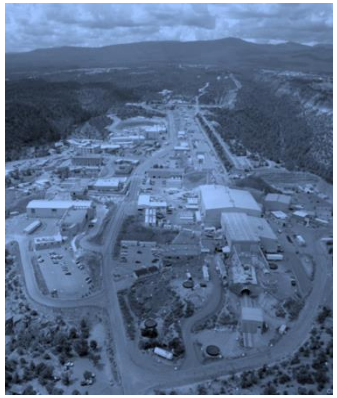

NOMAD
Modeling of the PDF: Hands-on PDFgui Exercises

NXS School Experiment

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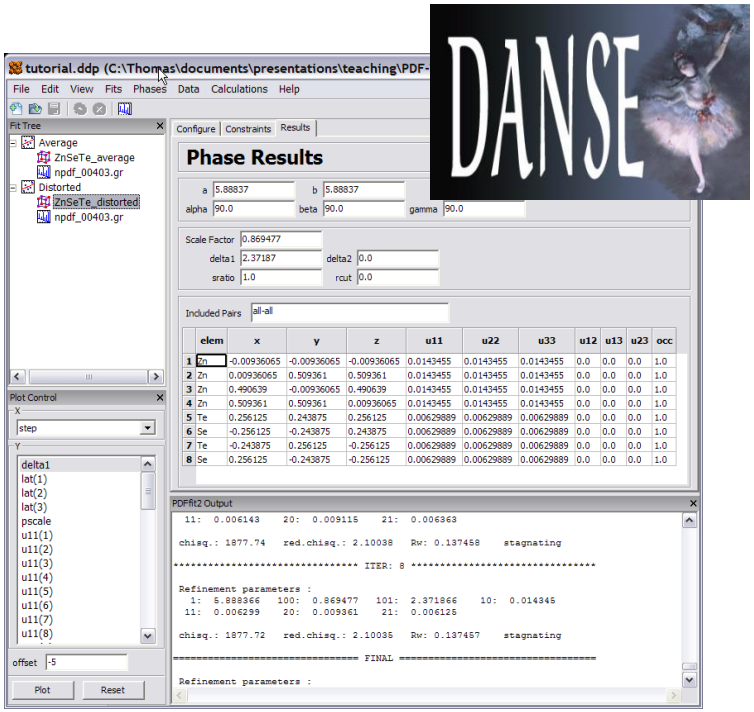
Overview

- PDFgui Parameters and Program Structure
- NOMAD Examples
  - Calibration Materials
  - SnO_2 Nanoparticles, In Situ Dehydration
- Additional Example: (on your own)
  - Jahn-Teller Distortion in $LaMnO_3$, A temperature series (neutron)
- Additional Example (on your own)
  - ZnSe Bulk (x-ray)
  - ZnSe Nano (x-ray)

PDFgui Software

Part of DANSE project.

http://www.diffpy.org/



- Calculation and refinement of small model system (< 1000 atoms)
- 'Rietveld' type parameters: *lattice parameters, atomic positions, displacement parameters, ..*
- Refinements as function of r range !
- Automatic refinement of multiple datasets as function of *T* or *x*
- Intuitive GUI
- Engine *pdffit2* can also be used in command mode

Parameters and Program Structure

PDFgui: Data set parameters

Set Parameters (or calibrated):

Refinement Range: Your selected range for real space refinement

Q_{max}: Finite data range used in the Fourier transform step

Q_{damp}: Gaussian dampening envelope due to limited Q-resolution

Q_{broad}: Peak broadening from increased intensity noise at high Q, often only significant for wide r-ranges

Refined Parameters:

dscale: data set scale factor

PDFgui: Phase parameters

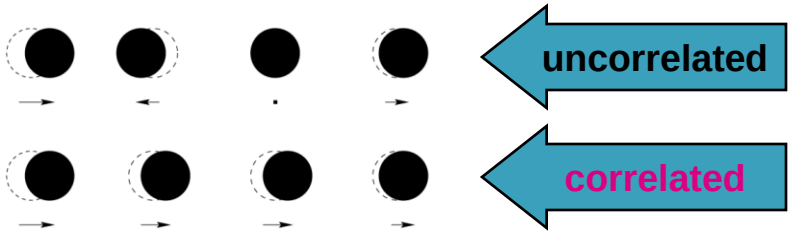
Refined Parameters:

pscale: scale factor of phase *Warning: correlated to dscale*

lattice parameters (*a*, *b*, *c*, *α*, *β*, *γ*)
For every atom *n:*

x[n]	x-position (fractional coordinates)
y[n]	y-position
z[n]	z-position
occ[n]	occupancy
u[*1*..*6*,n]	anisotropic thermal parameter U_{ij} (Å^{-2})

PDFgui: Peak width parameters



Results in sharpening of near neighbor peaks

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

delta1: 1/r contribution to peak sharpening (high temperature case) ($Å^{-1}$)

delta2: $1/r^2$ contribution to the peak sharpening (low temperature case) ($Å^{-2}$)

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

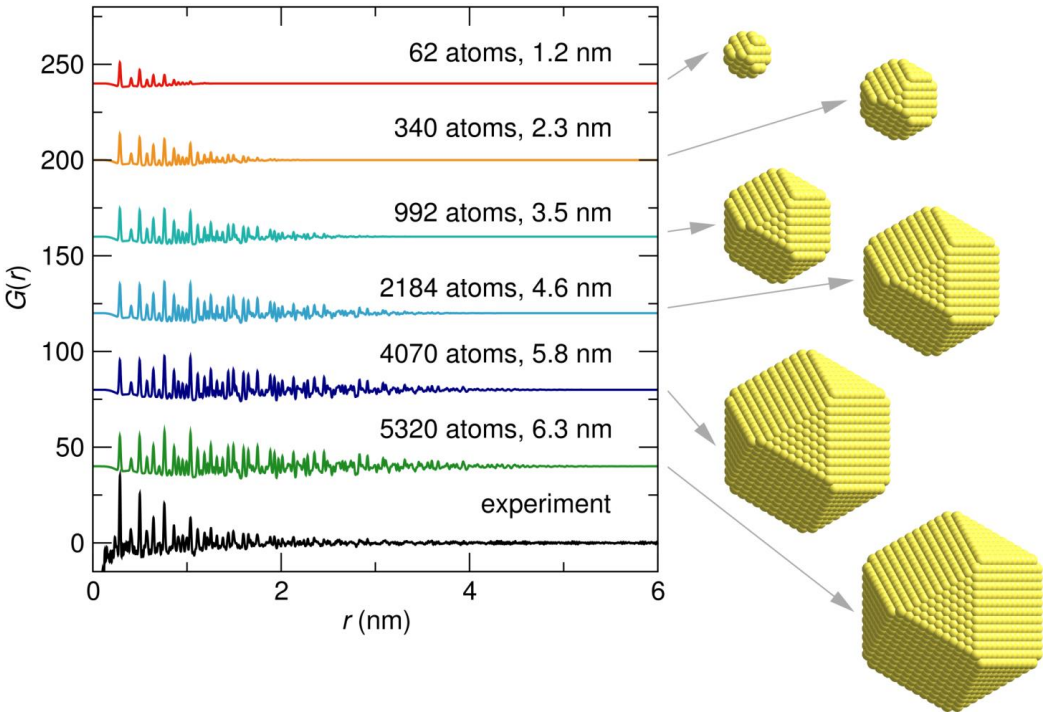
rcut: radius cuttoff for applying the sratio sharpening factor (Å)

Warning: strongly correlated, use more than one with caution

PDFfit: For nanoparticles

spdiameter: particle diameter for PDF shape damping function (Å)

stepcut: *r* value above which the PDF is truncated to zero (Å)



Ni Standard

NOMAD Data, Bulk Material

PDFgui example: Ni Bulk

We are starting with bulk Ni to obtain instrument resolution and dampening parameters. This way we can de-couple structural effects (disorder and size) from instrument effects in the experimental PDF.

Structural parameters for Ni (FCC Metal)

Spacegroup	Fm-3m
Lattice parameters	a = 3.52 Å
Atom coordinates	Ni 0 0 0

Steps:

1. Choose data and structural phase
2. Check peak positions
3. Choose refinement range
4. Refine

Refine:

1. dscale, a, b, c
2. U_{iso}, delta2
3. atom positions
4. Q_{damp}, Q_{broad}

PDFgui example: Ni Bulk

To get started…

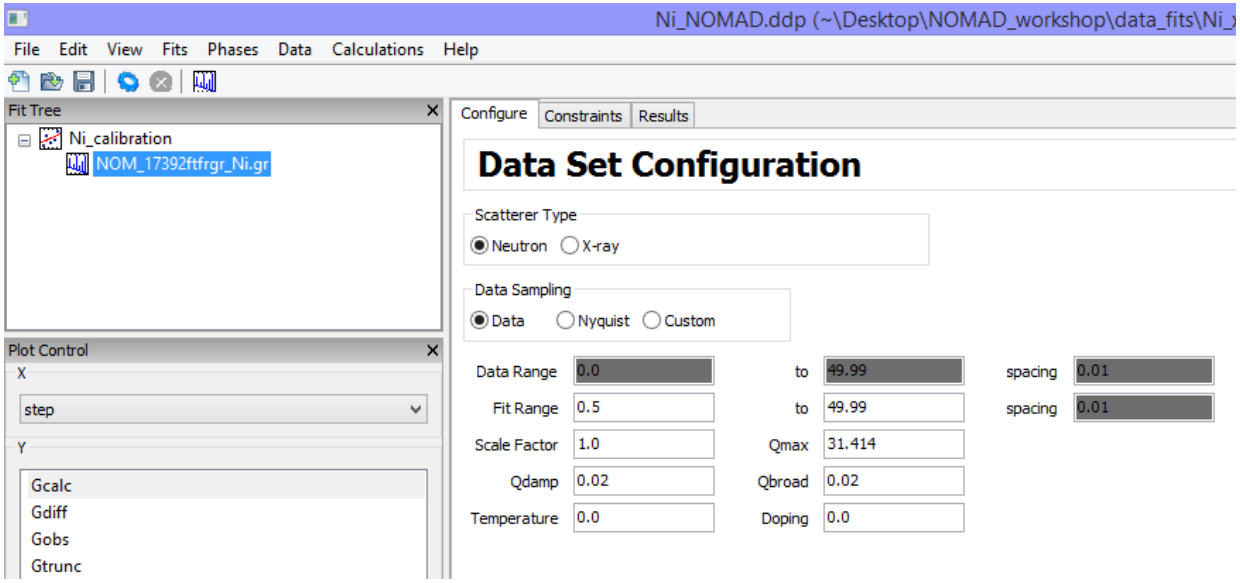
→Click on *Fits*

→ Select *"New Fit"* and name it in the *Fit Tree* Window

→Click on *Data*

→Select *"New Data Set"*

→Open File "*Ni.gr"



Data Set Configuration ("Configure" Tab)

→Enter Fit Range in Å (1 to 50)

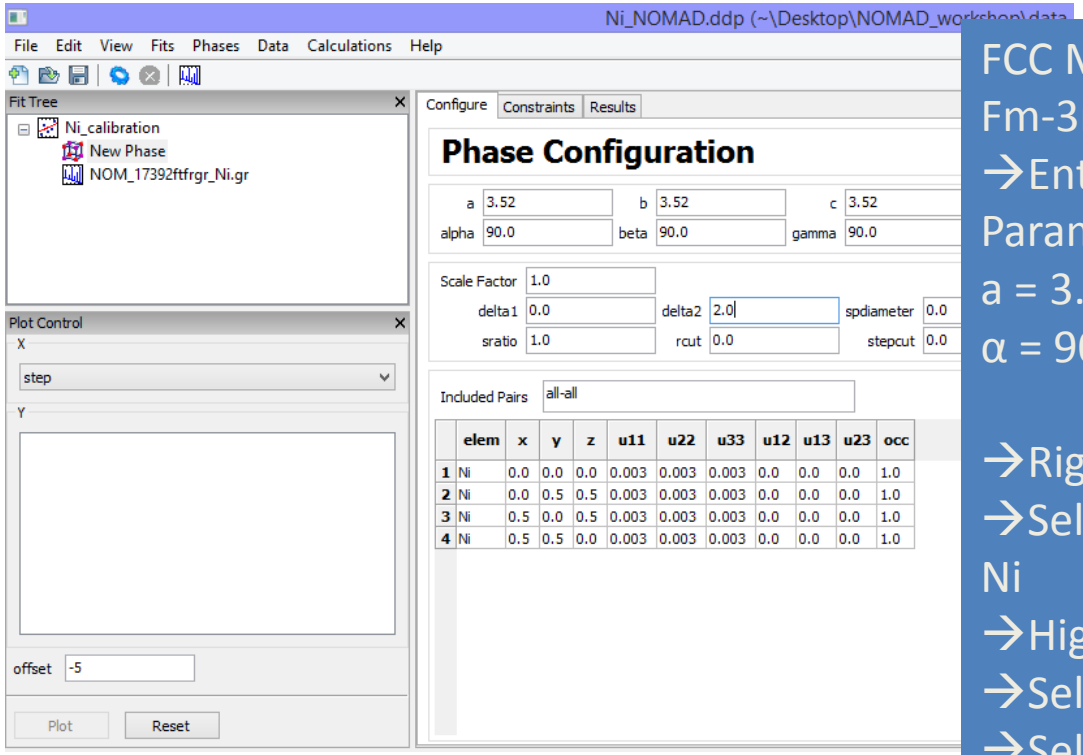
→Enter Starting Value for Q_{damp} in $Å^{-1}$ (0.02)

→Enter Starting Value for Q_{broad} $Å^{-1}$ (0.02)

PDFgui example: Ni Bulk

Phase Configuration ("Configure" Tab)

→*Phases*
→*New Phase*
→*"Create a new structure from scratch"*

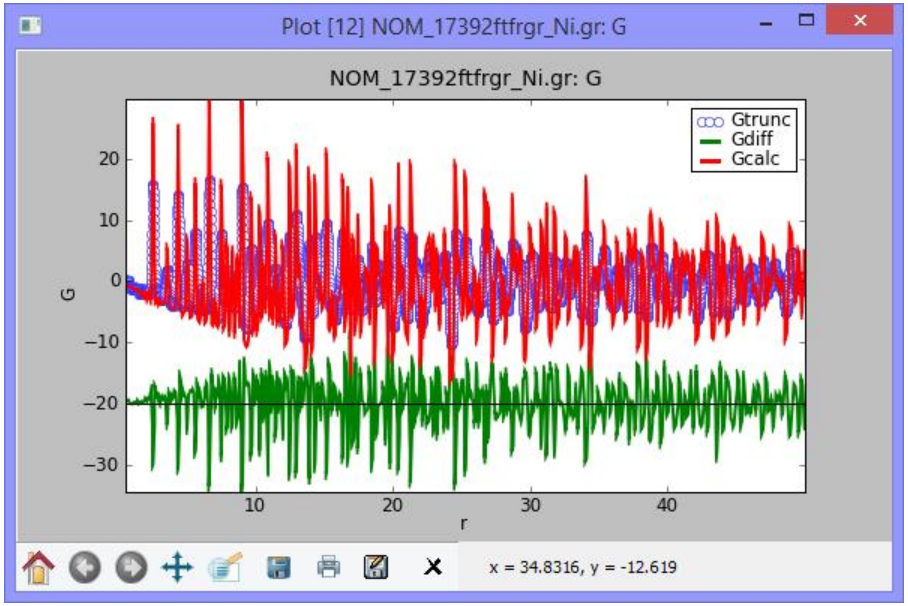


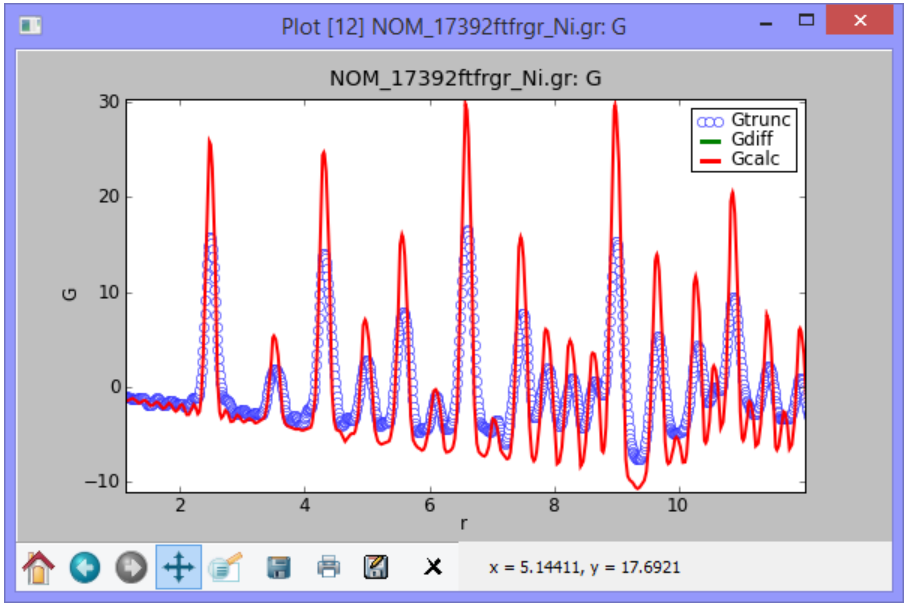
FCC Metal Crystal Structure
Fm-3m
→Enter Starting Values for Lattice Parameters:
a = 3.52, b = 3.52, c = 3.52
α = 90, β = 90, γ = 90

→Right Click "*elem*"
→Select *Insert Atoms* (you need one row)
Ni 0 0 0
→Highlight atom rows and Right Click
→Select "*Expand Space Group*"
→Select Fm-3m

→Enter Starting Value for Scale Factor: 1.0
→Enter Starting Value for delta2: 1.0

PDFgui example: Ni Bulk





Check Peak Positions:
I like to calculate the PDF of my starting structure and compare to data before defining refinement parameters (Do I have a good starting structure?).

→Click on the gear in the picture menu
→When calculation is complete, click on the plot in the picture menu (data, calculation, and difference curve are shown).

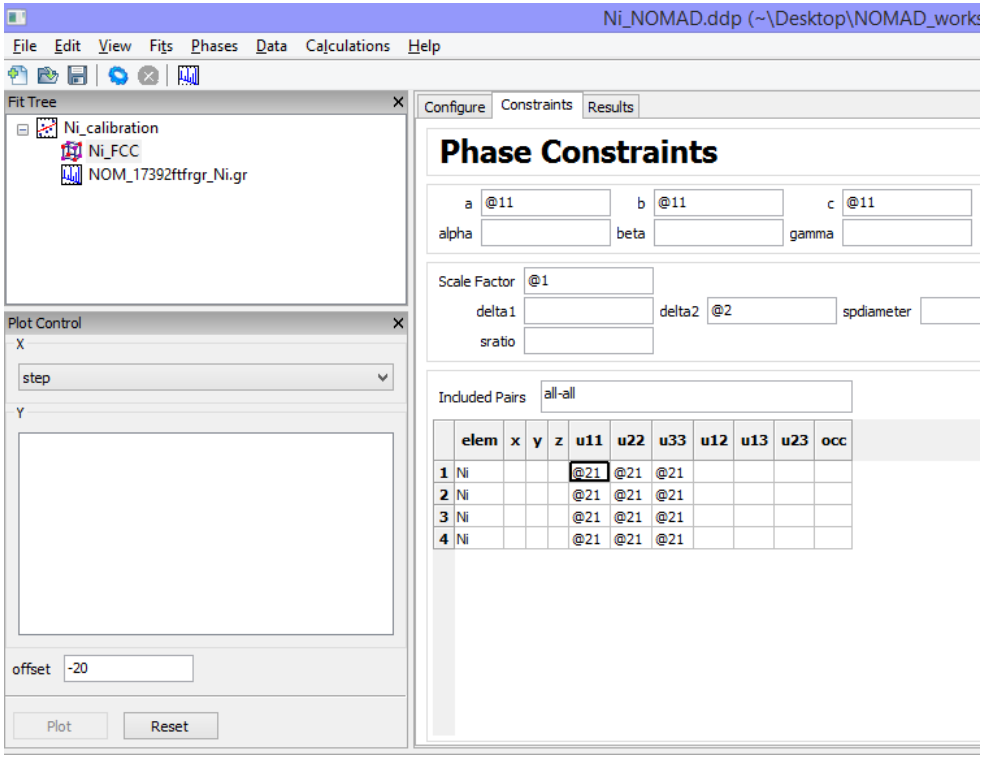
You can use the picture menu at the bottom of the plotting screen to pan, zoom, save the plot image, print the plot, or export the plot data.

→Looks like we have a good starting structure (peak positions and relative intensities roughly match the data).

Now we can enter refinement parameters…

PDFgui example: Ni Bulk

Phase Constraints ("Constraints" Tab)



→Enter "handles" for:

- lattice parameters (a = b = c)
- scale factor
- delta2 (or other peak width parameter)
- Isotropic atomic displacement parameters for each atom type (u11 = u22 = u33)

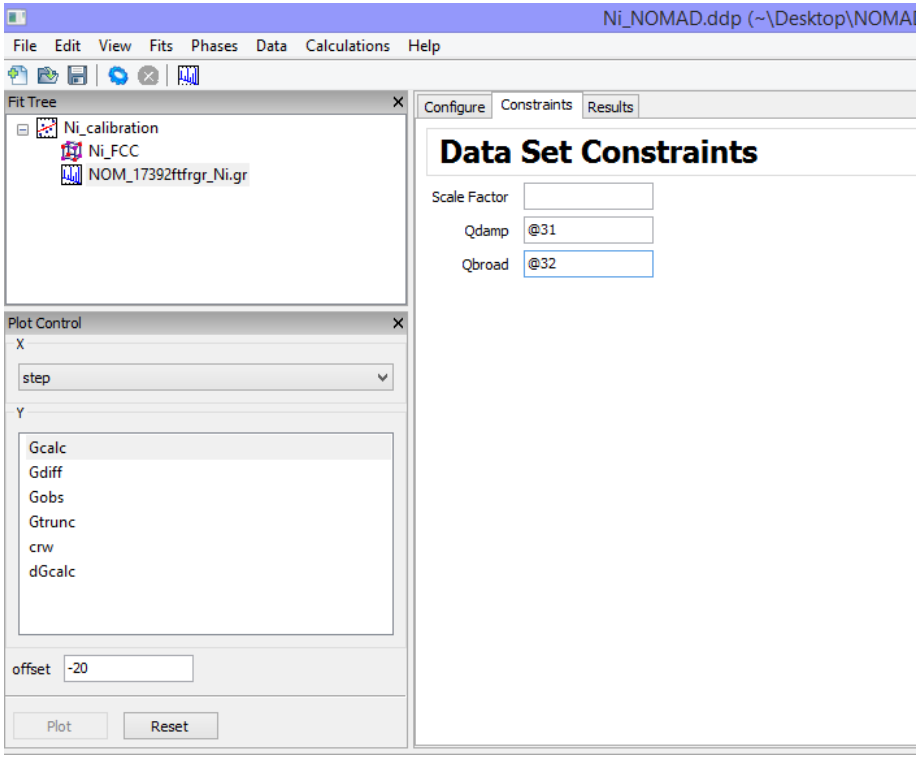
PDFgui example: Ni Bulk

Data Constraints ("Constraints" Tab)

→Enter "handles" for:

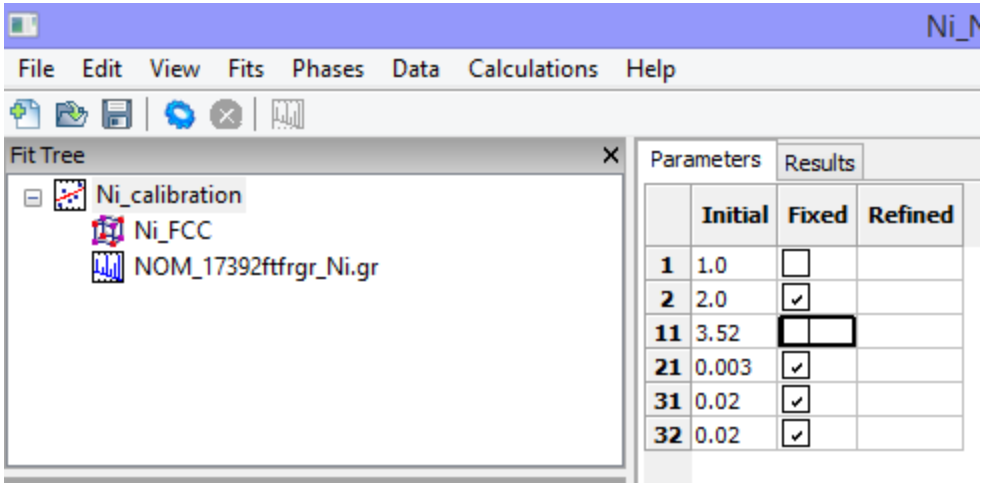
- Q_{damp}
- Q_{broad}

NOTE: When this is not a standard data set (meaning no expected disorder) it is not best practice to refine these parameters.



PDFgui example: Ni Bulk

Let's check our refinement parameters ("Parameters" Tab) before we start:
Here we can fix certain parameters, and refine certain parameters.

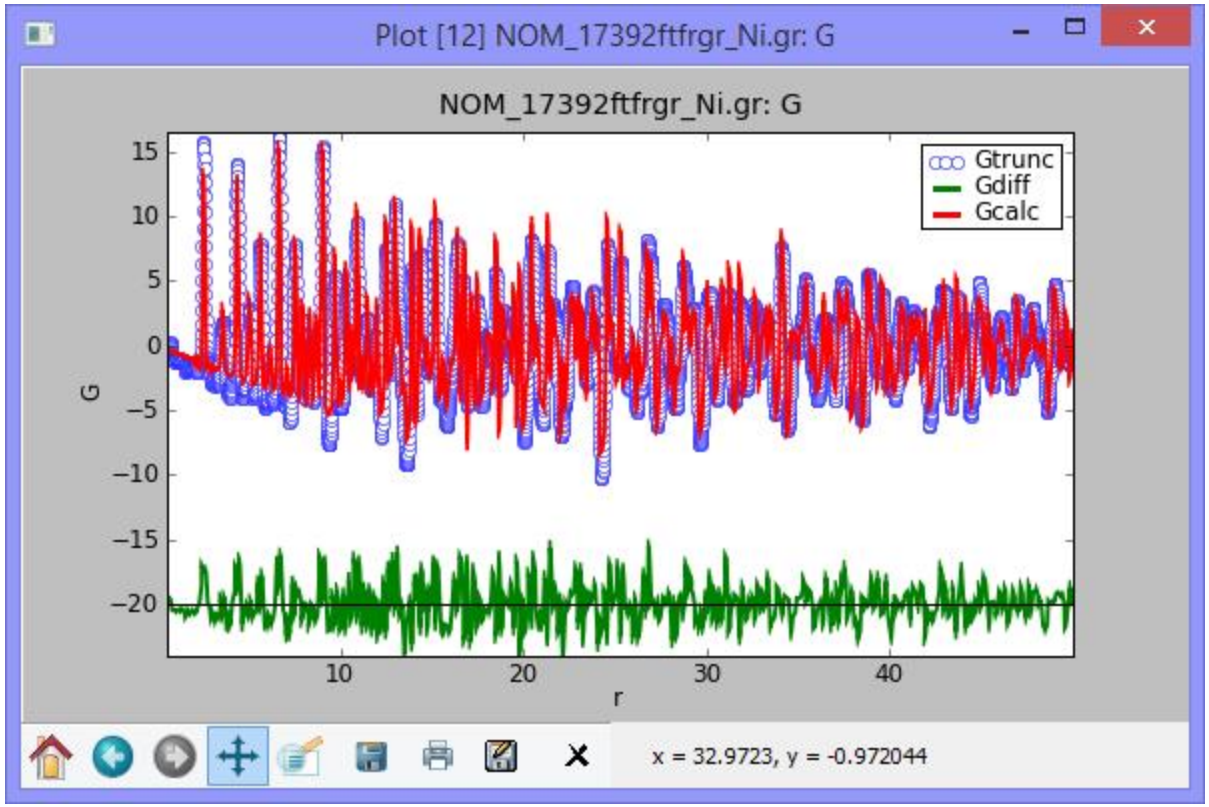


Kate's Recommended Order of Refinement:

1. **scale, a, b, c**
2. **U_{iso}, delta2**
3. **atom positions (not in this case)**
4. **Q_{damp}, Q_{broad} (only for standard data set)**

Click the gear in the picture menu when you have made your selection

PDFgui example: Ni Bulk



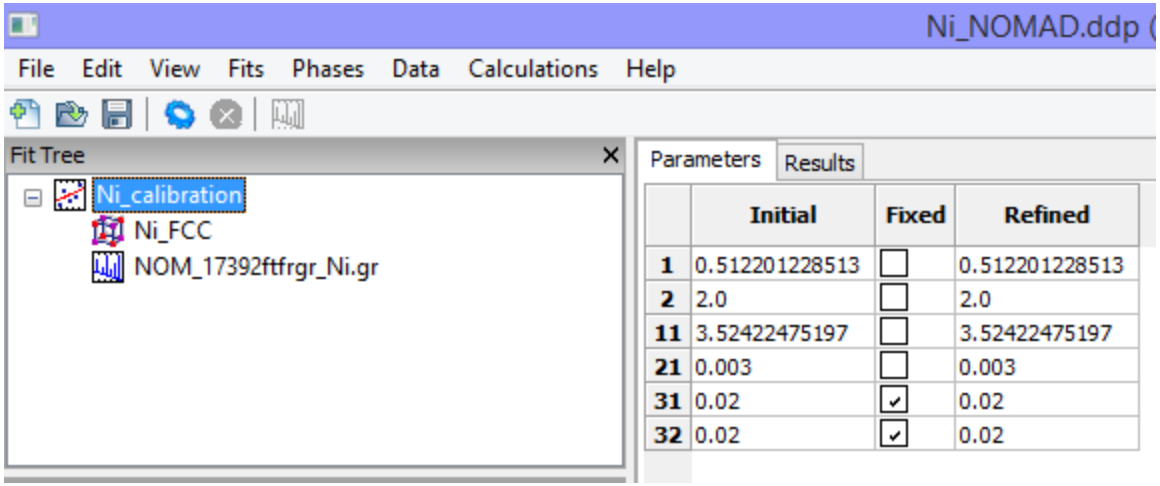
Kate's Recommended Order of Refinement:

1. scale, a, b, c

R_w goes from 1.01 to 0.37

Click the gear when you have made your selections.

PDFgui example: Ni Bulk



Highlight refined parameters

→ Right click and select "*Copy Refined to Initial*"

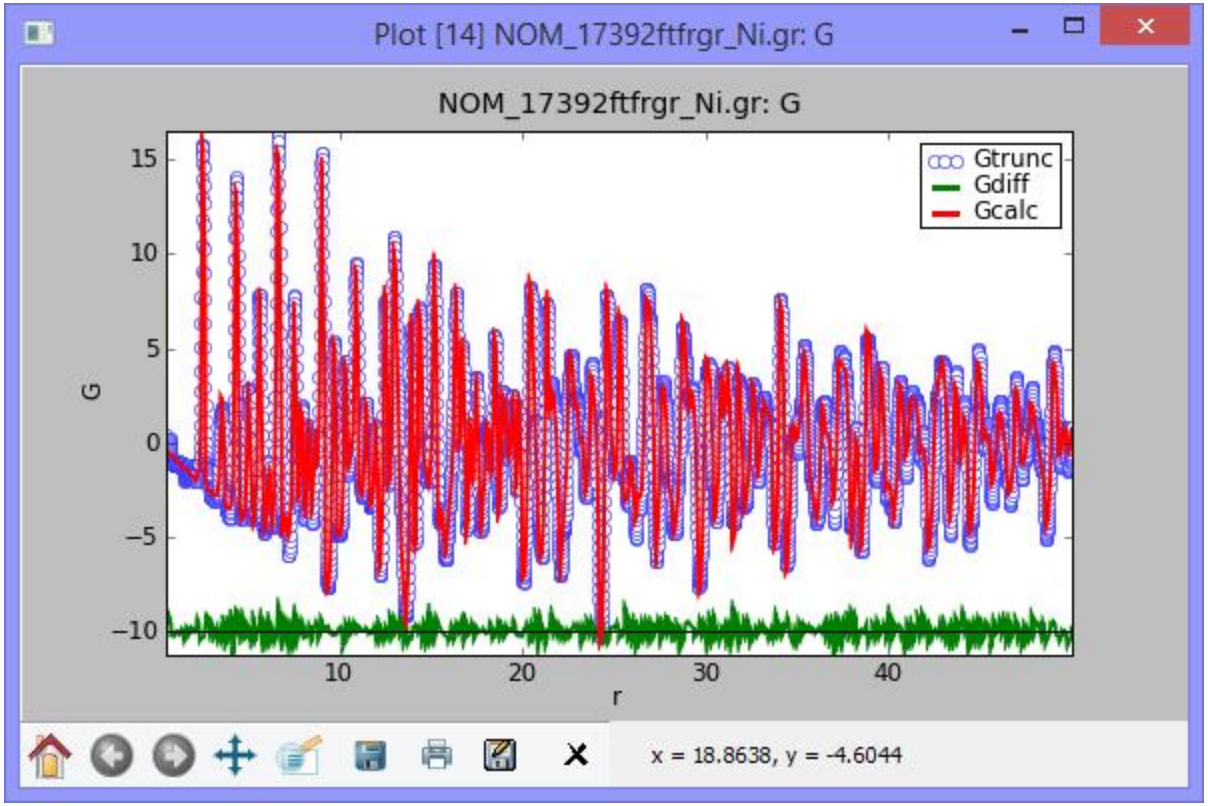
→ Continue adding parameters and running the refinement

1. scale, lattice parameters — *R_w goes from 1.01 to 0.37*
2. U_{iso}, delta2 — *R_w goes from 0.37 to 0.11*
3. atom positions (not in this case)
4. Q_{damp}, Q_{broad} (only for standard data set) — *R_w goes from 0.11 to 0.10*

PDFgui example: Ni Bulk

Final R_w = 10%

NOTE: This is supposed to be easy (it's a standard or calibration data set, after all! In most research samples lots of time is spent trying different models, and care should be taken to ensure you have not fallen into a "local minima".



Under "*Results*" Tab

scale factor	0.788(6)
delta2 factor	2.7 (1)
a	3.52433(8) Å
U_{iso}(Ni)	0.00589 (8) Å^2
Q_{damp}	0.0166(6) Å^{-1}
Q_{broad}	0.0259(6) Å^{-1}

These will now be set in the following example.

Some other PDFgui features

Fitting data series

→ Fits →Macros →temperature, doping, or *r*-series

Allows you to automatically create and run fits to multiple data sets in a series.

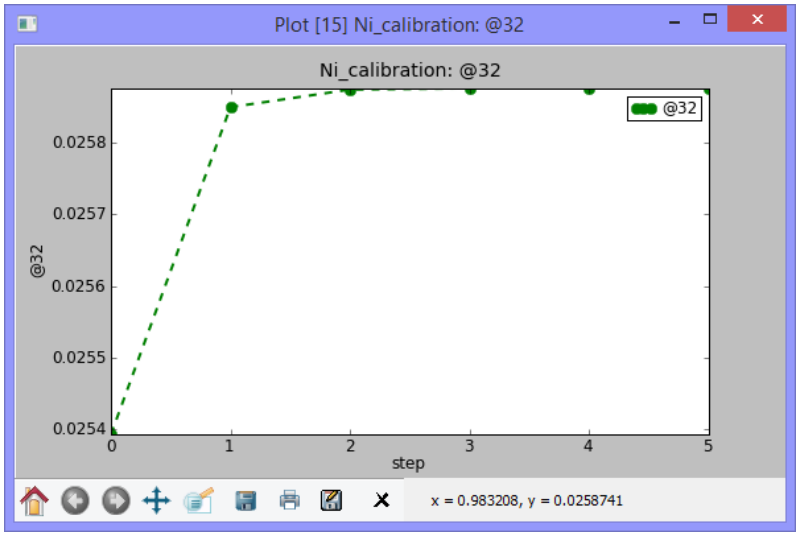
Visualization of structures

→Edit →Preferences →Structure viewer executable

Allows you to visualize a structure in your fit tree when it is highlighted and you click the plot icon.

Refinement progress

Options in the plot control window allow you to view parameter values and goodness of fit as a function of refinement iteration



Accessing initial and final structure information

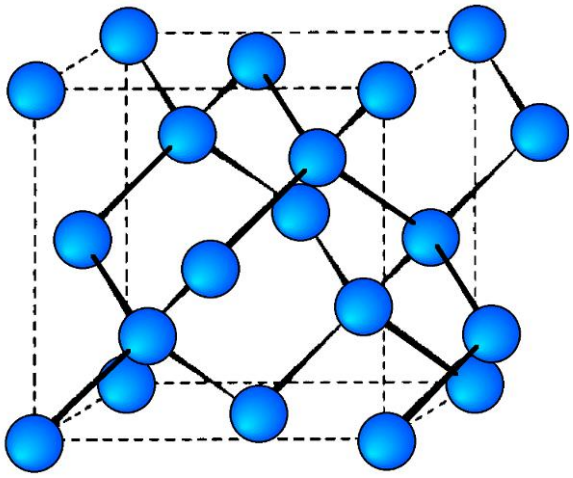
→ Phases

Allows you to calculate specific bond lengths and bond angles, and export or plot initial and final structures when a phase is highlighted.

See the manual for more.

PDFgui example: Diamond Powder

Can you fit the diamond data we just collected?



Structural parameters for C (diamond)

Spacegroup	Fd-3m
Lattice parameters	a = 3.57 Å
Atom coordinates	C 1/4 1/4 1/4

Steps:

1. Choose data and structural phase
2. Check peak positions
3. Choose refinement range
4. Refine

Refine:

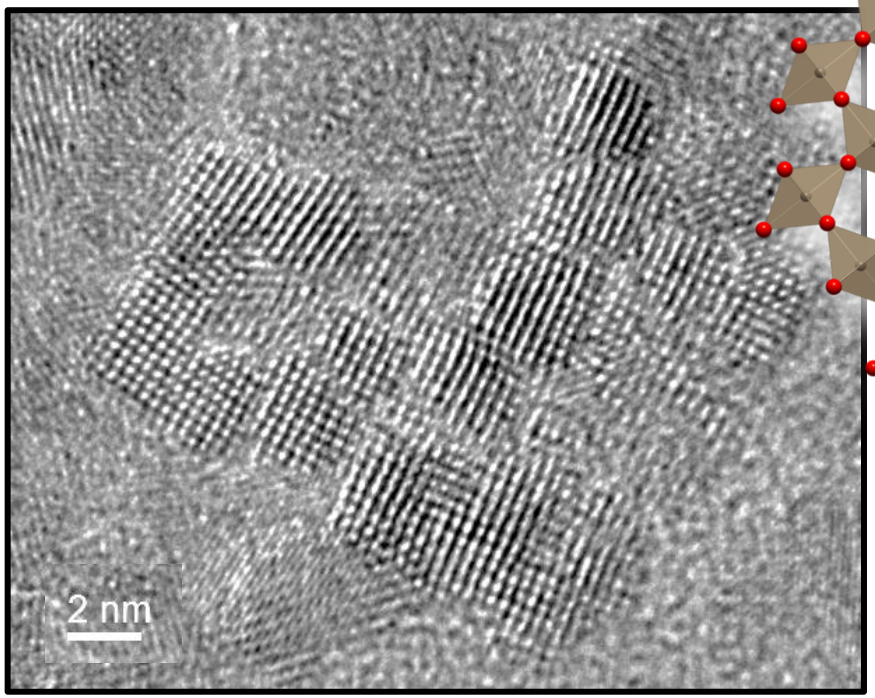
1. dscale, a, b, c
2. U_{iso}, delta2
3. atom positions
4. Q_{damp}, Q_{broad}

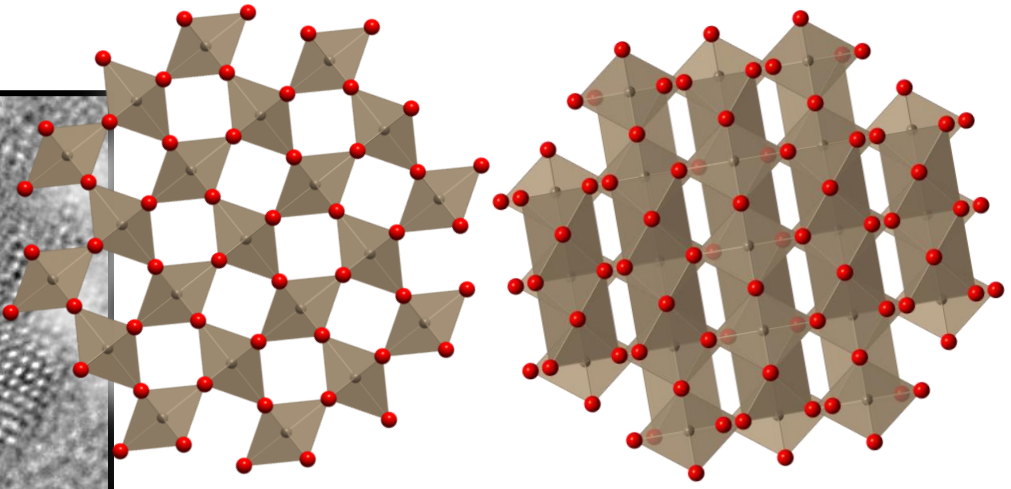
SnO_2 Nanocrystals

Neutron Data, Nanomaterial

Example: SnO_2 Nanocrystals

SnO_2 (cassiterite) nanocrystals capped with H_2O/OH or D_2O/OD groups



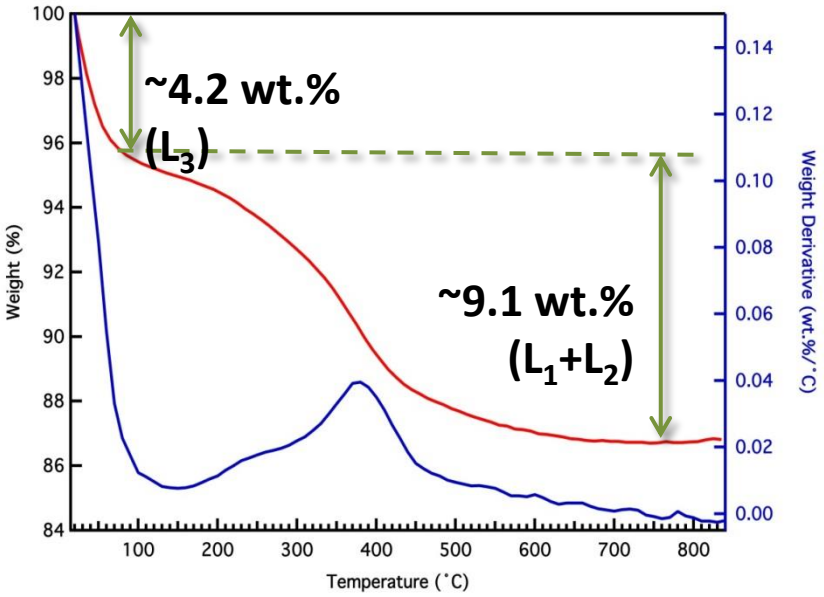


How many layers of water are actually formed?

What are the dynamics of dehydration?

How is water bonded to surfaces?

TGA suggests 2 steps dehydration



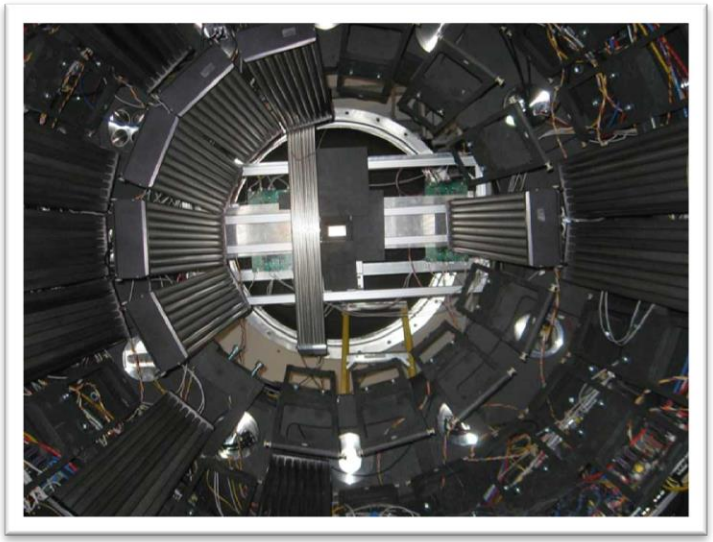
H.W. Wang, et al, *J. Am. Chem. Soc*., 2013, 135 , 6885–6895.

PDFgui example: SnO_2 Nanocrystals

Data collection at NOMAD, SNS
17 datasets between RT and 800˚C

60 minutes each

Q_{max} = 31.5 $Å^{-1}$



NOMAD

H.W. Wang, et al*, J. Am. Chem. Soc*., 2013, 135, 6885–6895.

Hsiu-Wen Wang

Wei Wang (synthesis)

Thomas Proffen and Mikhail Feygenson (NOMAD-NPDF)

Alexander Kolesnikov and Dave Wesolowski (SEQUOIA-INS)

Lukas Vlcek (MD model), Lawrence Allard (TEM), and Lawrence Anovitz

Example: SnO_2 Nanocrystals

File Names

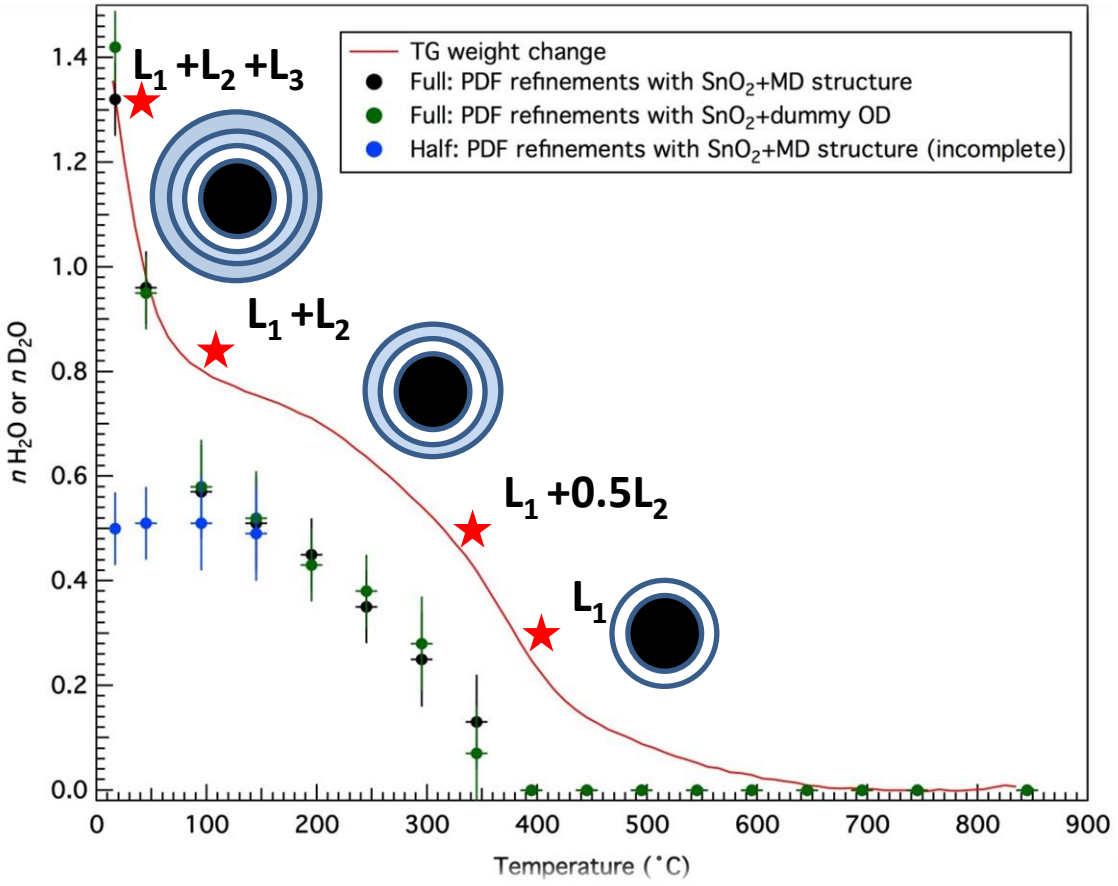
SnO2_PDFgui_room temp

#3: fully hydrated (L1+L2+L3 hydration layers)

#2: half hydrated (L1+0.48L2)

#1: dry sample (L1+0.25L2, i.e., the driest achievable states without introducing the growth)

#B: bulk SnO2



Example: SnO_2 Nanocrystals, Single Phase

Structural parameters for SnO_2 (Cassiterite)
(you can read in the structure from a cif or other format)

Spacegroup	P42/mnm
Lattice parameters	a=b=4.7 Å, c=3.2 Å
Atom coordinates	Sn (0, 0, 0) O (0.3, 0.3, 0)

Use:
Q_{damp}= 0.022 $Å^{-1}$
Q_{broad}= 0.024 $Å^{-1}$

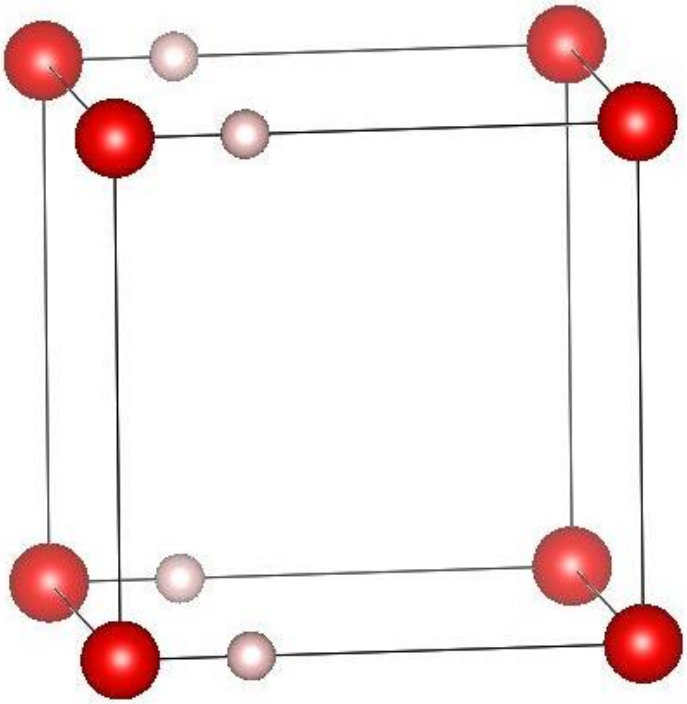
Steps:
1. choose data and phase
2. fix data set parameters
3. check peak positions
4. choose refinement range

Refine:
1. dscale, a, b, c
2. U_{iso}(Sn), U_{iso}(O), delta1, spdiam for nano
3. atom positions

Example: SnO_2 Nanocrystals, with Dummy OD Phase

Structural parameters for 'Dummy' OH Phase
(you can read in the structure from a cif or other format)

Spacegroup	P1
Lattice parameters	a=b=c=4 Å
Atom coordinates	O (0, 0, 0) D (0.25, 0, 0)



Steps:
1. Add second phase
2. Set stepcut = 1.9 Å

Refine:
1. pscale, *a*
2. U_{iso}, delta1
3. D *x* coordinate

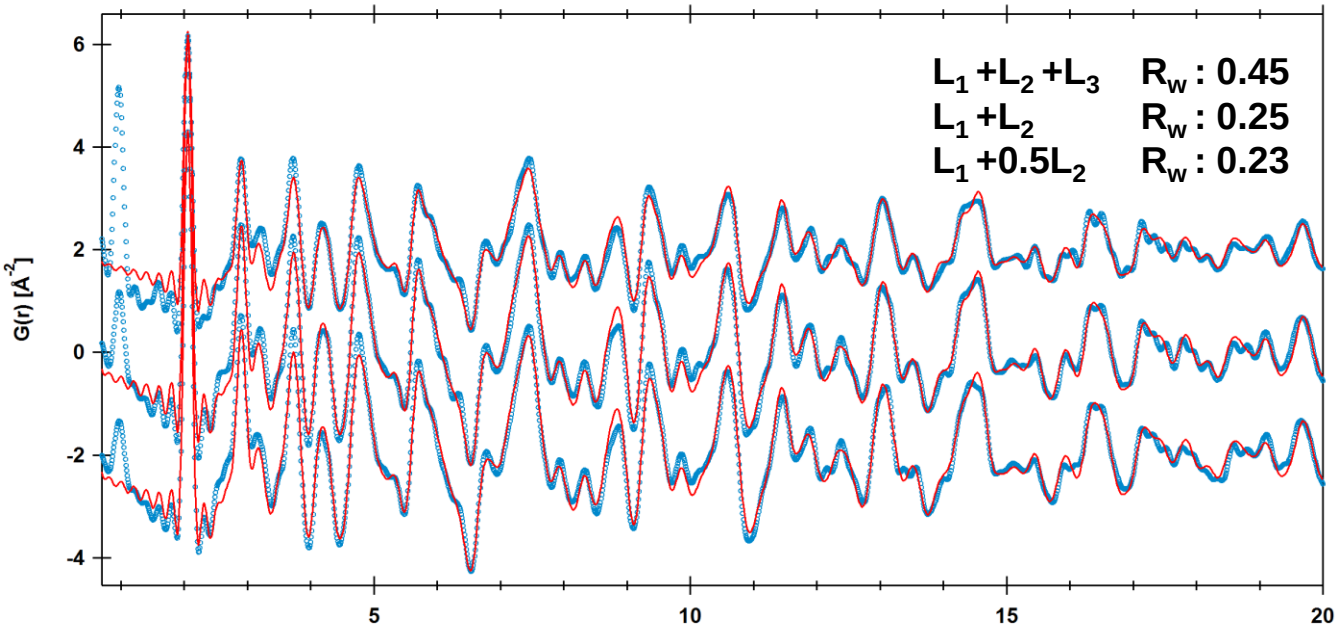
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

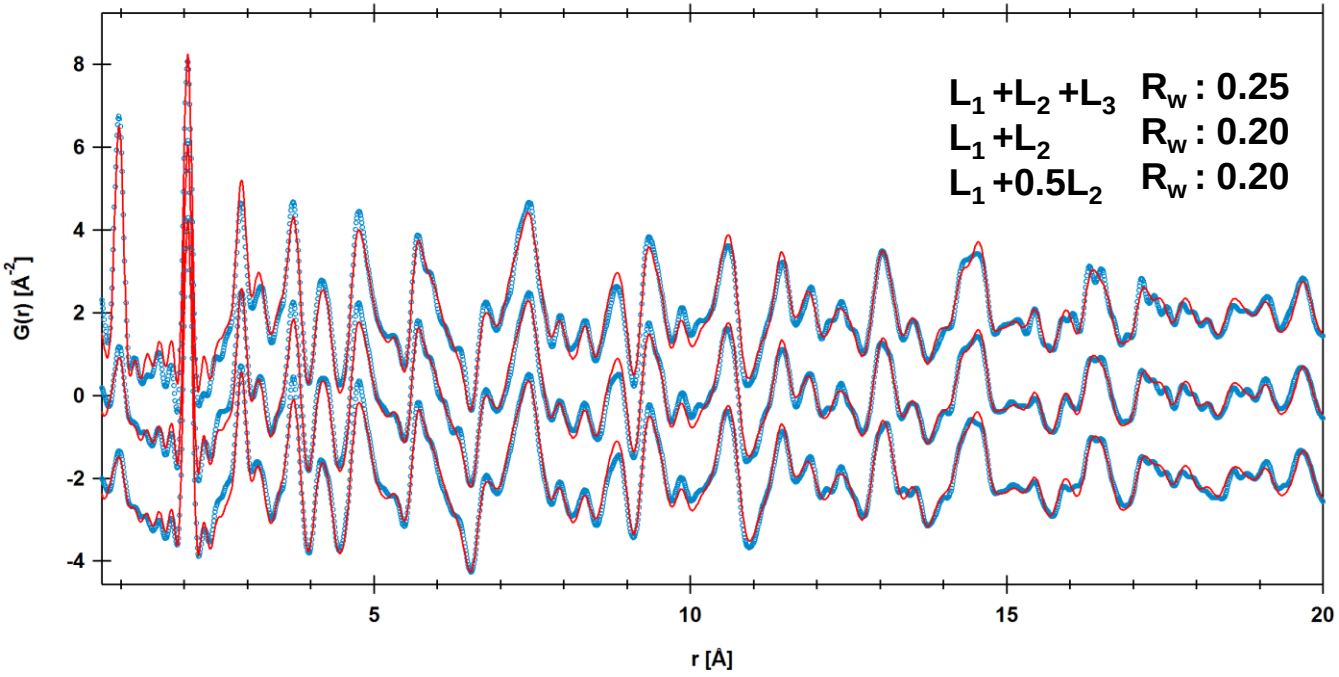
size = ~47 Å



Two phase model:

SnO_2 bulk + layered

MD water structure

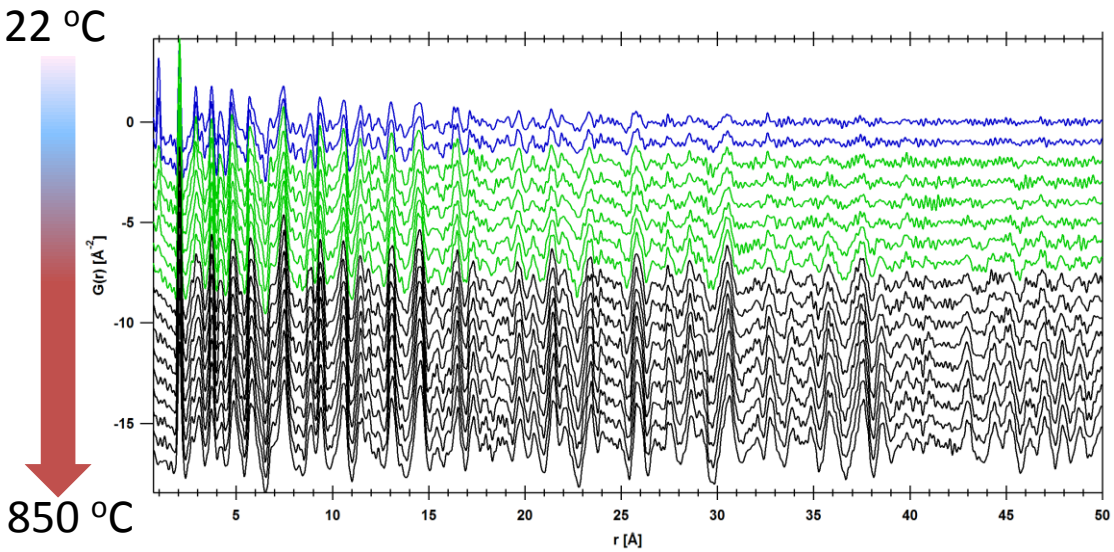


Example: SnO_2 Nanocrystals, Dehydration

#3 temps is the temperature sequence fits for sample #3

Temperatures from RT-350C are labeled

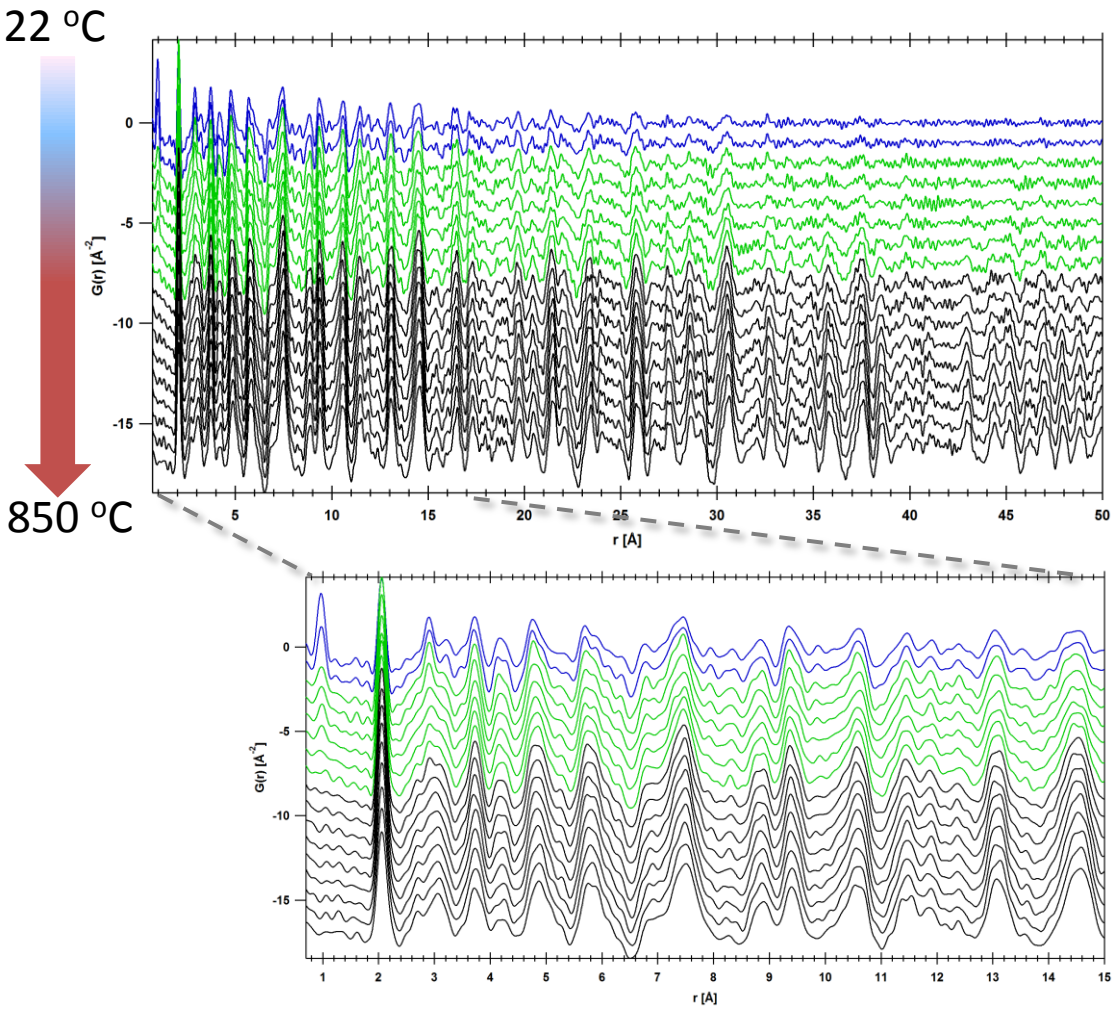
Within this temperature range (22-350C), you will see the growth of NPs as a function of hydration level (blue and green below)



Example: SnO_2 Nanocrystals

In situ Dehydration, NOMAD, SNS

- Starting with full coverage ($L_1 + L_2 + L_3$)
- Blue lines:
  22 and 50 ºC - $L_1 + L_2 + L_3$
- Green lines:
  50 to 350 ºC (with 50 ºC increments) - $L_1 + L_2$
- Black lines:
  400 to 850 ºC (with 50 ºC increments) – SnO_2 grain growth



H.W. Wang, et al, *J. Am. Chem. Soc*., 2013, 135 , 6885–6895.

Example: SnO_2 Nanocrystals

Fit the data series

→ Fits →Macros →temperature

Allows you to automatically create and run fits to multiple data sets in a series.

Extract features as a function of temperature easily
(particle size, Dummy OH phase fraction, etc.)