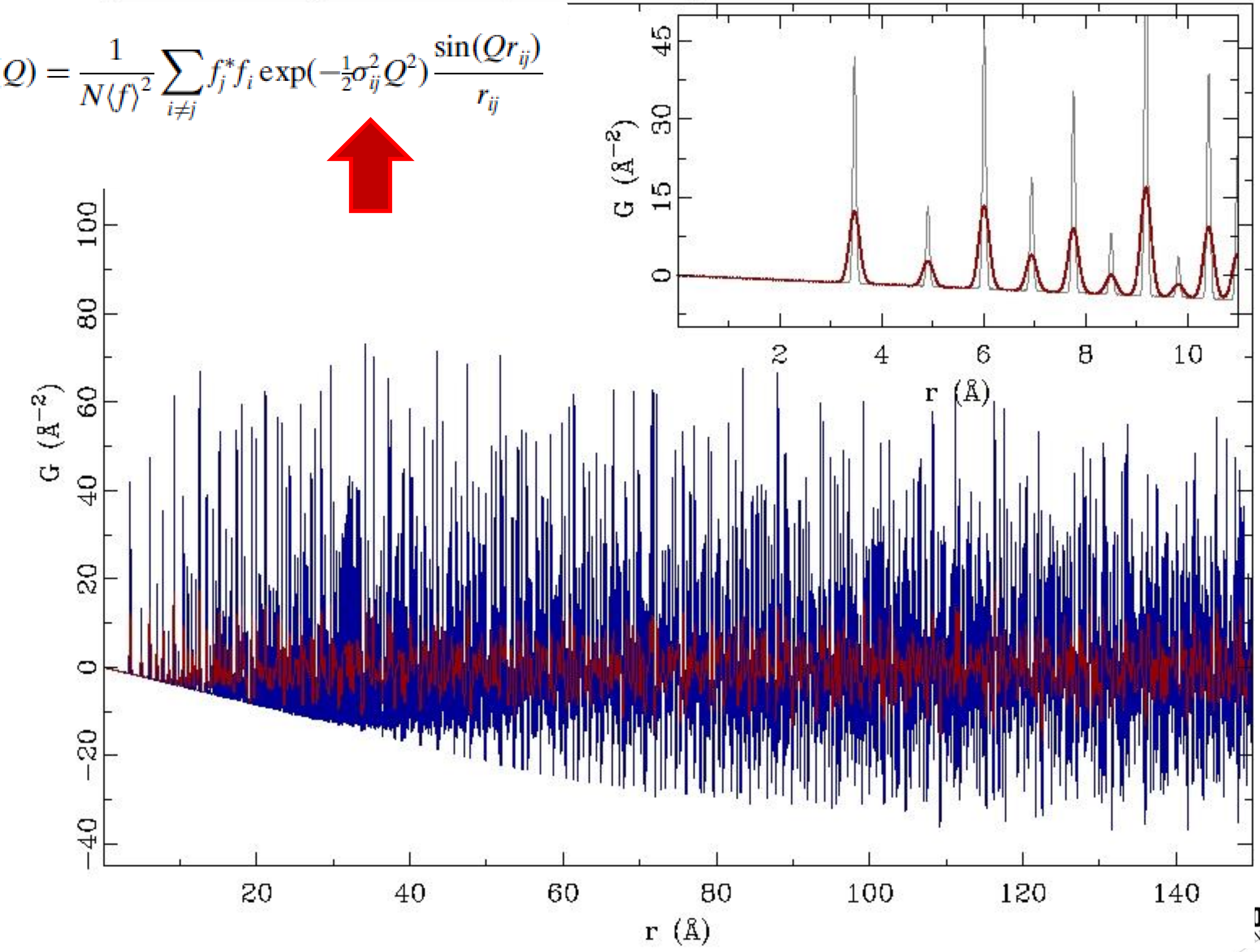
Some effects that should be accounted for

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

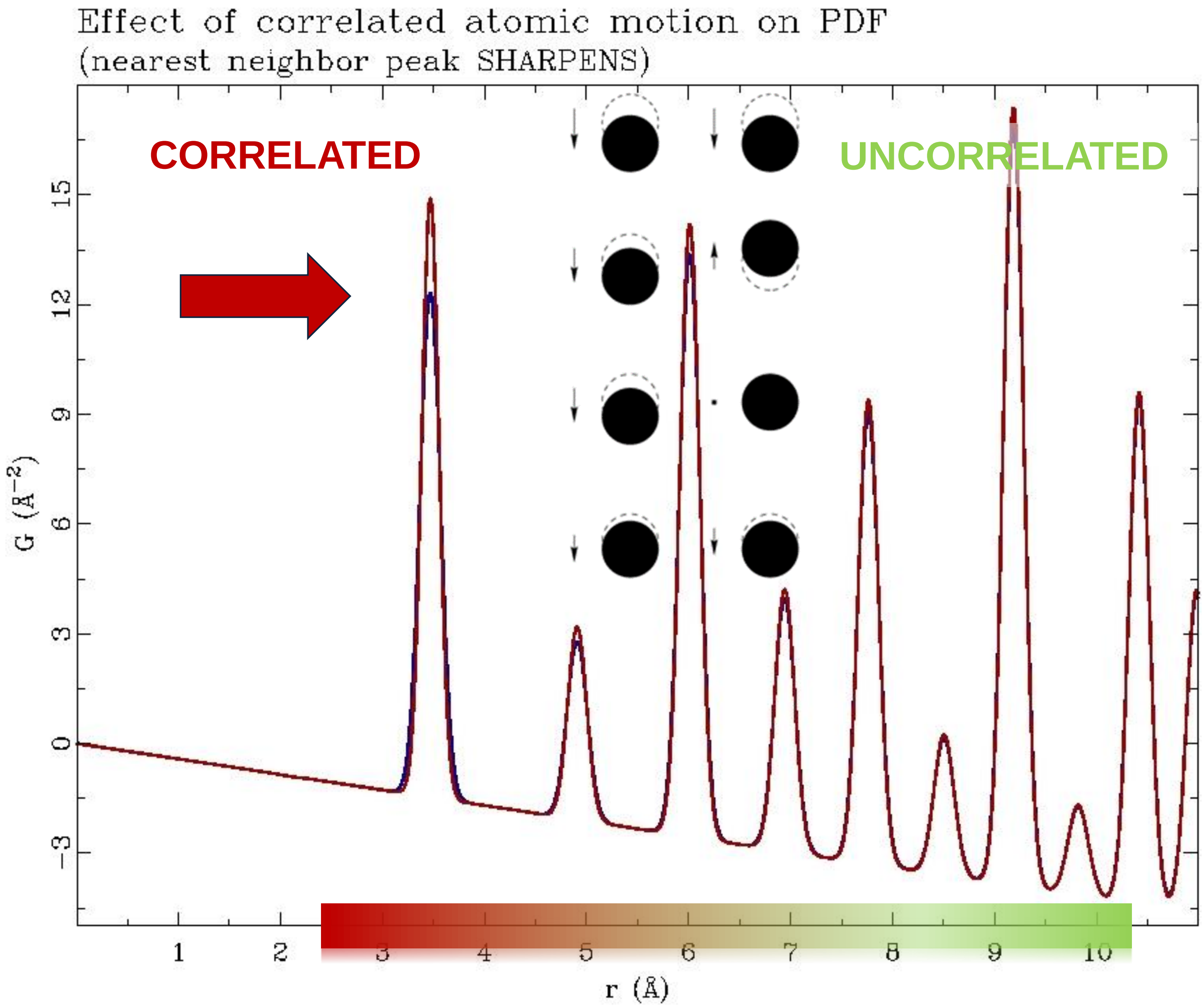
PDF: effect of thermal broadening

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

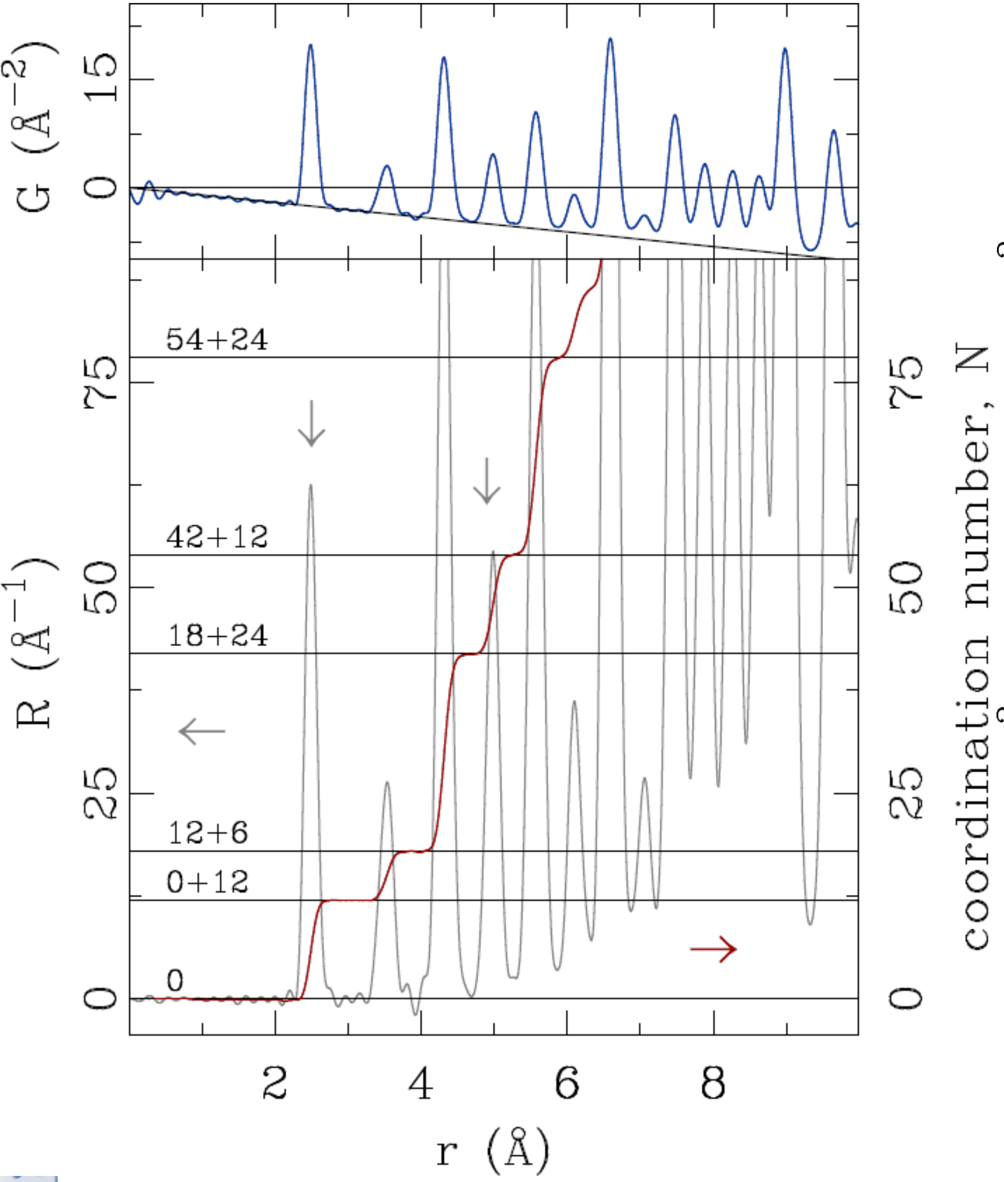
$$F(Q) = \frac{1}{N\langle f\rangle^2}\sum_{i\neq j} f_j^* f_i \exp(-\tfrac{1}{2}\sigma_{ij}^2 Q^2)\frac{\sin(Qr_{ij})}{r_{ij}}$$

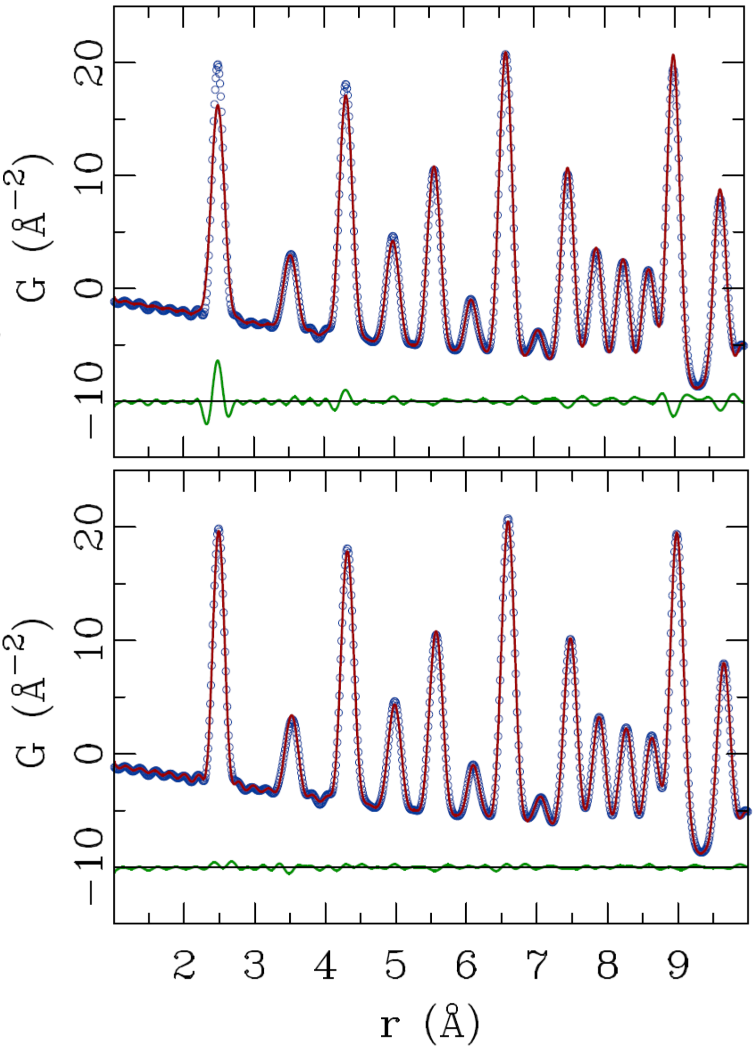


PDF: effect of correlated atomic motion



PDF: effect of correlated atomic motion

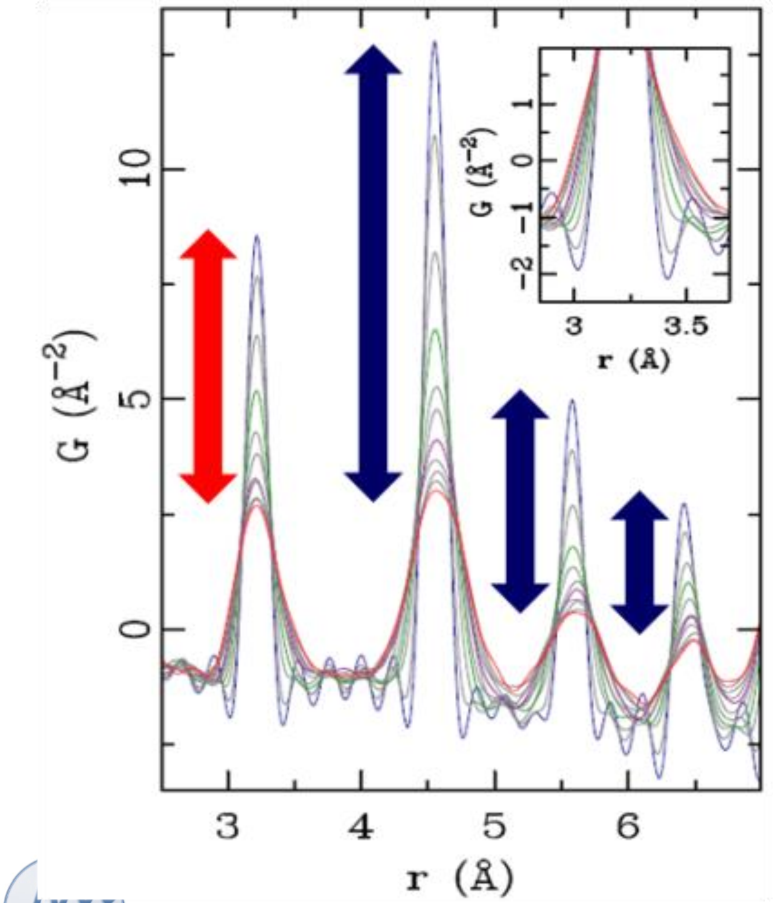




PDF: correlated atomic motion outlaws

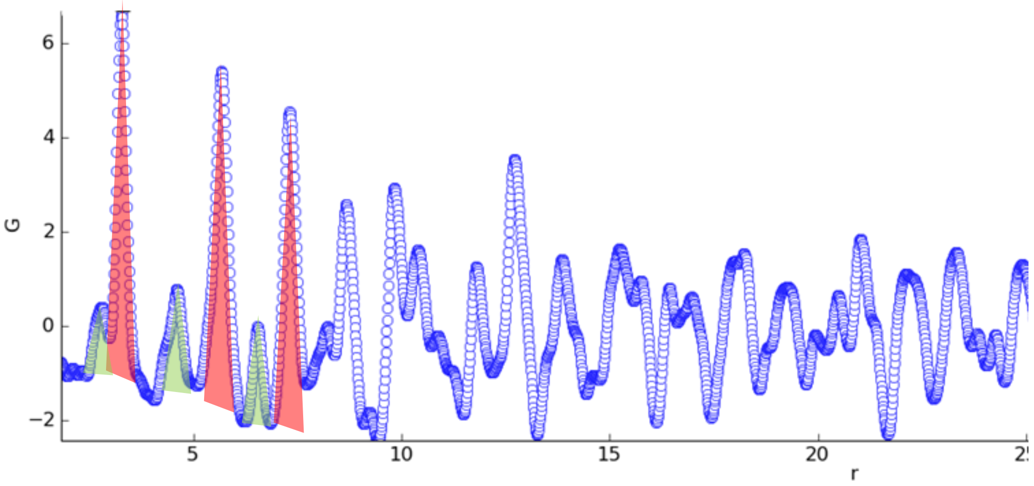
Weak effects
(e.g. PbTe)

break the rule



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

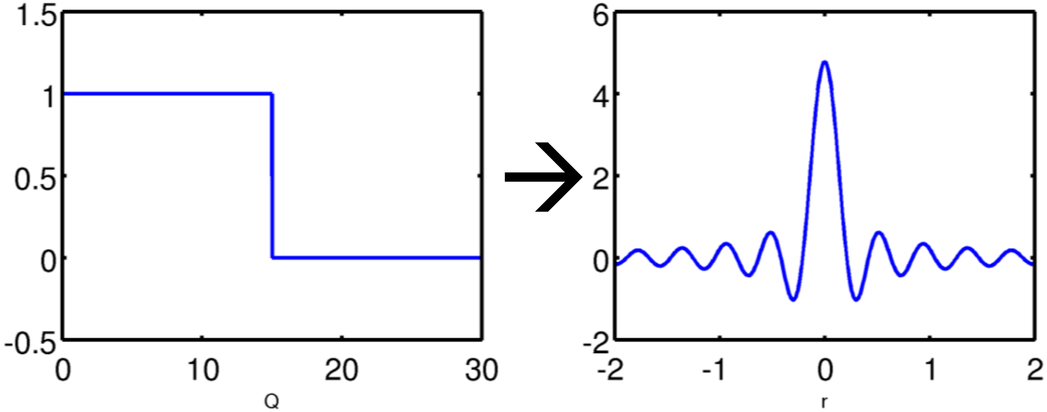
difficult to model



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

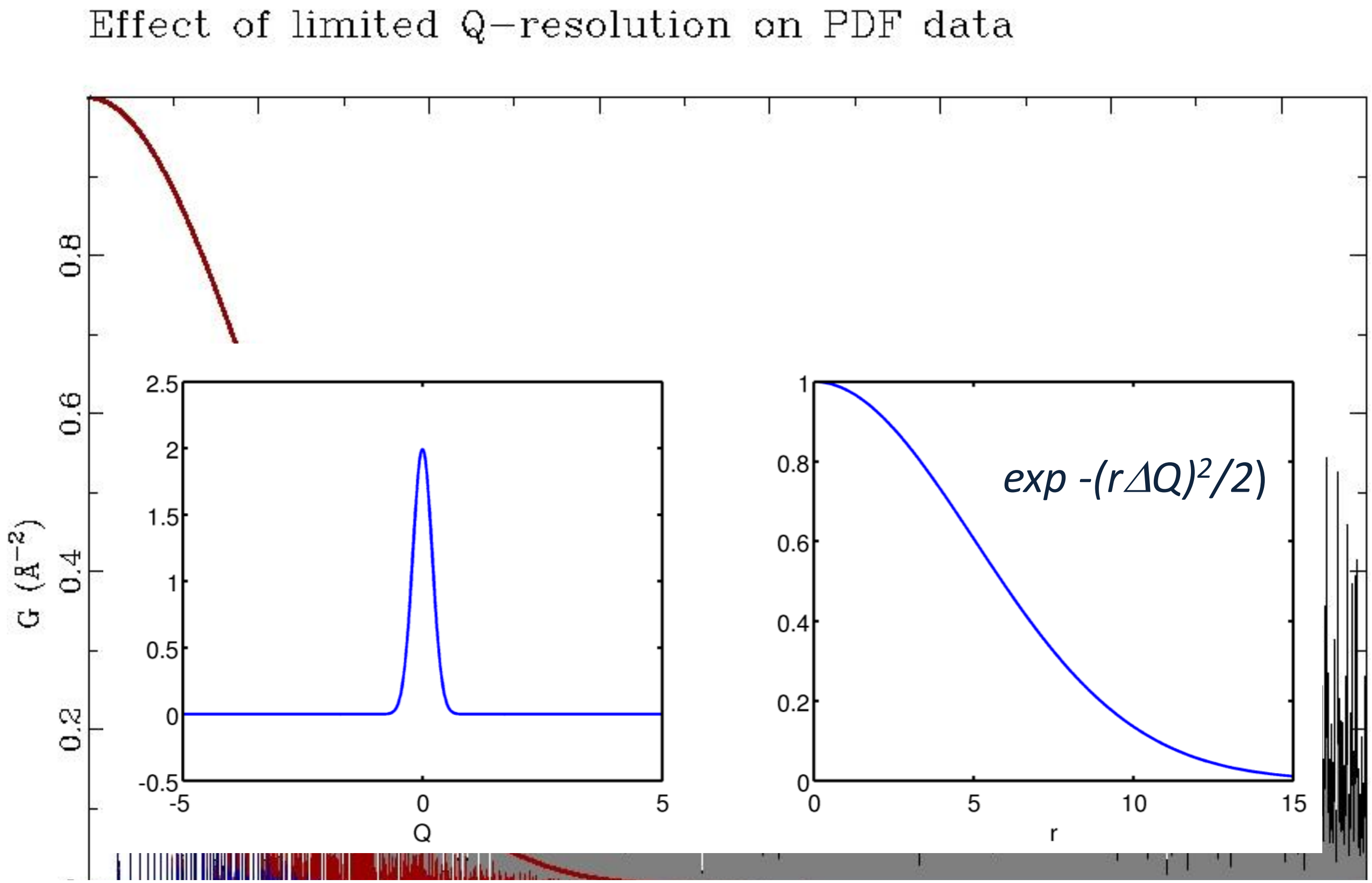
Effects from finite Q-range

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



- 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

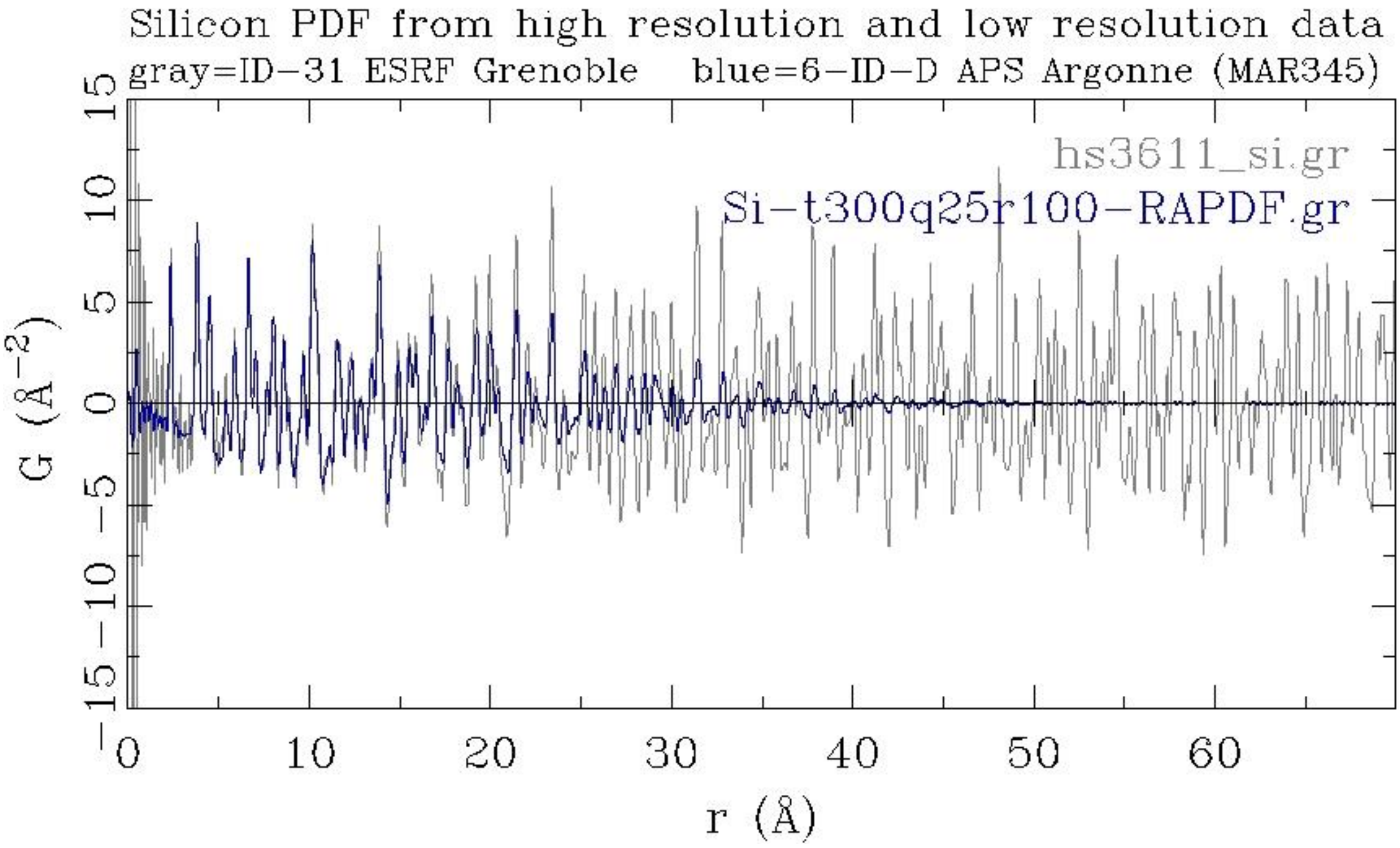
PDF: effect of the Q-space resolution



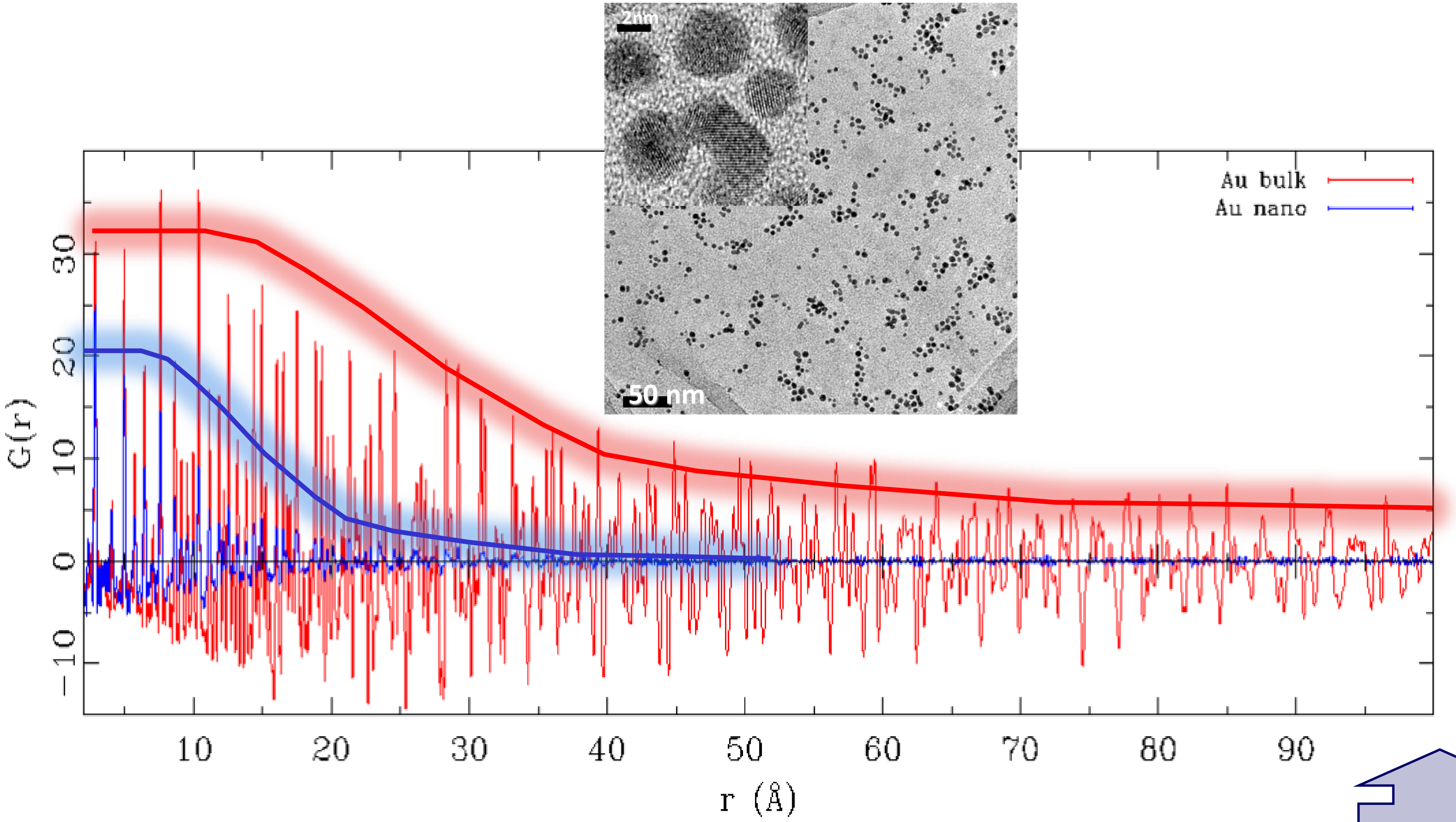
- ideal F(Q) is convoluted by Gaussian to simulate finite Q resolution
- *G(r)* gets multiplied by real-space Gaussian with reciprocal width
- For *G(r)* to have good *r*-range high resolution in *Q* is required

*Q-resolution defines PDF “**field of view**”*

PDF: effect of the Q-space resolution



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



100Å

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

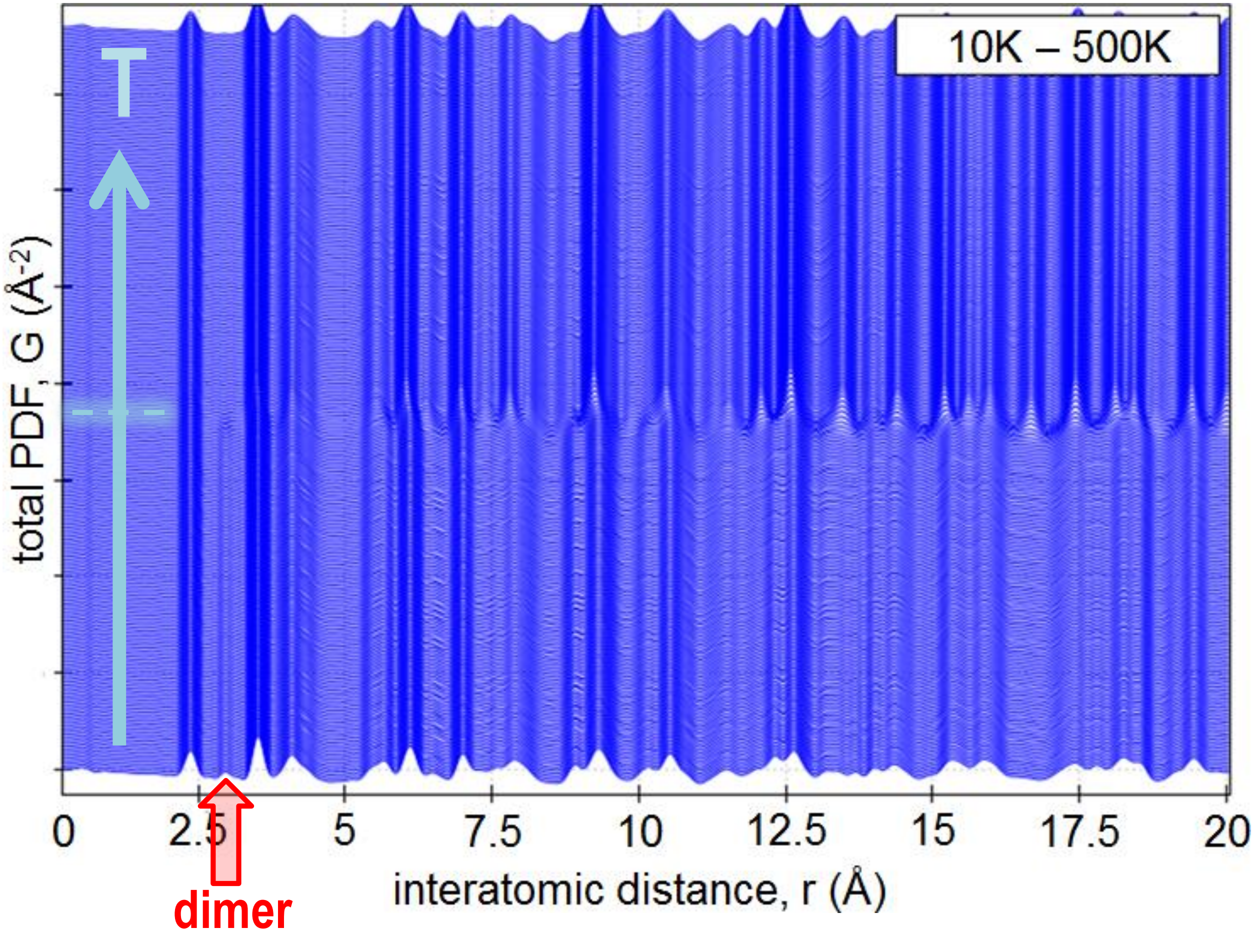
K.L. Page *et al*., *Chem. Phys. Lett.* **393**, 385 (2004).

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

Observing raw PDF: disappearance of dimers



Structure of Mystery compound 2 changes on all length scales on warming

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

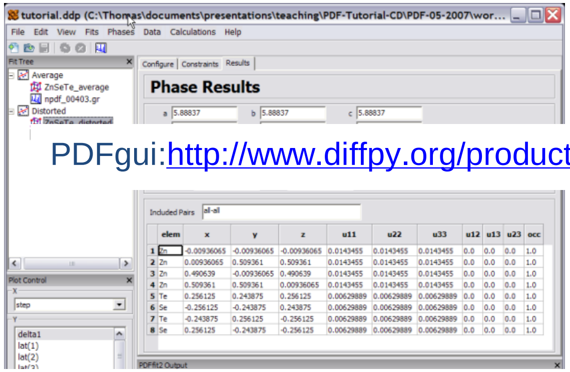
20000 + atoms
Fit X-ray and neutron *F(Q), G(r)* , Bragg profile
Constraints utilized
Static 3-D model of the structure (a snap-shot)

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



Phase Results

a 5.88837 b 5.88837 c 5.88837

Included Pairs all-all

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Zn	-0.00936065	-0.00936065	-0.00936065	0.0143455	0.0143455	0.0143455	0.0	0.0	0.0	1.0
2	Zn	0.00936065	0.509361	0.509361	0.0143455	0.0143455	0.0143455	0.0	0.0	0.0	1.0
3	Zn	0.490639	-0.00936065	0.490639	0.0143455	0.0143455	0.0143455	0.0	0.0	0.0	1.0
4	Zn	0.509361	0.509361	0.00936065	0.0143455	0.0143455	0.0143455	0.0	0.0	0.0	1.0
5	Te	0.256125	0.243875	0.256125	0.00629889	0.00629889	0.00629889	0.0	0.0	0.0	1.0
6	Se	-0.256125	-0.243875	0.243875	0.00629889	0.00629889	0.00629889	0.0	0.0	0.0	1.0
7	Te	-0.243875	0.256125	-0.256125	0.00629889	0.00629889	0.00629889	0.0	0.0	0.0	1.0
8	Se	0.256125	-0.243875	-0.256125	0.00629889	0.00629889	0.00629889	0.0	0.0	0.0	1.0

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

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

include symmetry operations, Monte Carlo simulation capabilities and the generation of domain structure to name just a few.

The second program is called PDFFIT. It is used for full profile refinements of the PDF based on an atomic structure. The program uses least squares and employs a very powerful way to implement constraints. Recently we have added a graphical users interface for simple refinements.

The next program is DIFFEV. This is a generic minimization program using an evolutionary algorithm. It is designed to work with the other programs in the package.

Finally the package contains a general plotting program called KUPLOT.

Thomas Proffen, Reinhard Neder and Simon Billinge

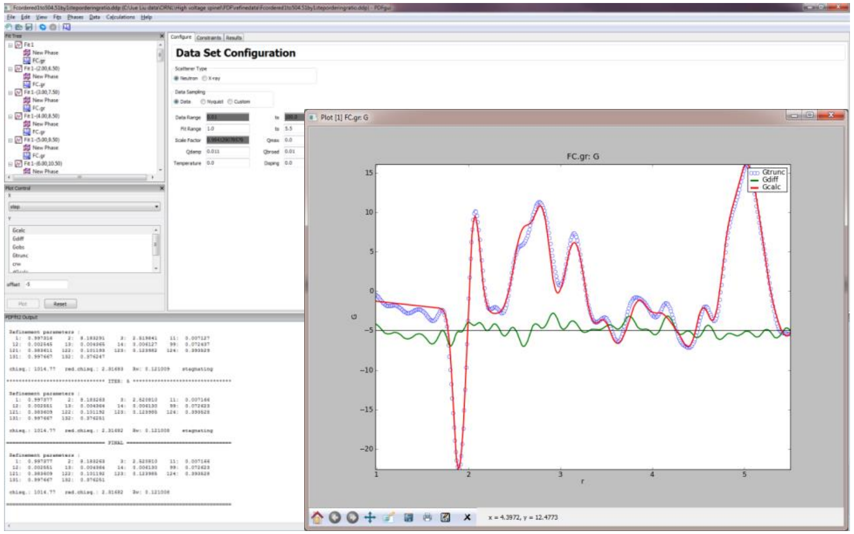
structure simulations, J. Appl. Crystallogr. 30, 171 (1997).

Th. Proffen and S. J. L. Billinge, PDFFIT a program for full profile structural refinement of the atomic pair distribution function, J. Appl. Crystallogr. 32, 572 (1999).

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

slide courtesy Katharine Page

“Small Box” software comparison



Data Set Configuration

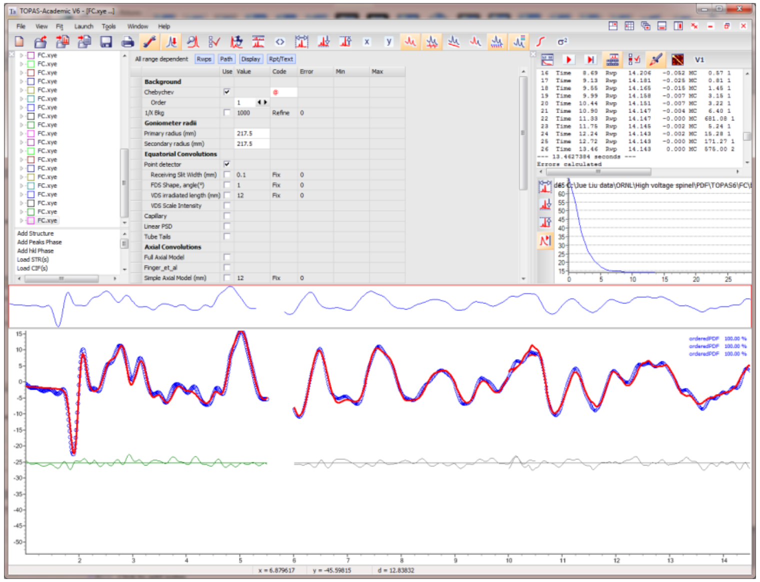
Scatterer Type: ● Neutron ○ X-ray

Data Sampling: ● Data ○ Nyquist ○ Custom

Fit Range: 1.0 to 5.5
Qmax: 0.0
Qdamp: 0.011
Qbroad: 0.01
Temperature: 0.0
Doping: 0.0
offset: -5

PDFgui http://www.diffpy.org/

- Slow refinement, e.g. for high-*r*
- Cumbersome outputs
+ Open Source and Free
+ GUI is Simple and User-friendly



	Use	Value	Code	Error	Min	Max
Background						
Chebychev	☑		@			
Order		1				
1/X Bkg	☐	1000	Refine	0		
Goniometer radii						
Primary radius (mm)		217.5				
Secondary radius (mm)		217.5				
Equatorial Convolutions						
Point detector	☑					
Receiving Slit Width (mm)	☐	0.1	Fix	0		
FDS Shape, angle(°)	☐	1	Fix	0		
VDS irradiated length (mm)	☐	12	Fix	0		
VDS Scale Intensity	☐					
Capillary	☐					
Linear PSD	☐					
Tube Tails	☐					
Axial Convolutions						
Full Axial Model	☐					
Finger_et_al	☐					
Simple Axial Model (mm)	☐	12	Fix	0		

```
16  Time   8.69  Rwp  14.206  -0.052 MC   0.57 1
17  Time   9.13  Rwp  14.181  -0.025 MC   0.81 1
18  Time   9.55  Rwp  14.165  -0.015 MC   1.45 1
19  Time   9.99  Rwp  14.158  -0.007 MC   3.15 1
20  Time  10.44  Rwp  14.151  -0.007 MC   3.22 1
21  Time  10.90  Rwp  14.147  -0.004 MC   6.40 1
22  Time  11.33  Rwp  14.147  -0.000 MC 681.08 1
23  Time  11.75  Rwp  14.145  -0.002 MC   5.24 1
24  Time  12.24  Rwp  14.143  -0.002 MC  15.28 1
25  Time  12.72  Rwp  14.143  -0.000 MC 171.27 1
26  Time  13.46  Rwp  14.143   0.000 MC 575.00 2
--- 13.4627384 seconds ---
Errors calculated
```

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")

Things 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

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

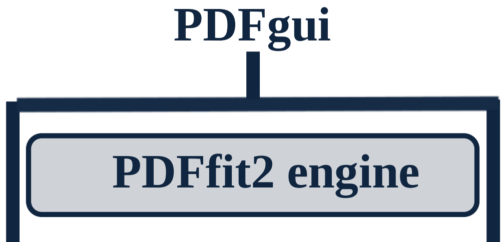
- least-squares refinement of p_i to minimize R_w
- Effects from setup (such as finite Q-resolution) or sample (correlated NN-motion) accounted for

$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}}$$

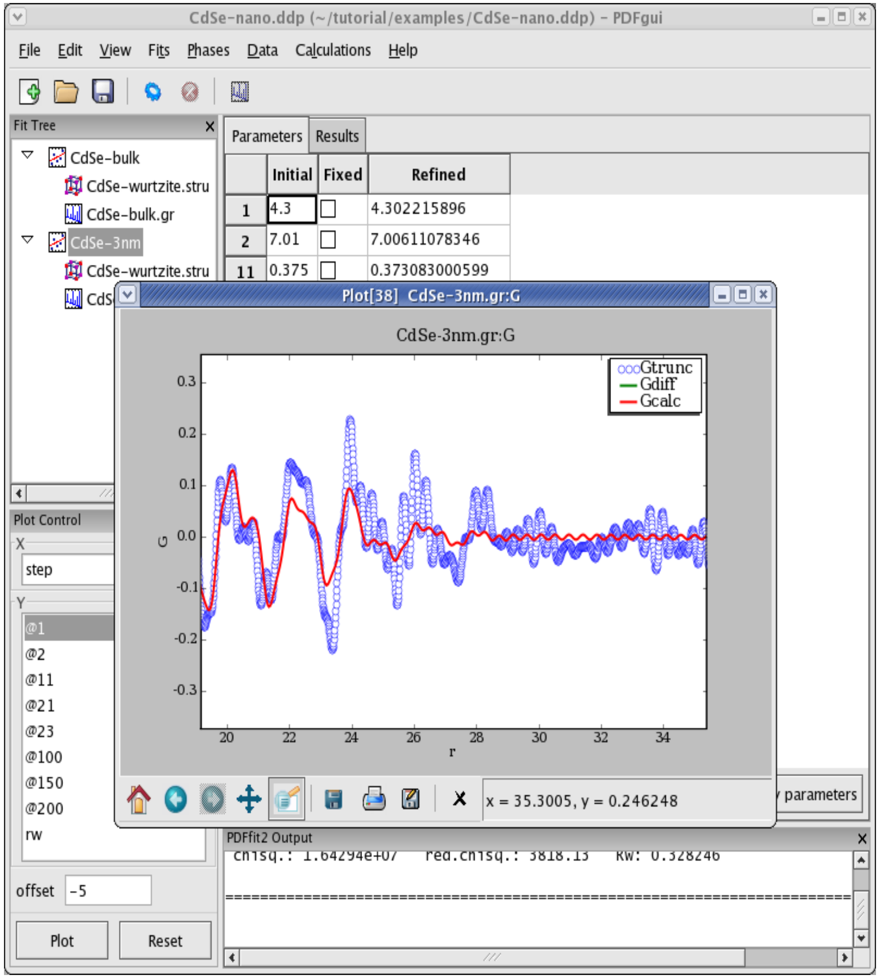
$$\sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

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



	Initial	Fixed	Refined
1	4.3	☐	4.302215896
2	7.01	☐	7.00611078346
11	0.375	☐	0.373083000599

X: step

offset: -5

x = 35.3005, y = 0.246248

```
 chisq.: 1.64294e+07    red.chisq.: 3818.13    Rw: 0.328246

==========================================================================
```

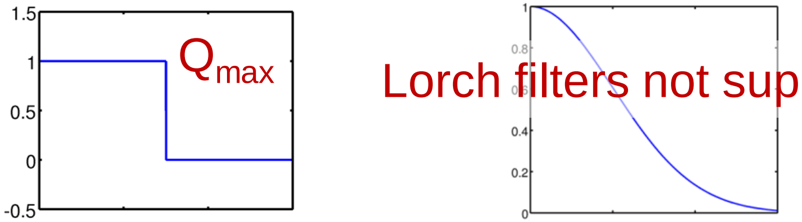
PDFgui

- 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 when r_{MAX} is large)
dscale refined	scale factor associated with dataset

PDFgui parameters and program structure

- **PDFgui parameters associated with PHASE**

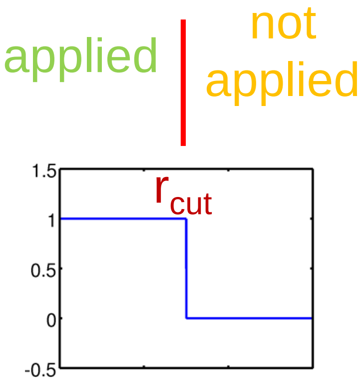
pscale refined	phase scale factor NOTE: could be redundant/correlated with dscale
a, b, c, α, β, γ refined	lattice parameters
x[n]	x-position (fractional coordinates)
y[n]	y-position
z[n]	z-position
occ[n]	site occupancy
u[*1*..*6*,n]	anisotropic displacement parameters U_{ij} [Å^{-2}]
refined (per symmetry)	

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\|

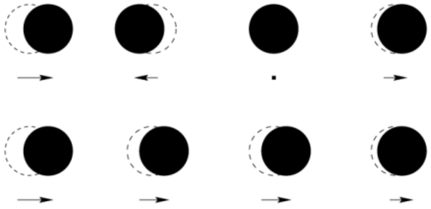
PDFgui parameters and program structure

- **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	peak width reduction for correlated motion (special cases of rigid structural units)
rcut constat	radius cuttoff for applying the sratio sharpening factor [Å]



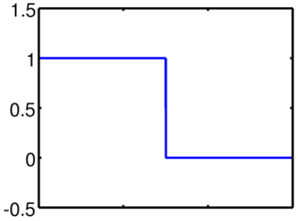
Note: Empirical correlated motion parameters are selected depending on material, they are very strongly correlated and affect other parameters

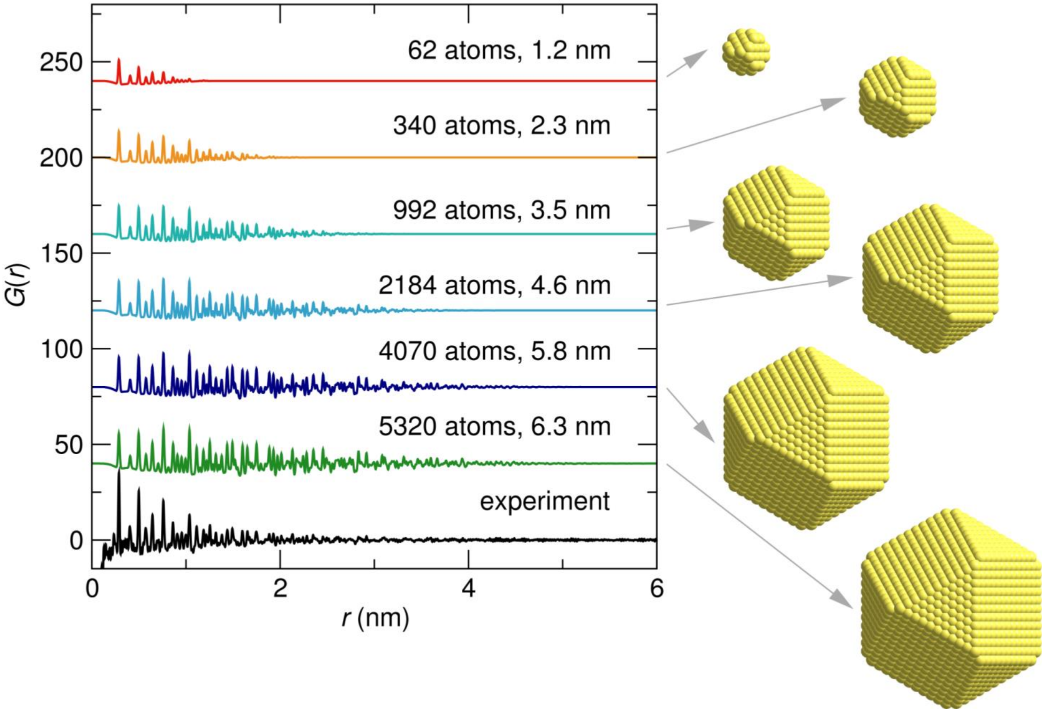


$$\sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

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.

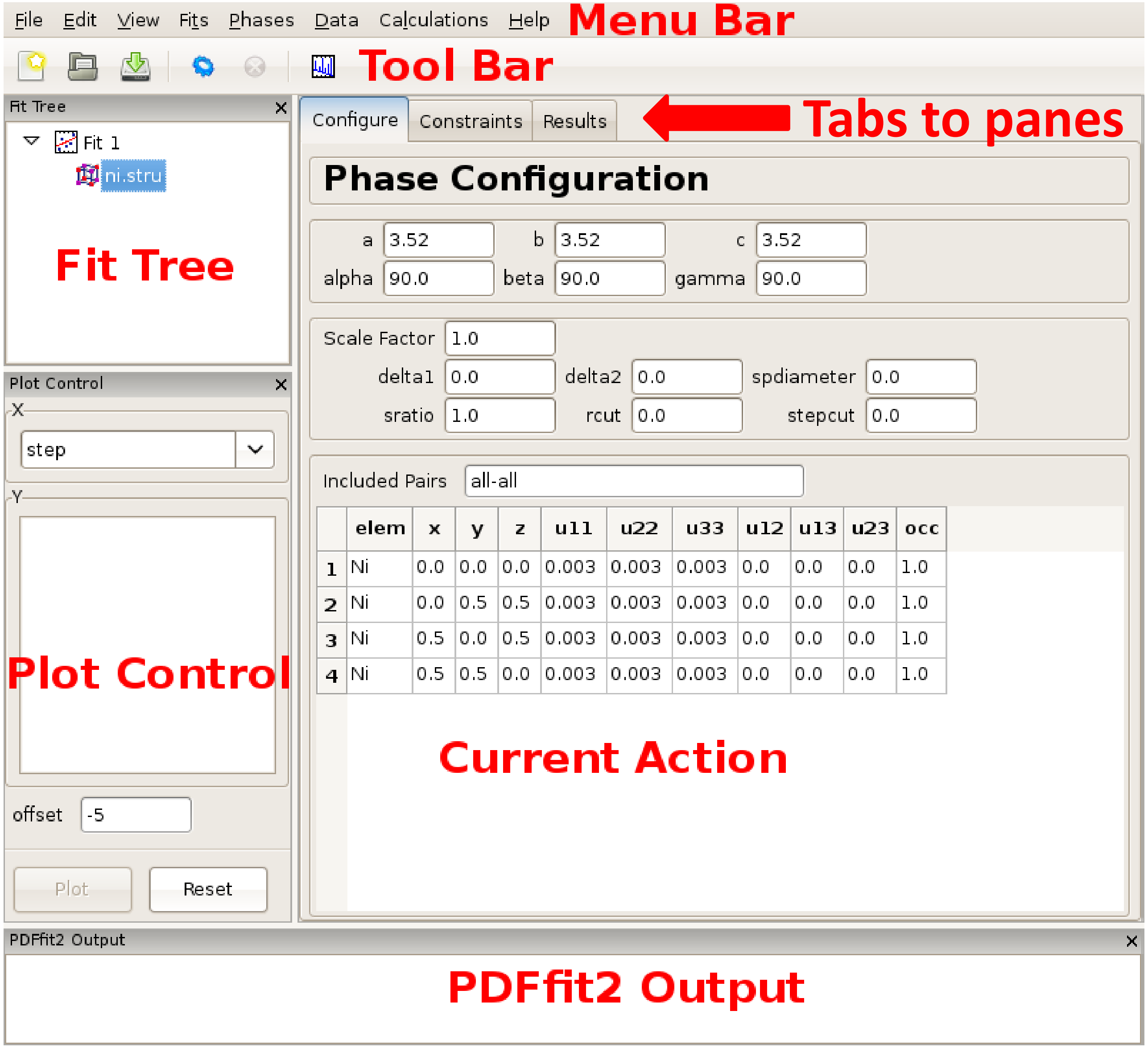
Variables that are assigned the same parameter number will be described by the same parameter.

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



Menu Bar

Tool Bar

Tabs to panes

Fit Tree

Plot Control

Current Action

PDFfit2 Output

Fit 1

ni.stru

X: step

Y:

offset -5

Phase Configuration

a 3.52
b 3.52
c 3.52
alpha 90.0
beta 90.0
gamma 90.0

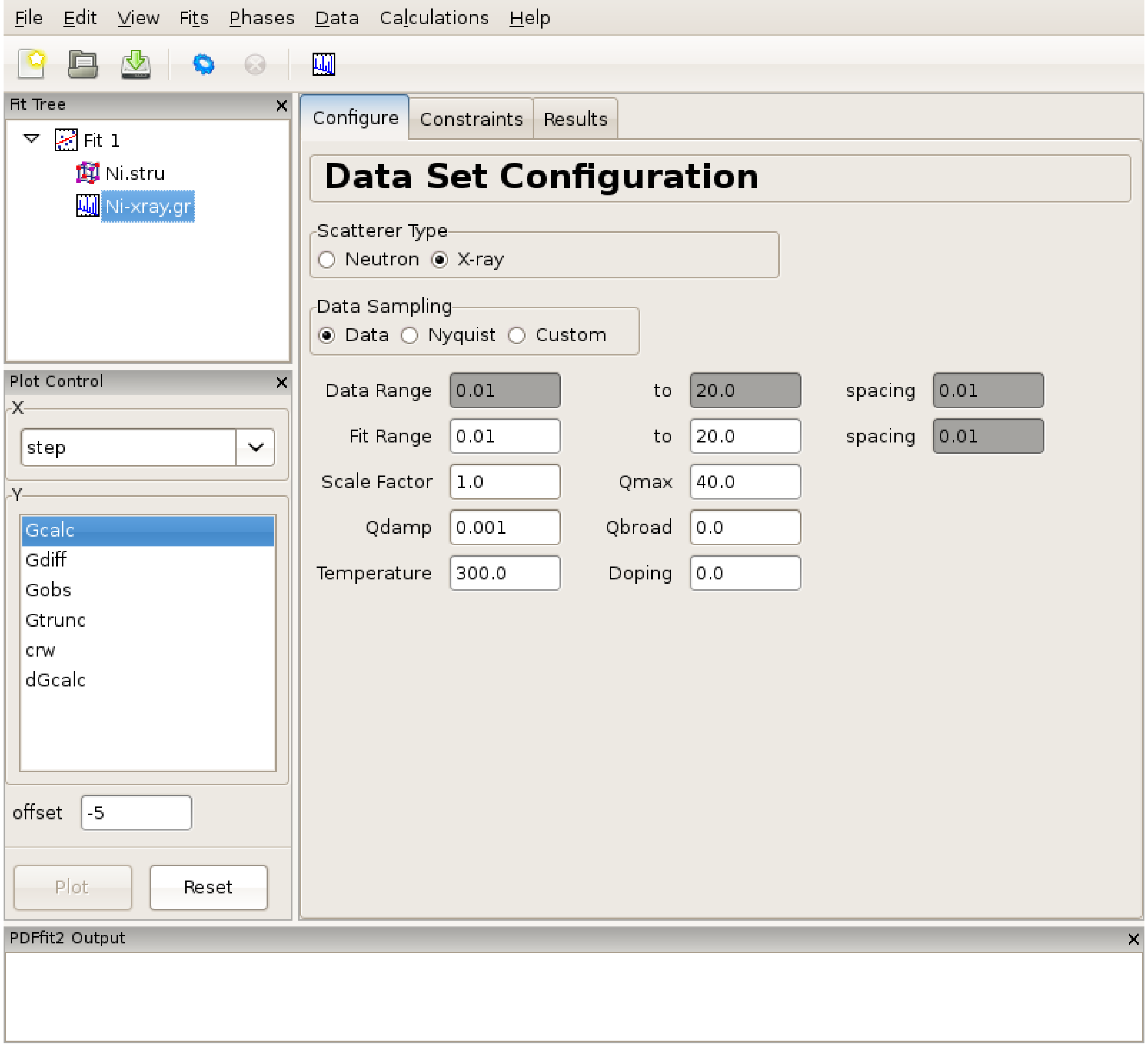
Scale Factor 1.0
delta1 0.0
delta2 0.0
spdiameter 0.0
sratio 1.0
rcut 0.0
stepcut 0.0

Included Pairs all-all

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Ni	0.0	0.0	0.0	0.003	0.003	0.003	0.0	0.0	0.0	1.0
2	Ni	0.0	0.5	0.5	0.003	0.003	0.003	0.0	0.0	0.0	1.0
3	Ni	0.5	0.0	0.5	0.003	0.003	0.003	0.0	0.0	0.0	1.0
4	Ni	0.5	0.5	0.0	0.003	0.003	0.003	0.0	0.0	0.0	1.0

Creating a simple fit using a preexisting struct file

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



Data Set Configuration

Scatterer Type

○ Neutron ● X-ray

Data Sampling

● Data ○ Nyquist ○ Custom

Data Range	0.01	to	20.0	spacing	0.01
Fit Range	0.01	to	20.0	spacing	0.01
Scale Factor	1.0	Qmax	40.0		
Qdamp	0.001	Qbroad	0.0		
Temperature	300.0	Doping	0.0		

X

step

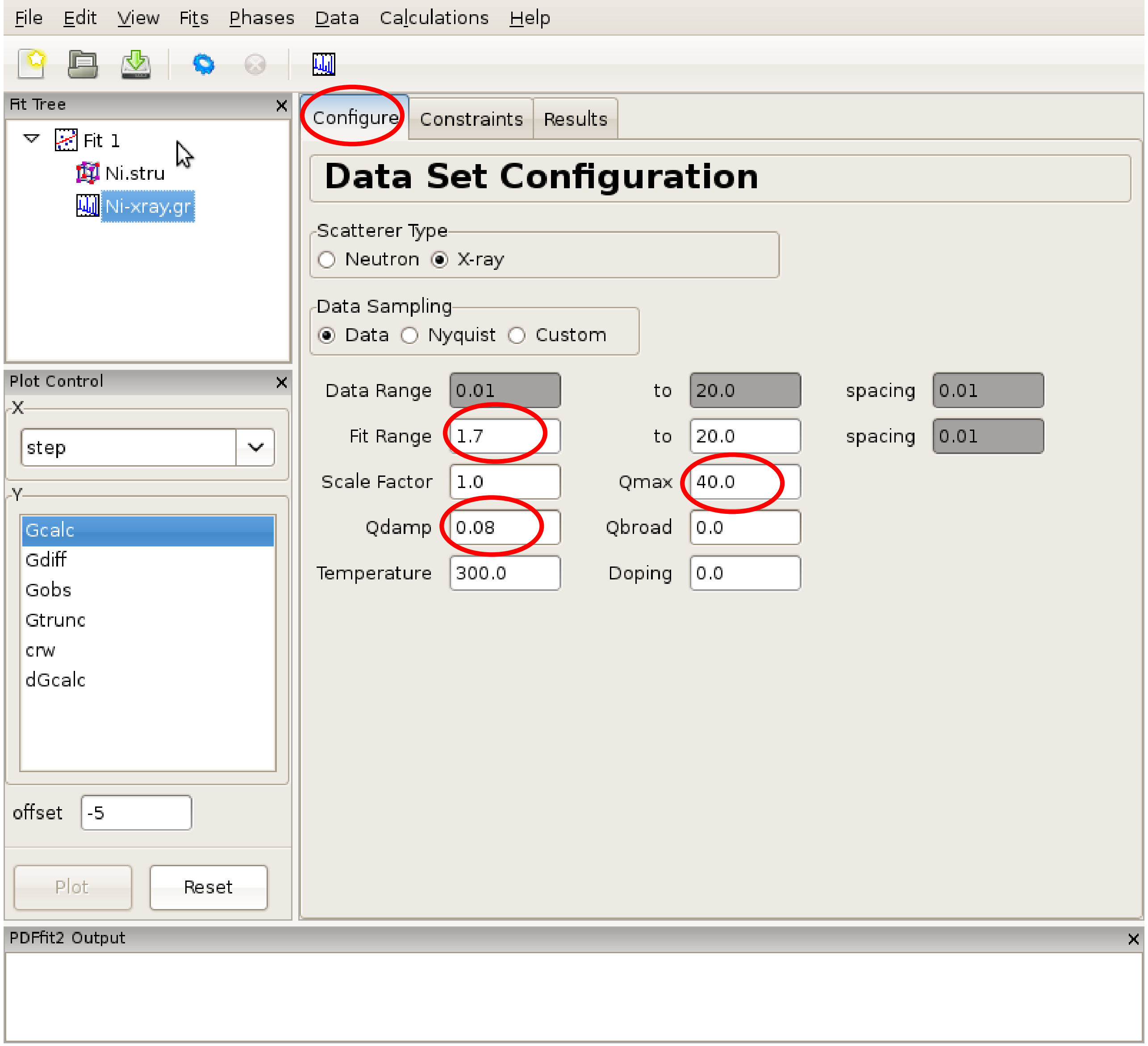
Y

- Gcalc
- Gdiff
- Gobs
- Gtrunc
- crw
- dGcalc

offset -5

Creating a simple fit using a preexisting struct file

Adjusting data set related configuration.



Data Set Configuration

Scatterer Type
○ Neutron ● X-ray

Data Sampling
● Data ○ Nyquist ○ Custom

Data Range 0.01 to 20.0 spacing 0.01

Fit Range 1.7 to 20.0 spacing 0.01

Scale Factor 1.0

Qmax 40.0

Qdamp 0.08

Qbroad 0.0

Temperature 300.0

Doping 0.0

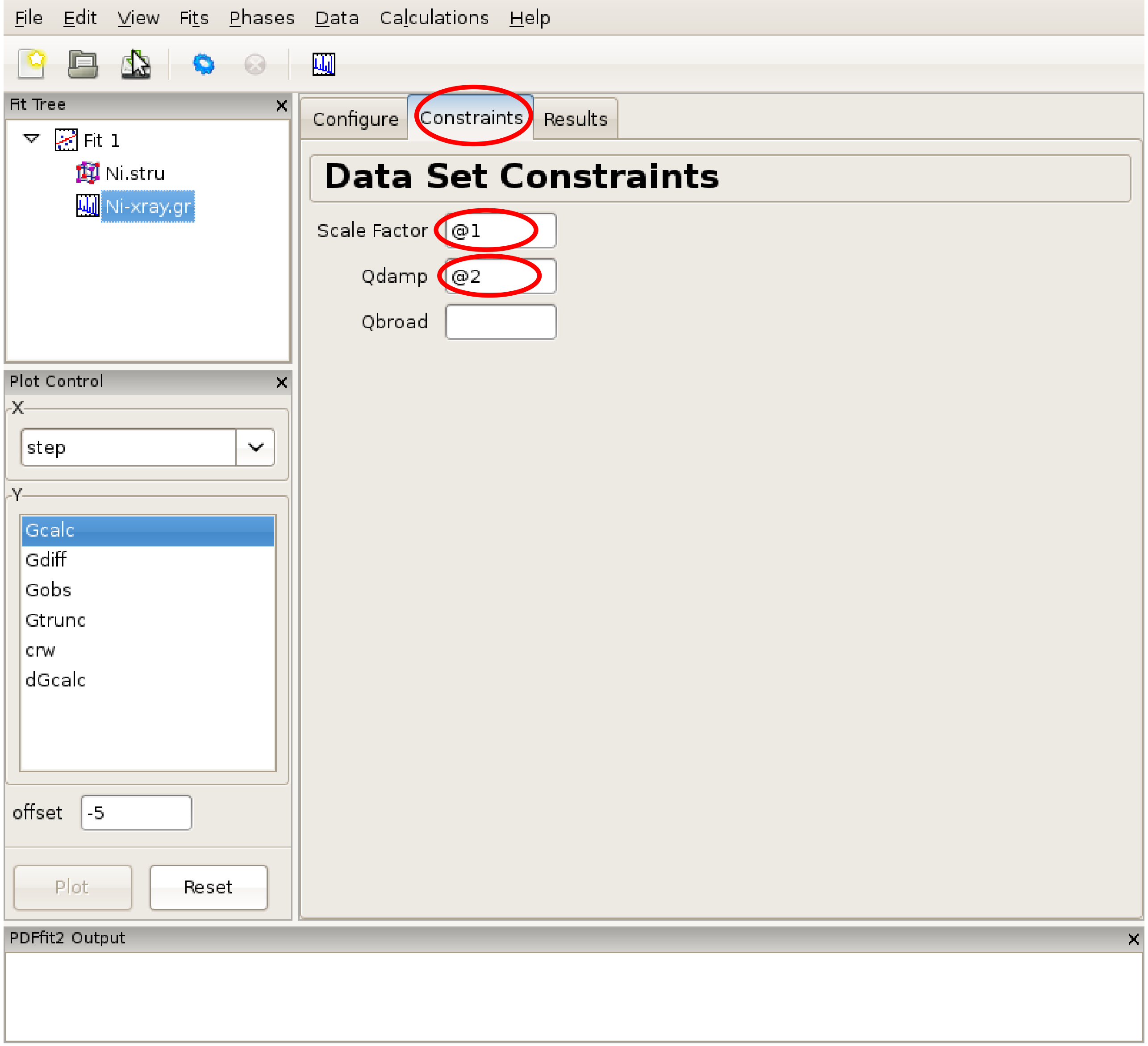
X: step

Y: Gcalc

offset -5

Creating a simple fit using a preexisting struct file

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



Data Set Constraints

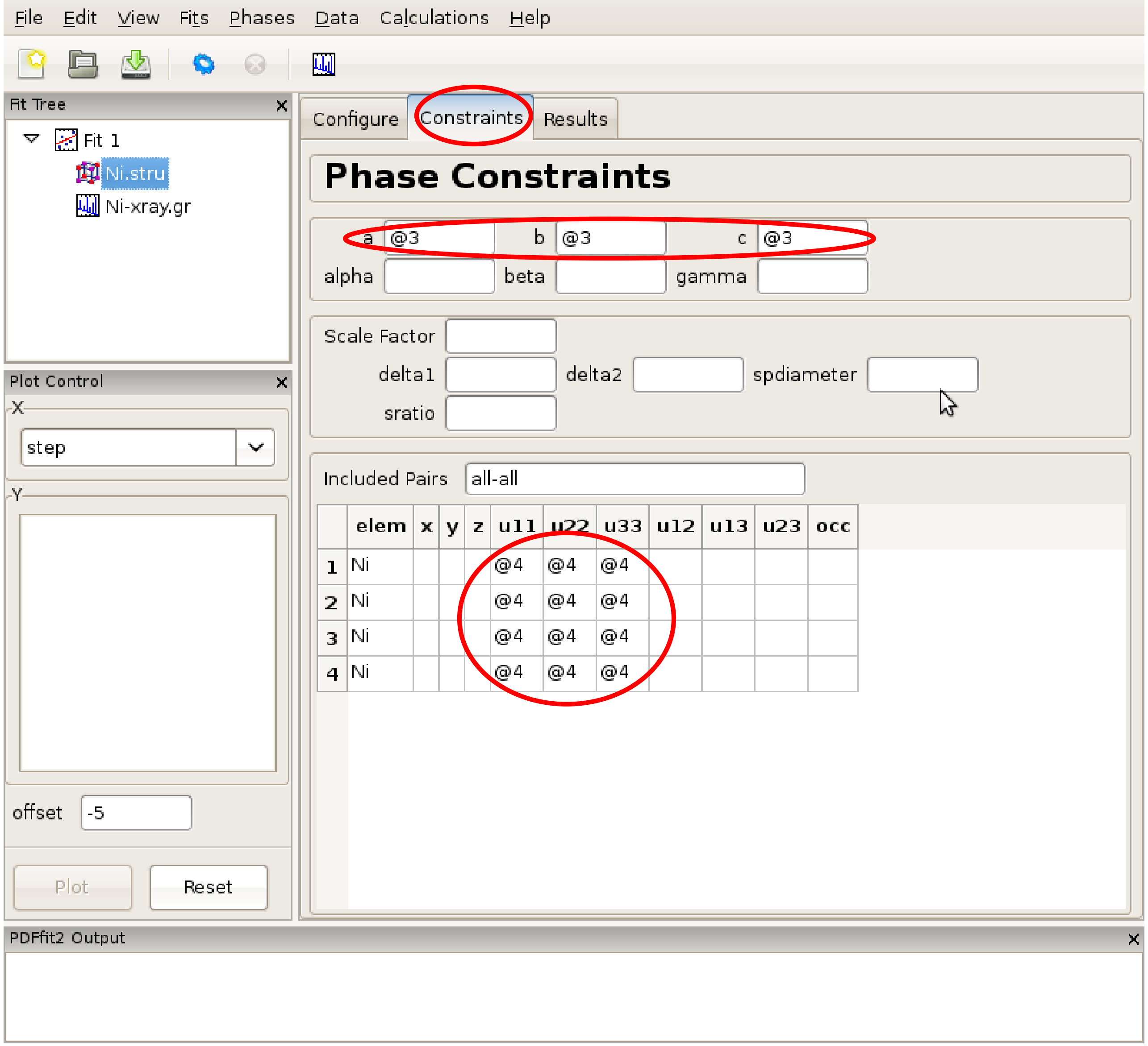
Scale Factor @1

Qdamp @2

Qbroad

Creating a simple fit using a preexisting structure file

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



Phase Constraints

a @3
b @3
c @3
alpha
beta
gamma

Scale Factor
delta1
delta2
spdiameter
sratio

Included Pairs all-all

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Ni				@4	@4	@4				
2	Ni				@4	@4	@4				
3	Ni				@4	@4	@4				
4	Ni				@4	@4	@4				

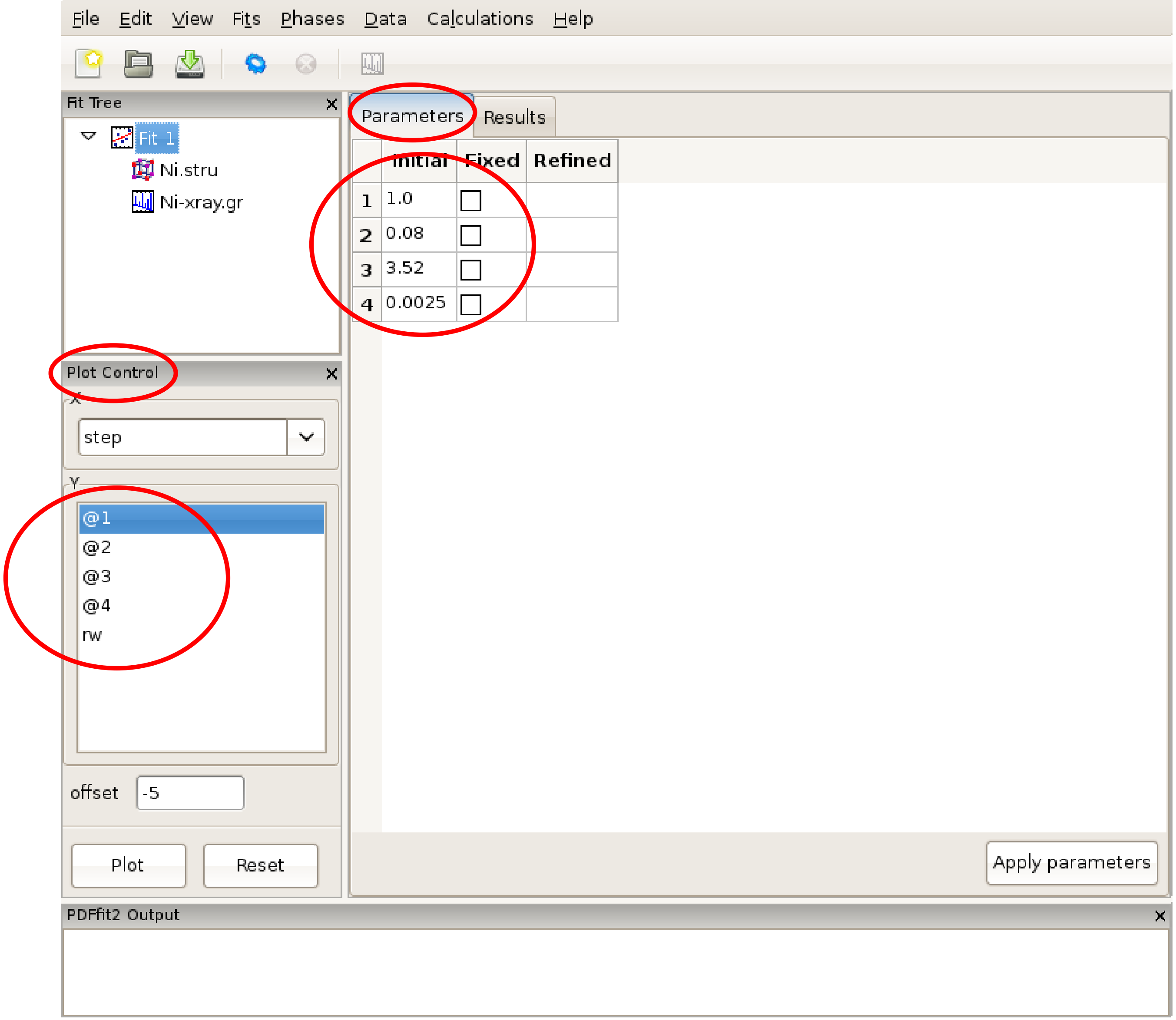
X step

Y

offset -5

Creating a simple fit using a preexisting struct file

Reviewing the fit parameters and conditions

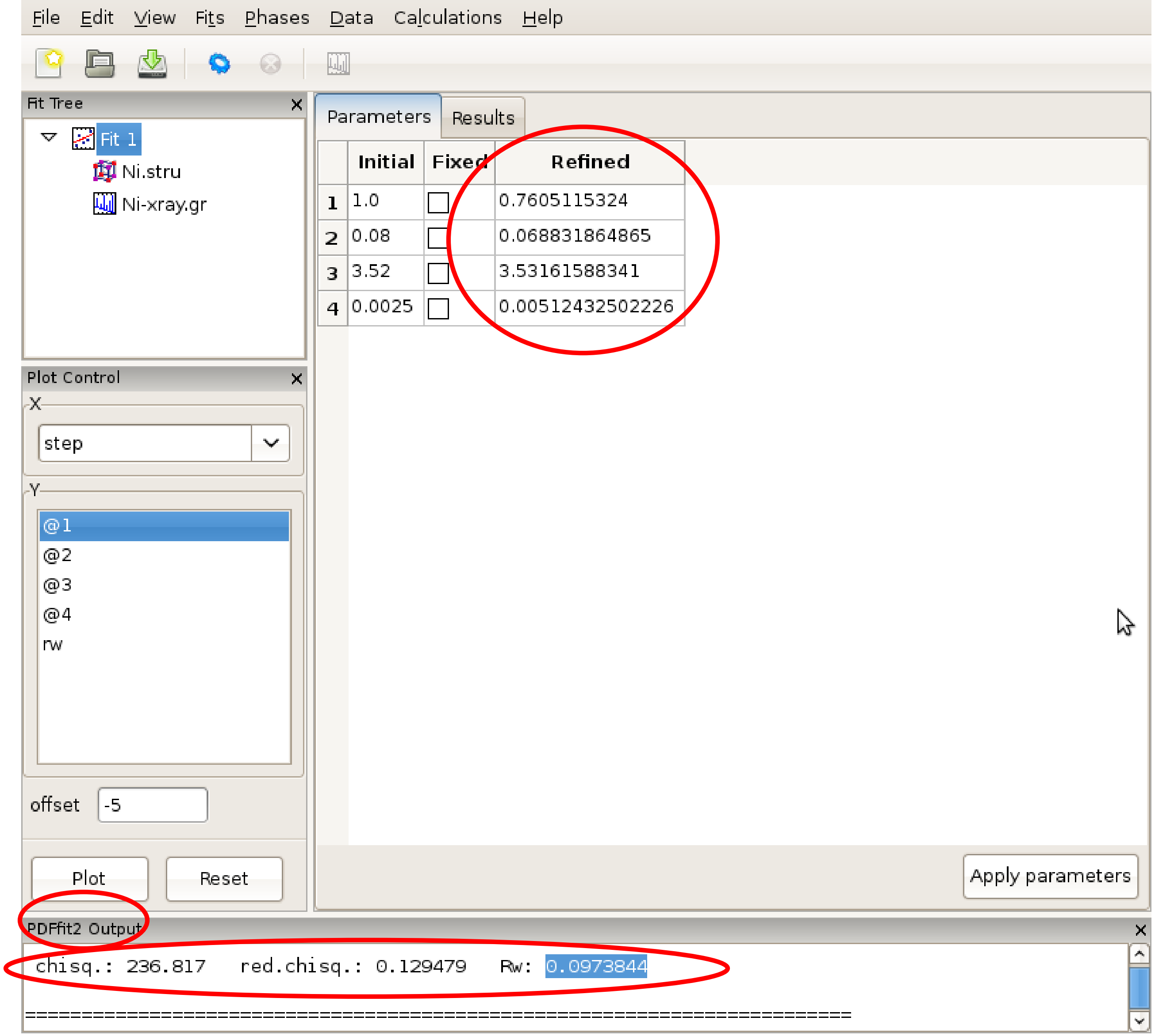


offset -5

	Initial	Fixed	Refined
1	1.0	☐	
2	0.08	☐	
3	3.52	☐	
4	0.0025	☐	

Creating a simple fit using a preexisting struct file

The refinement progress is displayed in the PDFfit2 Output panel.



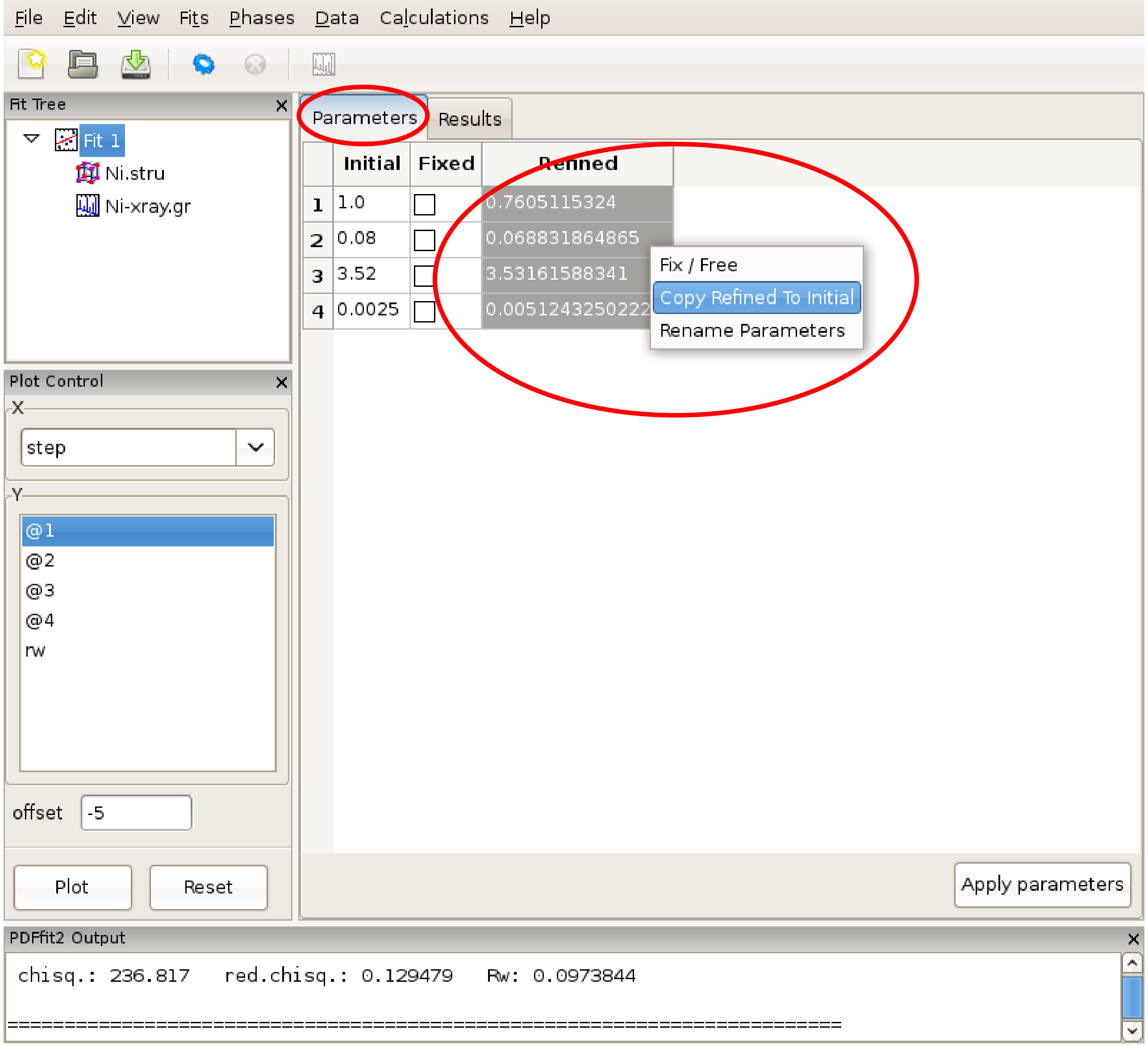
	Initial	Fixed	Refined
1	1.0	☐	0.7605115324
2	0.08	☐	0.068831864865
3	3.52	☐	3.53161588341
4	0.0025	☐	0.00512432502226

```
chisq.: 236.817    red.chisq.: 0.129479    Rw: 0.0973844

==========================================================================
```

Creating a simple fit using a preexisting struct file

Updating the set of initial values of refined parameters.



	Initial	Fixed	Refined
1	1.0	☐	0.7605115324
2	0.08	☐	0.068831864865
3	3.52	☐	3.53161588341
4	0.0025	☐	0.0051243250222

X: step

Y: @1, @2, @3, @4, rw

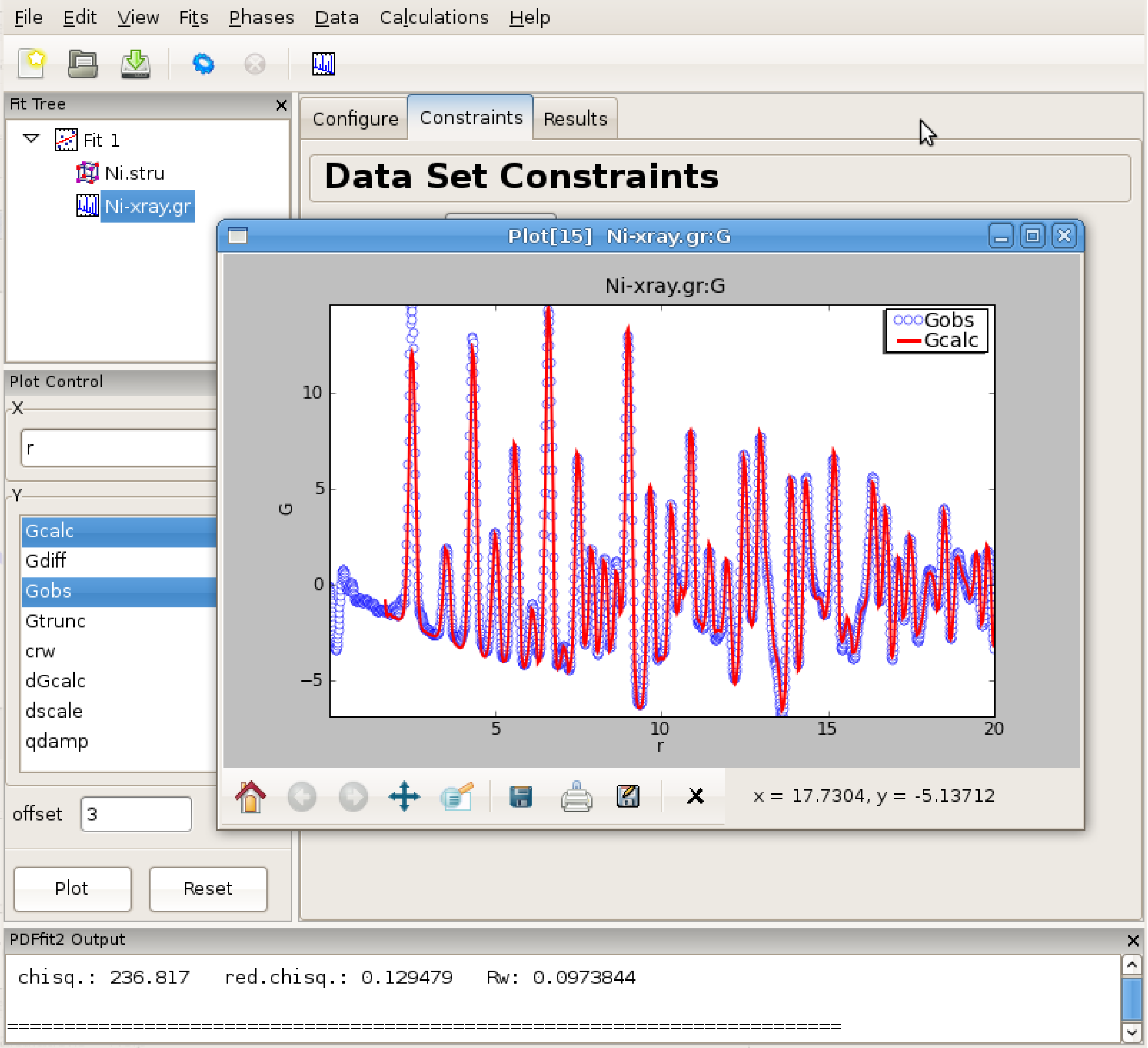
offset: -5

```
chisq.: 236.817   red.chisq.: 0.129479   Rw: 0.0973844

==========================================================================
```

Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a fit.



X: r

Y: Gcalc, Gobs

offset 3

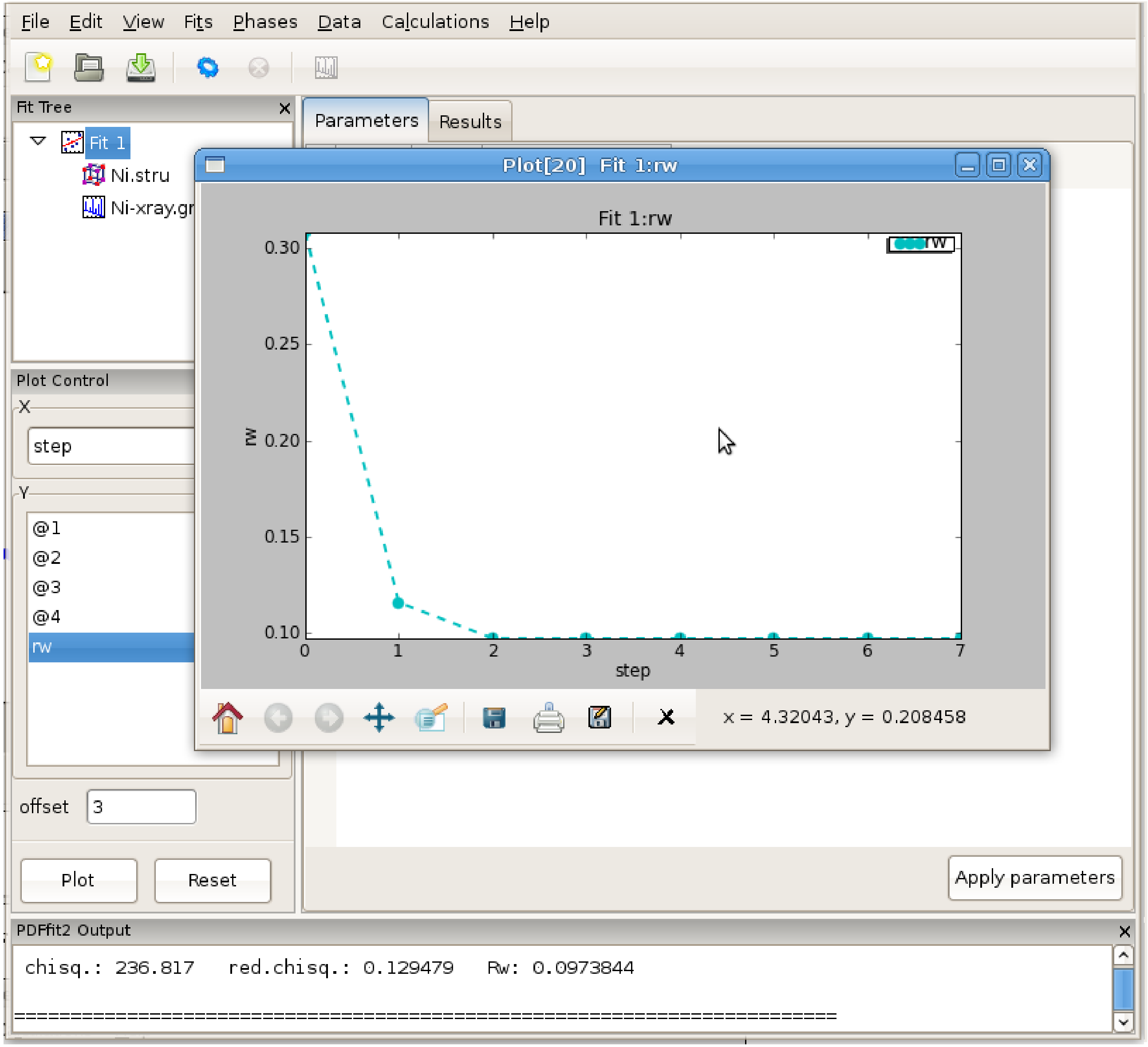
```
x = 17.7304, y = -5.13712
```

```
chisq.: 236.817    red.chisq.: 0.129479    Rw: 0.0973844

==========================================================================
```

Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a parameter.



X: step

offset: 3

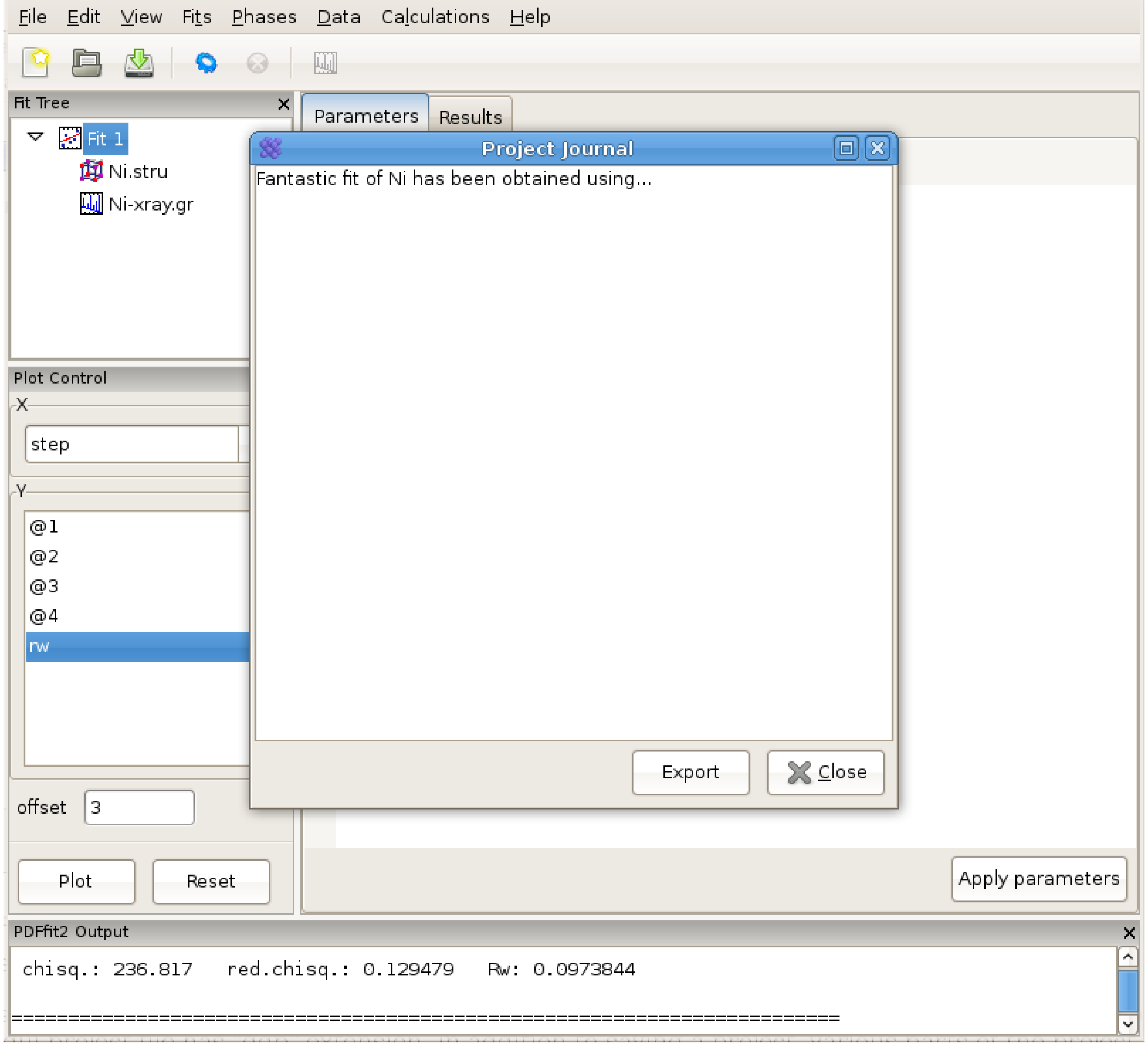
```
x = 4.32043, y = 0.208458
```

```
chisq.: 236.817    red.chisq.: 0.129479    Rw: 0.0973844

=========================================================================
```

Creating a simple fit using a preexisting struct file

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



Fantastic fit of Ni has been obtained using...

X: step

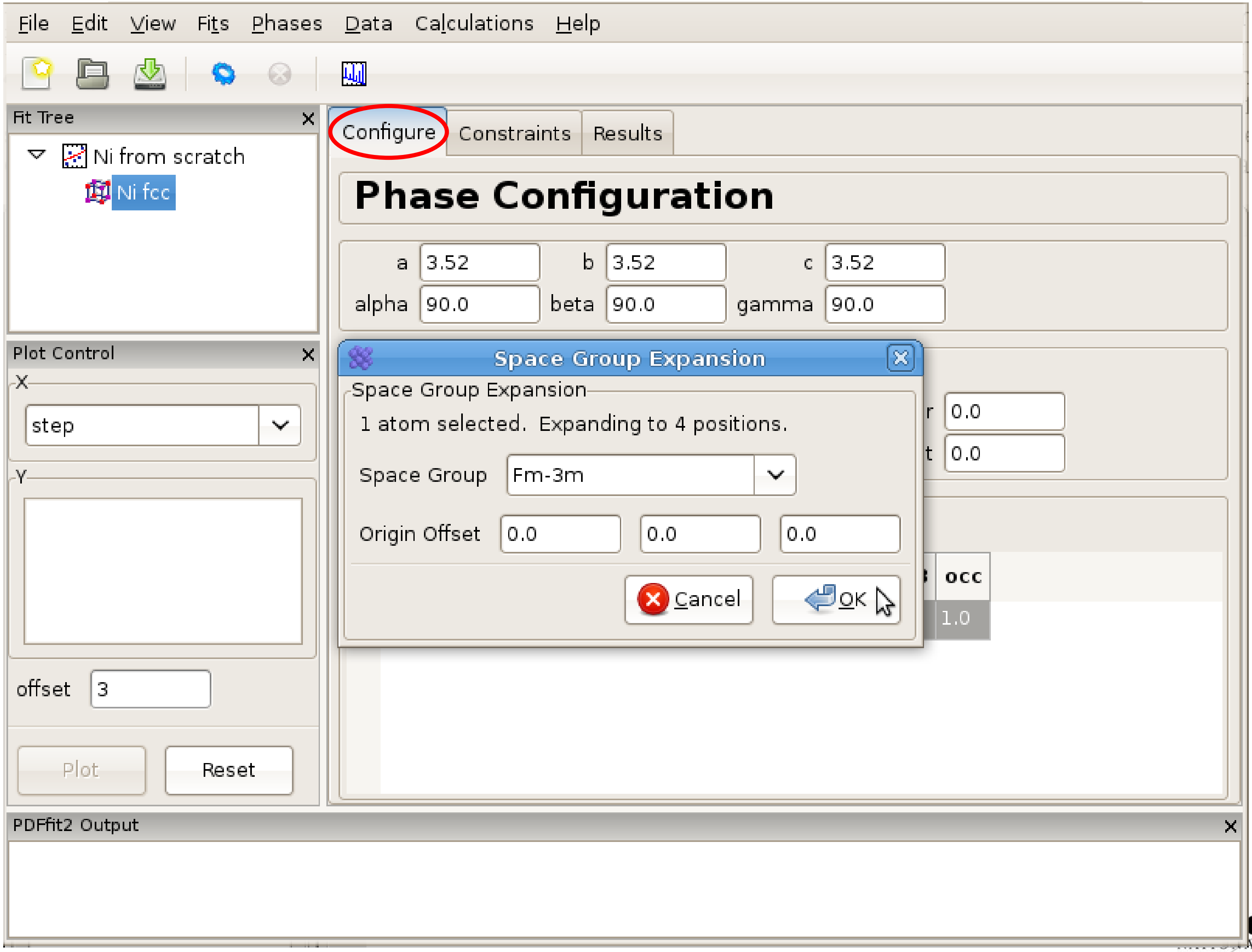
offset: 3

```
chisq.: 236.817    red.chisq.: 0.129479    Rw: 0.0973844

=========================================================================
```

Building structure model using crystal symmetry

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



Phase Configuration

a 3.52
b 3.52
c 3.52
alpha 90.0
beta 90.0
gamma 90.0

r 0.0
t 0.0

Space Group Expansion

Space Group Expansion

1 atom selected. Expanding to 4 positions.

Space Group Fm-3m

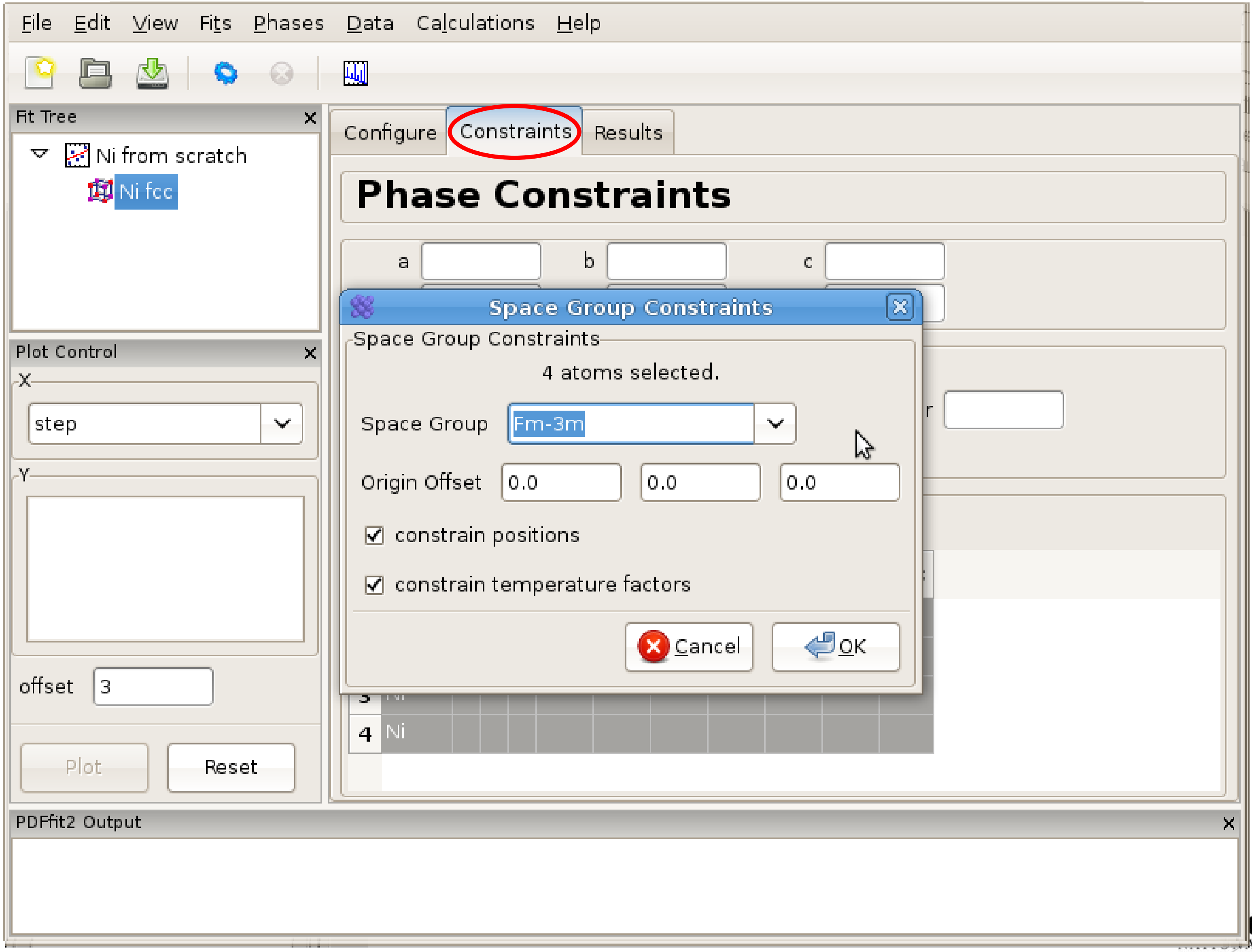
Origin Offset 0.0 0.0 0.0

X step

offset 3

Building structure model using crystal symmetry

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



Space Group Constraints

4 atoms selected.

Space Group: Fm-3m

Origin Offset: 0.0 0.0 0.0

☑ constrain positions

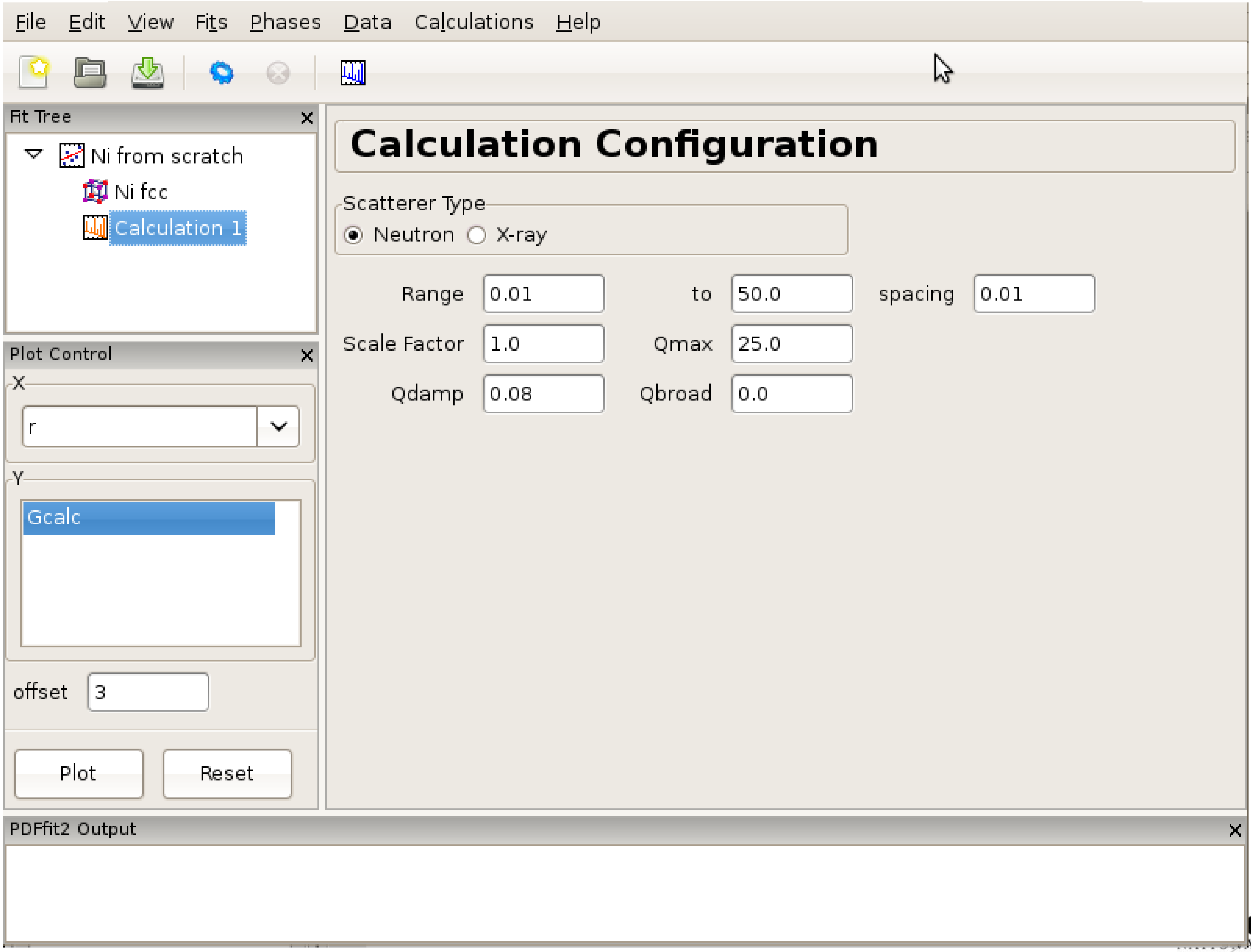
☑ constrain temperature factors

X: step

offset: 3

Calculating PDF from a structure

An example of the calculation configuration panel.



Calculation Configuration

Scatterer Type

● Neutron ○ X-ray

Range 0.01 to 50.0 spacing 0.01

Scale Factor 1.0

Qmax 25.0

Qdamp 0.08

Qbroad 0.0

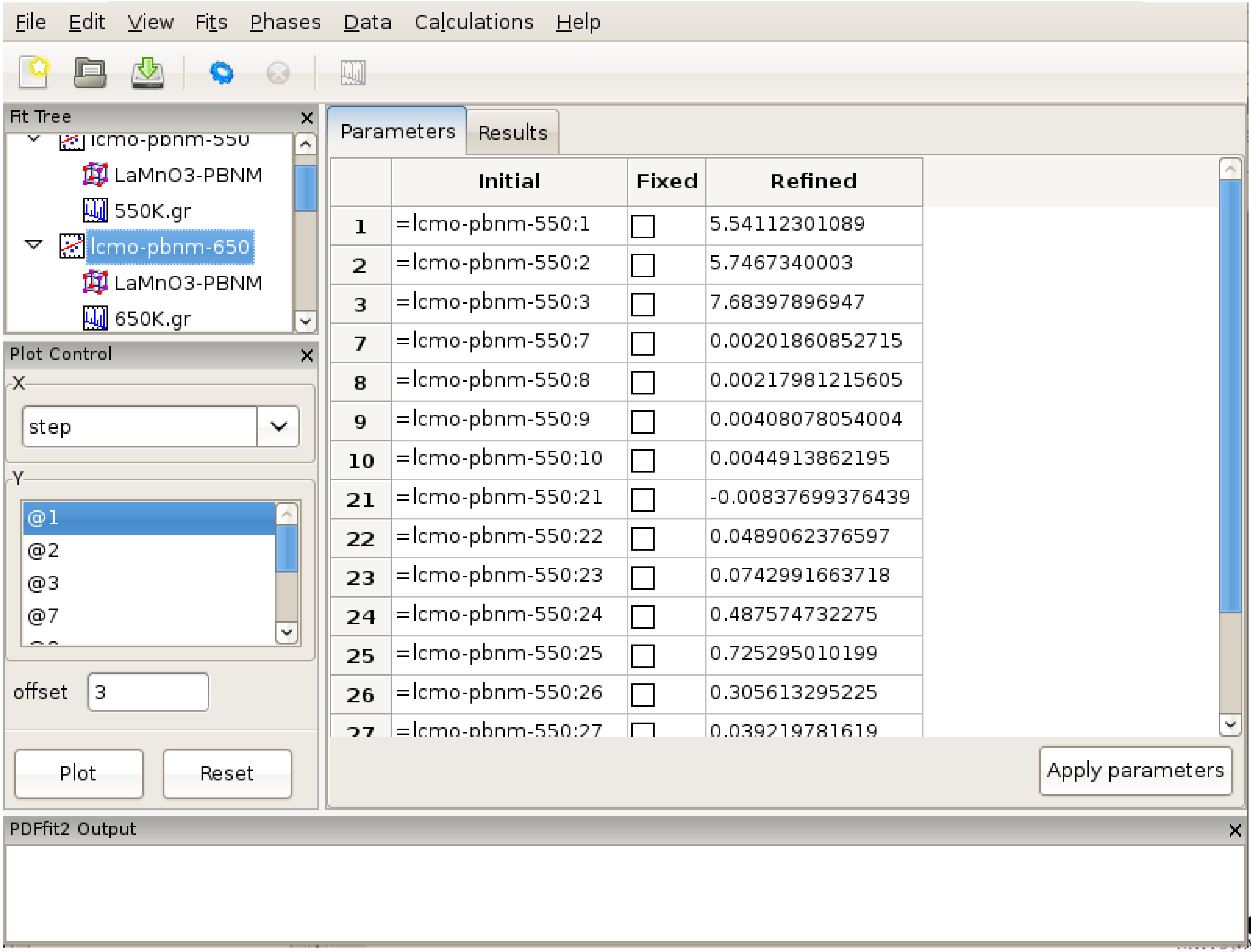
X: r

Y: Gcalc

offset 3

Multistage fitting

Sequential refinement where fits are chronologically linked



Fit Tree:

- lcmo-pbnm-550
  - LaMnO3-PBNM
  - 550K.gr
- lcmo-pbnm-650
  - LaMnO3-PBNM
  - 650K.gr

X: step

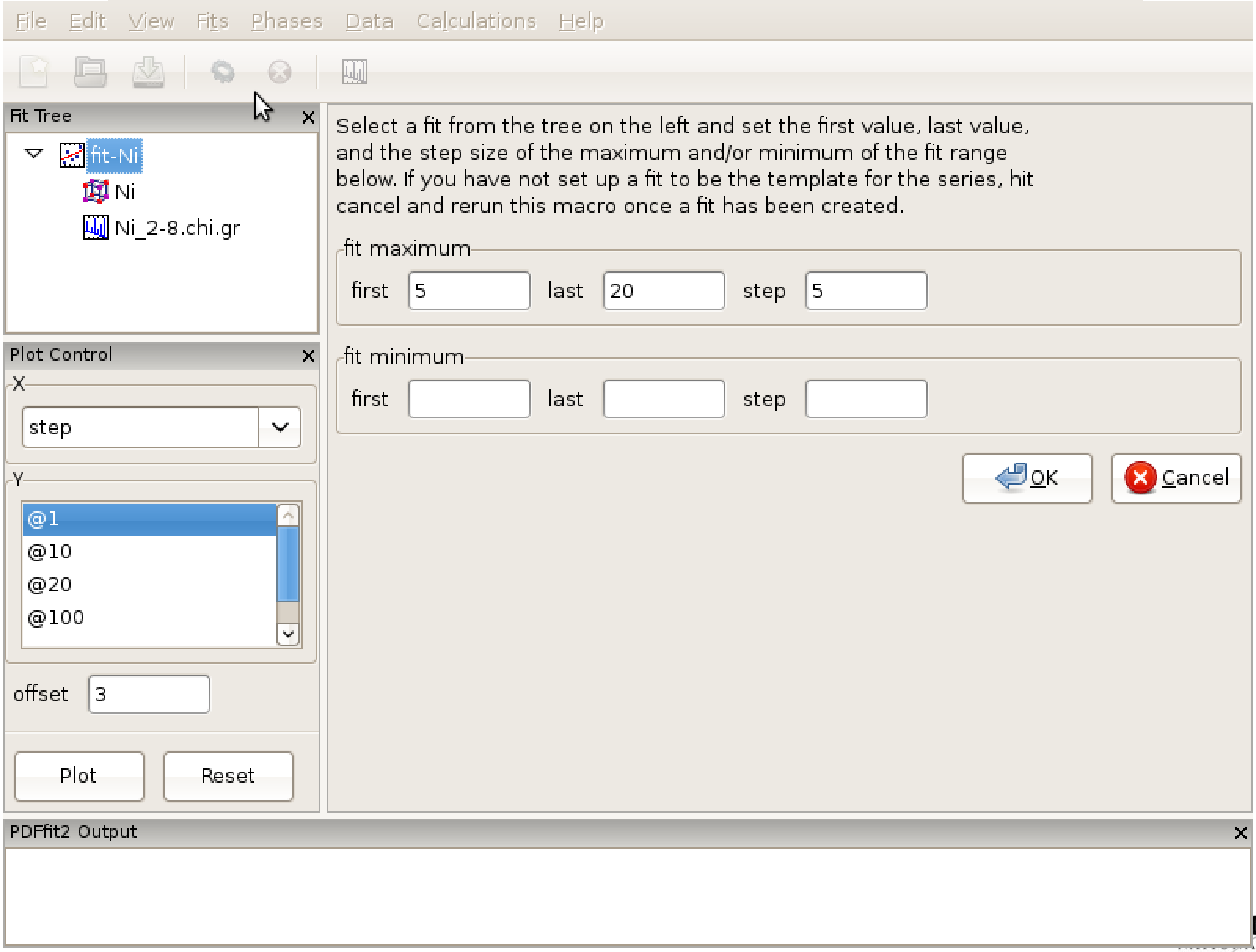
Y: @1, @2, @3, @7

offset: 3

	Initial	Fixed	Refined
1	=lcmo-pbnm-550:1	☐	5.54112301089
2	=lcmo-pbnm-550:2	☐	5.7467340003
3	=lcmo-pbnm-550:3	☐	7.68397896947
7	=lcmo-pbnm-550:7	☐	0.00201860852715
8	=lcmo-pbnm-550:8	☐	0.00217981215605
9	=lcmo-pbnm-550:9	☐	0.00408078054004
10	=lcmo-pbnm-550:10	☐	0.0044913862195
21	=lcmo-pbnm-550:21	☐	-0.00837699376439
22	=lcmo-pbnm-550:22	☐	0.0489062376597
23	=lcmo-pbnm-550:23	☐	0.0742991663718
24	=lcmo-pbnm-550:24	☐	0.487574732275
25	=lcmo-pbnm-550:25	☐	0.725295010199
26	=lcmo-pbnm-550:26	☐	0.305613295225
27	=lcmo-pbnm-550:27	☐	0.039219781619

Sequential fitting of incremental r-series

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



Select a fit from the tree on the left and set the first value, last value, and the step size of the maximum and/or minimum of the fit range below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created.

fit maximum

first 5 last 20 step 5

fit minimum

first last step

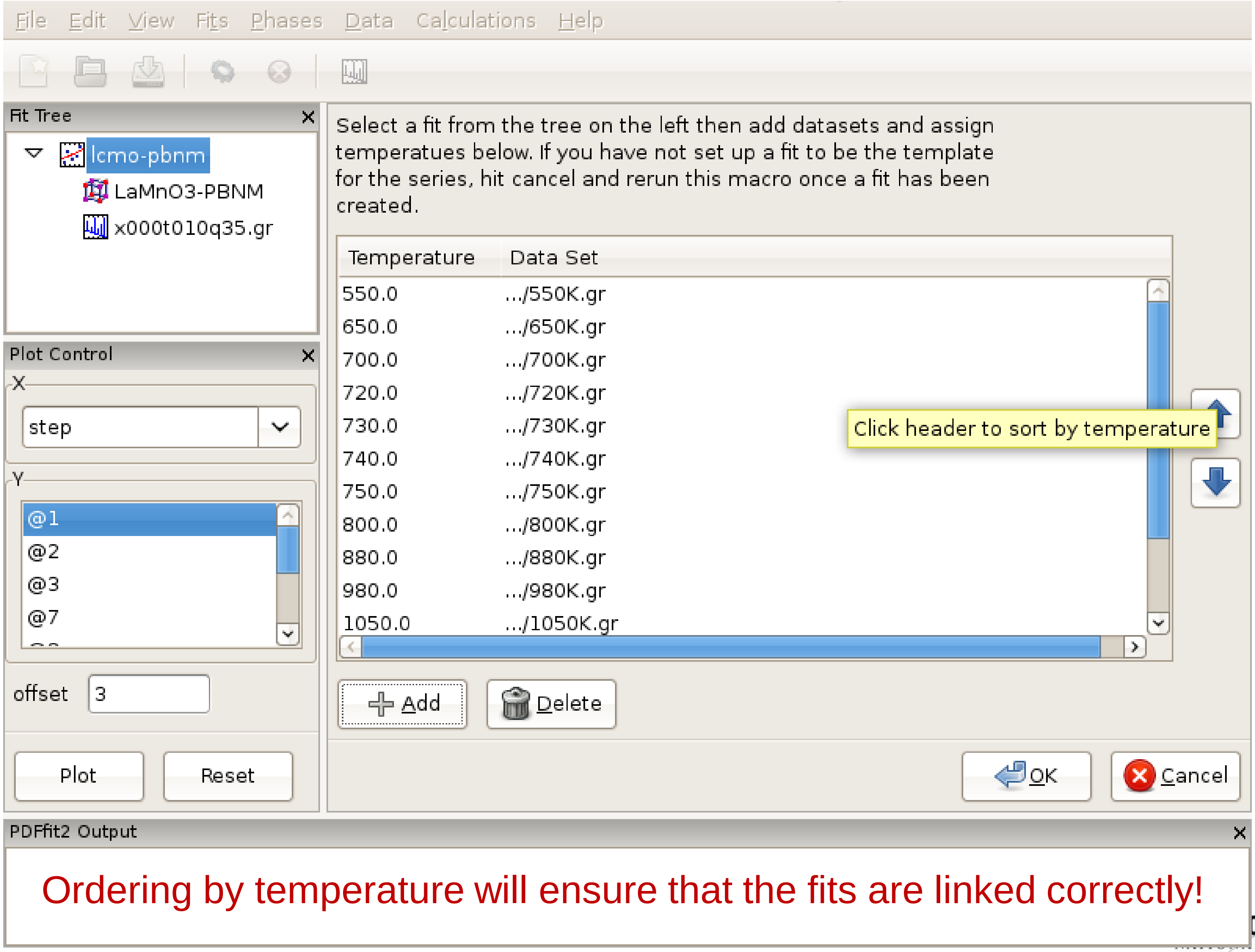
X: step

Y: @1, @10, @20, @100

offset 3

Sequential fitting of temperature series

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



Select a fit from the tree on the left then add datasets and assign temperatues below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created.

Temperature	Data Set
550.0	.../550K.gr
650.0	.../650K.gr
700.0	.../700K.gr
720.0	.../720K.gr
730.0	.../730K.gr
740.0	.../740K.gr
750.0	.../750K.gr
800.0	.../800K.gr
880.0	.../880K.gr
980.0	.../980K.gr
1050.0	.../1050K.gr

Click header to sort by temperature

X: step

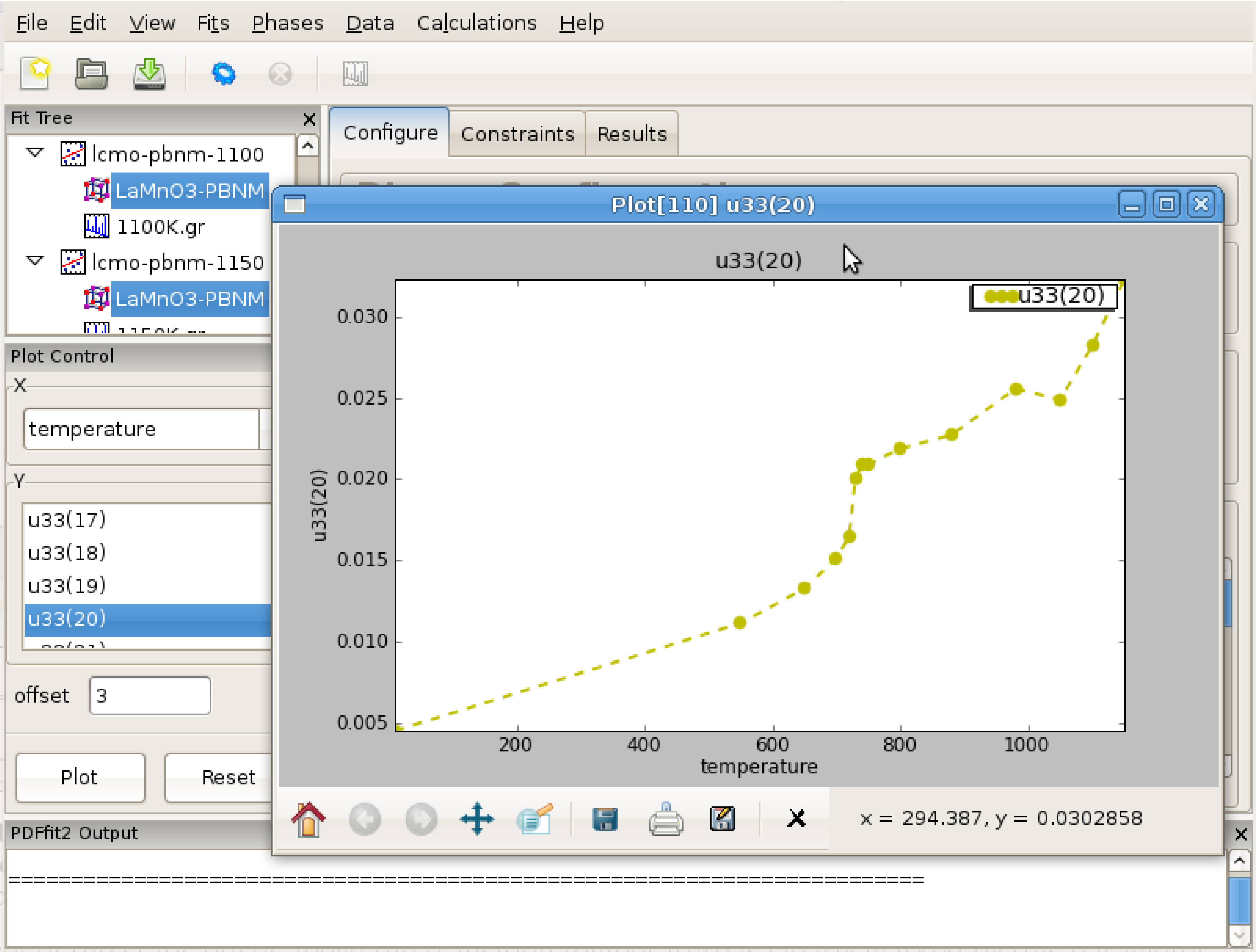
Y: @1 @2 @3 @7

offset: 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



X: temperature

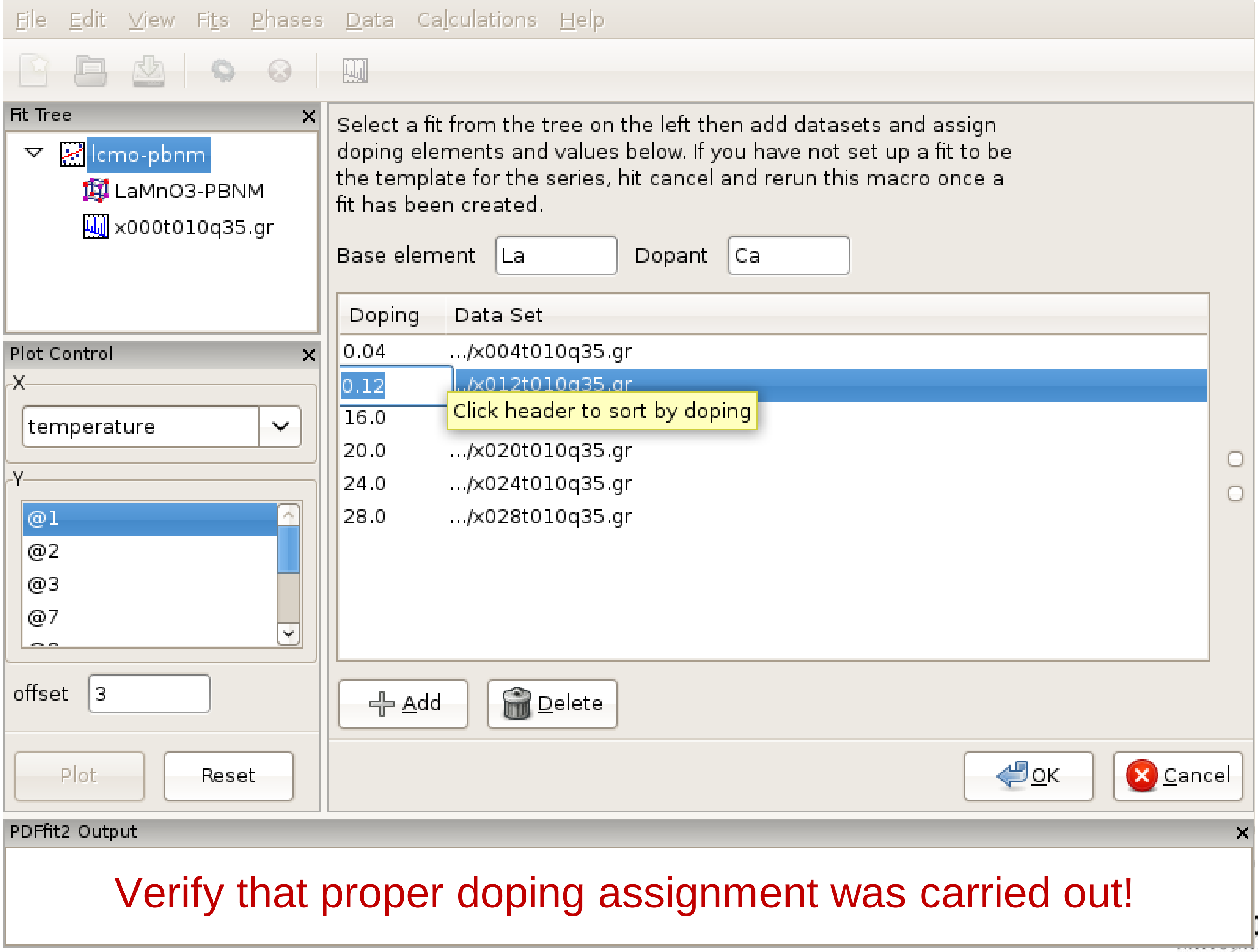
offset: 3

```
x = 294.387, y = 0.0302858
```

```
=============================================================================
```

Sequential fitting of doping series

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



Select a fit from the tree on the left then add datasets and assign doping elements and values below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created.

Base element: La

Dopant: Ca

Doping	Data Set
0.04	…/x004t010q35.gr
0.12	…/x012t010q35.gr
16.0	
20.0	…/x020t010q35.gr
24.0	…/x024t010q35.gr
28.0	…/x028t010q35.gr

Click header to sort by doping

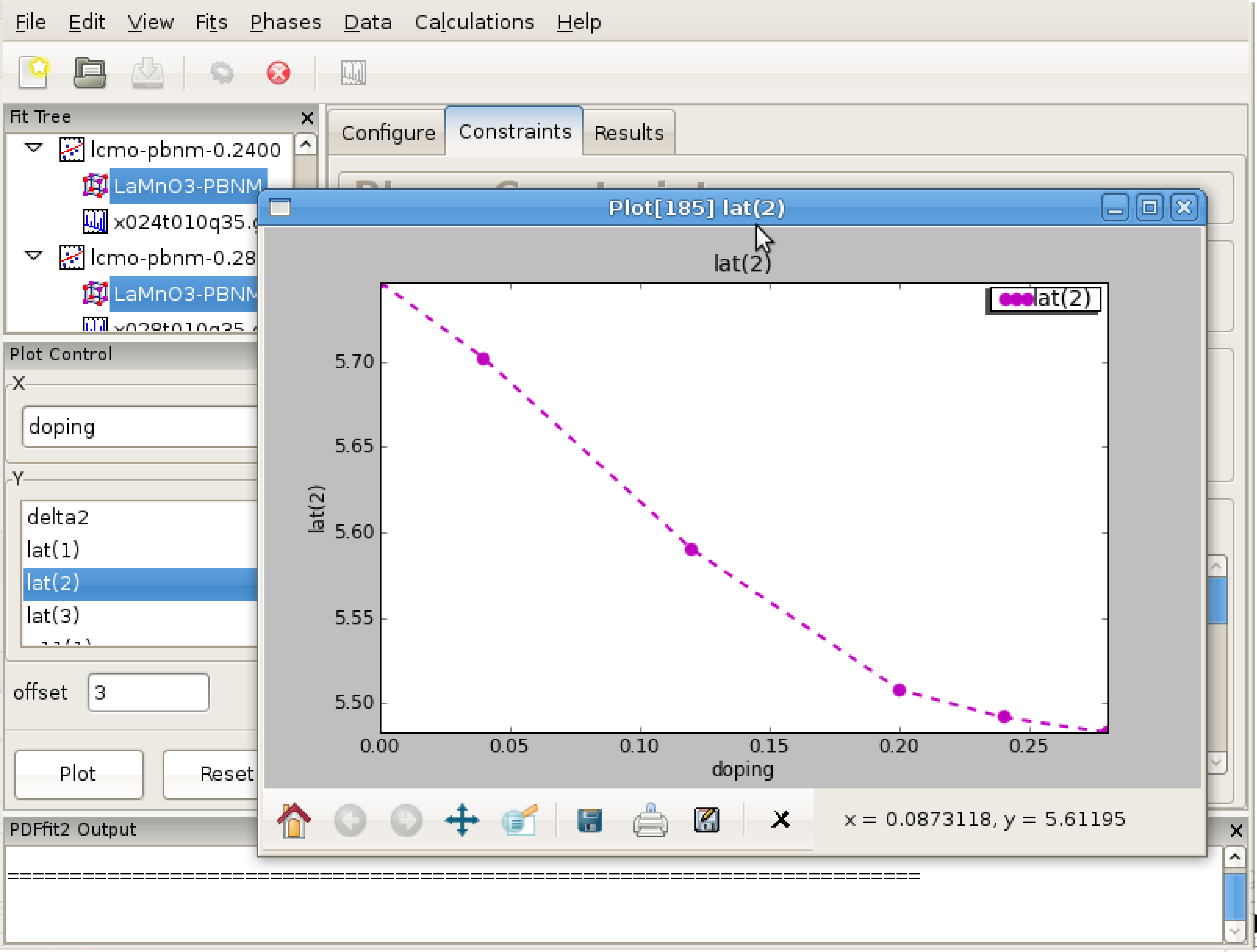
X: temperature

offset: 3

Verify that proper doping assignment was carried out!

Sequential fitting of doping series

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



- lcmo-pbnm-0.2400
  - LaMnO3-PBNM
  - x024t010q35.
- lcmo-pbnm-0.28
  - LaMnO3-PBNM
  - x028t010q35.

X: doping

Y:
- delta2
- lat(1)
- lat(2)
- lat(3)

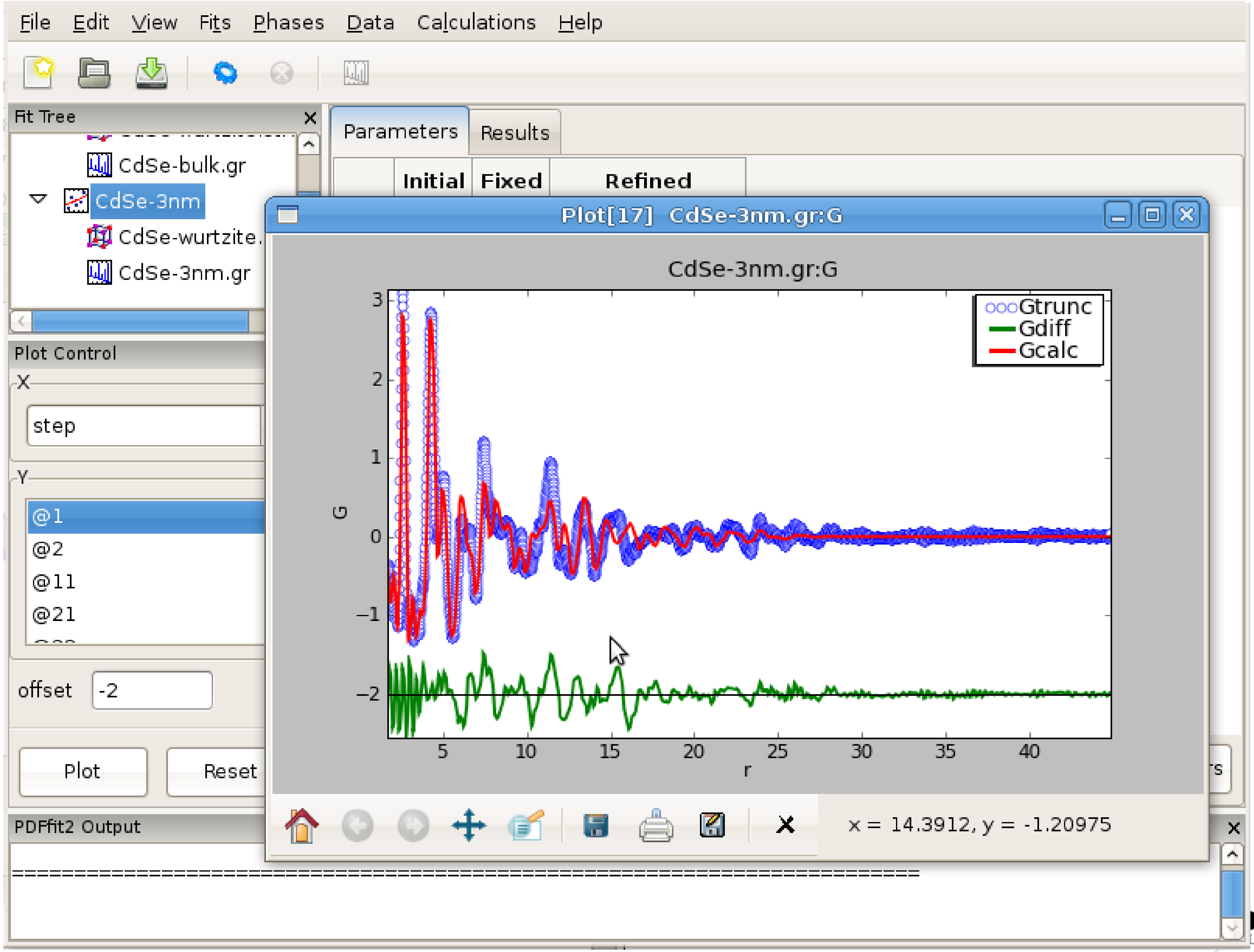
offset 3

x = 0.0873118, y = 5.61195

```
==========================================================================
```

Nanoparticle structure: spherical!

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



X: step

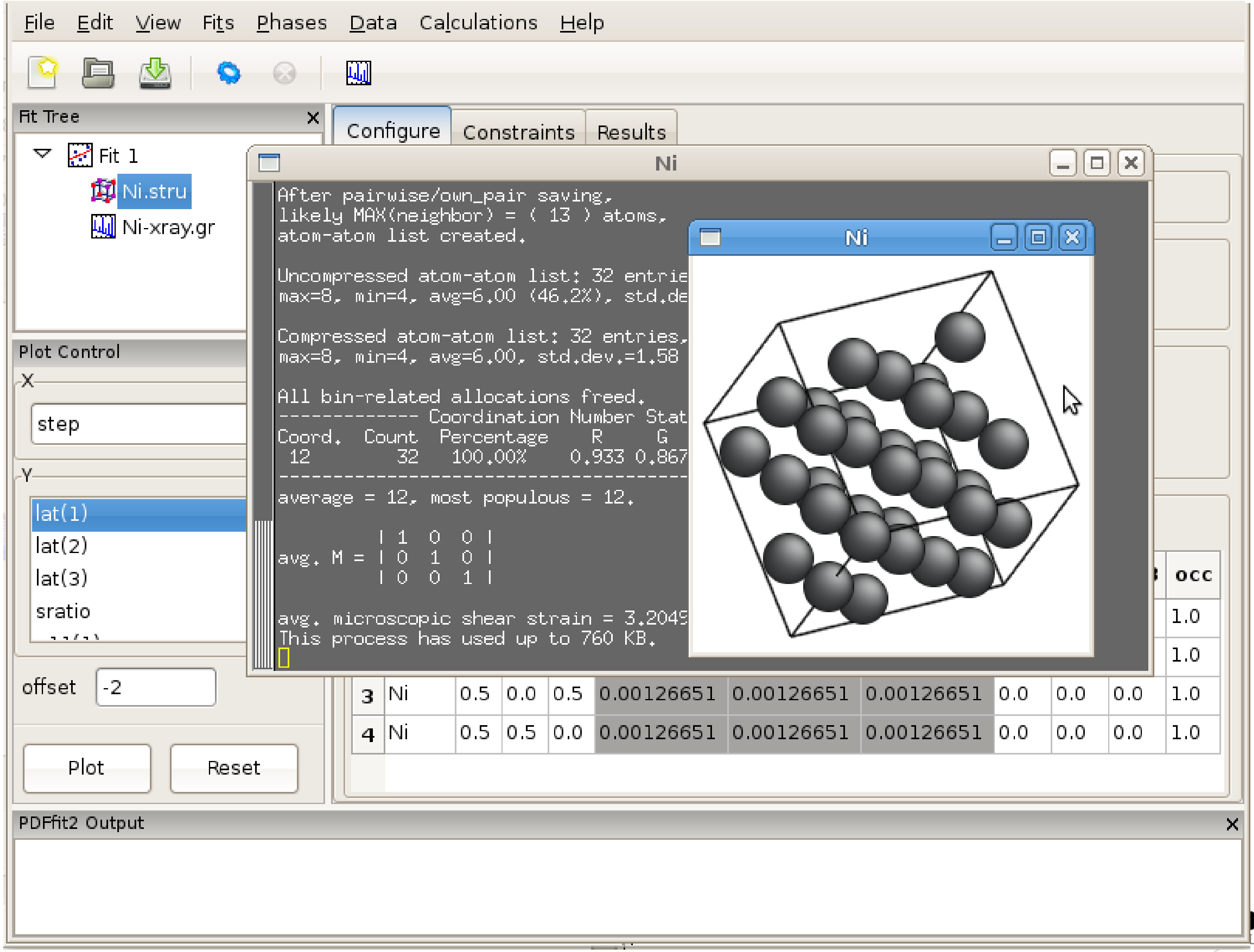
offset: -2

x = 14.3912, y = -1.20975

```
==========================================================================
```

Displaying the structure

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



```
After pairwise/own_pair saving,
likely MAX(neighbor) = ( 13 ) atoms,
atom-atom list created.

Uncompressed atom-atom list: 32 entrie
max=8, min=4, avg=6.00 (46.2%), std.de

Compressed atom-atom list: 32 entries,
max=8, min=4, avg=6.00, std.dev.=1.58

All bin-related allocations freed.
------------- Coordination Number Stat
Coord.  Count  Percentage    R     G
 12        32    100.00%    0.933 0.867
---------------------------------------
average = 12, most populous = 12.

            | 1  0  0 |
avg. M =    | 0  1  0 |
            | 0  0  1 |

avg. microscopic shear strain = 3.2049
This process has used up to 760 KB.
```

											occ
											1.0
											1.0
3	Ni	0.5	0.0	0.5	0.00126651	0.00126651	0.00126651	0.0	0.0	0.0	1.0
4	Ni	0.5	0.5	0.0	0.00126651	0.00126651	0.00126651	0.0	0.0	0.0	1.0

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-X-ray co-refinement
    - Ni/Si mixture refinement; phase analysis

    - Ni T-dependence sequential refinement
    - $LaMnO_3$ T-dependence sequential refinement – complex system
    - $Cu(Ir_{0.88}Cr_{0.12})S_4$ 100K data fitting - r-dependent sequential refinement
    - Nanoparticle examples: CeO_2 and CdSe systems

Live PDFgui Demo (*time permitting*)