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Judging quality: Catching common refinement problems

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Outline

- What are [some of] the Rietveld R-factors and what do they measure
- Graphical analysis of Rietveld fits
  - Background problems
  - Unindexed peaks (lowered symmetry or 2nd phase?)
  - Poor fit of peak shapes
  - Refereeing: using & plotting fits from CIF

Rietveld R-factors

- Weighted Profile R_{wp}
  - Valuable
- Unweighted R_p
  - Unimportant
- Expected R_{exp}
  - Statistically best R_{wp}
- Reduced χ^2
  - $\chi^2 = (R_{wp} / R_{exp})^2$
  - $\chi^2 \geq 1$ & $\chi^2 \cong 1$
- Integrated Intensity R_{Bragg}, R_F, R_{F^2}
  - no statistical basis
  - compare to single xtal
- Durbin-Watson
  - error correlation in adjacent points
    - *0 completely correlated*
    - *2 errors purely random*
  - not terribly important

See:
- Pages 168-9 in 2001 GSAS manual
- B.H. Toby, "R-factors in Rietveld Analysis: How good is good enough?" *Powder Diffraction*. 21(1): 67-70 (2006).

R-factor Computation

- $[R_{wp}]^2 \equiv \Sigma\, \sigma_i^{-2}(I_{obs,i} - I_{calc,i})^2 \,/\, \Sigma\, \sigma_i^{-2}(I_{obs,i})^2$
- *If all errors are statistical, then on average,* $|\langle I_{obs,i} - I_{calc,i} \rangle| = \sigma_I$.
  Expected R_{wp} *(≡* R_{exp}*)*

  $[R_{exp}]^2 = N_{obs} \,/\, \Sigma\, \sigma_i^{-2}(I_{obs,i})^2$

  $[R_{exp}]^2 = (N_{obs} - N_{var}) \,/\, \Sigma\, \sigma_i^{-2}(I_{obs,i})^2$
- *reduced* $\chi^2 \equiv [R_{wp}]^2 / [R_{exp}]^2$
  ==> 1 in statistical limit

  $\chi^2 = [\Sigma\, \sigma_i^{-2}(I_{obs,i} - I_{calc,i})^2] \,/\, [N_{obs} - N_{var}]$

χ^2 in GSAS includes other things

- GSAS includes all "histograms" (including soft constraints) in χ^2
  - useful to report contribution of soft constraints to total χ^2
- GSAS includes the fit to fixed background points & their standard uncertainties (née esd) in χ^2 -- I have no idea why.

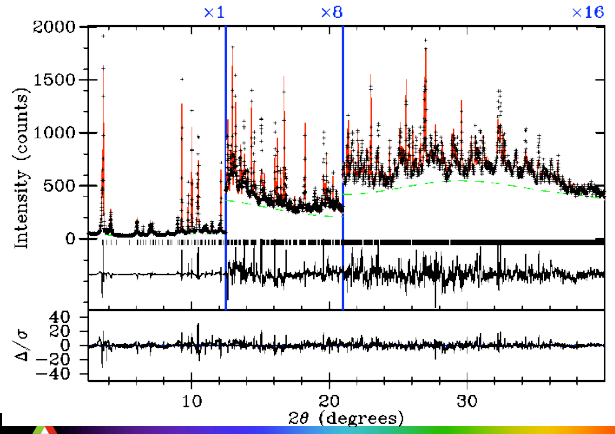
R-factors are not absolute

Problem: *Profile R-factors measure GOF for structure + peak shape +background*

- With very good counting statistics, minor profile problems ==> high R_{wp} & χ^2 values
- With poor counting statistics & high backgrounds, good R_{wp} & χ^2 values come from fitting background

Solution: ***Judge quality from a plot of the fit!***

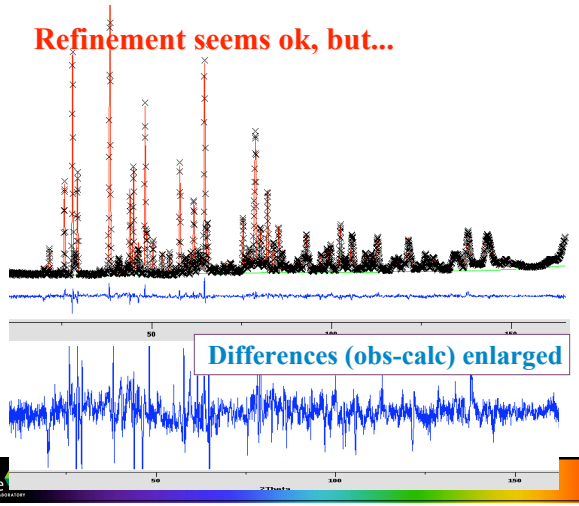
Plot of fit ("Rietveld plot")



Common Problems in Fits, Viewed Graphically

- Background is poorly fit
- Extra peaks (intensity where none is seen)
- peak width problems
  - need to use additional terms
  - asymmetric peak broadening
  - "irregular" peak shapes
- Poor intensity match

Refinement seems ok, but...



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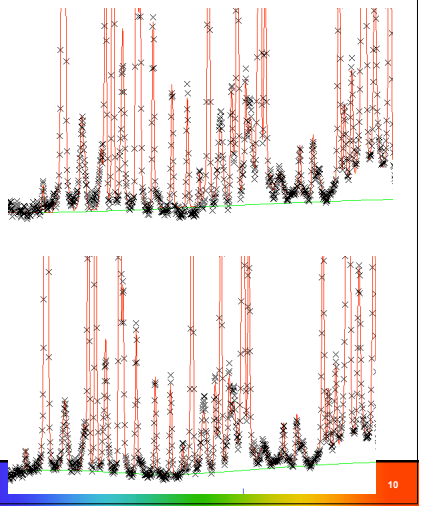
9

Also with more magnification:

Note how background "cuts through" the data points -- background should go average or below (with peak tails)!

Adding more terms to polynomial:

Better fit!



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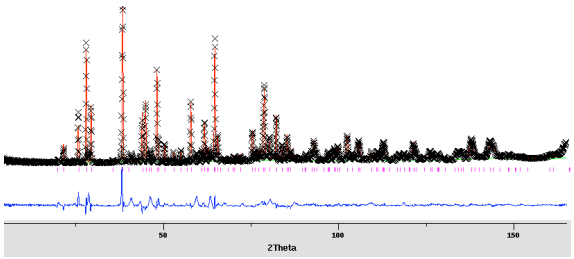
10

Next problem:

Not a great fit, (though better than previous)

Why is the fit not better?



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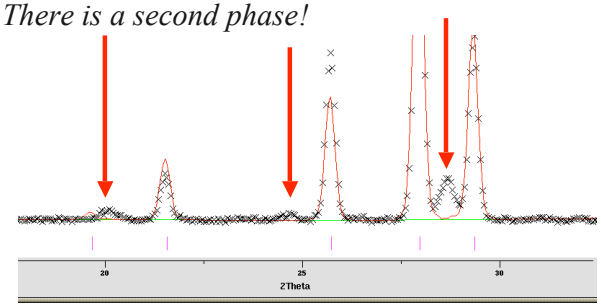
11

Enlarged section: Note the unindexed peaks.

There is a second phase!



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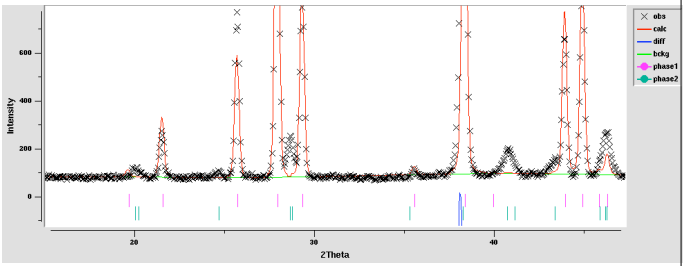
12

2nd phase has significant overlap with 1st (structurally related?)

This would likely bias the model for the 1st phase!



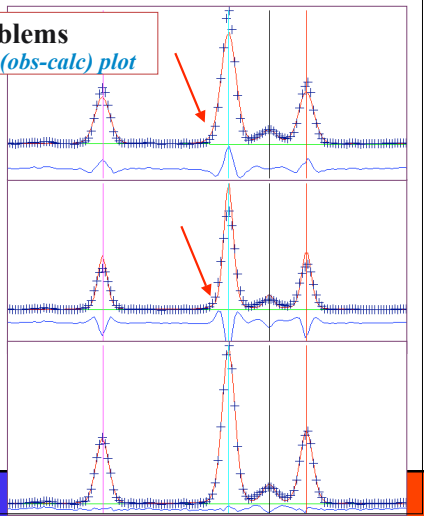
Other Common Problems

note shape of difference (obs-calc) plot

Peak shape is too wide

Peak shape is too narrow

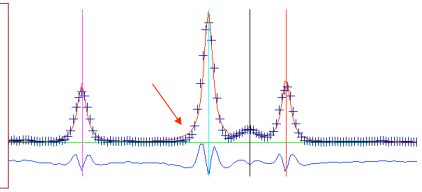
Pretty good



Peak tails don't match

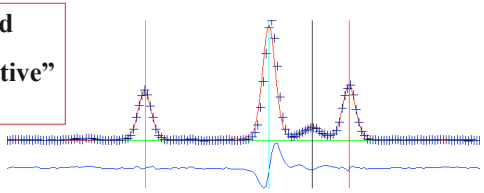
Fit is Lorentzian
Data are ~Gaussian

(opposite is more common)



Peak is shifted

(note "derivative" appearance)



Refereeing powder diffraction fits

- As a referee, you have a unique role to ensure quality
- You need to look closely at the fit in a magnified plot
- How?
  - Request raw data & fit in a CIF (pdCIF)
  - Use pdCIFplot to view the fit at any level of detail you want

pdCIFplot software (part of CIFTOOLS, free runs on Windows, Linux & Mac)
http://www.ncnr.nist.gov/programs/crystallography/software/cif/ciftools.html

pdCIFplot intro:
http://www.ncnr.nist.gov/programs/crystallography/software/cif/pdCIFplot.html

B.H. Toby, "Inspecting Rietveld Fits from pdCIF: pdCIFplot". Journal of Applied Crystallography. ***36****(5): p. 1285-7* ***(2003)*** *[2 citations].*

Wrap up

- Use R-factors to compare different fits on a single data set, but don't worry about their magnitude
- Do ask why χ^2 is not 1, but if the problem is not having systematic variations in the intensity fitting, don't worry too much.
- Look carefully at plots of fits -- small discrepancies can indicate big problems
- As a referee, insist on getting pdCIF files and use pdCIFplot to examine fits