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'

	<u>ı.</u>	Rietica						
	Fil	e Edit	Model	Rietveld	Information	Help		
		New] 🔘
4	2	Open						
р	t 🔳	Save						
	1	Save /	As					2
		; Close						
		Impor	t					•
R	b	Expor	t					► E
		Prefer	ences					
	2	Print						
	2	Print P	Preview					
Ī	-	Page	Setup					to a

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 \rightarrow Import \rightarrow Diffraction data
- 3. File \rightarrow Export \rightarrow 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 \rightarrow Open

Open Experimental Data

- 7. Open '.xy' file
- 8. Experimental data occurs (1.1)
- 9. Close Plot (1.2) $^{1.2}$





Example 1 BASICS: Li_xNi_{1-x}O

$Li_xNi_{1-x}O$

- $\text{Li}_x \text{Ni}_{1-x} \text{O}$ 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 \rightarrow New
- $\text{Li}_x \text{Ni}_{1-x} \text{O}$ has one phase (2.1) with three distinct atoms (2.2)
- Go to Model \rightarrow General
- Change
 - Read data using format: 'xy'
 (3.1)
- Include:
 - 'Obs.&Calc. Intensities' (3.2)
 - 'Symmetry Operators' (3.3)

	New Input
	Histograms
	The input file should contain 1 🚖 histograms
	Histogram 1 💼 is a data file 💌
	using the following setup Cu Ka X-ray machine
2.1	Make the rest of the histograms the same: Set
· · ·	Phases 2.2
	There are 1 🜩 phases
	Phase 1 \bigcirc is a structure \checkmark with β \bigcirc atoms
	OK Cancel

Title: A New refinement		
Options Number of Cycles: 30 Use summation in PO Print U's instead of B's Bond Distances and Angles: Min Å: 0.000 Max Å: 0.000 Read Separate Data Read Syncrotron Data tead data using format: xy	Refinement Strategy Newton-Raphson Marquart 0.00000 Damping and Limits x.y.z,B,n: 0.90 B11,B22B23: 0.90 ubc,S,Z,P,Biso: 0.90 UVW,LAsy: 0.90 S.3 Asymmetry Limit F^2 Limit 0.10	Output File Options Plot File options: ILL Plot File Fourier File options: No Fourier File Recycle LeBail Obs. & Calc. Intensitie Line Printer Plot Reflection List Correlation Matrix Input Step Intensitie Merged Reflection Symmetry (Overston

Phases

- Go to Model \rightarrow Phases
- For $\text{Li}_x \text{Ni}_{1-x} O$
- 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 <u>http://www.cryst.ehu.es/</u> →WYCKPOS→choose→Space group
- Find the occupied sites and insert them. For *Fm-3m*:
 - 4a (0,0,0) (4.3)
 - $4b (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) (4.3)$



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 \rightarrow 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)





Phase:

hkl:

d:

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)

Histograms			×
Histogram1			
X-ray CW	▼ Data. ▼	Polynomial 5th order	•
Data min-max: 10	.50000 80.00000	6 terms 💌 Offset: 0	
Data step:	0.050000	Par: Value:	•
Histogram Scale:	1.0	B-1 0	
Zero:	0	BU 1E-5	
Wavelength 1:	1.54051	B2 0 🗆	
Wavelength 2:	1.54433	B3 0	-
Ratio:	0.5	Excluded Regions:	
Sample Displace:	0	Start Stop	R
Base Width:	7	2	
Hist. Weighting:	1	3	
Polarization:	1	5	-
Illumination:		Incident Cooptrum	
	,		2
		OK Cancel Helr	, 1

7.1

Lattice Parameters

- Go to Model \rightarrow 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

🖶 Phases				
Phase1				
Title: LiNiO		Calculation Method:	Normal	•
Space Group: FM3	M	Lattice: Cubic	a: 3.90000	a: 90.0
Phase Scale: 1E-06	~	Gen Mult: 192	b: 3.90000	b: 90.0
Overall Thermal: 0.000	00	Z: 1	c: 3.90000	g: 90.0
# Mult Name Type	x y	z B	n	B11 B22
1 4 LI LI	0.0000 🗆 0.00	0000 🗆 0.00000 🗆 0.	.60000 🗆 0.50000 🗖	0.00000 🗆 0.00000
2 4 NI NI	0.0000 🗆 0.00	0000 🗆 0.00000 🗆 0.	.60000 🗆 0.50000 🗆	0.00000 🗆 0.00000
3 4 <u>O</u> O	0.50000 🗖 0.50	0000 🗖 0.50000 🗖 0.	.60000 🗖 1.00000 🗖	0.00000 🔲 0.00000

8,1



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 \rightarrow Phases
- Check the boxes for vary the occupations (9.1)

Ph	ases											\mathbf{I}			
has	e1														
Title:	LiNi)			_		Cal	cula	tion Metho	od:		No	rmal		•
Space Group: FM3M				•	Latt	ice:	Cubic		a:	3.8	9890		e a		
Phase Scale: 1.62546E-06			~	Ger	n Mu	ult: 192		b:	3.8	9890	Г	b			
Overall Thermal:		rmal:	0.00000				Z:		1		C:	3.8	9890	Тг	g
#	Mult	Name	Туре	x		у			z		В		n	V	B1
1	4	LI	LI	0.00000		0.00	000		0.00000		0.60000		0.50	000	☑ 0.0
2	4	NI	NI	0.00000		0.00	000		0.00000		0.60000		0.50	000	☑ 0.0
3	4	0	0	0.50000		0.50	000		0.50000		0.60000		1.00	000	0.

9.1

Constraints

- Go to Model \rightarrow 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

10.1

- Go to Model \rightarrow 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

Histograms						X
Histogram1						
X-ray CW	▼ Data	•	Polyn	omial 5th ord	er	•
Data min-max: 10.	50000 80.000	00	6 term	s 🔻	Offset	0
Data step:	0.050000	_ /	Par:	Value:		•
Histogram Scale:	1.0		B-1	0		
Zero:	0	-	B0 B1	42.0418		
Wavelength 1:	1.54051	- -	B2	0		
Wavelength 2:	1.54433		B3	0		•
Ratio:	0.5	_	Exclud	ed Regions:		
Sample Displace:	0	_	1 Sta	art S	Stop	_
Base Width:	7	-	2			
Hist. Weighting:	1	_	3			
Polarization:	1		5			•
Illumination:			Incide	ent Spectrum	Form	Factors



Sample Displacement

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

X Histograms Histogram1 X-ray CW ▼ Data Ŧ Polynemial 5th order • 10.00000 80.00000 0 6 ter ns Data min-max: • Offset: 0.020000 Data step: Pa Value: 0 1.0 Histogram Scale: 42.0418 0 Zero: B1 B2 0 1.54051 Wavelength 1: B3 1.54433 Wavelength 2: Excluded Regions: 0.5 Ratio: Start Stop 0 Sample Displace: 1.0 1 2 3 Base Width: Hist. Weighting: 4 Polarization: Illumination: Form Factors OK Cancel Help

11.1

Peak Shape

- Go to Model \rightarrow 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 \rightarrow Sample
- Press PlotFWHM (12.5) \rightarrow FWHM has to be positive

ларс		12.1		
1 2.4				
ample				
Histogram1	1			
PeakShape: Pseudo-Voigt (How. Asym)	•	μ: 0.0	0000	
Ge clathrates	12.3			
Instrumental PeakShape		Preferred Orie	entation	
U: 0.01000 🔽 Game, 0.20000		Model:	March Mode	- ▼
V: -0.00500 [▼ Gam1: 0.00000		PO HKL:	0.0 0.0	1.0
W: 0.02000 [- Gam2: 0.00000		P0 Value:	1.00000	
Asy1: 0.02000		Absorption		
		Model:	Cylindrical	•
	12	Absor. R:	0.00000	
	12.	4	,	
Broadening Model: Delta-a/a Model	•			
Sample Dependant Peakshape		Extinction		
delta-a/a: 0.00000		Extinction	0.0000	
AHKI 0.0 0.0 1.0		Exunction:	10.00000	
12.5				
			1	
Plot FWHM		OK	Cancel	Help

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 \rightarrow 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
- $\gamma = \gamma_0 + \gamma_1(2\theta) + \gamma_2(2\theta)^2$
- $\gamma=0$ peak shape is Gaussian
- $\gamma=1$ peak shape is Lorentzian

istogram1	
eakShape: Pseudo-Voigt (How. Asym)	Ψ μ: 0.00000
Instrumental PeakShape	Preferred Orientation
U: 0.00980 Gam0: 0.20000	Model: March Model 💌
V: -0.00600 Gam1: 0.00000	PO HKL: 0.0 0.0 1.0
W: 0.03100 Gam2: 0.00000	PO Value: 1.00000
Asy1: 0.02000	Absorption
	Model: Cylindrical -
	Absor. R: 0.00000
Broadening Model: Delta-a/a Model Sample Dependant Peakshape delta-a/a: 0.00000	Extinction Extinction: 0.00000
AHKL: 0.0 0.0 1.0	

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

14.1	
Sample	X
Histogram1	
PeakShape: Pseudo-Voigt (How. Asym)	μ: 0.00000
LiNiO	
Instrumental PeakShape	Preferred Orientation
U: 0.00980 🗖 Grm0: 0.36410 🗖	Model: March Model 💌
V: -0.00600 🗆 Gam1: 0.00000	PO HKL: 0.0 0.0 1.0
W: 0.03100 Gam2: 0.00000	PO Value: 1.00000
Asy1: 0.02000	Absorption
	Model: Cylindrical
	Absor. R: 0.00000
Broadening Model: Delta-a/a Model	
-Sample Dependent Poskchang	
	Extinction
	Extinction: 0.00000
AHKL: 0.0 0.0 1.0	
Plot FWHM	OK Cancel Help

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 \rightarrow 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



15.1



Goodness of Refinement

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

1	. 1	11.97	16.3	30	12.57	I.	1.858	1
SUMY	DIF	SUMY	OBS	SUM	YCALC	SUM	VYOBSSQ	I
0.104	7E+05	0.874	3E+05	0.85	10E+05	0.8	743E+05	0.3
CORREI	ATION	MATRIX	(=					
	1	2	3	4	5	6	7	1
1	100	1	25	22	14	-4	4	-3
2	1	100	1	0	2	-1	2	(
3	25	1	100	87	50	-10	10	-
4	22	0	87	100	83	-8	8	-
5	14	2	50	83	100	-5	5	-2
6	-4	-1	-10	-8	-5	100	-99	9
7	4	2	10	8	5	-99	100	-9
8	-2	0	-8	-6	-2	99	-99	10
9	-96	0	-12	-11	-7	3	-1	
10	-4	-13	-6	-1	-5	7	-5	:
AVERAG	E INTE	ENSITY	DIFFE	RENCE	FOR PA	TTERN,	,	
GIVEN	FOR BI	LOCKS C	F 20 (OBSERV	ATIONS	-		
	1	5.9	2	8.2	3	7.3	4	9.6
	11	4.9	12	4.9	13	8.0	14	7.8
	21	5.4	22	5.4	23	2.8	24	1.8
	31	5.4	32	4.1	33	0.2	34	2.1
Find							×	
								. 6
1 Find w	hat b	ragg				F	ind Mext	1 :
	teh u hele i		-	Direction			Cancel	1
j Ma	tch whole	word only		Direction			ouncer	

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.t xt'
- 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)





17.2 17.3 17.4 17.5 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 8*a*, 32*e*, and 96*g* 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 \rightarrow Phases
- Check box for vary Phase Scale
- Each atom on a different site has its own position
 - 8*a*: (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)

Pha	ases													
hase	1													
Title:	Geo	lathrates	6		Calculation Method:					Normal				
Space Group:		FD3M	▼ Lattice: Cubic					a: [a: 15.2					
Phase Scale:		1E-6	X			Gen Mult: 192			b: [15.2		Г		
Overall Thermal:		rmal:	0.00000				Z:		1		с: [15.3	2	
#	Mult	Name	Туре	x		У			z		в		n	Г
1	16	Ge1	Ge	0.875		0.87	5		0.875		0.60000		1.00000	
2	16	Ge2	Ge	0.7815		0.78	15		0.7815		0.60000		1.00000	
3	16	Ge3	Ge	0.81667		0.81	667		0.6296		0.60000		1.00000	
4	16	Na1	Na	0 375		0 37	' 5		0.375		0 60000		1.00000	



[1] A. M. Guloy et al. Nature 443 (2006). Jan-Hendrik Poehls · Dalhousie University

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



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Background

- The background of this example is more complex
- Go to Model \rightarrow 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

Histograms			×
Histogram1			
X-ray CW	Data	Polynomial 5th order	19.2
Data min-max: 10	.00000 80.00000	6 terms ▼ Offset: 0	
Data step:	0.020000	Par: Value:	-
Histogram Scale:	1.0		19.1
Zero:	0	B1 0	
Wavelength 1:	1.54051	B2 0	19.3
Wavelength 2:	1.54433	B3 0	
Ratio:	0.5	Excluded Regions:	19.4
Sample Displace:	0	Start Stop	19 5
Base Width:	7	2	
Hist. Weighting:	1	3	
Polarization	1	4	_1
Were the state of		Ma	nual ei
illumination:		Incident Spectrum Form Factors	
			1
		OK Cancel Help	

Lattice Parameters, Thermal & Zero

- Go to Model \rightarrow 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 \rightarrow 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. Jan-Hendrik Poehls · Dalhousie University

Excluding Peaks

- Find in MATCH the positions of Ge
- Go to Model \rightarrow Histograms
- Exclude the regions where the Ge peaks are (exclude a larger region) under Excluded Regions (22.1)
- Go to Rietveld \rightarrow 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

-								
	Histograms					1	×	
	Histogram1							
	X-ray CW	▼ Data	•	Polynomial	5th order		•	
	Data min-max	0.00000	30.00000	6 terms	-)ffset	0	
	Data step:	0.020000		Part Val		,		
	Histogram Scale:	1.0		B-1 30	47.55	~		
	Zero:	0.03		B0 -34	16.24 8222			
	Wavelength 1:	1.54051		B2 -0.	265708			
	Wavelength 2:	1.54433		B3 0.0	00145998		-	
	Ratio:	0.5		Excluded to	egions:			
	Sample Displace:	0		Start 26.5000	Stop 0 28.10	000	_	
	Base Width:	7		2 42.9000	45.50	000		
	Hist. Weighting:	1		4 52.8000	0 54.40	000		
	Polarization:	1		5			•	
	Illumination:			Incident Sp	ectrum	Form Fa	actors	
				ОК	Cance		Help	
				OK	Cance		Help	
dit	Chart Help			OK	Cance		Help	
dit	Chart Help	Histogram	1 💌	ОК	Cance		Help	>
dit	Chart Help	Histogram	1 💌	<u>ОК</u>	Cance		Help	
dit	Chart Help P R M P	Histogram	1 <u>v</u> 1t		Cance		Help	>
dit	Chart Help 2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Histogram	1 💌		Cance		Help	
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dit @	Chart Help	Histogram refinemer	1 ▼ nt				Help	>
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37

Jan-Hendrik Poehls · Dalhousie University

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 \rightarrow New
- Change 'a structure' to 'an extraction' (23.1)
- Go to Model \rightarrow General
 - Same procedure (see Slide 9)
- Go to Model \rightarrow 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



Calculation Method:

192

B

Lattice: Cubic

Z

Gen Mult:

23.1

Hases Phases

Title: Ge clathrates

Space Group:

Phase Scale:

Overall Thermal:

0

FD3M

0.00000

0.01

Mult Name Type

-

a: 90.0

b: 90.0

q: 90.0

B11

Recycle

B22

Le Bail

a: 15.20000

b: 15.20000

c: 15.20000

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)