XRD Refinement using Rietica

Jan-Hendrik Poehls
Mary Anne White Group
Dalhousie University

DALHOUSIE *University*

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Introduction

- For crystal structure characterization x-ray diffraction (XRD) is a common technique
- Experimental data can be qualitatively compared using, *e.g.*, diverse data bases (MATCH) or using calculated pattern (CrystalDiffract)
- For quantitative analyses experimental data has to be refined (*e.g.*, Rietveld refinement using the software Rietica)
- Rietveld refinement can give many aspects of the structure (atomic positions, occupations) and exclude measurement uncertainties (*e.g.*, sample displacement)
- It is a least squares approach
- A free Rietveld refinement software is Rietica (Free download: http://www.rietica.org/download.htm)

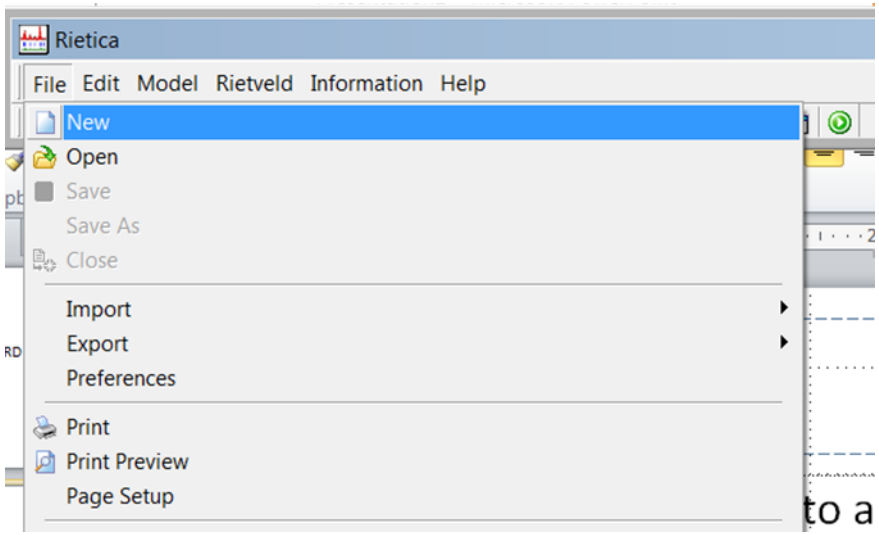
Content

Three examples are given:

- 1. Example: BASICS ($Li_xNi_{1-x}O$)
  - General procedure to refine simple XRD patterns (including two atoms occupy the same atomic position)
- 2. Example: ADVANCED (Ge clathrates)
  - Refinement of complex structures (including atomic positions are not fixed and occupations are not completely filled)
- 3. Example: QUALITATIVE ANALYSIS
  - Fast qualitative analysis of space group and lattice parameters

Open Rietica

- Open Rietica
- Open New Data (File→ New)
- Indicate the number of phases and the number of atoms
- Each atom with different position has to be included
- Save input file as ‘yyyymmdd_material.inp’



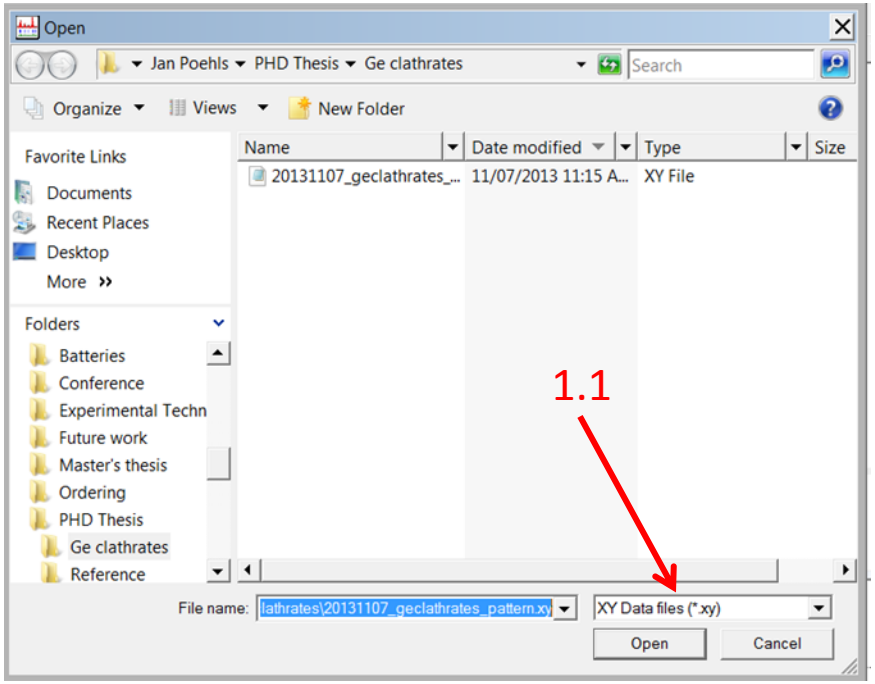
Open Experimental Data

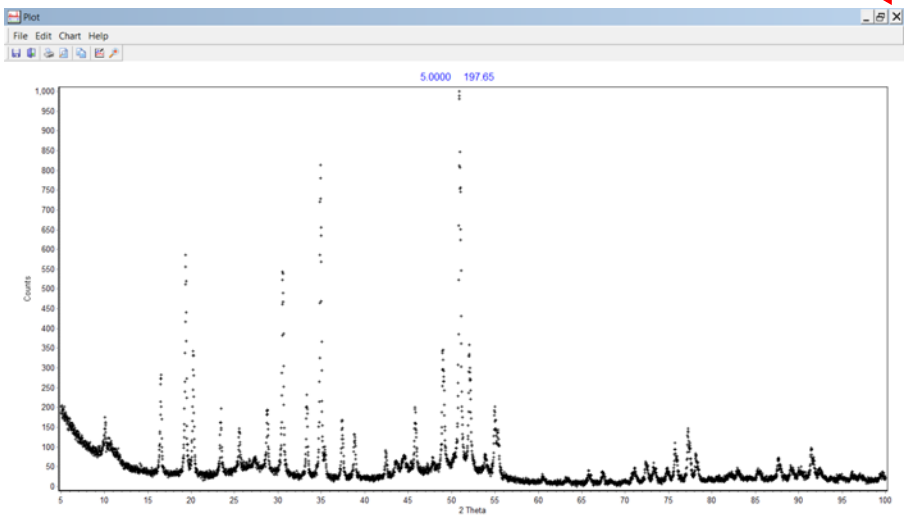
- XRD pattern has to be a ‘.xy’ file
- Best way to get a ‘.xy’ file is:

1. Open the software ‘MATCH’
2. File→Import→Diffraction data
3. File→Export→Profile data
4. Save as type: ‘Profile (2 columns: 2theta/d intensity)’
5. File name: ‘yyyymmdd_material_pattern.dat’
6. Change ‘.dat’ file to ‘.xy’ manually
7. Go to Rietica: File→Open

Open Experimental Data

7. Open '.xy' file
8. Experimental data occurs (1.1)
9. Close Plot (1.2)



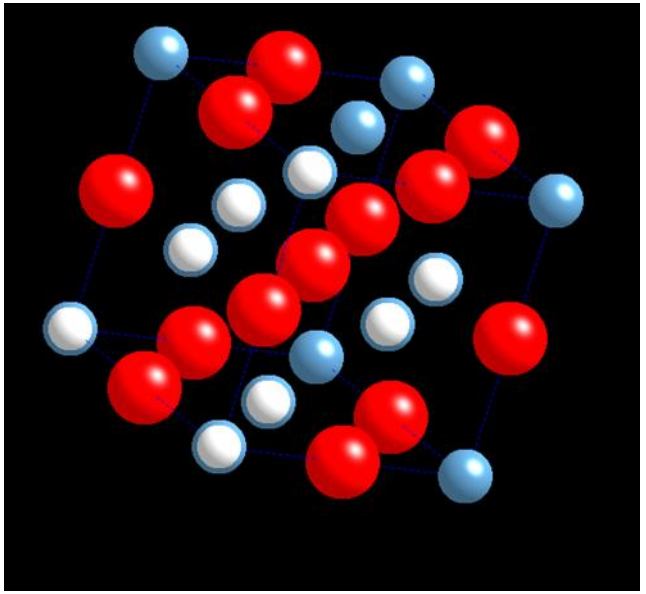


Example 1

BASICS: $Li_xNi_{1-x}O$

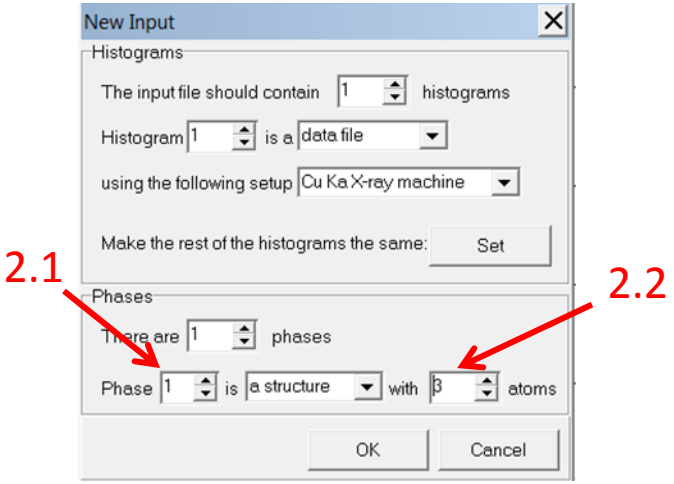
$Li_xNi_{1-x}O$

- $Li_xNi_{1-x}O$ has a rock salt structure (*Fm-3m*)
- Cations sit on the *4a* sites and oxygen sits on *4b* sites
- Lattice parameter is about 3.9 Å
- Information about space groups, occupation sites and lattice parameters can be found in MATCH, manuscripts
- Open data base for crystal structures:
  - http://www.crystallography.net
  - http://www.webmineral.com

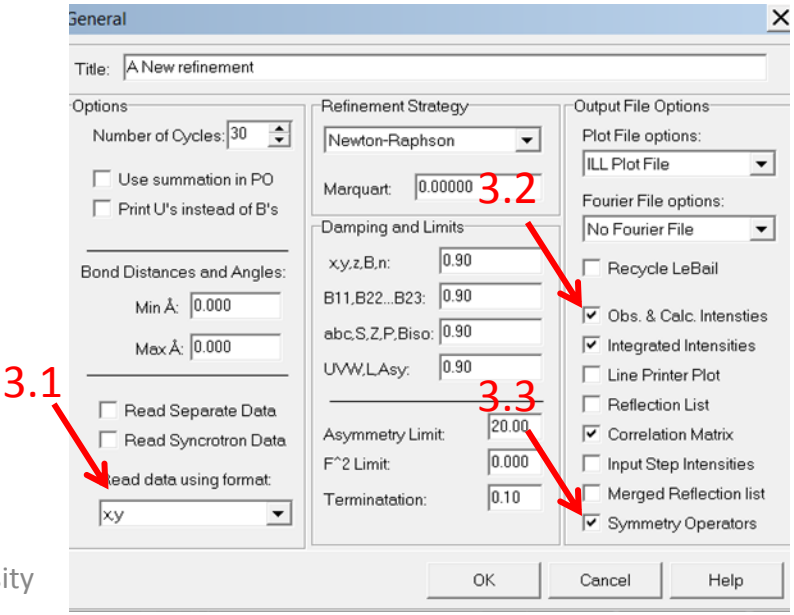


General Settings

- Go to File→New
- $Li_xNi_{1-x}O$ has one phase (2.1) with three distinct atoms (2.2)

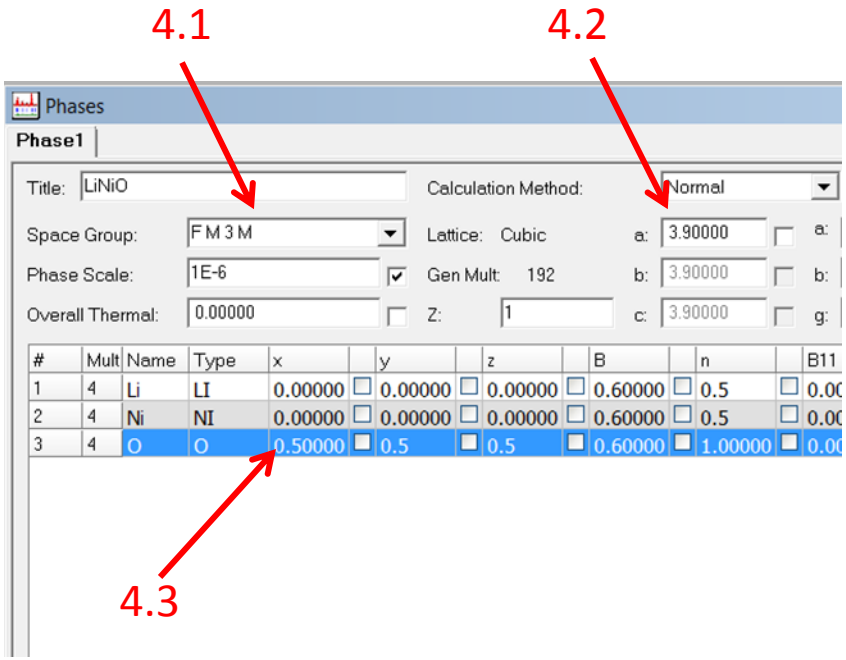


- Go to Model→General
- Change
  - Read data using format: 'xy' (3.1)
- Include:
  - 'Obs.&Calc. Intensities' (3.2)
  - 'Symmetry Operators' (3.3)



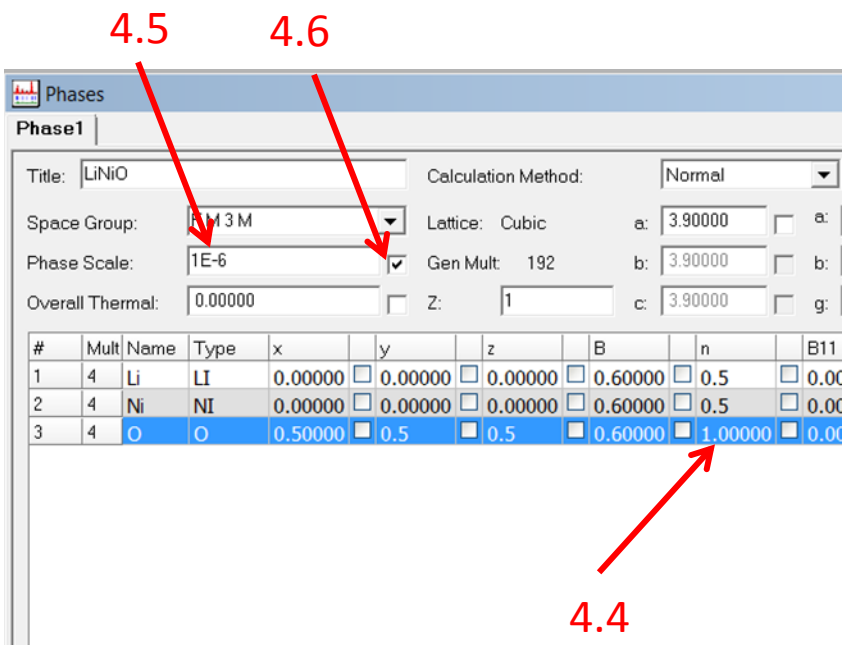
Phases

- Go to Model→Phases
- For $Li_xNi_{1-x}O$
- Space group: *Fm-3m* (4.1)
- Lattice parameter set to 3.9 Å (4.2)
- Atomic positions (Wyckoff positions)
  - Space groups and occupied sites have to be known
- Go to http://www.cryst.ehu.es/ →WYCKPOS→choose→Space group
- Find the occupied sites and insert them. For *Fm-3m:*
  - *4a* (0,0,0) (4.3)
  - *4b* (½,½,½) (4.3)



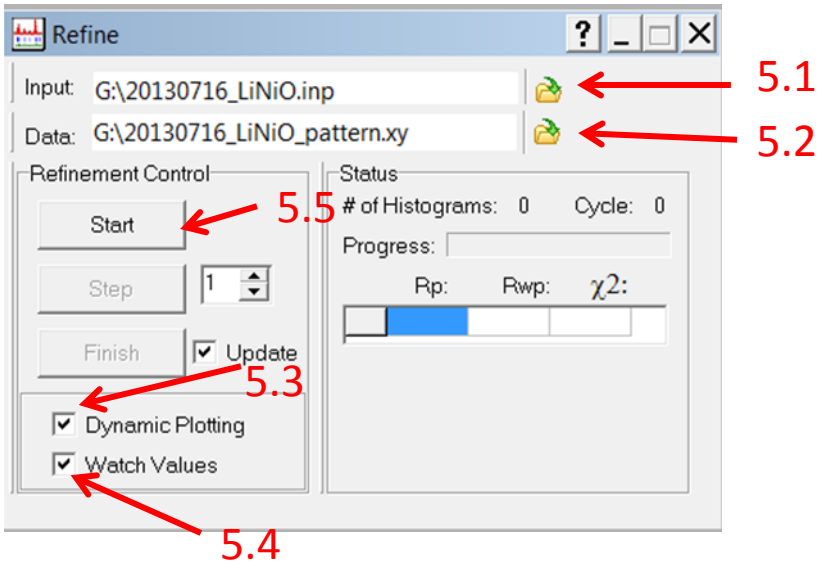
Phases

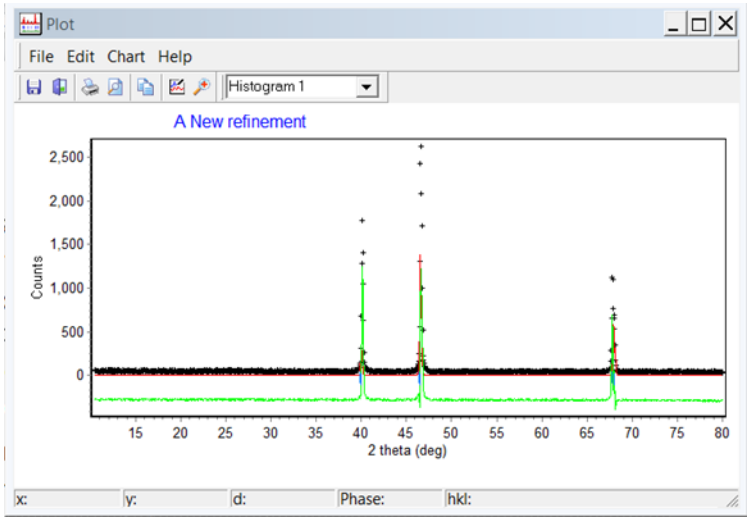
- Occupation is for oxygen 1 and we assume $x = 0.5$ as initial value (4.4)
- Phase scale is changed to 1E-6 because the intensities are in general much lower than the expected one (4.5)
- Check box to vary Phase scale (4.6)



First Refinement

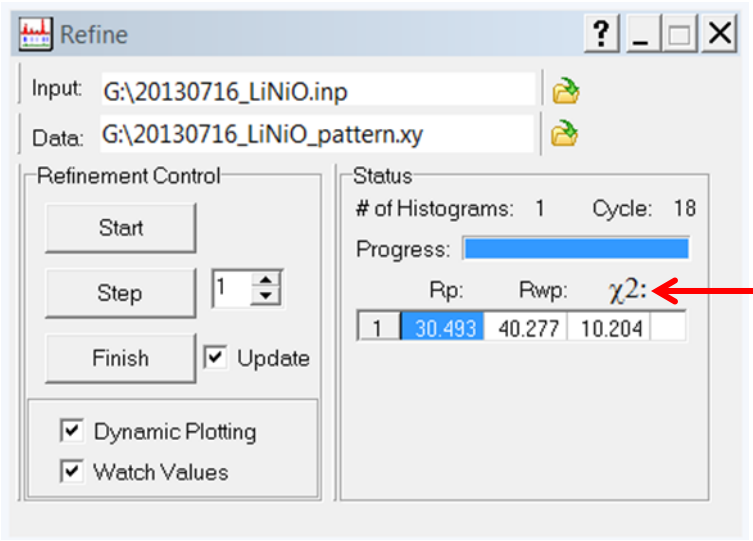
- Go to Rietveld→Refine
- Be sure: '.inp' file is in Input (5.1) and '.xy' file is in Data (5.2)
- Check the boxes:
  - Dynamic plotting (to see data and refined pattern) (5.3)
  - Watch values (to see the goodness of refined parameters) (5.4)
- Press 'Start' (5.5)
- Press 'Step' and three curves are shown:
  - Experimental data (black)
  - Refinement (red)
  - Difference (green)

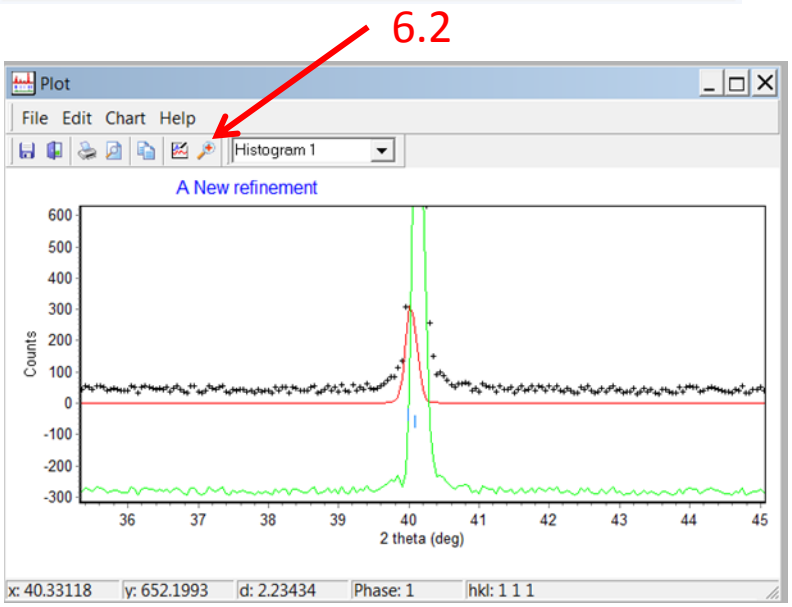




First Refinement

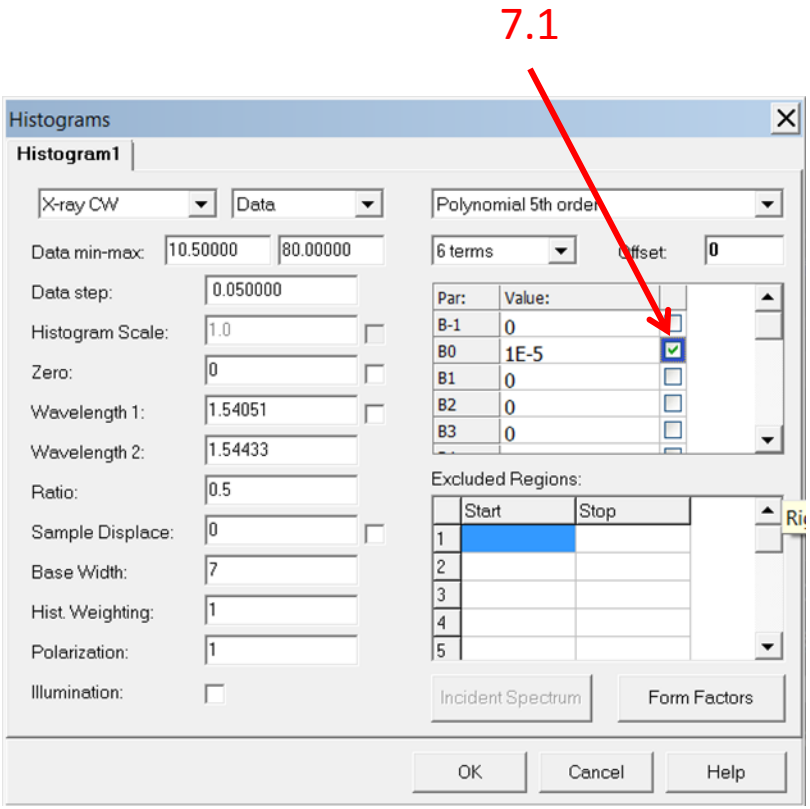
- Look if refined peaks are close to experimental one (if not go back to Model→Phases and change manually the lattice parameter)
- Press several times 'Step' until χ^2 doesn't change anymore (6.1)
- After each refinement save a backup of your input file (Always have one original and one backup input file)
- Zoom in (6.2) and look if the background of the experimental data is the same as the refined pattern
- If refinement is good, press 'Finish'. If not close window.





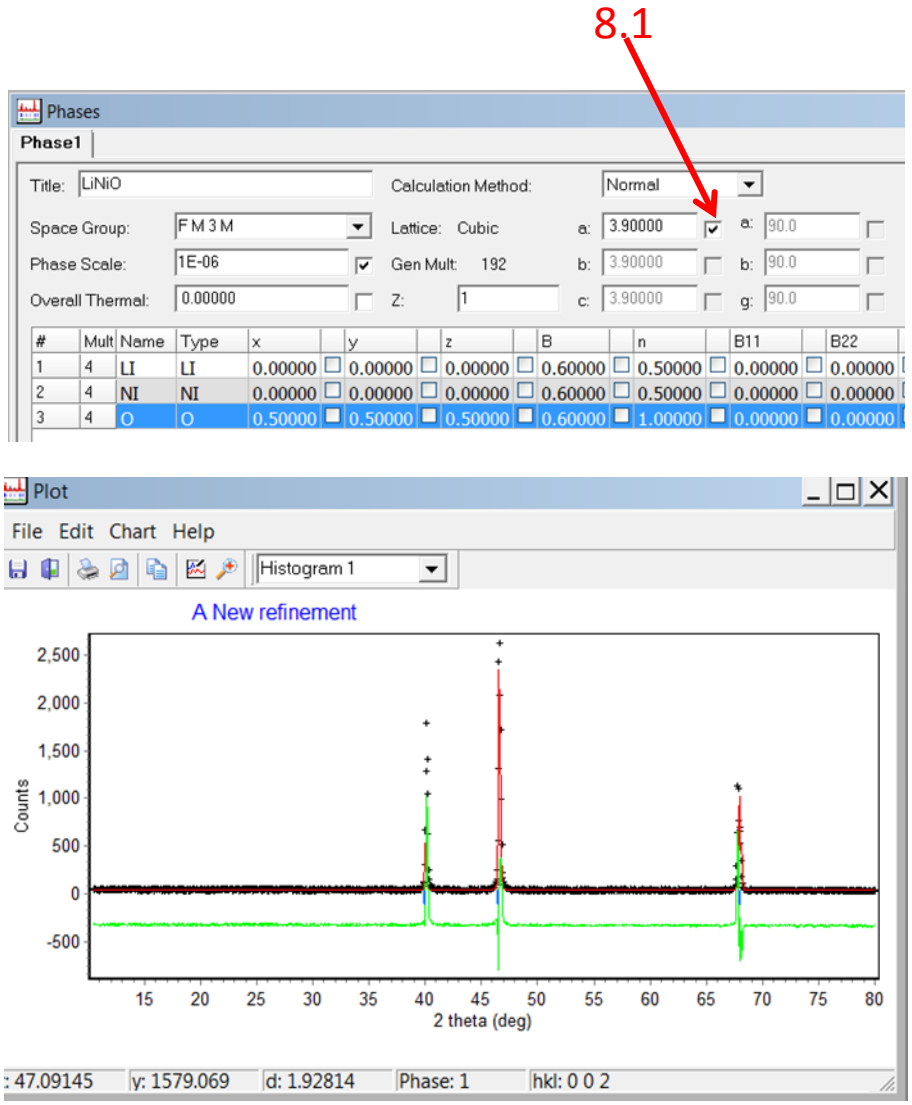
Background

- Go to Model→Histograms
- Check box for vary B0 (constant Background shift) (7.1)
- Go back to Rietveld→Refine
- For procedure (see Slide 12-13)
- IMPORTANT: In general use Polynomial 5th order and B0 (plus maximal 2 more parameters)



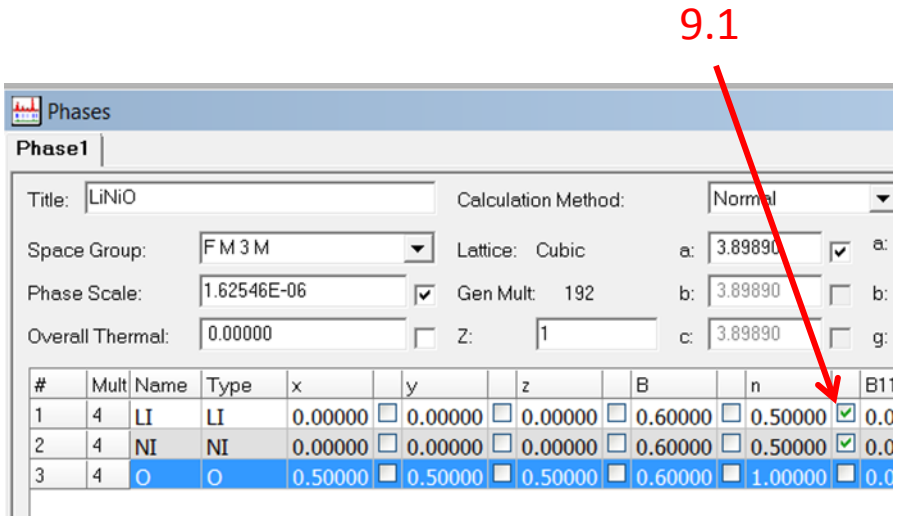
Lattice Parameters

- Go to Model→Phases
- Check the box to vary the lattice parameters (8.1)
- Refine parameters
- Peak positions of the refined data should be the same for the experimental data
- Intensities should look similar



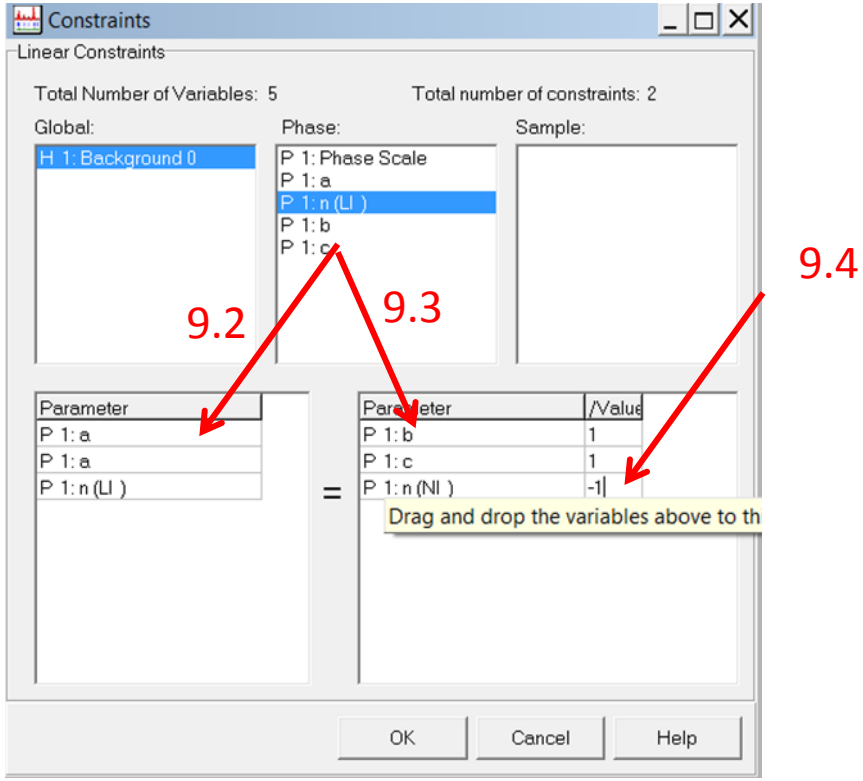
Occupations

- In some cases different atoms can occupy the same atomic positions (*e.g.*, Li and Ni on *4a* sites in LiNiO) or lattice positions are not fully occupied (*e.g.*, Li intercalation in Li-ion batteries) → Change the occupation for the refinement
- For $Li_xNi_{1-x}O$ occupation of Li and Ni should be equal to one
- Go to Model→Phases
- Check the boxes for vary the occupations (9.1)



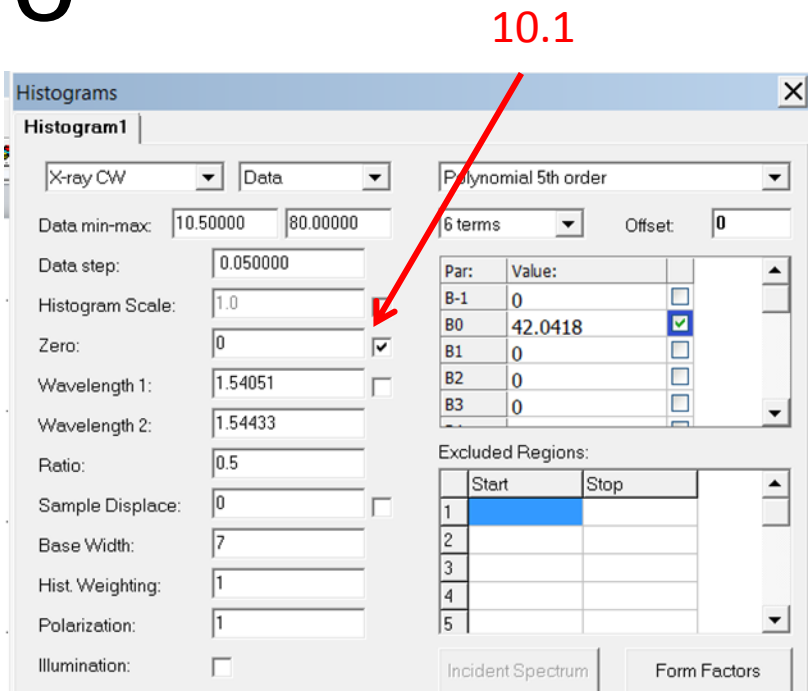
Constraints

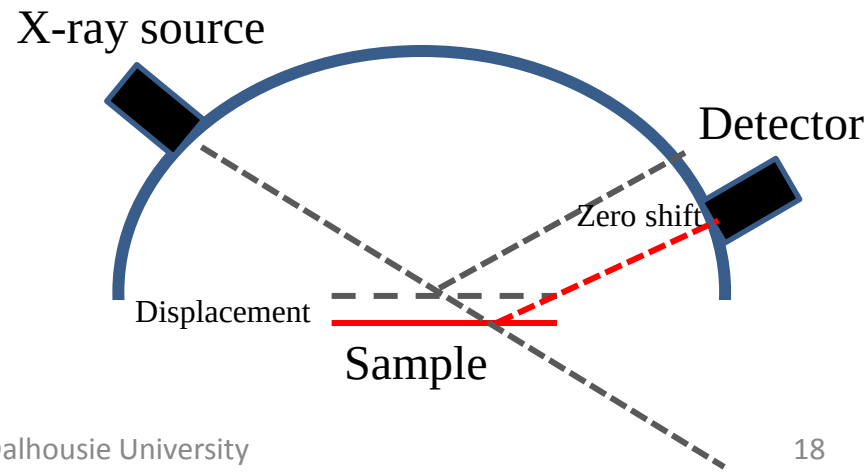
- Go to Model→Constaints
- Drag P 1:n(LI) (9.2) and P 1:n(NI) (9.3) from Phase
- Set /Value to -1 (9.4)
- Refine parameters
- IMPORTANT: Different occupation leads to different intensities of the peaks



Zero

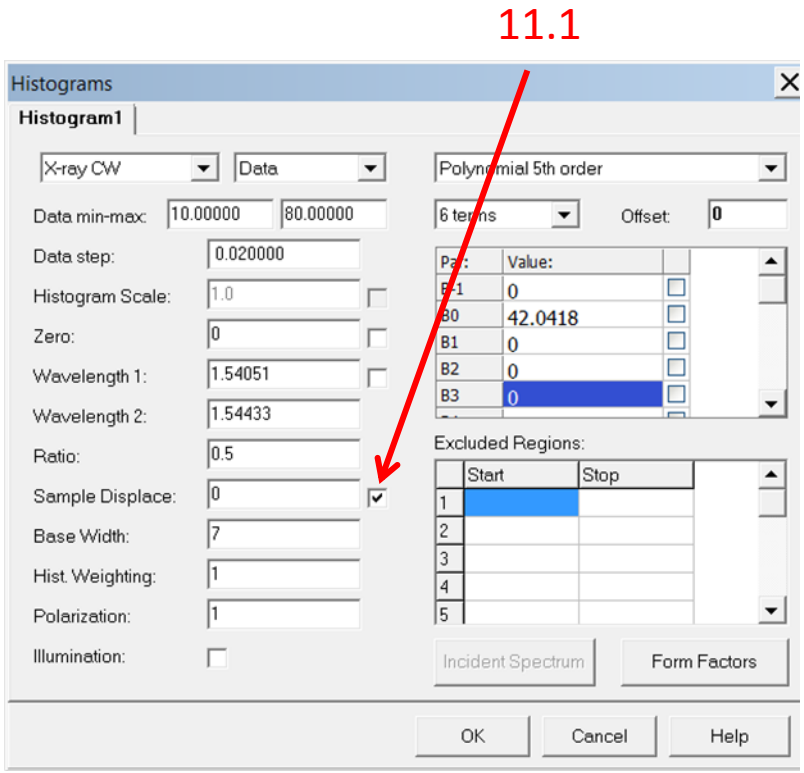
- Go to Model→Histograms
- Check the box to vary Zero (10.1)
- Refine parameters
- If you want to have default values, press right click→Use Instrument→Cu Ka X-ray machine
- IMPORTANT: Sample might have a different height than the zero point of the detector





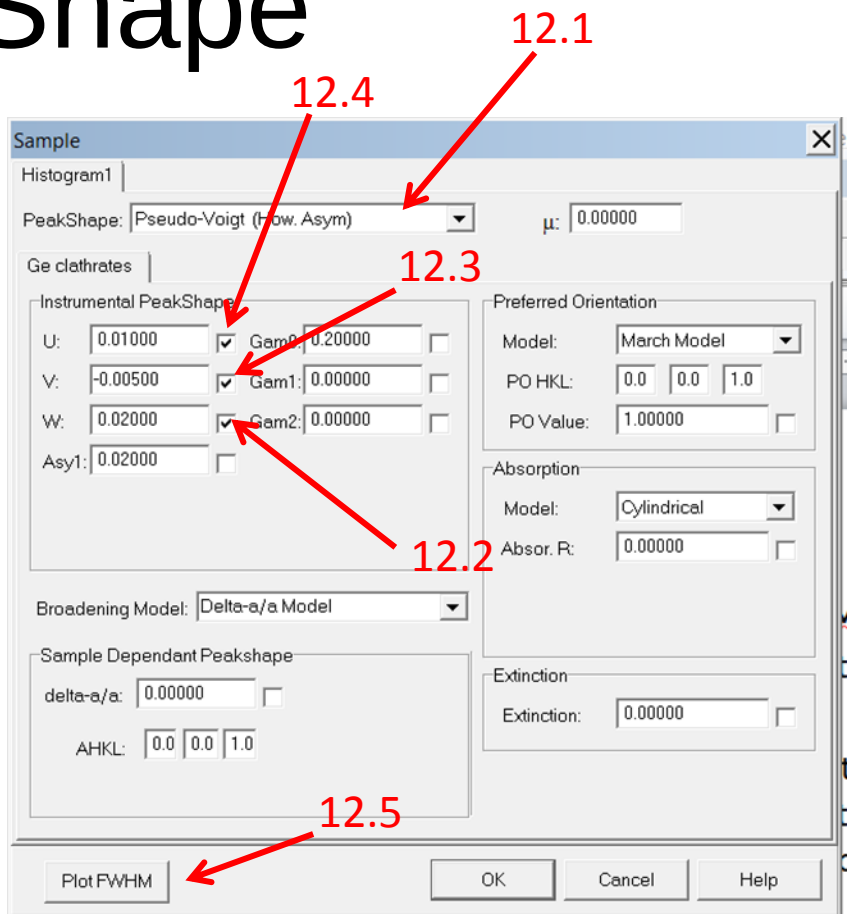
Sample Displacement

- Go to Model→Histograms
- Check to vary Sample Displacement (11.1)
- Refine paramaters
- In contrast to ‘Zero’ ‘Sample Displacement’ is angle-dependent (with increasing angles the uncertainty increases)
- IMPORTANT: **NEVER** vary ‘Zero’ **AND** ‘Sample Displacement’ simultaneously for one pattern



Peak Shape

- Go to Model→Sample
- PeakShape: Pseudo-Voigt (How. Asym) (12.1)
- Check the boxes in this order:
  1. Only W (12.2)
  2. Only V (12.3)
  3. Only U (12.4)
- Refine every time parameters
- Go back to Model→Sample
- Press PlotFWHM (12.5) → FWHM has to be positive

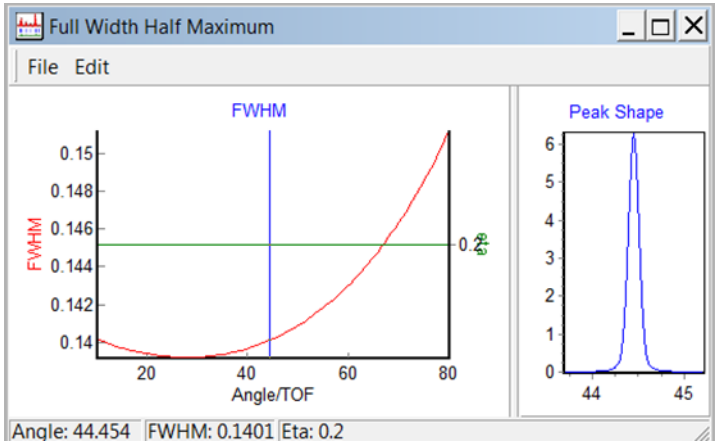


UVW (Cagliotti Parameters)

- U, V, and W gives the full width at half maximum (FHWM):

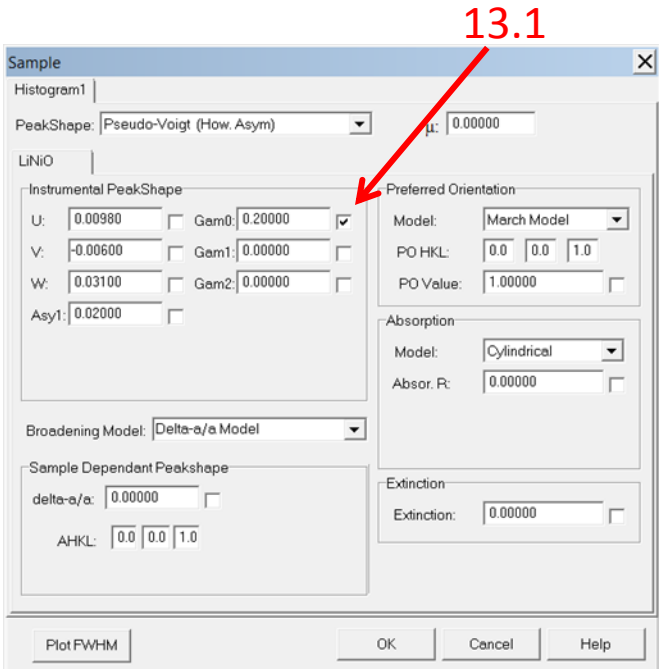
$$FWHM^2 = U\tan^2\theta + V\tan\theta + W$$

- At higher angles the peaks are broader and therefore, the broadening and intensity of peaks might be angle dependent
- IMPORTANT: When the peaks are broader, the intensity of the peaks decreases



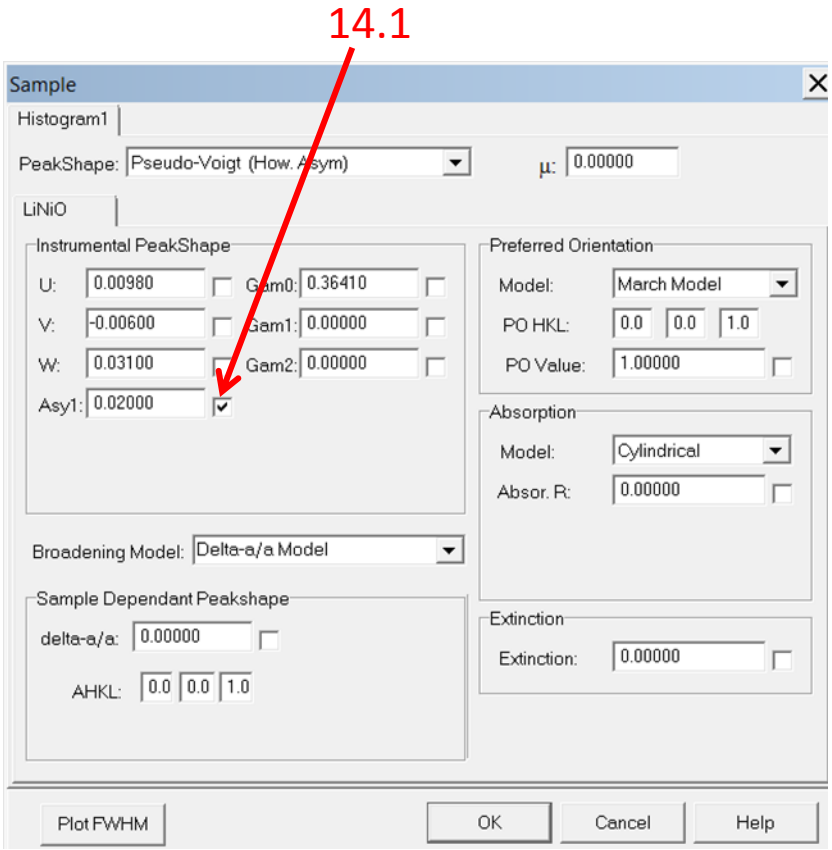
Gamma Function

- Go to Model→Sample
- Check the box for vary only gamma0 (do not refine gamma1 and gamma 2 if you don't need to) (13.1)
- Uncheck U, V, and W
- Refine parameter
- $\gamma = \gamma_0 + \gamma_1(2\theta) + \gamma_2(2\theta)^2$
- γ=0 peak shape is Gaussian
- γ=1 peak shape is Lorentzian



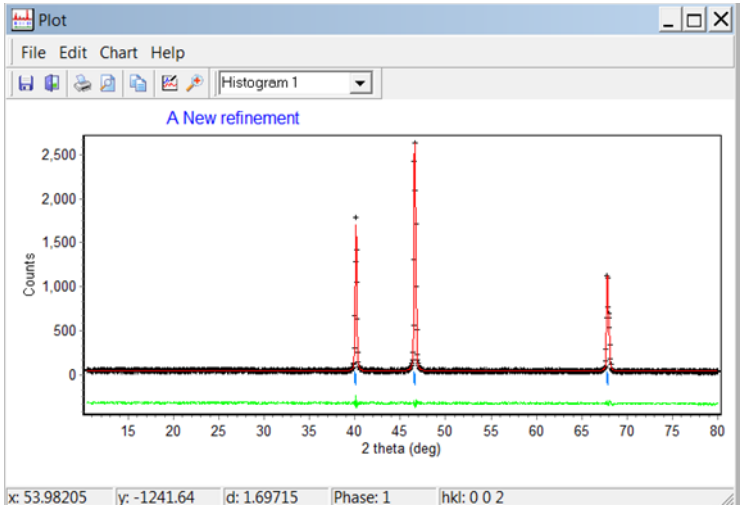
Asymmetric Peaks

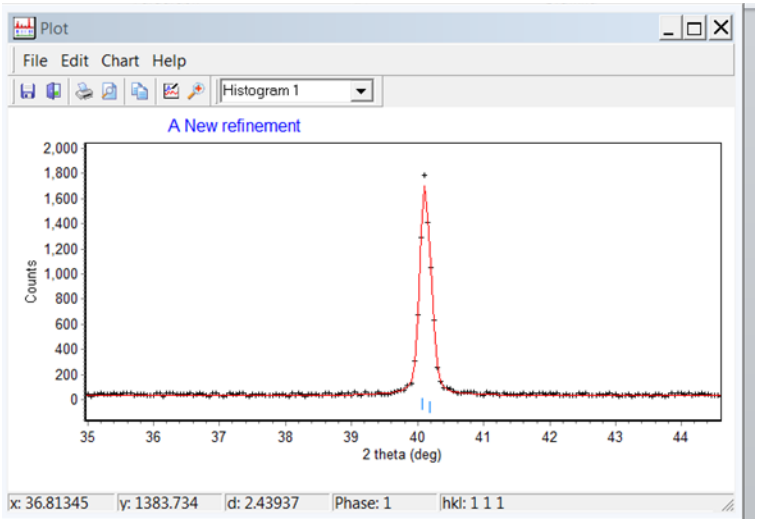
- Zoom in to the refinement at low angles and see if the experimental peaks are asymmetric
- If peaks are asymmetric, go to Model→Sample
- Check box to vary only Asy1 (14.1)
- Refine parameters
- IMPORTANT: Peaks can be asymmetric because of two parameters:
  - *S/L*: source size to the sample-detector distance ratio
  - *D/L*: detector size to the sample-detector distance ratio



Peak Shape

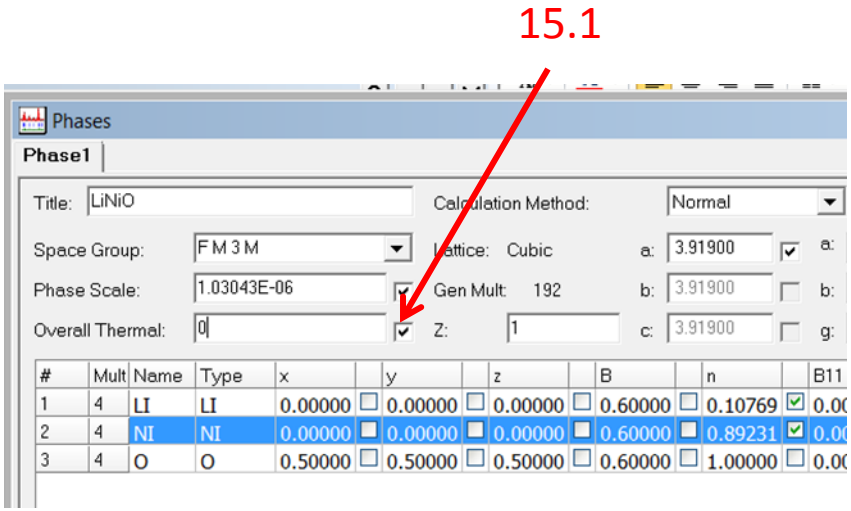
- Repeat slides 20-23 at least five times and refine only one parameter
- Refine only V+W
- Refine only V+W+U
- Refine only V+W+U+gamma0
- (Refine V+W+U+gamma0+Asy1 if necessary)

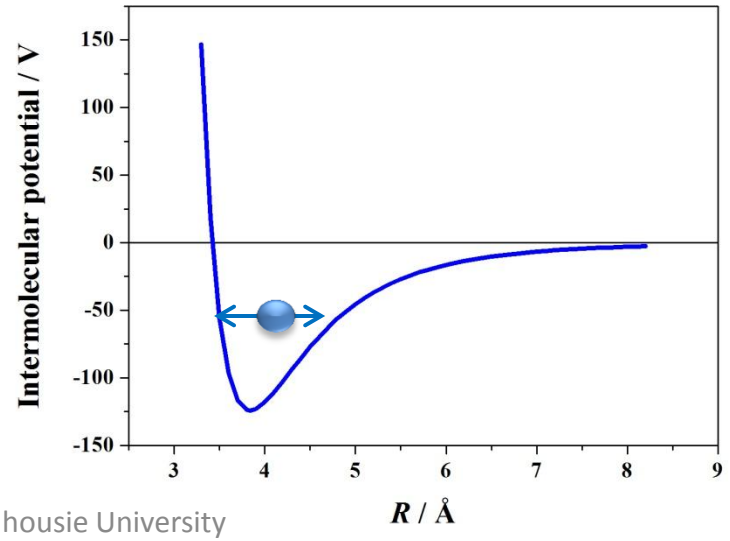




Thermal Parameters

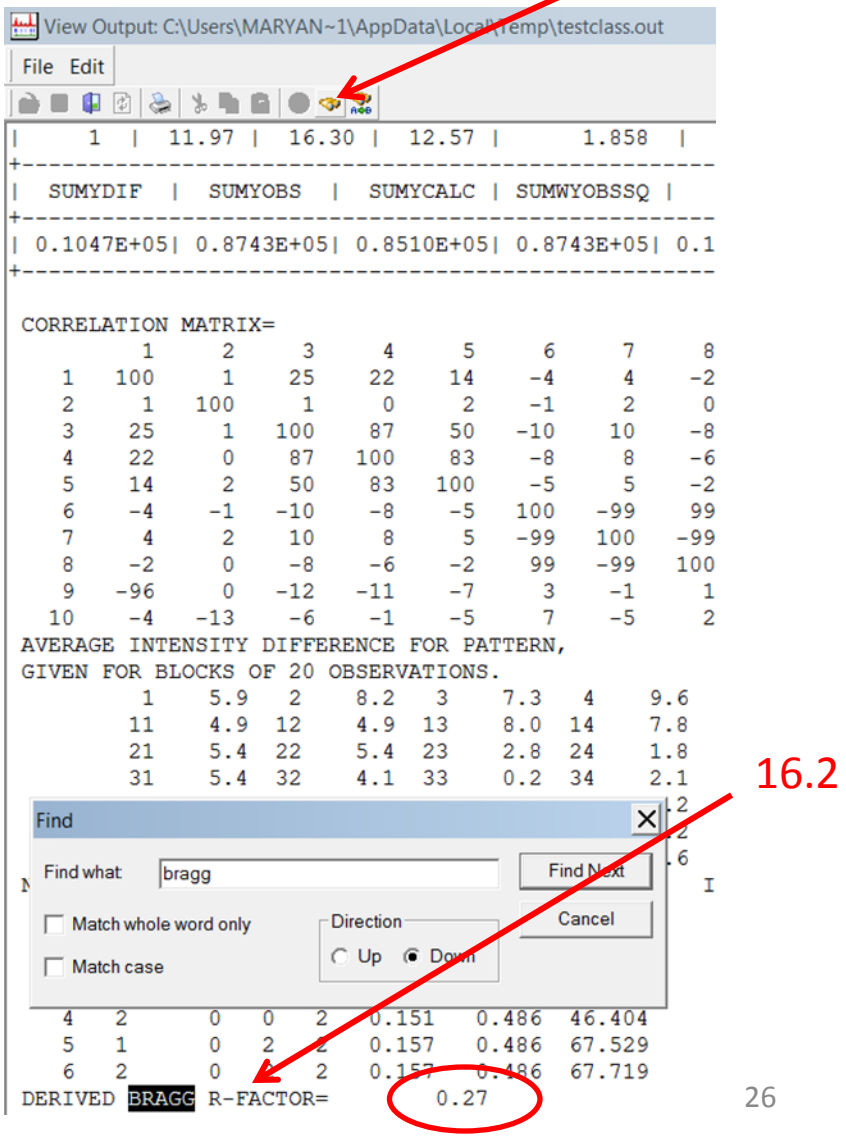
- Go to Model→Phases
- Check the box to vary overall thermal (15.1)
- Refine parameters
- IMPORTANT: Due to increased temperature electrons and atoms are in motion and therefore, the scattering factor is reduced. This leads to broadening of the peaks. Overall Thermal corrects isotropic thermal motions





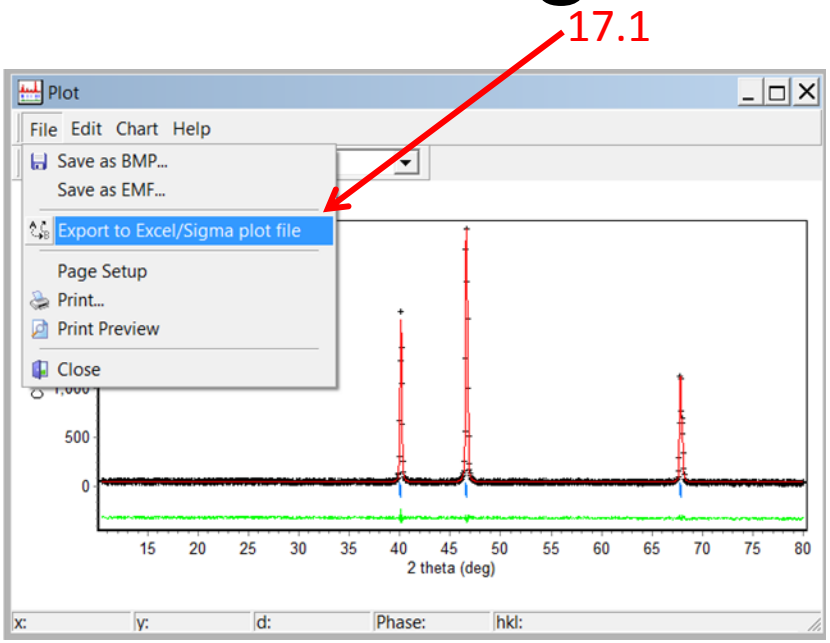
Goodness of Refinement

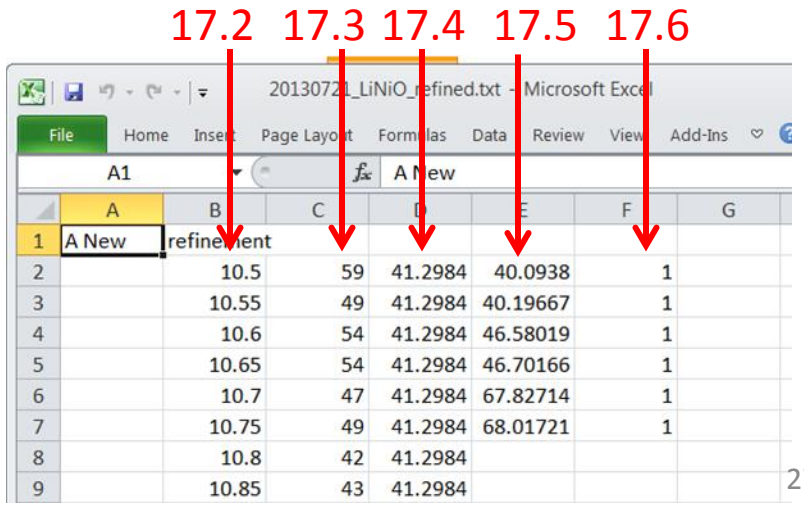
- Go to Information→ View Output
- Go to Edit→Find (16.1)
- Search: Bragg
- Derived Bragg R-factor should be optimal below 2 (16.2)



Export Data for Plotting

- Refine your data and go to File→Export to Excel/Sigma plot file on the panel 'Plot' (17.1)
- Save file as: 'yyyymmdd_material_refined.txt'
- Text file can be open in Microsoft Excel, Origin, or Grapher
- Five columns:
  - 2θ angle (17.2)
  - Intensity of experiment (17.3)
  - Intensity of refinement (17.4)
  - 2θ angle of peak position (17.5)
  - Peak position (17.6)



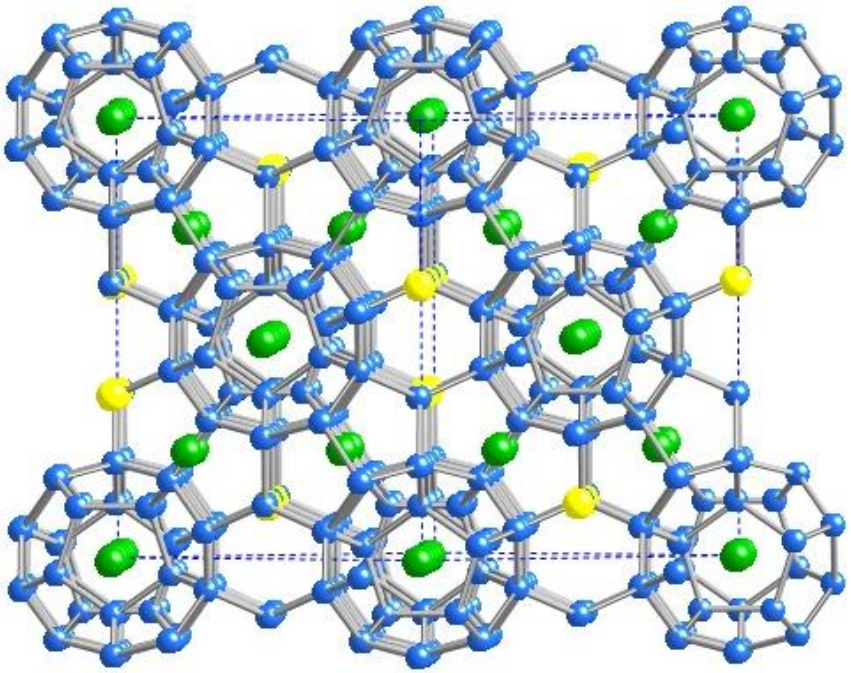


Example 2

ADVANCED: Ge clathrates

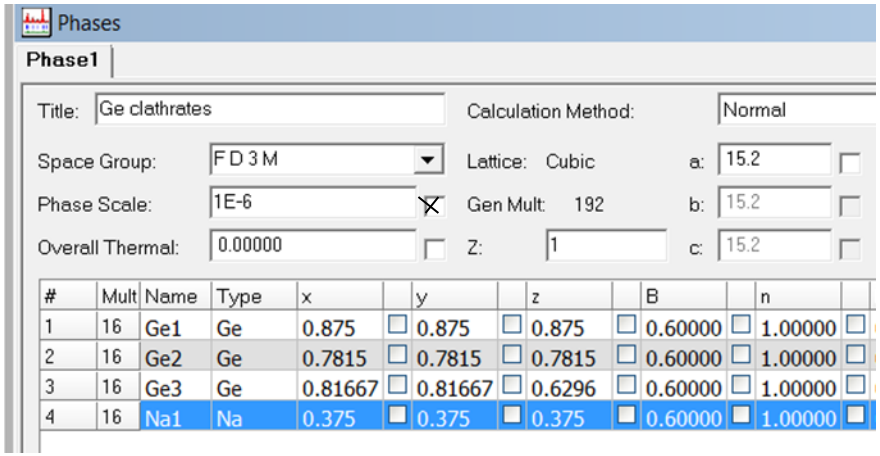
Ge Clathrates

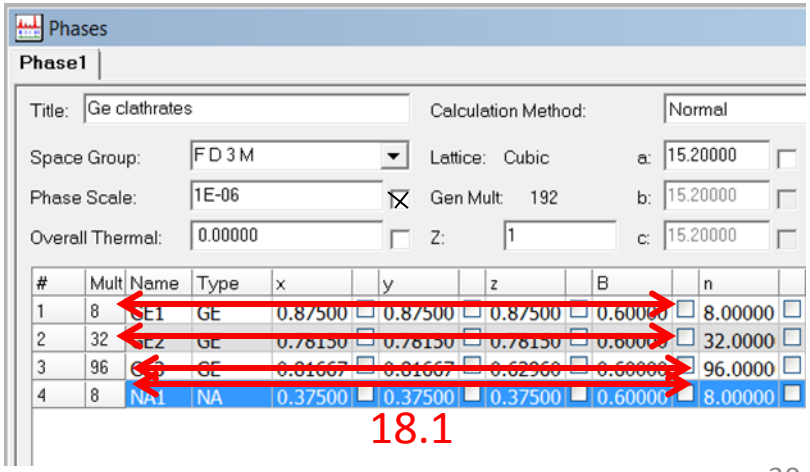
- Ge type II clathrates have 136 Ge and maximum 24 Na atoms
- They have a cubic structure (Fd-3m) with a lattice length of about 15.2 Å
- Ge is on *8a*, *32e*, and *96g* sites
- If the Na concentration is low, Na is only on *8b* sites, but with higher concentrations Na will go also on *16c* sites



Phases

- Go to Model→Phases
- Check box for vary Phase Scale
- Each atom on a different site has its own position
  - *8a*: (3/7,3/7,3/7)
  - *8b*: (7/8,7/8,7/8)
  - *16c*: (0,0,0) [We assume a low concentration of Na]
  - *32e*: (*x*,*x*,*x*)
  - *96g*: (*x*,*x*,*z*)
- *x*, and *z* are taken from a manuscript [1]
- Press OK and reopen Phases
- Maximal occupation of the atoms are shown by the multipliers
  - → Occupation has to fit with multipliers (18.1)

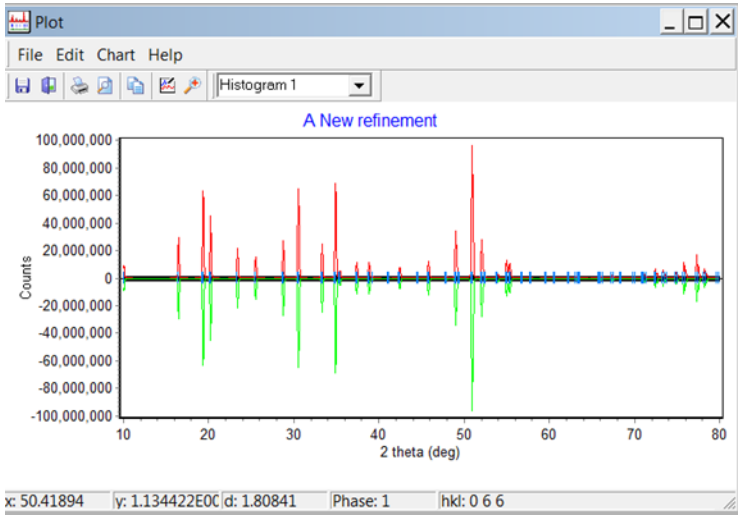


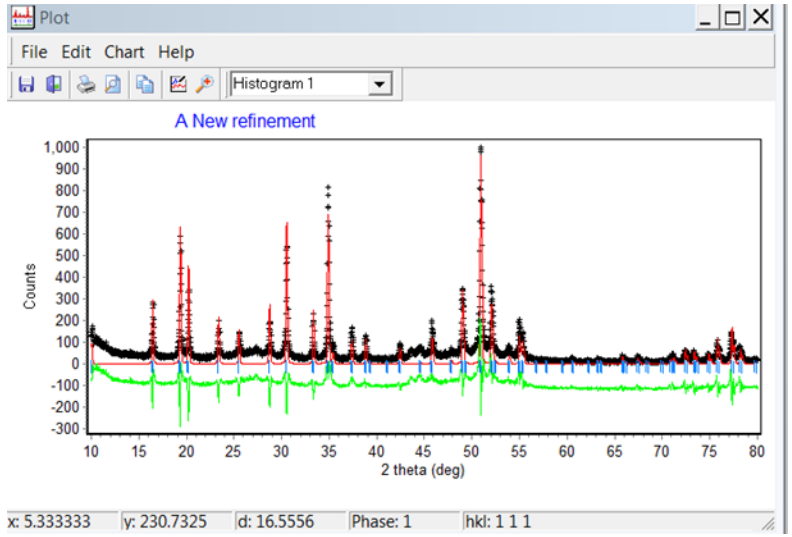


[1] A. M. Guloy *et al. Nature* 443 (2006).

Intensity

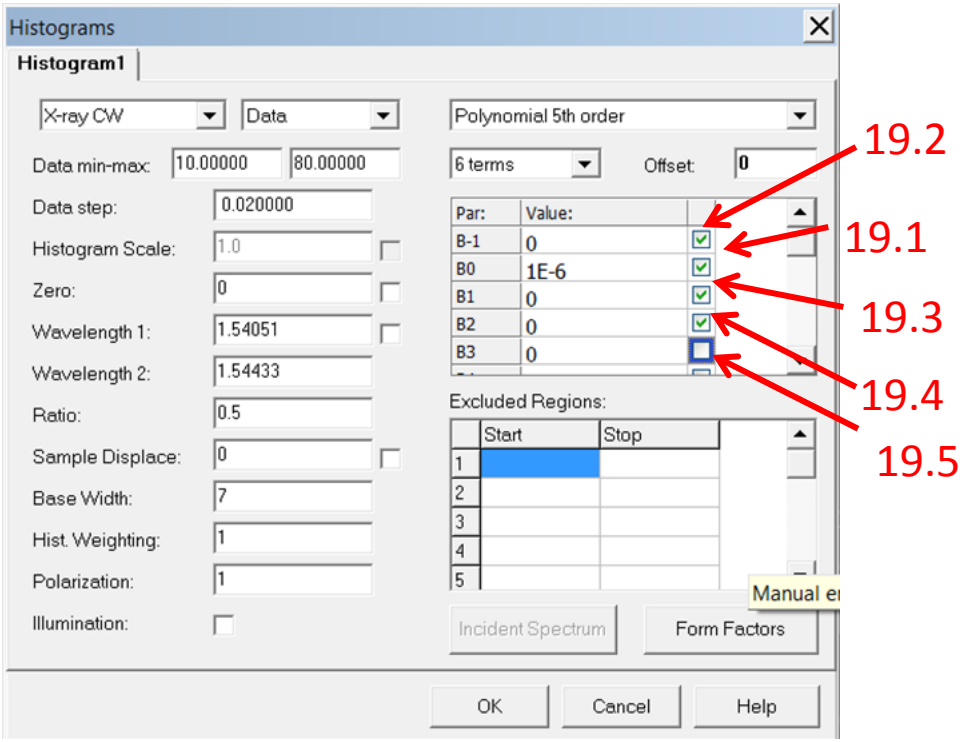
- Refine the parameters
- If the intensity of the refined pattern is too small or too large, go to Model→Phases
- Refine the phase scale until refined and experimental pattern look similar





Background

- The background of this example is more complex
- Go to Model→Histograms
- Check the boxes in the following order and refine them:
  1. Only B0 (19.1)
  2. Only B-1 (19.2)
  3. Only B1 (19.3)
  4. Only B2 (19.4)
  5. Only B3 (19.5)
- Repeat 1-5 steps at least three times
- Then B0+B-1, B0+B-1, B0+B-1+B1, B0+B-1+B1+B2+B3
- IMPORTANT: If there is a tail at low angles, B-1 has to be refined

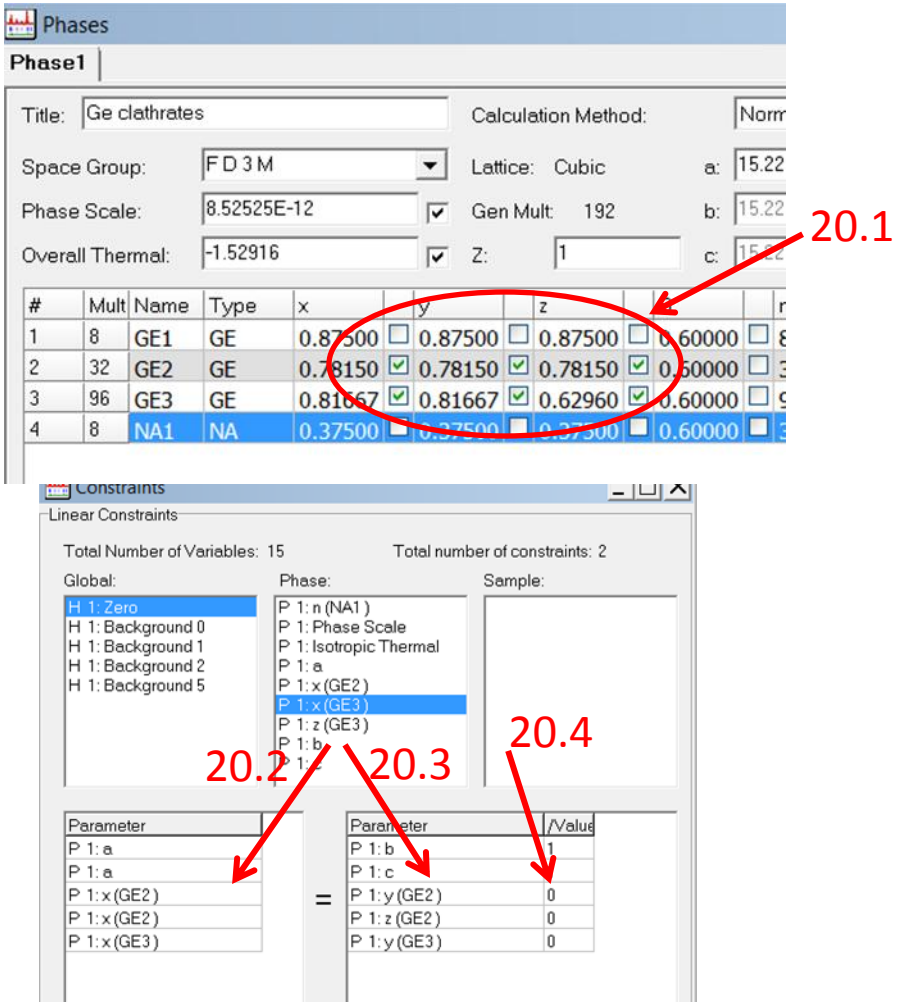


Lattice Parameters, Thermal & Zero

- Go to Model→Phases
- Check boxes for lattice parameters (Lengths and angles) (see Slide 15)
- Refine these parameters
- Only Na content is tunable and therefore, check the box to vary the occupation of Na (see Slide 16)
- Refine this parameter
- Check the box to vary Zero OR Sample Displacement (see Slide 18-19) and refine
- Refine peak shape (see Slide 20-24)
- Check the box to vary Overall Thermal (see Slide 25) and refine

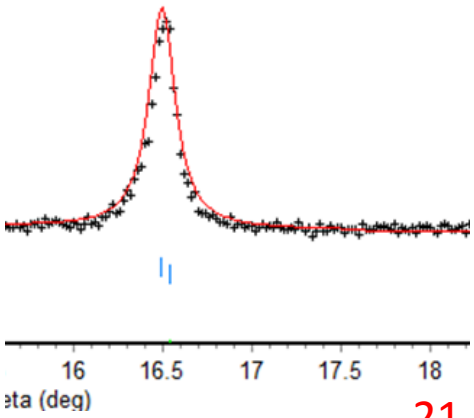
Constraints

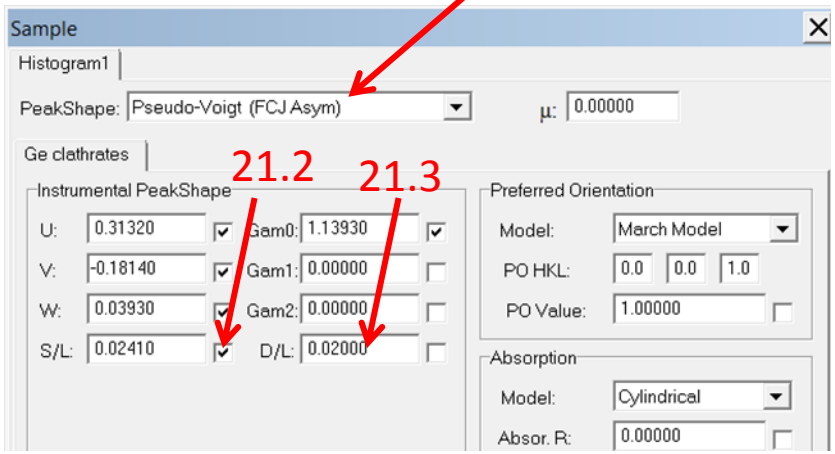
- Positions of atoms are not given exactly for *32e* & *96g* → Slightly different position → change in scattering factor → change in intensity
- Check boxes to vary positions (20.1)
- Go to Model→Constraints
- Drag parameters down, so that for *32e* $x=y=z$ and for *96g* $x=y$ (20.2, 20.3) (/Value has to be set to 0 (20.4))



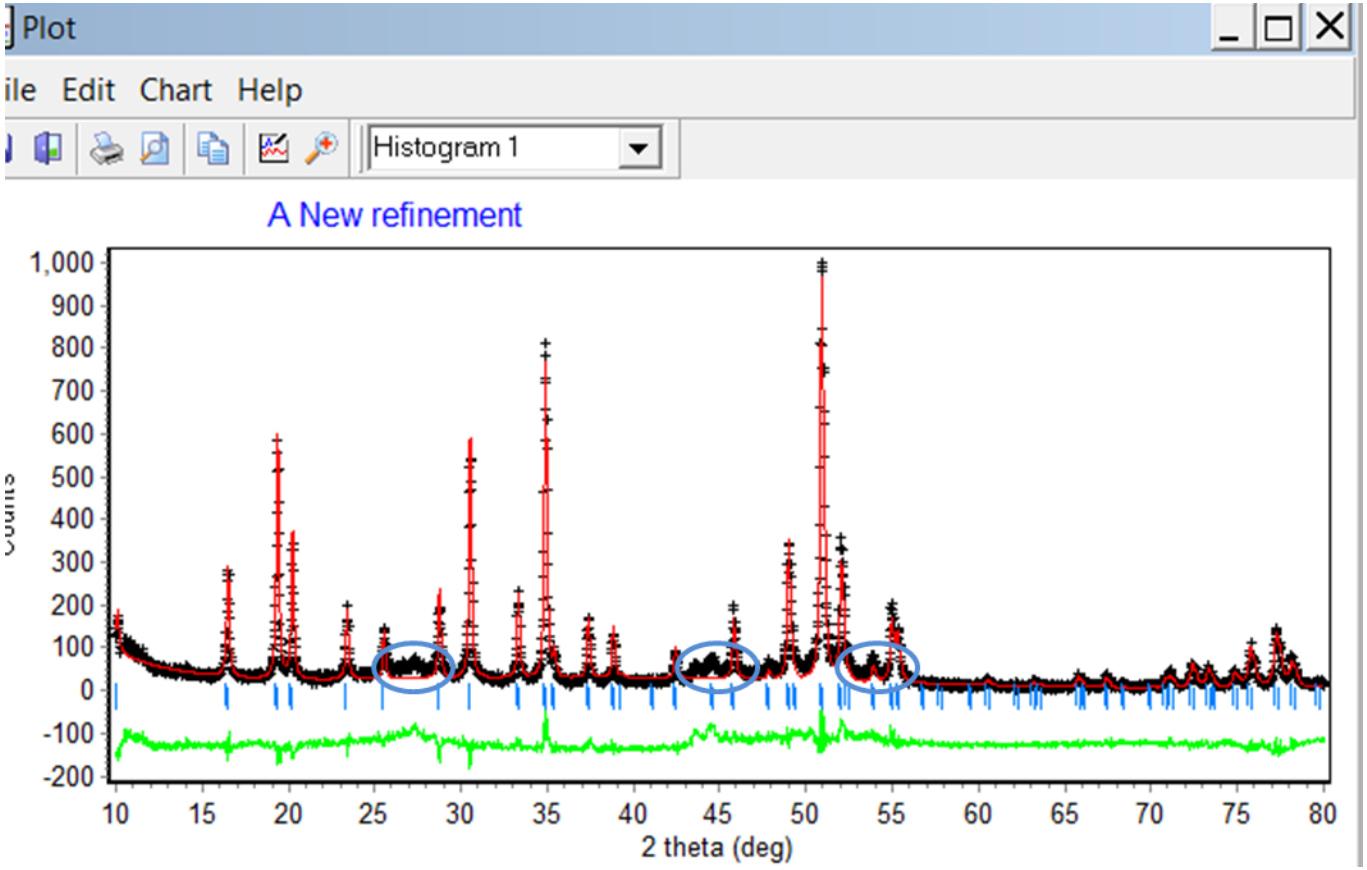
Advanced Refinement

- If the shape of the peak at low angles is not symmetric (Zoom in)
- Go to Model→Sample and change PeakShape to Pseudo-Voigt (FCJ Asym) (21.1)
  - Uncheck box to vary *S/L* (21.2)
  - Increase *D/L* by the same amount as reducing *S/L* (the peak will shift to the right side) (21.3)





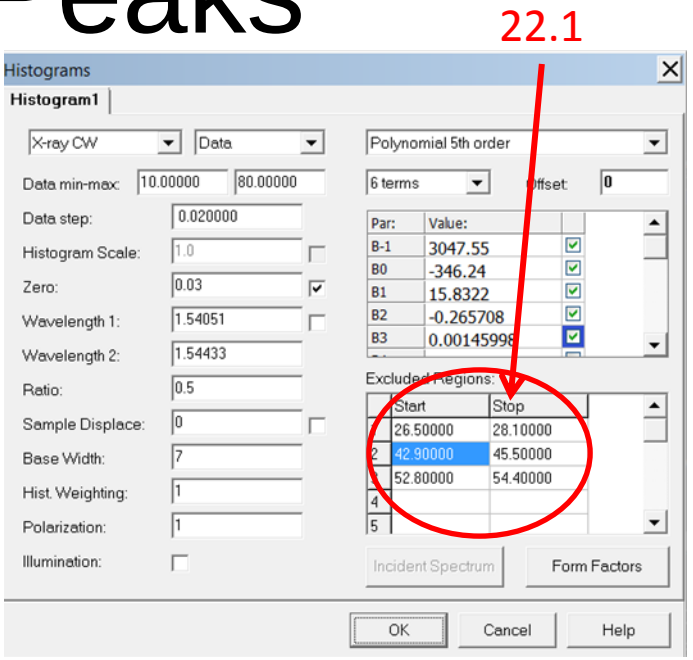
Excluding Peaks

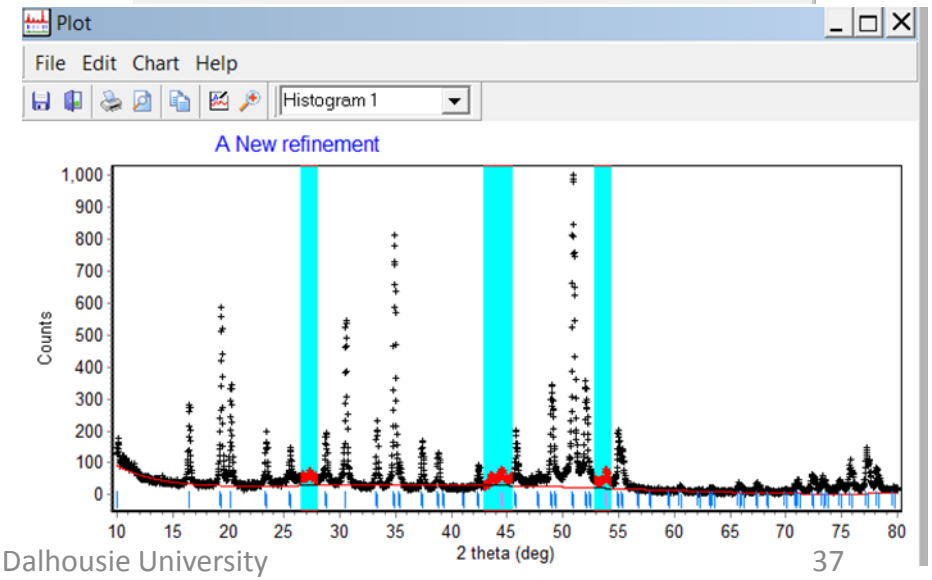


Also small peaks of polycrystalline Ge are shown. Some peaks are overlapping. However, the experimental data have enough other peaks, and polycrystalline Ge peaks can be excluded.

Excluding Peaks

- Find in MATCH the positions of Ge
- Go to Model→Histograms
- Exclude the regions where the Ge peaks are (exclude a larger region) under Excluded Regions (22.1)
- Go to Rietveld→Refine and press only ‘Start’
- Look if total area of the peaks is excluded
- If so, press ‘Step’. If not, close window and change excluded regions





Example 3

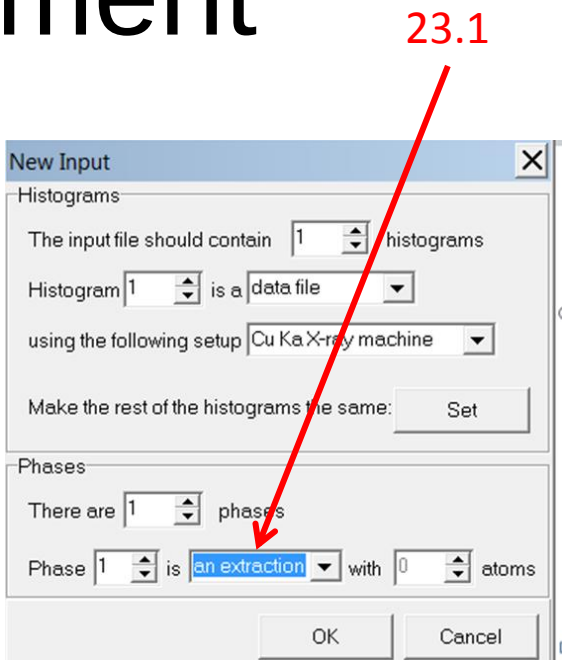
QUALITATIVE ANALYSIS: Clathrates

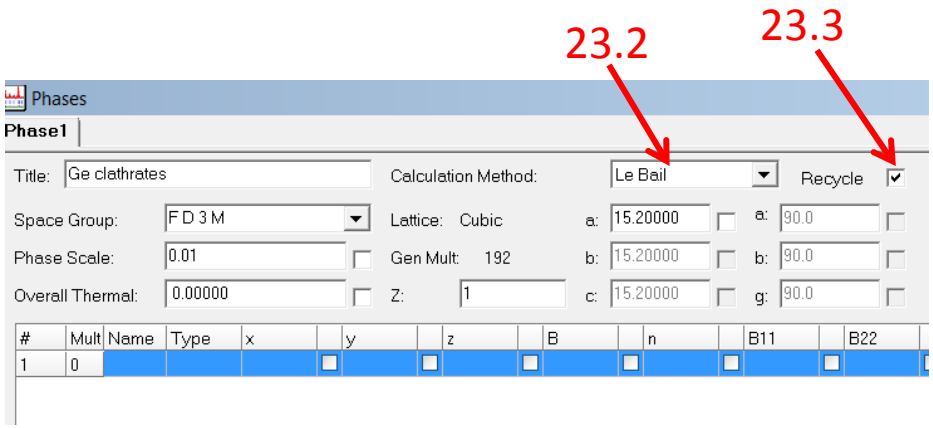
Qualitative Analysis

- Qualitative analyses provide information about the lattice parameter and the space group, but no information about the atomic positions or occupations
- For unknown materials it is a quick analysis

LeBail Refinement

- Go to File→New
- Change ‘a structure’ to ‘an extraction’ (23.1)
- Go to Model→General
  - Same procedure (see Slide 9)
- Go to Model→Phases
  - Check Calculation Method is LeBail (23.2) and the box ‘recycled’ is checked (23.3)
  - Change only lattice parameters & space group
- Refine parameters
- IMPORTANT: **NEVER** check the boxes for Phase Scale and Overall Thermal





Refinement

- Check the boxes for the background (see Slide 14 and 32)
- During refinement press ‘Step’ if χ^2 decreases and ‘Finish’ if χ^2 increases
- Check the box/es for lattice parameters (see Slide 15)
- Check the box for Zero or Sample Displacement (see Slide 18-19)
- Check the boxes for peak shape (see Slide 20-24)

Conclusions

- Rietica refinement is a powerful tool for quantitative and fast qualitative analyses of crystal structures
- Shown strategies might be slightly changed depending on the experimental data
- Refine parameters sequentially
- Do not refine several parameters at once or parameters which you don’t know
- For further questions, please contact: Jan Poehls (Jan.Poehls@Dal.ca)