Rietveld refinement

CHAN PARK, MSE, Seoul National University

Hugo M. Rietveld

Robert L. Snyder

Denver X-ray Conference 2003

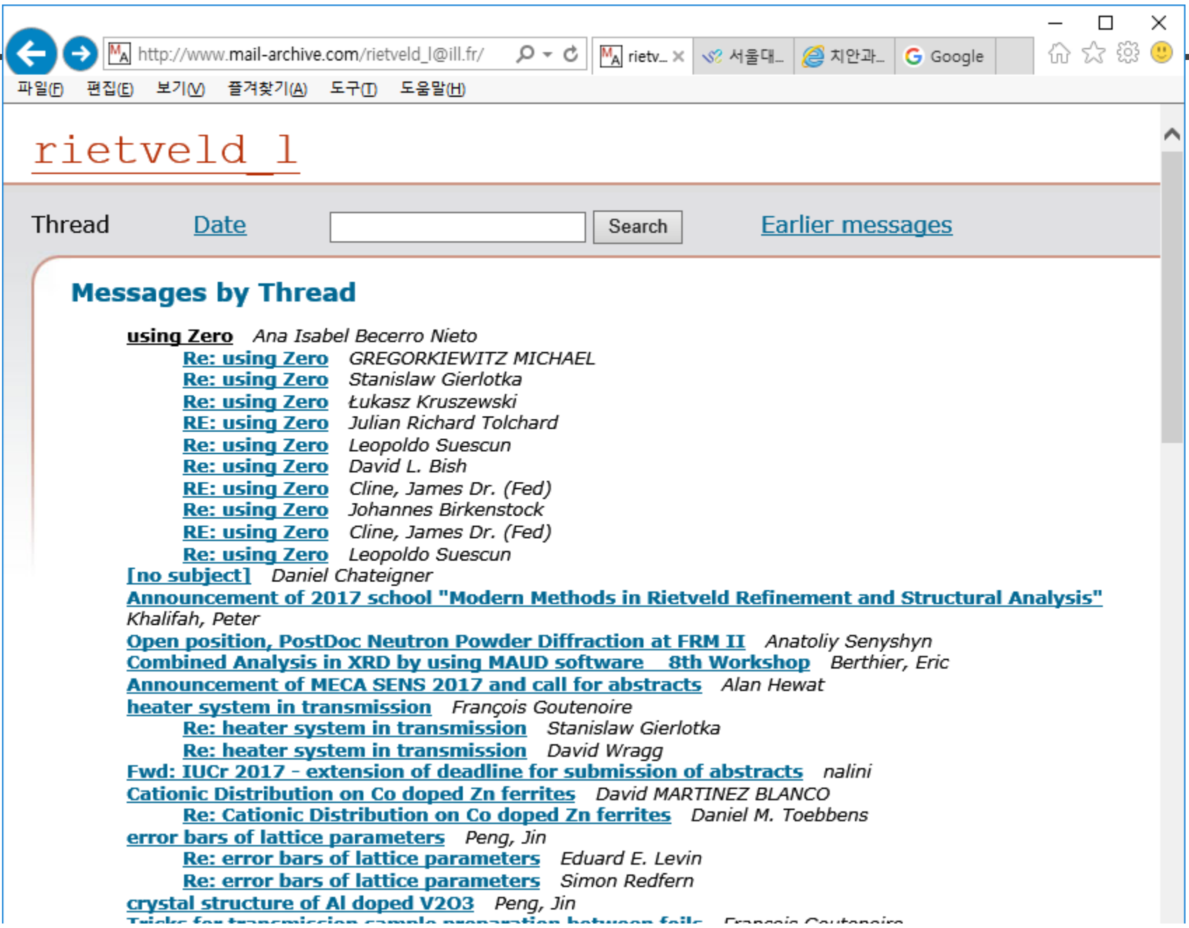
- Rietveld Refinement Guidelines J. Appl. Cryst. (1999), 32 36-50 McCusker et al.
- http://home.wxs.nl/~rietv025/
- Join “Rietveld Method Users Mailing List”

  Can get info on how to join → www.mail-archive.com/rietveld_l@ill.fr/info.html

  The mail archive → www.mail-archive.com/rietveld_l@ill.fr/

Most materials in this file are from

- R. A. Young, The Rietveld Method
- V.K. Pecharsky and P.Y. Zavalij, Fundamentals of powder diffraction and structural characterization of materials, 2nd ed.
- tutorial materials of ICDD



rietveld_l

Thread Date Earlier messages

Messages by Thread

using Zero *Ana Isabel Becerro Nieto*
  - **Re: using Zero** *GREGORKIEWITZ MICHAEL*
  - **Re: using Zero** *Stanislaw Gierlotka*
  - **Re: using Zero** *Łukasz Kruszewski*
  - **RE: using Zero** *Julian Richard Tolchard*
  - **Re: using Zero** *Leopoldo Suescun*
  - **Re: using Zero** *David L. Bish*
  - **RE: using Zero** *Cline, James Dr. (Fed)*
  - **Re: using Zero** *Johannes Birkenstock*
  - **RE: using Zero** *Cline, James Dr. (Fed)*
  - **Re: using Zero** *Leopoldo Suescun*

[no subject] *Daniel Chateigner*

Announcement of 2017 school "Modern Methods in Rietveld Refinement and Structural Analysis" *Khalifah, Peter*

Open position, PostDoc Neutron Powder Diffraction at FRM II *Anatoliy Senyshyn*

Combined Analysis in XRD by using MAUD software 8th Workshop *Berthier, Eric*

Announcement of MECA SENS 2017 and call for abstracts *Alan Hewat*

heater system in transmission *François Goutenoire*
  - **Re: heater system in transmission** *Stanislaw Gierlotka*
  - **Re: heater system in transmission** *David Wragg*

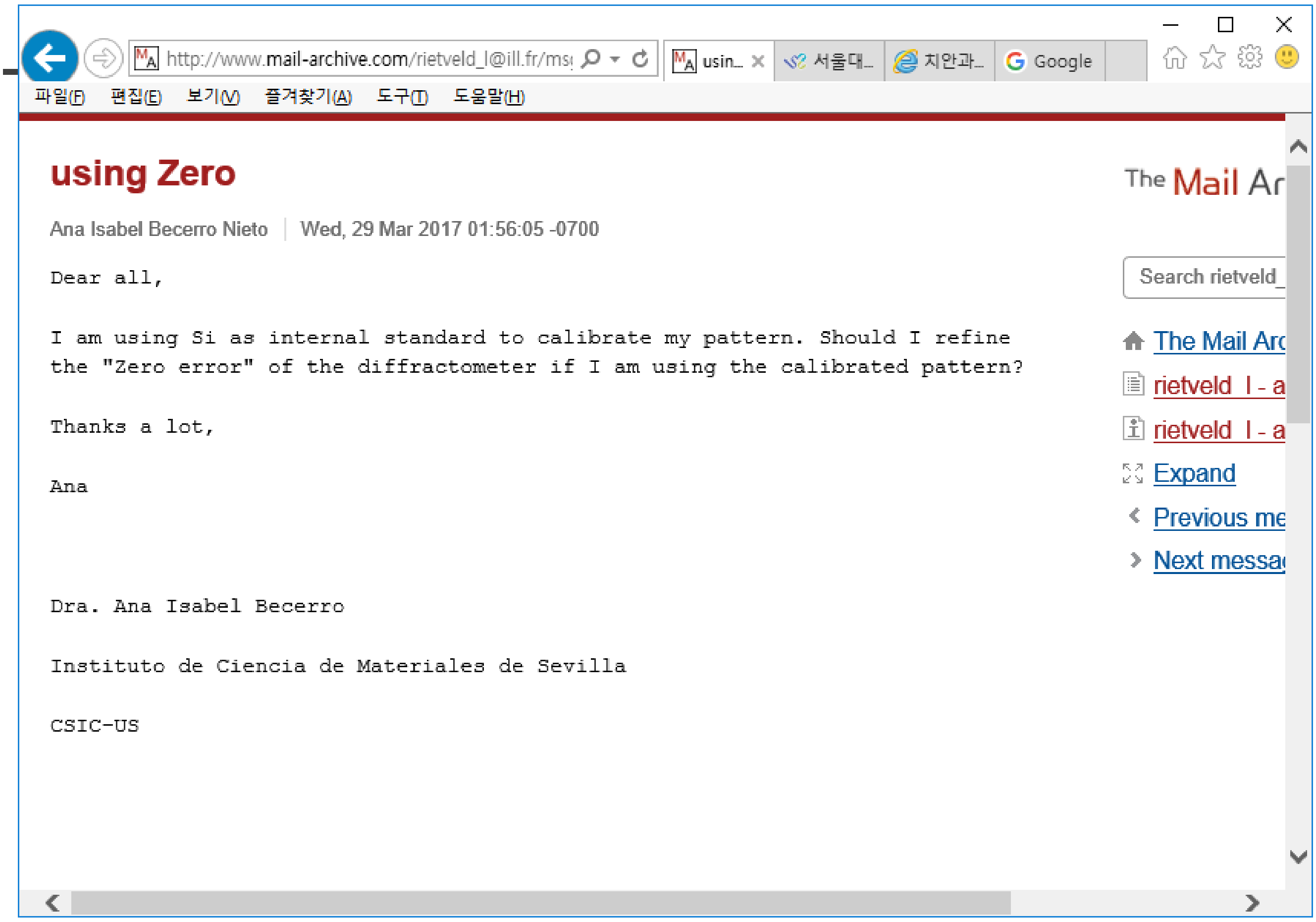
Fwd: IUCr 2017 - extension of deadline for submission of abstracts *nalini*

Cationic Distribution on Co doped Zn ferrites *David MARTINEZ BLANCO*
  - **Re: Cationic Distribution on Co doped Zn ferrites** *Daniel M. Toebbens*

error bars of lattice parameters *Peng, Jin*
  - **Re: error bars of lattice parameters** *Eduard E. Levin*
  - **Re: error bars of lattice parameters** *Simon Redfern*

crystal structure of Al doped V2O3 *Peng, Jin*

Tricks for transmission sample preparation between foils *François Goutenoire*



using Zero

Ana Isabel Becerro Nieto | Wed, 29 Mar 2017 01:56:05 -0700

```
Dear all,

I am using Si as internal standard to calibrate my pattern. Should I refine
the "Zero error" of the diffractometer if I am using the calibrated pattern?

Thanks a lot,

Ana



Dra. Ana Isabel Becerro

Instituto de Ciencia de Materiales de Sevilla

CSIC-US
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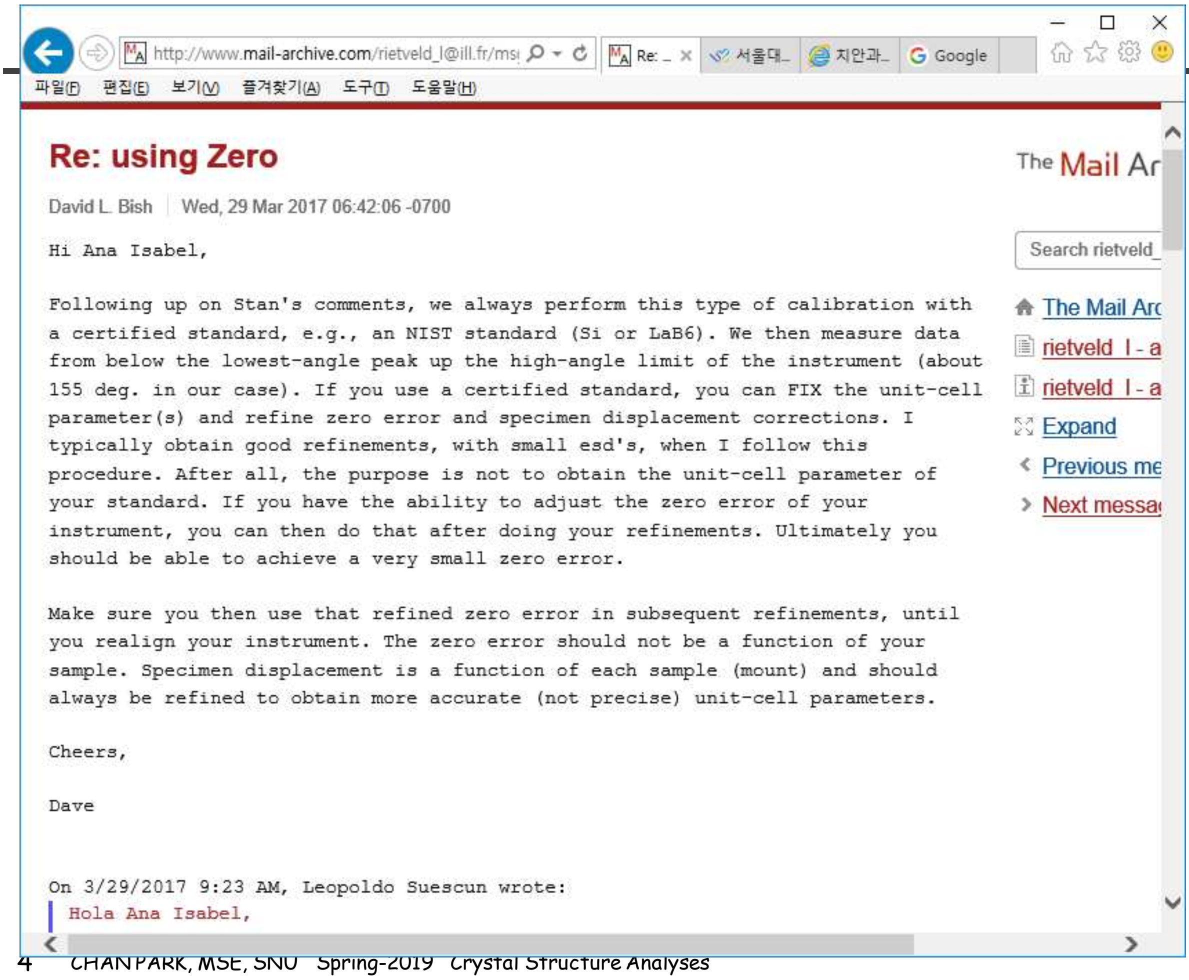

Re: using Zero

David L. Bish | Wed, 29 Mar 2017 06:42:06 -0700

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Hi Ana Isabel,

Following up on Stan's comments, we always perform this type of calibration with
a certified standard, e.g., an NIST standard (Si or LaB6). We then measure data
from below the lowest-angle peak up the high-angle limit of the instrument (about
155 deg. in our case). If you use a certified standard, you can FIX the unit-cell
parameter(s) and refine zero error and specimen displacement corrections. I
typically obtain good refinements, with small esd's, when I follow this
procedure. After all, the purpose is not to obtain the unit-cell parameter of
your standard. If you have the ability to adjust the zero error of your
instrument, you can then do that after doing your refinements. Ultimately you
should be able to achieve a very small zero error.

Make sure you then use that refined zero error in subsequent refinements, until
you realign your instrument. The zero error should not be a function of your
sample. Specimen displacement is a function of each sample (mount) and should
always be refined to obtain more accurate (not precise) unit-cell parameters.

Cheers,

Dave


On 3/29/2017 9:23 AM, Leopoldo Suescun wrote:
| Hola Ana Isabel,
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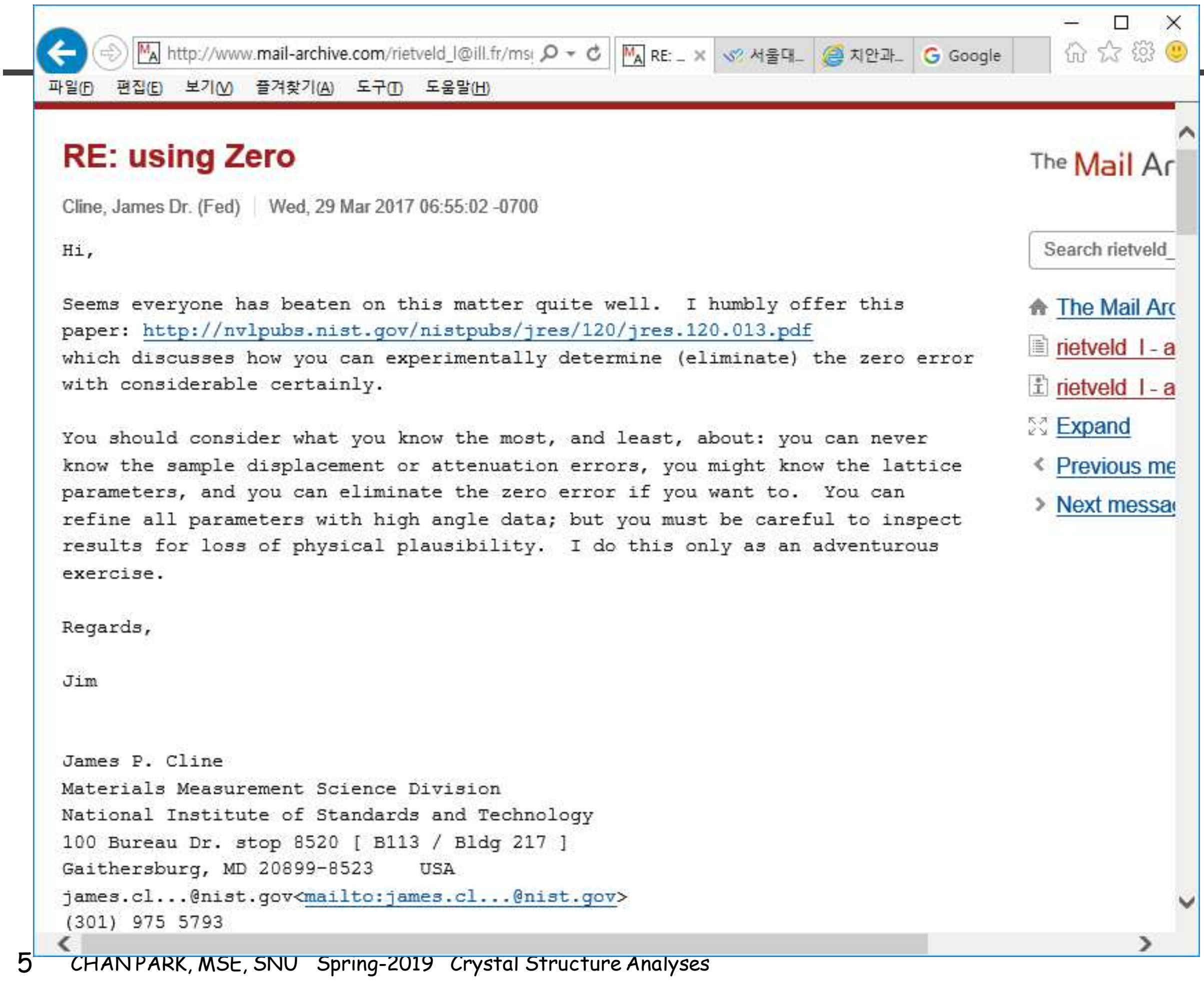

RE: using Zero

Cline, James Dr. (Fed) | Wed, 29 Mar 2017 06:55:02 -0700

Hi,

Seems everyone has beaten on this matter quite well. I humbly offer this paper: http://nvlpubs.nist.gov/nistpubs/jres/120/jres.120.013.pdf which discusses how you can experimentally determine (eliminate) the zero error with considerable certainly.

You should consider what you know the most, and least, about: you can never know the sample displacement or attenuation errors, you might know the lattice parameters, and you can eliminate the zero error if you want to. You can refine all parameters with high angle data; but you must be careful to inspect results for loss of physical plausibility. I do this only as an adventurous exercise.

Regards,

Jim

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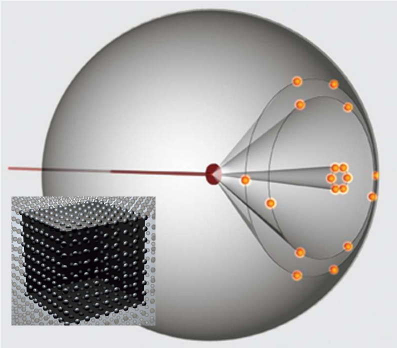
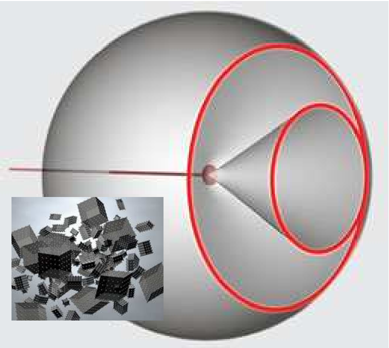
Debye rings from ---- & Rietveld

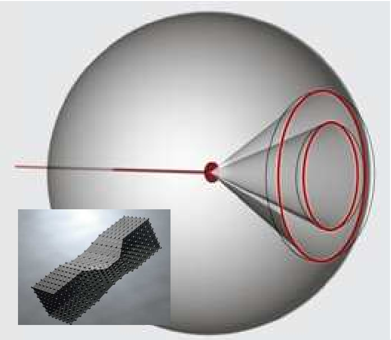
single crystal



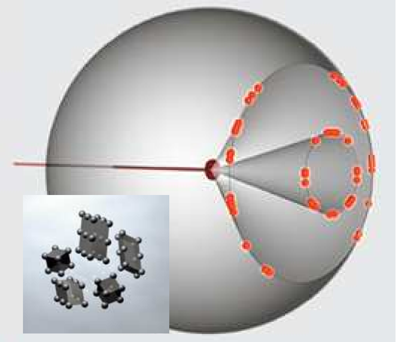
powder



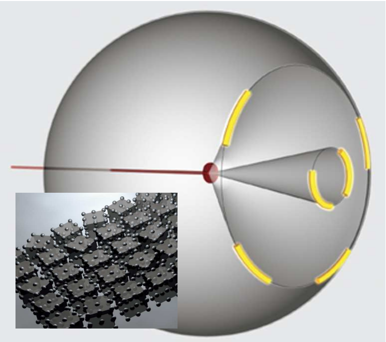
strained material



small volume



textured material



Jon Giencke

What we can do with XRD

- **Identification of unknown phases (phase-ID)**
- **Quantitative phase analysis (QPA)**
- Accurate lattice parameter measurement
- % crystallinity
- Crystal size
- Internal elastic strains
- Preferred orientation measurement
- Residual stress analysis
- Order-disorder transitions
- Cation site disorder
- Structure of thin films
- Micro-diffraction (phase identification, texture, stress…)
- Crystal structure determination
- Crystal structure refinement

What Rietveld can do

- Analysis of the whole diffraction pattern
  - ✓ Profile fitting is included
  - ✓ Not only the integrated intensities

- Refinement of the structure parameters from diffraction data
  - ✓ Quantitative phase analysis (crystalline and amorphous)
  - ✓ Lattice parameters
  - ✓ Atomic positions and occupancies
  - ✓ Temperature vibrations (isotropic and anisotropic)
- Other information
  - ✓ Grain size and micro-strain (isotropic and anisotropic)
  - ✓ Stacking fault and twin
  - ✓ Magnetic moments (neutrons)

- Not intended for the structure solution
  - ✓ The structure model must be known before starting the Rietveld refinement

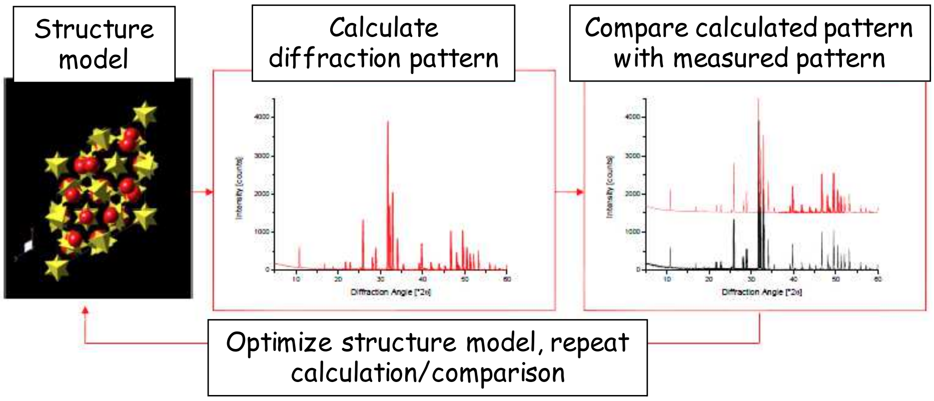
Why the Rietveld refinement is widely used?

- Pros
  - ✓ It uses directly the measured intensities points
  - ✓ It uses the entire spectrum (as wide as possible)
  - ✓ Less sensible to model errors
  - ✓ Less sensible to experimental errors

- Cons
  - ✓ It requires a model
  - ✓ It needs a wide spectrum
  - ✓ Rietveld programs are not easy to use
  - ✓ Rietveld refinements require experience (1-2 years?)

from presentation of Luca Lutterotti

Rietveld refinement

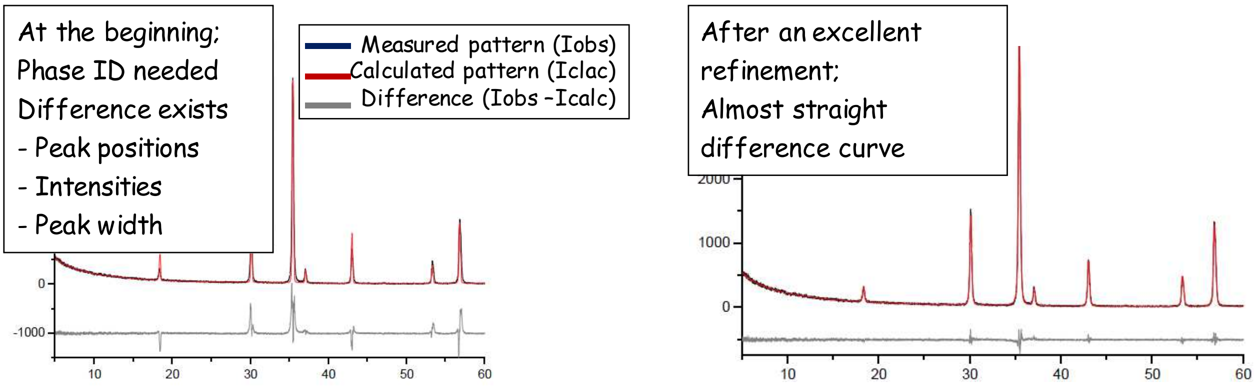


Structure model

Calculate diffraction pattern

Compare calculated pattern with measured pattern

Optimize structure model, repeat calculation/comparison



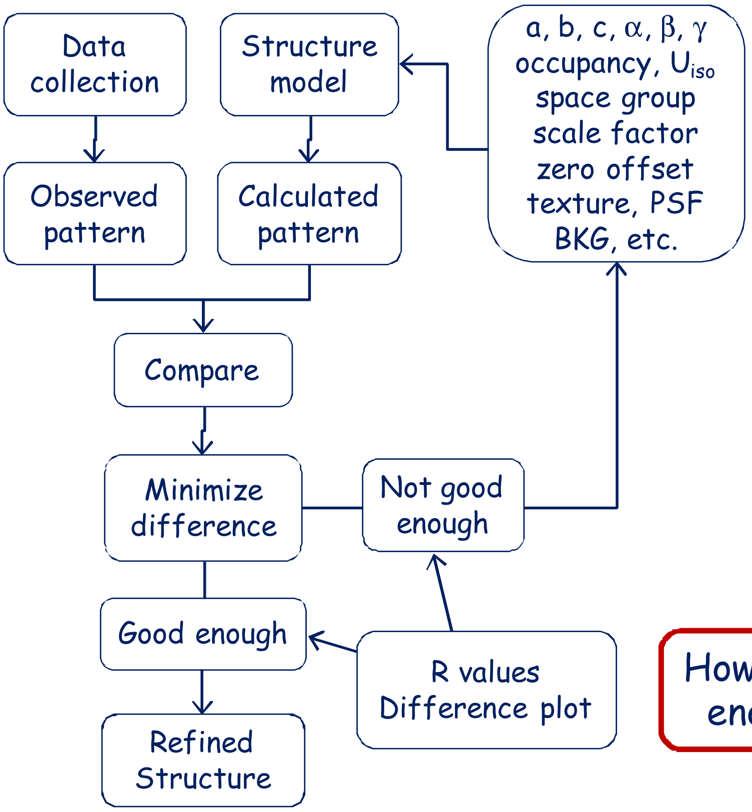
At the beginning;
Phase ID needed
Difference exists
- Peak positions
- Intensities
- Peak width

After an excellent refinement;
Almost straight difference curve

Minimize differences between calculated and observed pattern by least-squares method

From presentation of Nicola Döbelin, RMS Foundation, Switzerland

Rietveld refinement


Data collection

Structure model

Observed pattern

Calculated pattern

a, b, c, α, β, γ
occupancy, U_{iso}
space group
scale factor
zero offset
texture, PSF
BKG, etc.

Compare

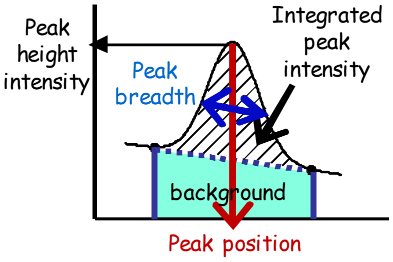
Minimize difference

Not good enough

Good enough

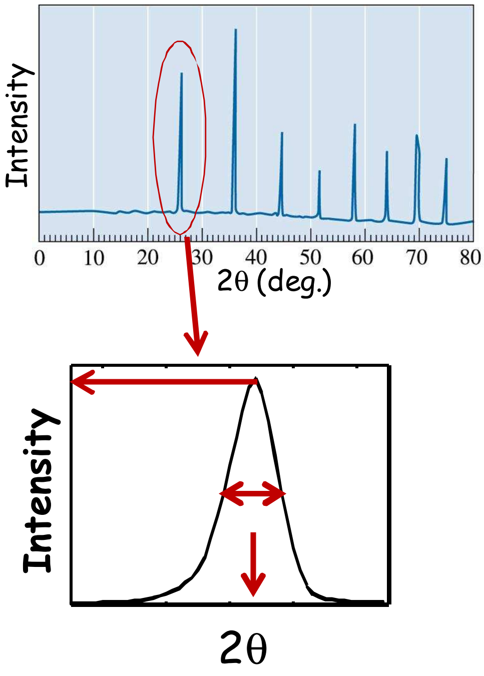
R values
Difference plot

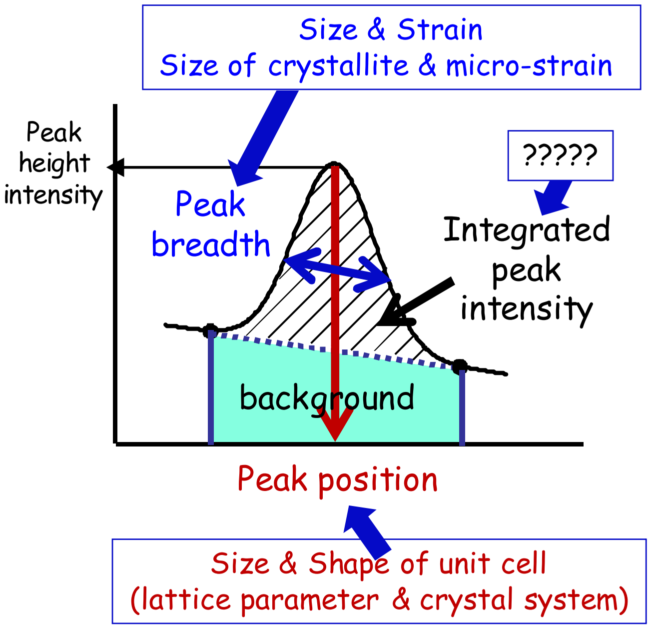
Refined Structure



How good is good enough ??????

θ–2θ scan > 2θ, intensity, peak breadth




Size & Strain
Size of crystallite & micro-strain

?????

Size & Shape of unit cell
(lattice parameter & crystal system)

Position, intensity, shape → Xtal structure, physical state, etc.

Factors affecting the relative intensity of XRD peaks

- Structure sensitive
  - ✓ Atomic scattering factor
  - ✓ Structure factor
  - ✓ Polarization
  - ✓ Multiplicity
  - ✓ Temperature
- Sample sensitive
  - ✓ Absorption
  - ✓ Crystallite size
  - ✓ Degree of crystallinity
  - ✓ Particle orientation
- Instrument sensitive
  - ✓ Absolute intensities
    - Source intensity
    - Diffractometer efficiency
    - Take-off angle of tube
    - Receiving slit width
    - Axial divergence allowed
  - ✓ Relative intensities
    - Divergence slit aperture
    - Detector dead-time
- Measurement sensitive
  - ✓ Method of peak area measurement
  - ✓ Method of background subtraction
  - ✓ $\alpha 2$ stripping or not
  - ✓ Degree of data smoothing employed

Bish & Post Chap 3

What determines the intensities?

- Structure
  - ✓ Atomic positions
  - ✓ Occupancies
  - ✓ Atomic scattering factors
  - ✓ Thermal/disorder parameters
  - ✓ Lattice parameters
  - ✓ Symmetry
- Global Parameters
  - ✓ Concentration
  - ✓ Incident intensity
  - ✓ Background
  - ✓ Extinction
  - ✓ Absorption
  - ✓ Preferred orientation
  - ✓ Multiplicity
  - ✓ Lp factor
  - ✓ Profile function
  - ✓ Diffractometer parameters

Intensity diffracted by a single phase powder specimen in a diffractometer

$$I(hkl) = \left(\frac{I_o A \lambda^3}{32\pi r}\right)\left[\left(\frac{\mu_o}{4\pi}\right)^2 \frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right)$$

- I(hkl) = integrated intensity per unit length of diffraction line
- I_0 = intensity of incident beam
- A = crosssectional area of incident beam
- r = radius of diffractometer circle
- V = volume of unit cell
- F(hkl) = structure factor
- p = multiplicity factor
- e^{-2M}; temperature factor
- μ = linear absorption coefficient

Factors affecting observed intensity to depart from the theoretical one (important in quantitative phase analysis)

Preferred orientation (texture)
Microabsorption
Extinction

Rietveld refinement

- What is the **goal** of Rietveld Refinement?
  - ✓ to obtain an accurate crystal structure
- What is the **basic idea** of a Rietveld Refinement?
  - ✓ To fit the entire diffraction pattern at once, optimizing the agreement between calculated and observed patterns
- **What input** is needed to carry out a Rietveld Refinement?
  - ✓ Correct space group symmetry
  - ✓ Reasonably accurate unit cell dimensions
  - ✓ Approximate starting positions of the atoms (correct Wyckoff sites)
- The Rietveld Method is a refinement technique, not a structure solution method → A good starting model is required

Structure model

- (X-ray or neutron) Powder diffraction pattern can be modeled from
  - ✓ Crystallographic Model: describes size, symmetry of unit cell, atomic positions, thermal parameters and occupancy
  - ✓ Instrumental Model: describes optics and set-up of diffractometer
  - ✓ Profile Model: describes peak shape

- Rietveld refinement
  - ✓ The difference between the observed and calculated data is minimized iteratively until getting satisfactory answer, i.e. **a good fit between experimental and calculated pattern** is obtained
  - ✓ Performs a **least square minimization** of the **weighted differences between calculated pattern and observed data** by computing the **shifts** in the **adjustable parameters** for the model

How do we get the model?

- Commercial Databases
  - ✓ **Powder Diffraction File (PDF)**
  - ✓ **Inorganic Crystal Structure Database (ICSD)**
  - ✓ Linus Pauling File (LPF)
  - ✓ NIST Structural Database (metals, alloys, intermetallics)
  - ✓ Cambridge Structure Database (CSD) (organic materials)
- Free Online Databases
  - ✓ Crystallography Open Database (www.crystallography.net)
  - ✓ CRYSTMET (cds.dl.ac.uk/cds/datasets/crys/mdf/llmdf.html) (???)
  - ✓ ICSD- 4% available as demo at (icsd.ill.eu/icsd/index.html)
  - ✓ Mincryst (database.iem.ac.ru/mincryst/index.php)
  - ✓ American Mineralogist (www.minsocam.org/MSA/Crystal_Database.html)
  - ✓ WebMineral (www.webmineral.com)
  - ✓ Protein Data Bank (www.rcsb.org/pdb/home/home.do)
  - ✓ Nucleic Acid Database (ndbserver.rutgers.edu)
  - ✓ Database of Zeolite Structures (www.iza-structure.org/databases)

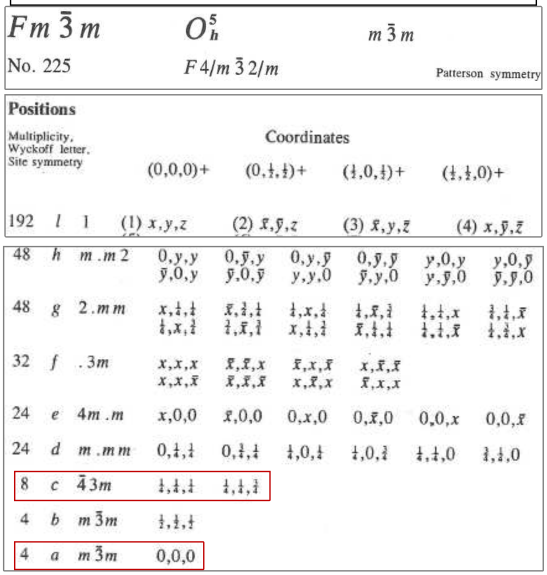
- Primary literature (Acta Crystallographica, etc.)
- *ab initio* structure determination

Structure model

- Cubic ZrO_2
- Space Group Fm-3m (225)
- Lattice Parameter a=5.11

Atom	**Wyckoff Site**	x	y	z	**B_{iso}**	**occupancy**
Zr	4a	0	0	0	1.14	1
O	8c	0.25	0.25	0.25	2.4	1

International Tables for Crystallography, Volume A: Space-group symmetry



$Fm\bar{3}m$ O_h^5 $m\bar{3}m$

No. 225 $F\,4/m\,\bar{3}\,2/m$ Patterson symmetry

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates					
			$(0,0,0)+$	$(0,\frac{1}{2},\frac{1}{2})+$	$(\frac{1}{2},0,\frac{1}{2})+$	$(\frac{1}{2},\frac{1}{2},0)+$		
192	*l*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$		
48	*h*	$m.m2$	$0,y,y$ $\bar{y},0,y$	$0,\bar{y},y$ $\bar{y},0,\bar{y}$	$0,y,\bar{y}$ $y,y,0$	$0,\bar{y},\bar{y}$ $\bar{y},y,0$	$y,0,y$ $y,\bar{y},0$	$y,0,\bar{y}$ $\bar{y},\bar{y},0$
48	*g*	$2.mm$	$x,\frac{1}{4},\frac{1}{4}$ $\frac{1}{4},x,\frac{3}{4}$	$\bar{x},\frac{3}{4},\frac{1}{4}$ $\frac{3}{4},\bar{x},\frac{3}{4}$	$\frac{1}{4},x,\frac{1}{4}$ $x,\frac{1}{4},\frac{3}{4}$	$\frac{1}{4},\bar{x},\frac{3}{4}$ $\bar{x},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},x$ $\frac{1}{4},\frac{1}{4},\bar{x}$	$\frac{3}{4},\frac{1}{4},\bar{x}$ $\frac{1}{4},\frac{3}{4},x$
32	*f*	$.3m$	x,x,x $x,x,\bar{x}$	$\bar{x},\bar{x},x$ $\bar{x},\bar{x},\bar{x}$	$\bar{x},x,\bar{x}$ $x,\bar{x},x$	$x,\bar{x},\bar{x}$ $\bar{x},x,x$		
24	*e*	$4m.m$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
24	*d*	$m.mm$	$0,\frac{1}{4},\frac{1}{4}$	$0,\frac{3}{4},\frac{1}{4}$	$\frac{1}{4},0,\frac{1}{4}$	$\frac{1}{4},0,\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{1}{4},0$
8	*c*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$				
4	*b*	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
4	*a*	$m\bar{3}m$	$0,0,0$					

Temperature factor

B_{iso}, U_{iso}, B_{ij}, U_{ij}, b_{ij}

$$f = f_0 \exp\left[-\frac{B\sin^2\theta}{\lambda^2}\right]$$

$$B = 8\pi^2 U^2$$

- Site occupancy = 1; every equivalent position of that site is occupied by that atom
- Site occupancy < 1; some of the sites are vacant
  - Site occupancy = 0.5; half of that site is occupied by the atom
- two atoms occupying the same site will each have a fractional site occupancy

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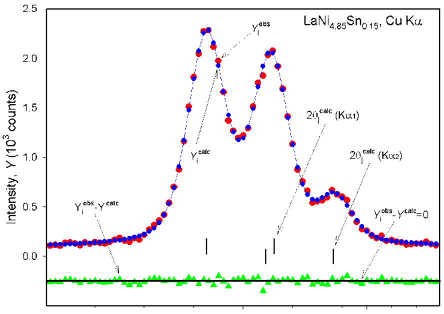
Mathematical Basis



Pecharsky Figure 15.10

- S_y is the function to minimize

$$S_y = \sum w_i\,(Y_i - Y_{ci})^2$$

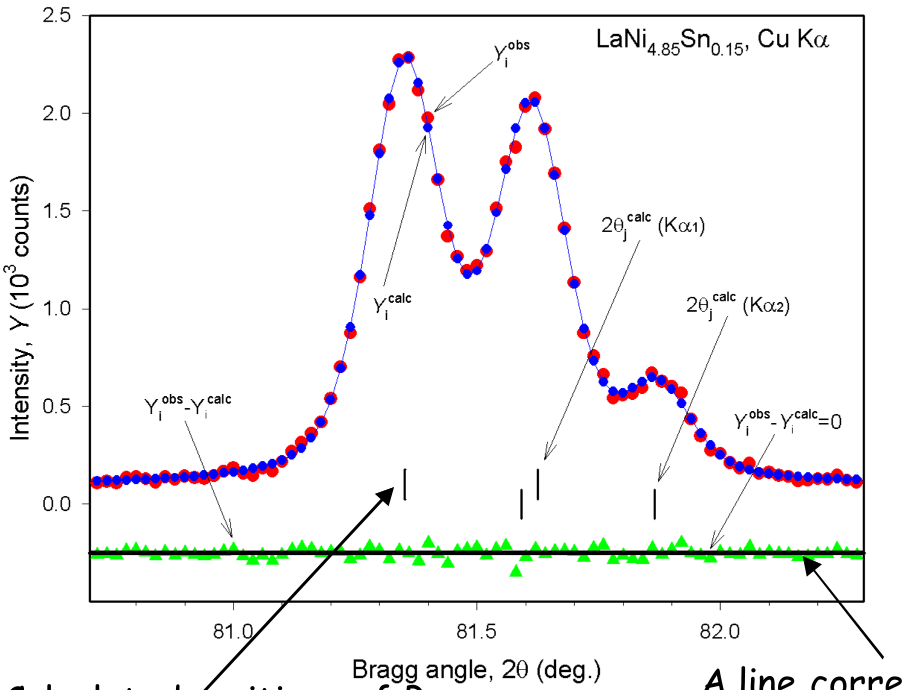
  - ✓ w_i weighting factor = $1 / y_i$
  - ✓ Y_i, Y_{ci} = observed, calculated intensity at the i^{th} step
- S_y = 0 in perfectly ideal case
- Y_{ci} is a combination of many factors

$$Y_{ci} = s \sum L_K\,|F_K|^2\,\varphi\,(2\theta - 2\theta_K)\,P_K\,A\ + y_b$$

  - ✓ s = scale factor K = Miller indices for a given reflection
  - ✓ L_K = Lorentz, polarization and multiplicity factors
  - ✓ φ = Reflection profile function P_K = Preferred orientation function
  - ✓ A = Absorption factor F_K = Structure factor for the Kth reflection
  - ✓ y_{bi} = Background intensity at point I
- Parameters not included in Y_{ci} equation
  - ✓ Unit cell parameters (a,b,c;α,β,γ): can be refined but are not included in equation → should be close to real cell parameters
  - ✓ Space Group: cannot be refined. Must be right (if not?)
- Modify structural model to match observed data
  - ✓ L-S minimization → normal matrix (derivatives of all y_{ci} with each adjustable parameter)

Pecharsky, Figure 15.10

Result plot of Rietveld refinement



Observed I

Calculated I

Difference between observed & calculated I

Calculated positions of Bragg peaks of each phase

A line corresponding to $Y_i^{obs} - Y_i^{calc} = 0$

Pecharsky, Figure 15.10

Mathematical Basis

- Elements of normal matrix:

$$M_{jk} = -\sum_i 2w_i \left[(y_i - y_{ci}) \frac{\partial^2 y_{ci}}{\partial \chi_j \cdot \partial \chi_k} - \left(\frac{\partial y_{ci}}{\partial \chi_j} \right) \left(\frac{\partial y_{ci}}{\partial \chi_k} \right) \right]$$

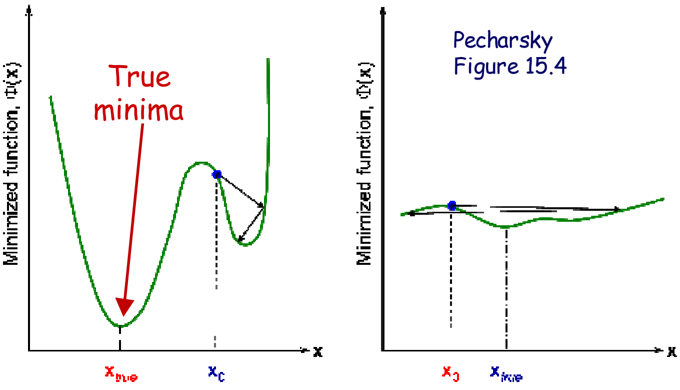
Where x_j and x_k are a set of adjustable parameters

- ✓ Solve for x_j and x_k by matrix inversion, where matrix is (m x m) (m = # of parameters)
- ✓ This is non-linear → solution is computed with iterative shifts (Newton-Raphson Method)

- ✓ e.g. $$\Delta \chi_k = \sum M_{jk}^{-1} \frac{\partial S_y}{\partial \chi_k}$$
- ✓ Hopefully the shifts in parameters will yield the best values

- BUT beware of false minima:

→ Starting model must be close to correct model



Pecharsky Figure 15.4

For non-linear least square minimization, see Pecharsky chapter 15.5

Structural complexity

- How complex can a crystal structure be, to accurately refine the structure with the Rietveld method?

- Depends upon several factors
  - ✓ Quality of the sample (sharp peaks or broad, diffracts out to what value of d)
  - ✓ Quality of the instrument (the larger peak intensities, the better → need high resolution and large coverage of Q space)
  - ✓ Heavy peak overlap that can severely limit accuracy
  - ✓ Soft constraints, rigid bodies, etc. are ways to get information where full unconstrained refinement is not accurate

- In the best cases, structures with 150-200 atomic parameters have been accurately refined

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Achievements

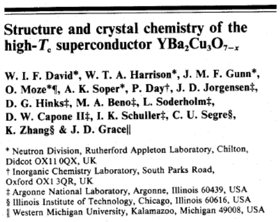
- Major contribution to almost every hot area of “hard” materials in the last 30 years
  - ✓ High temperature superconductors
    - Much of the solid state chemistry of these materials was worked using neutron diffraction and Rietveld refinement
  - ✓ Buckyballs (C60)
    - The structure of bucky balls was first determined by Rietveld analysis using neutrons
    - The structure of C60 and its metal doped variants have all been examined using the Rietveld method
  - ✓ Colossal Magnetoresistance (CMR) Thermoelectrics
  - ✓ Hydrogen Storage Batteries
  - ✓ …………………

- Now making an inroad in biological science and organic materials
  - ✓ Drugs, polymers, proteins?

Achievements

High T_c superconductors

- Much of the solid state chemistry of these materials was worked using neutron diffraction and Rietveld refinement



Structure and crystal chemistry of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$

W. I. F. David*, W. T. A. Harrison*, J. M. F. Gunn*, O. Moze*¶, A. K. Soper*, P. Day†, J. D. Jorgensen‡, D. G. Hinks‡, M. A. Beno‡, L. Soderholm‡, D. W. Capone II‡, I. K. Schuller‡, C. U. Segre§, K. Zhang§ & J. D. Grace‖

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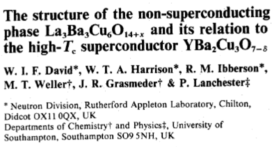
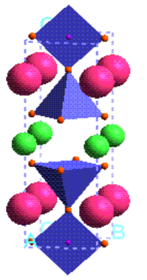


The structure of the non-superconducting phase $La_3Ba_3Cu_6O_{14+x}$ and its relation to the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$

W. I. F. David*, W. T. A. Harrison*, R. M. Ibberson*, M. T. Weller†, J. R. Grasmeder† & P. Lanchester‡

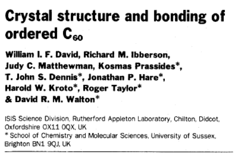
* Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK
Departments of Chemistry† and Physics‡, University of Southampton, Southampton SO9 5NH, UK



$YBa_2Cu_3O_7$

C_{60} - Buckminsterfullerene

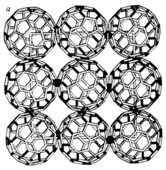
- The structure of C_{60} and its metal doped variants have all been examined using the Rietveld method



Crystal structure and bonding of ordered C_{60}

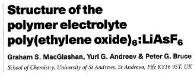
William I. F. David, Richard M. Ibberson, Judy C. Matthewman, Kosmas Prassides*, T. John S. Dennis*, Jonathan P. Hare*, Harold W. Kroto*, Roger Taylor* & David R. M. Walton*

ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK
* School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK



Polymer electrolytes

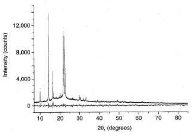
- Powerful solution procedures combined with constrained Rietveld refinements reveal details of electrolyte structure

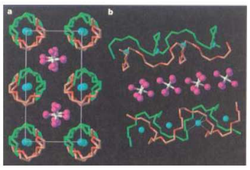


Structure of the polymer electrolyte poly(ethylene oxide)$_6$:$LiAsF_6$

Graham S. MacGlashan, Yuri G. Andreev & Peter G. Bruce

School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

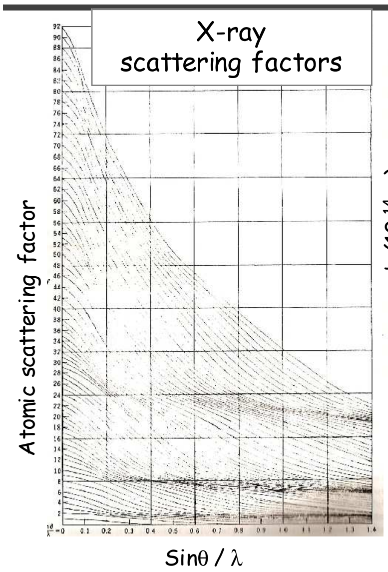


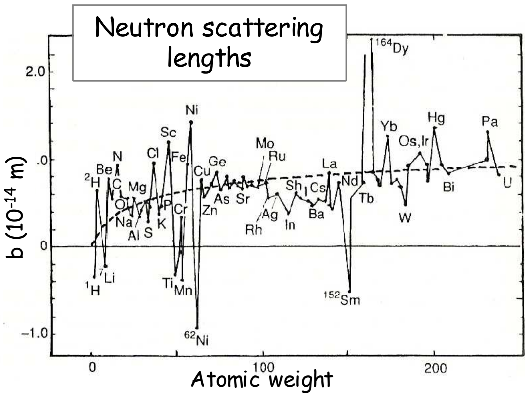


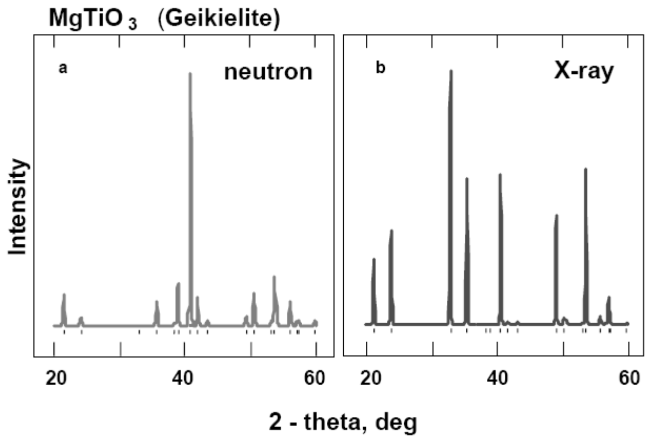
The limits of Rietveld refinement?

- We have to consider structural complexity, data quality and what we already know
- Structural complexity is determined by unit cell size & symmetry
- Data quality includes factors such as:
  - ✓ How many resolved peaks do we have?
  - ✓ Is both neutron and X-ray data available?
- Existing information
  - ✓ Bond lengths
  - ✓ Chemical composition
- A reasonable structural model is needed before starting

Neutron & X-ray Diffraction







The Rietveld Method, RA Young

Non-refinable parameters in the Rietveld method

- Space group
- Chemical composition
- Analytical function describing the shape of the diffraction profiles
- Wavelength of the radiation (can be refined for the synchrotron data)
- Intensity ratio in $K_{\alpha1}$, $K_{\alpha2}$ doublet
- Origin of the polynomial function describing the background

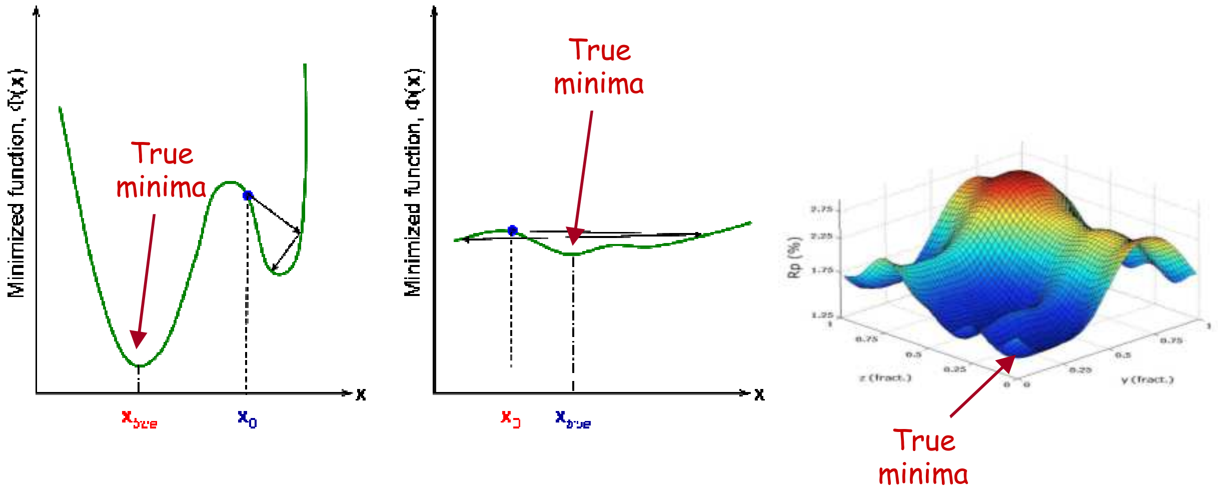
Refinement Strategies

- To get accurate results, we must model *all* the quantities correctly (correlations)
- The advantage of the Rietveld method is that it uses all the information in the powder pattern, and yields the most information
- Examining the nature of the errors in the difference plot can give insight into the source of the errors

---

False minima

- The least squares "response surface" can be flat, and prone to false minima, so care is needed
- It is also possible to ask too much from the data
- We need to remember that we are fitting a model to data, and that our answers will only be as good as the model is appropriate



Pecharsky Figure 15.4

Sample for Rietveld refinement

- Need a powder, but…
- Random is best, but…
- Resolution – more is better, but can generate size/strain by trying to get powder
- Phase purity

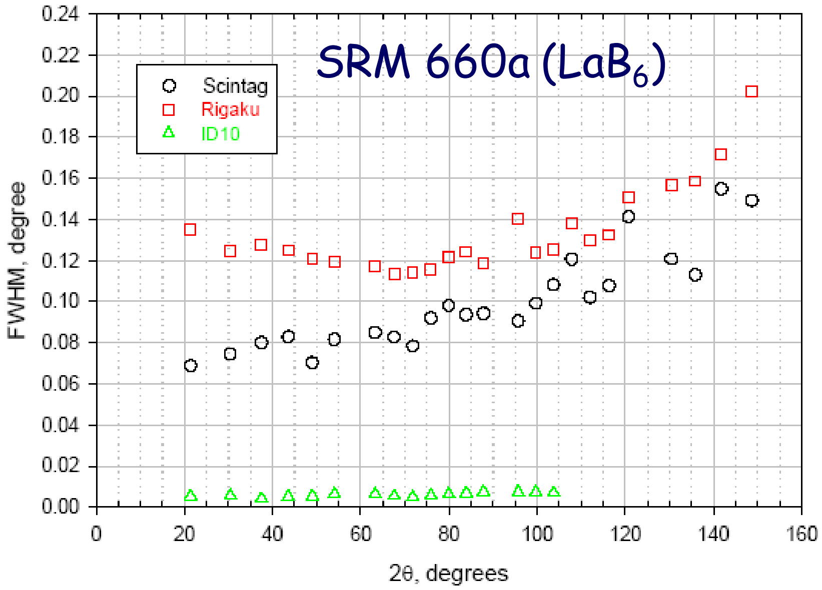
- An advantage of the Rietveld method is that ideal samples are rare, and the method provides a way of dealing with real samples.

Instrument & data collection

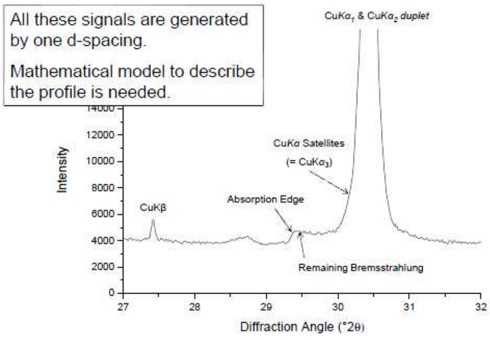
- Instrument
  - ✓ Alignment/systematic errors
  - ✓ Zero, displacement, transparency
  - ✓ Wavelength
  - ✓ Profile function
- Data Collection
  - ✓ Compromises!
  - ✓ Fixed step sizes
  - ✓ Wide 2θ range
  - ✓ ≥ 5 steps across FWHM of sharpest peaks
  - ✓ Constant or variable counting time
  - ✓ 5k ~ 10k counts for strongest peaks

Instrument Profile Function

- ➢ Some programs require one
- ➢ Helps interpret refined values
- ➢ Use a sample free of size and strain broadening – SRM 660a (LaB_6) or SRM 1976 (corundum plate)



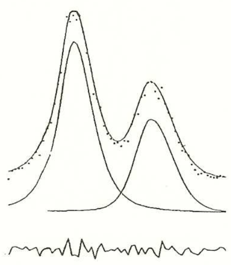
Peak shape modelling



All these signals are generated by one d-spacing.

Mathematical model to describe the profile is needed.

From presentation of Nicola Döbelin, RMS Foundation, Switzerland



The Rietveld Method, RA Young

- ➢ Analytical profile fitting
- ➢ Direct convolution approach

Analytical profile fitting

- ➢ fit a numerical function (profile shape function; PSF) to a measured diffraction pattern
- ➢ PSF → 2θ, I, FWHM
- ➢ An optimization algorithm is employed to adjust parameters of PSF until the difference between the measured and calculated lines are minimized

Direct convolution approach

(Fundamental Parameters Approach)

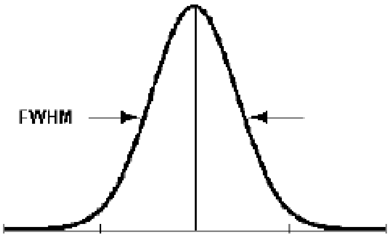
- ➢ profiles are generated by convolution where various functions are convoluted to form the observed profile shape
- ➢ Calculate peak profile from device configuration

Full Width Half Maximum

- All peak shape functions incorporate dependence on half width of Bragg peaks or FWHM
- FWHM shows angular dependence expressed by the Caglioti function

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

- H = half width
- U, V, W = refinable parameters



Analytical profile shape functions (PSFs)

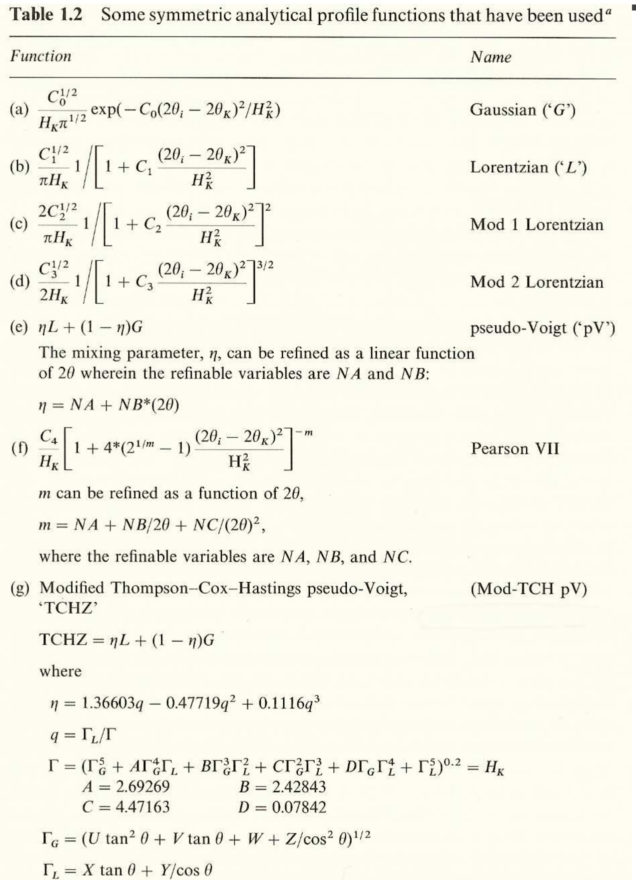


Table 1.2 Some symmetric analytical profile functions that have been used[a]

Function	*Name*
(a) $\frac{C_0^{1/2}}{H_K \pi^{1/2}} \exp(-C_0(2\theta_i - 2\theta_K)^2/H_K^2)$	Gaussian ('G')
(b) $\frac{C_1^{1/2}}{\pi H_K} 1 \Big/ \left[1 + C_1 \frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]$	Lorentzian ('L')
(c) $\frac{2C_2^{1/2}}{\pi H_K} 1 \Big/ \left[1 + C_2 \frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]^2$	Mod 1 Lorentzian
(d) $\frac{C_3^{1/2}}{2H_K} 1 \Big/ \left[1 + C_3 \frac{(2\theta_i - 2\theta_K)^2}{H_K^2}\right]^{3/2}$	Mod 2 Lorentzian
(e) $\eta L + (1 - \eta)G$ The mixing parameter, η, can be refined as a linear function of 2θ wherein the refinable variables are NA and NB: $\eta = NA + NB^*(2\theta)$	pseudo-Voigt ('pV')
(f) $\frac{C_4}{H_K}\left[1 + 4^*(2^{1/m} - 1)\frac{(2\theta_i - 2\theta_K)^2}{\mathrm{H}_K^2}\right]^{-m}$ m can be refined as a function of 2θ, $m = NA + NB/2\theta + NC/(2\theta)^2$, where the refinable variables are NA, NB, and NC.	Pearson VII
(g) Modified Thompson–Cox–Hastings pseudo-Voigt, 'TCHZ' $\mathrm{TCHZ} = \eta L + (1 - \eta)G$ where $\eta = 1.36603q - 0.47719q^2 + 0.1116q^3$ $q = \Gamma_L/\Gamma$ $\Gamma = (\Gamma_G^5 + A\Gamma_G^4\Gamma_L + B\Gamma_G^3\Gamma_L^2 + C\Gamma_G^2\Gamma_L^3 + D\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{0.2} = H_K$ $A = 2.69269$ $B = 2.42843$ $C = 4.47163$ $D = 0.07842$ $\Gamma_G = (U \tan^2\theta + V \tan\theta + W + Z/\cos^2\theta)^{1/2}$ $\Gamma_L = X \tan\theta + Y/\cos\theta$	(Mod-TCH pV)

- Gaussian
- Lorentzian
- Modified Lorentzian
- Intermediate Lorentzian
- Pseudo-Voigt
- Pearson VII
- Split Pearson VII

The Rietveld Method, RA Young

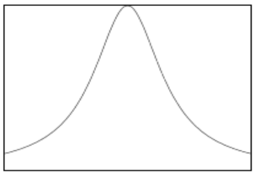
Analytical profile fitting > Gaussian, Lorentzian, Pseudo Voigt profile

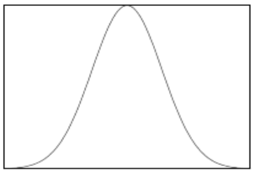
- Most instruments are more Gaussian at low angles and more Lorentzian at high angles (wavelength dispersion)

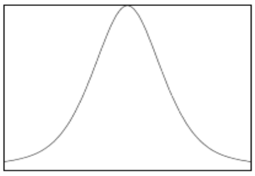
Pseudo Voigt profile; nL + (1-n)G

Lorentzian profile

Gaussian profile

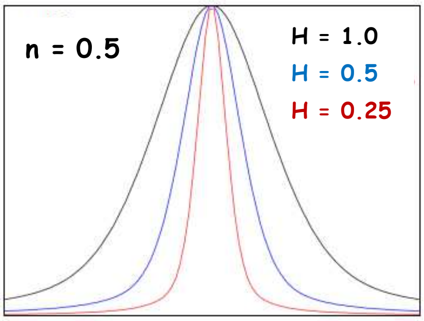

Lorentzian (n = 1.0)


Gaussian (n = 0)


Pseudo Voigt (n = 0.5)

Same FWHM (H) in

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



From presentation of Nicola Döbelin, RMS Foundation, Switzerland

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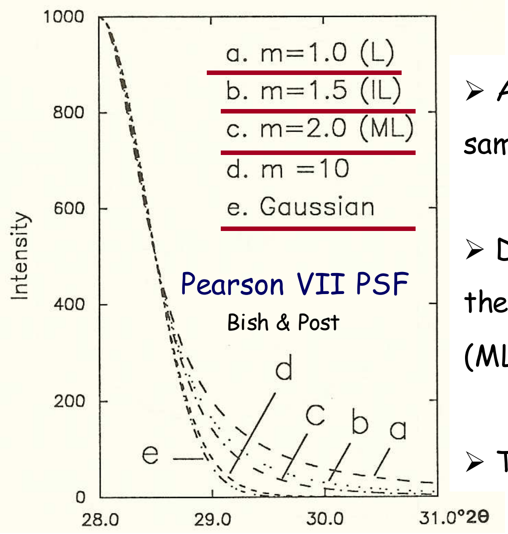
Analytical profile fitting > Pearson VII profiles

$$\text{(f)}\quad \frac{C_4}{H_K}\left[1+4^*(2^{1/m}-1)\frac{(2\theta_i-2\theta_K)^2}{H_K^2}\right]^{-m}$$

m can be refined as a function of 2θ,

$m = NA + NB/2\theta + NC/(2\theta)^2$,

where the refinable variables are NA, NB, and NC.



- A series of Pearson VII profiles generated with the same fwhm but with different values of exponent m
- Depending on the value of m, the function replicates the Intermediate Lorenzian (IL), Modified Lorenzian (ML), and pure Lorenzian (L) profiles.
- The shape is essentially Gaussian when m > ~ 10

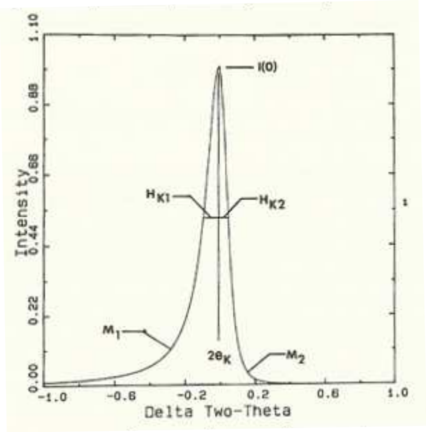
Bish & Post

The Rietveld Method, RA Young

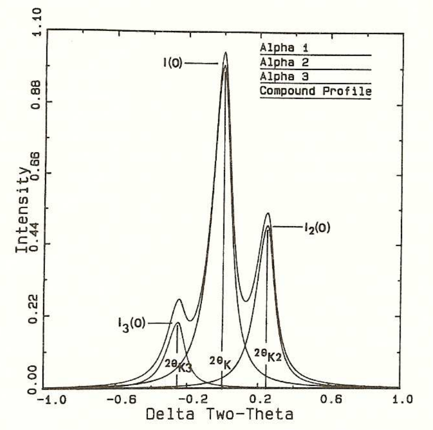
Analytical profile fitting > Split Pearson VII

- The two half profiles share a common Bragg angle $2\theta_K$ and peak intensity.

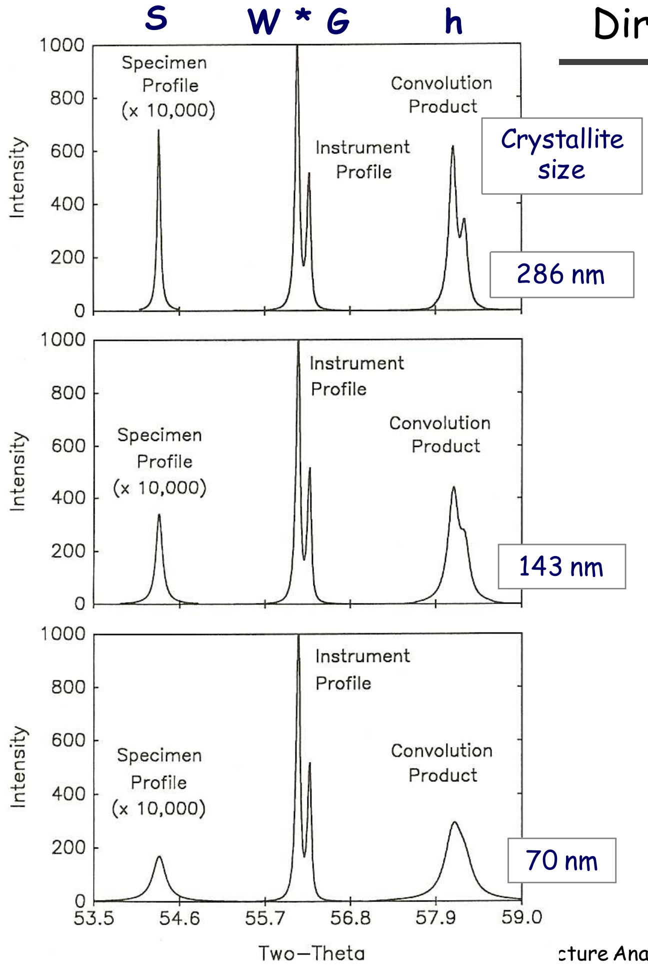
- Their different fwhm's H_K, and exponents M, allow the profile to model an asymmetric line



The Rietveld Method, RA Young



The Rietveld Method, RA Young



Direct convolution approach

$$h = (W * G) * S$$

- Line shape ← convolution of (W*G) and (S) contributions

W*G; instrument

S; specimen

S; Intrinsic profile (specimen profile)
W; Spectral distribution (radiation source contribution)
G; Instrumental contribution

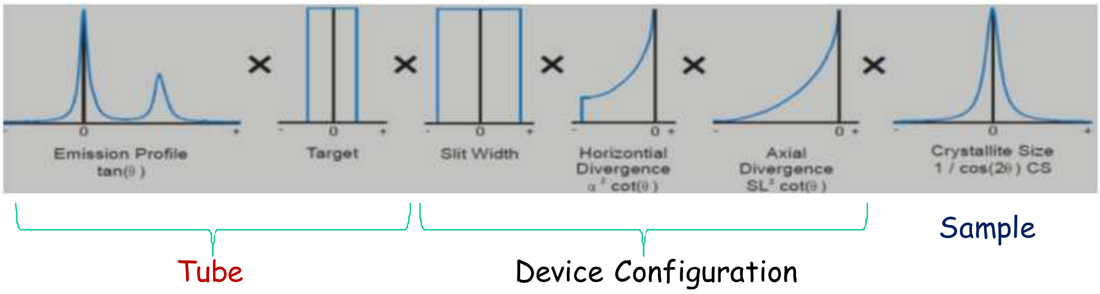
Intergrated intensity of the peak remains the same while the peak broadens and the peak intensity decreases

Need to know precisely the nature of <u>contributions from both instrument & specimen</u>

Bish & Post

Direct convolution approach > Fundamental Parameters Approach (FPA)

- Calculate the peak profile from the device configuration
- Take into account the contributions of:
  - ✓ Source emission profile (X-ray wavelength distribution from Tube)
  - ✓ Every optical element in the beam path (position, size, etc.)
  - ✓ Sample contributions (peak broadening due to crystallite size & strain)



FPA needs:

- Very detailed and complete description of the instrument configuration
- Very well aligned instrument

From presentation of Nicola Döbelin, RMS Foundation, Switzerland

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Factors that affect the integrated peak **intensity** and **not the peak shape**

- Background fitting (this should not affect the apparent Bragg intensities if it is done correctly)
- Extinction
- Preferred Orientation (Texture)
- Absorption & Surface Roughness
- Other Geometric Factors

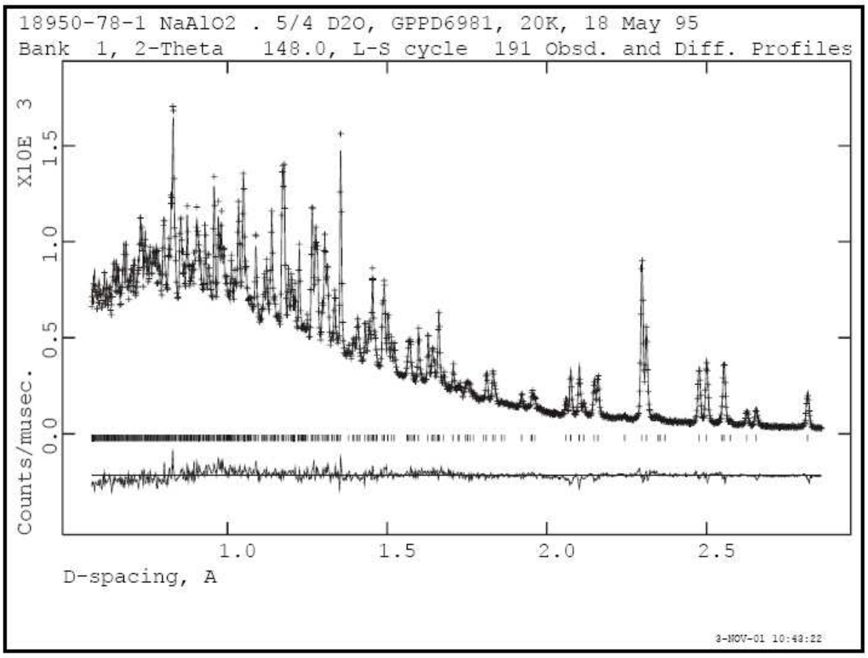
Background

- Crucial to get right – affects integrated intensities (and thus the structure) – especially the displacement coefficients
- Interacts with the profile function
- **<u>Use as few parameters as possible</u>**
- Crystalline sample – slowly varying
- Background parameters are <u>highly-correlated</u>

- Manually subtracted - not recommended, distorts the weighting scheme for the observations
- Fit to a function - many possibilities
  - ✓ Polynomials
  - ✓ Chebyschev power series
  - ✓ Linear interpolation between selected points
  - ✓ Debye equation - amorphous background
  - Fourier series – empirical
  - Exponential expansions
  - Read from file

Background

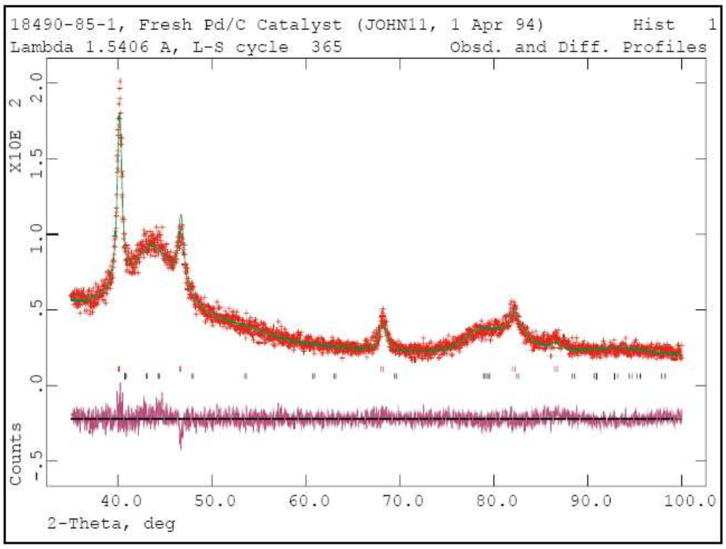
$NaAlO_2 (D_2O)_{5/4}$



- Where is the background? (by eye – always too high!)
- Power series – some unreasonable U
- Change to pair correlation function (X-ray showed some amorphous material), get reasonable distances, U – even anisotropic!

Background

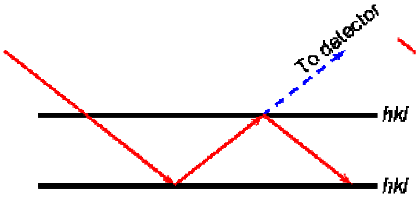
Pd/C Catalyst



- Pair correlation function has trouble modeling "sharp" amorphous components
- A combination of very small particle crystalline graphite and a cosine Fourier series works well (at cost of greater time)
- A good candidate for reading the background from a file

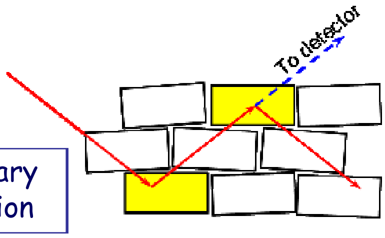
Extinction

- A reduction in the observed intensity of a diffracted peak as a consequence of
  - ✓ Loss of incident beam intensity as it propagates through a specimen due to some of the intensity being diffracted (secondary extinction) – not an issue with powder samples
  - ✓ Loss of diffracted beam intensity due to interference within a crystal (mosaic block) – can be an issue with powders
- Extinction is most obvious for the strongest reflections
- Extinction corrections are not important for small crystals and "normal" radiation wavelengths
  - ✓ <u>The grains in a powder that is ideally suited for Rietveld analysis are always "small" (< 10 μm)</u>
  - ✓ However, in time-of-flight neutron diffraction experiments the large d-spacing reflections are measured with long wavelength neutrons → This can lead to extinction problems for these experiments



Primary Extinction

Secondary extinction



Pecharsky page 200

Texture

- Ideally, for Rietveld refinement, the crystals in your sample should have a random distribution of orientations
- If the sample does not display a random distribution of orientations it is said to be textured or to show preferred orientation
  - ✓ This changes the measured peak intensities from what you would expect for a random powder
  - ✓ This can lead to problems with the Rietveld analysis unless it is either modeled or a new random sample is prepared
- Several models can be used to correct texture
- The simplest is by March and Dollase
  - ✓ crystallites in the sample are assumed to be rod or disk like
  - ✓ sample is assumed to have cylindrical symmetry

Texture > March Dollase function

- Can be applied to both needle and plate shaped crystals and is explicitly correct when the sample has cylindrical symmetry along the diffraction vector and is a reasonable approximation when the cylinder axis is perpendicular to the diffraction plane (In-plane, Out-of-plane texture)

  → it covers the two most common diffraction geometries for powder diffraction; Debye-Scherrer geometry as used in neutron diffraction and Bragg-Brentano geometry as used for most X-ray powder diffractometers

- It is especially effective when the sample is rotated about the appropriate axis to ensure cylindrical symmetry

$$O_{ph} = \frac{1}{M_p} \sum_{j=1}^{M_p} \left(R_o^2 \cos^2 A_j + \frac{\sin^2 A_j}{R_o} \right)^{-3/2}$$

- O_{ph} = preferred orientation correction
- A_j = angle between the preferred orientation axis and the reflection vector
- M_p = multiplicity

- The refinable coefficient, R_o, gives the effective sample compression or extension along the cylinder axis due to preferred orientation
- If there is no preferred orientation then $R_o = 1.0$

Texture > other models

- The March-Dollase model assumes a nice simple distribution of crystal orientations
- In some real samples (rolled steel plates, wires, welds, deformed rocks), the distribution can be very complex
  - ✓ We may need to correct for the effects of a complex texture on our powder pattern
- a model based on spherical harmonics function can be used to treat the effects of complex textures
  - ✓ Can be used not just as a correction but as a way of learning about texture in engineering or geological samples

---

Absorption Corrections

- X-rays
  - ✓ For thick flat plate samples in symmetrical reflection geometry, the effect of absorption on the observed intensities is independent of 2Θ
    - Unless microabsorption/surface roughness is an issue
  - ✓ But for very low absorption thick samples, the peak positions may not be exactly where you would expect them to be
- Neutrons: experiments are typically done on cylindrical samples (Debye-Scherrer geometry)
  - ✓ Absorption depends on 2Θ and λ, but for many samples this is a small effect (most elements do not absorb neutrons strongly)
  - ✓ Attenuation due to multiple scattering can be a bigger effect than true absorption
- X-ray experiments in Debye-Scherrer geometry may be strongly affected by absorption

Absorption models

- Most Rietveld programs include a correction for absorption in cylindrical specimens
  - ✓ Frequently Hewat's model is used
    - not suitable for samples with $\mu t > 1$
    - OK for most neutron samples, but not for Debye-Scherrer X-ray samples
  - ✓ A model developed by Lobanov and alte de Veiga is suitable for $\mu t < 30$
  - ✓ Do not refine the absorption correction term for constant wavelength data - It correlates very strongly with your atomic displacement parameters

---

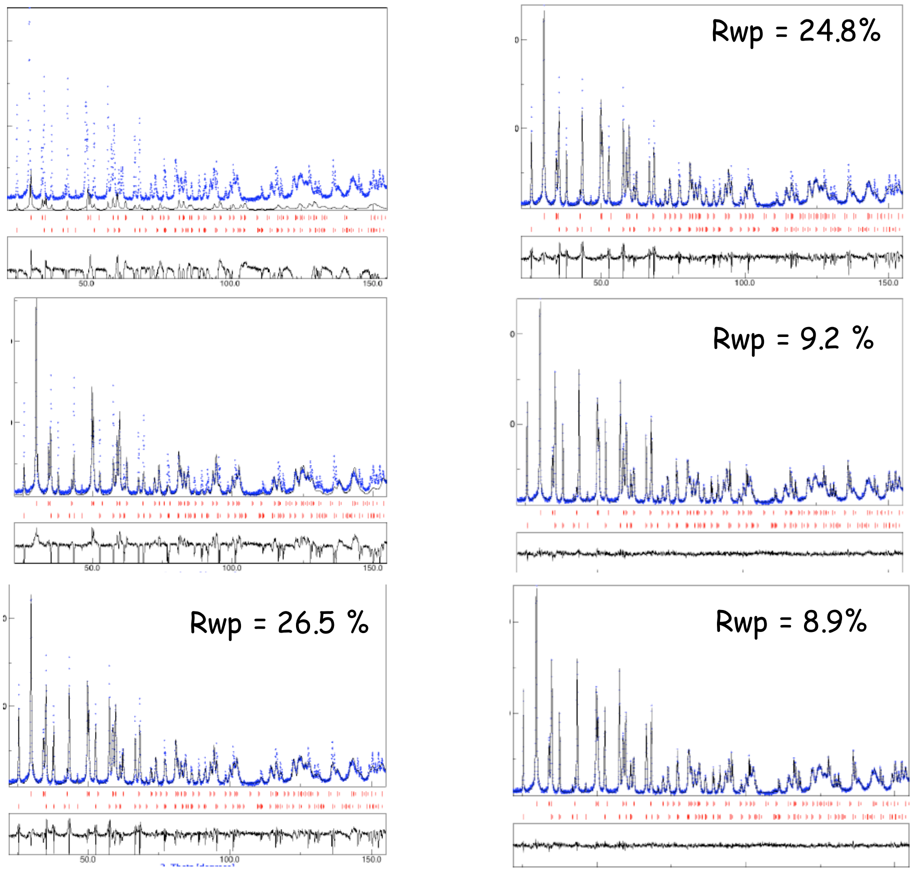
Surface Roughness

- Non-uniform sample density as a function of depth below the surface
  - ✓ Is often a problem with highly absorbing flat plate samples (many specimens with Cu Kα radiation)
  - ✓ If not dealt with, it will give atomic displacement parameters that are lower than they should be as surface roughness leads to a reduction in the intensity of the low angle reflections
- GSAS has available two different models
  - ✓ Suortti model $SR = 1 - pe^{-q} + pe^{-q/\sin\theta}$
  - ✓ Pitschke, et al. model $SR = 1 - pq(1-q) - (pq/\sin\theta)(1-q/\sin\theta)$
  - ✓ p and q are parameters which are often not very stable in refinement

Rietveld refinement procedure > Rietveld programs

- First select the appropriate Rietveld program; depending on what you need to analyze you can find the best program.
- Rietveld programs
  - ✓ GSAS: widely used; very good for crystal structure refinement and TOF neutron; not easy to use but there is a lot of knowledge around; a friendly graphical interface available with Expgui
  - ✓ FullProf: best for magnetic materials; good for crystal structure refinements; no graphical interface.
  - ✓ Maud: for material scientists; good for quantitative phase analysis, size-strain and texture; best in the case of texture/strain problems; come with a graphical user interface
  - ✓ Rietan, Arit, Brass, DBWS, XRS-82, XND etc.
- commercial programs
  - ✓ Bruker TOPAS (also an academic)
  - ✓ Rigaku PDXL
  - ✓ PANalytical High Score Plus
  - ✓ MDI Jade

Rietveld refinement procedure



Refinement Strategy

- Data Collection: High resolution, high intensities
  - ✓ Long time per 2θ step
  - ✓ Wide 2θ range
  - ✓ Large sample volume

- Initial Model: As close as possible to expected answer
  - ✓ Accurate cell parameters
  - ✓ Profile settings representative of instrument
  - ✓ Reasonable values for coefficients in background function

---

Refinement Strategy > Tips and tricks (on the course of the refinement)

Instrumental parameters

- Scale factor (always)
- Background (1)
- Line broadening and shape (3)
- Zero shift (4)
- Sample displacement or transparency (5)
- Preferred orientation (7)
- Surface absorption (7)
- Extinction (7)

Structure parameters

- Scale factor (always)
- Lattice parameter (2)
- Atomic co-ordinates (6)
- Temperature factors (8)
- Occupancies (8)

Never refine (4) & (5) together
(3) 2θ < 100, W is enough; 2θ > 100, refine W & V; 2θ > 135, include U

Refinement Strategy > Tips and tricks (how to obtain reliable data)

- Use only well-adjusted diffractometer
  - ✓ Bad adjustment causes the line shift and broadening; the latter cannot be corrected in the Rietveld programs
- Use only fine powders
  - ✓ Coarse powder "randomises" the integral intensities
  - ✓ Coarse powder causes problems with rough surface
- Use sufficient counting time
  - ✓ The error in intensity is proportional to $N^{\frac{1}{2}}$ as for the Poisson distribution
- Apply dead-time correction
  - ✓ For strong diffraction lines, the use of the dead-time correction is strongly recommended

---

Refinement Strategy > Tips and tricks

- First get a good experiment/spectrum.
- Know your sample as much as possible.
- Do not refine too many parameters.
- Always try first to manually fit the spectrum as much as possible.
- Never stop at the first result.
- Look carefully and constantly at the visual fit/plot and residuals during refinement process (no "blind" refinement).
- Zoom in the plot and look at the residuals. Try to understand what is causing a bad fit.
- Use all the indices and check parameter errors.
- Check the physical/chemical meaning of the result.

From presentation of Luca Lutterotti

Refinement Strategy > In the Rietveld refinement, **don't**

- refine parameters which are fixed by the structure relations (fractional co-ordinates, lattice parameters(????))
- refine all three parameters describing the line broadening concurrently (U, V and W of Caglioti function)
- refine the anisotropic temperature factors from X-ray powder diffraction data
- use diffraction patterns measured in a narrow range
- forget that the number of structure parameters being refined cannot be larger than the number of lines

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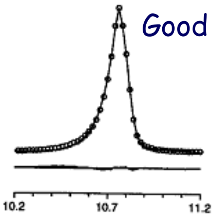
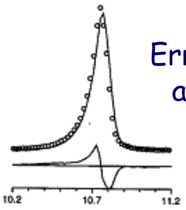
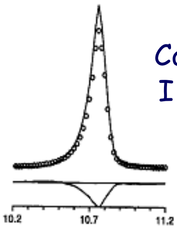
Refinement Strategies > Difference plot



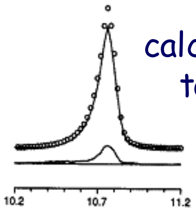
Good fit



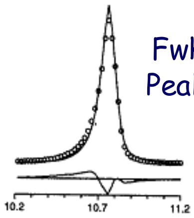
Error in calculated angular position 2θ too large



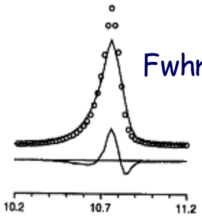
Calculated I too high



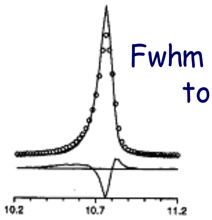
calculated I too low



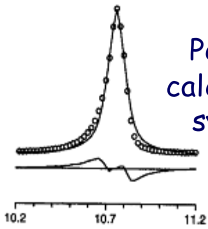
Fwhm too small Peak asymmetry too small



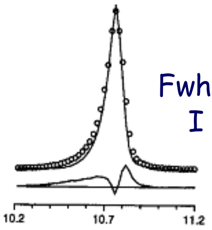
Fwhm calculated too high



Fwhm calculated too small



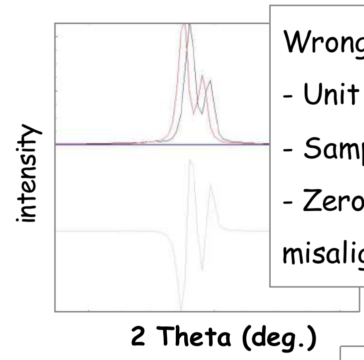
Peak shape calculated too symmetric



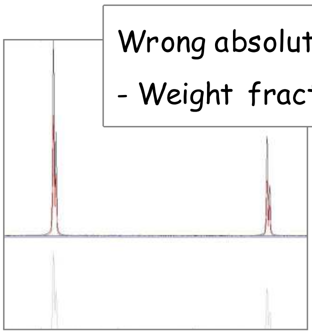
Fwhm too small I too small

Pecharsky chapter 15.6.1

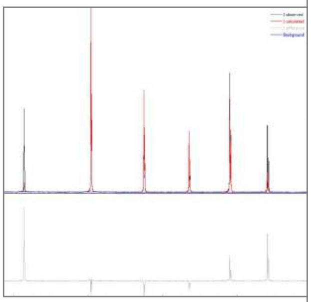
Refinement Strategies > Difference plot



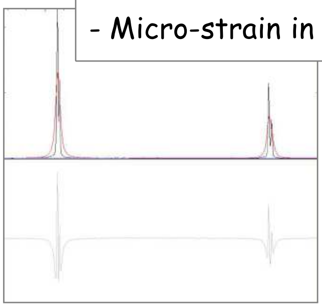
Wrong peak positions:
- Unit cell dimensions
- Sample height displacement
- Zero-shift (instrument misalignment)



Wrong absolute intensities:
- Weight fraction (scaling)



Wrong relative intensities:
- Preferred orientation
- Graininess
- Atomic species
- Atomic coordinates
- Site occupancies
- Thermal displacement parameters



Wrong peak width:
- Crystallite size
- Micro-strain in crystal structure

From presentation of Nicola Döbelin, RMS Foundation, Switzerland

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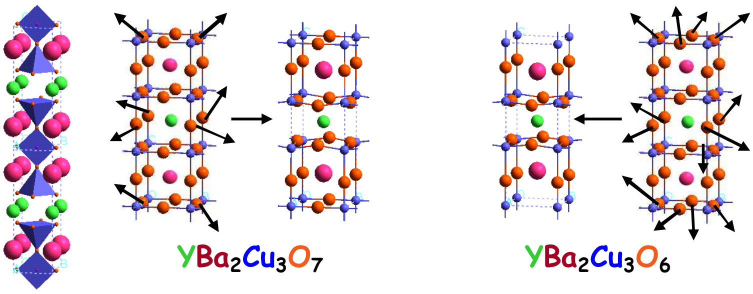
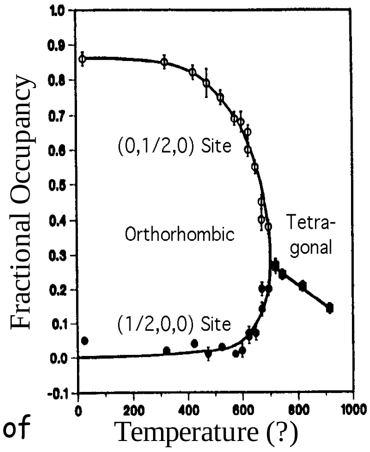
Refinement Strategies

Effect in diffraction pattern	Origin in crystal structure model
Wrong peak positions	Unit cell dimensions
	Sample height displacement
	Zero-shift
Wrong absolute intensities	Weight fraction (scaling)
Wrong relative intensities	Preferred orientation
	Atomic species / Substitutions
	Atomic coordinates
	Site occupancies
	Thermal displacement parameters
Wrong peak width	Crystallite size
	Lattice strain

From presentation of Nicola Döbelin, RMS Foundation, Switzerland

Example; $YBa_2Cu_3O_{7-x}$ (YBCO)

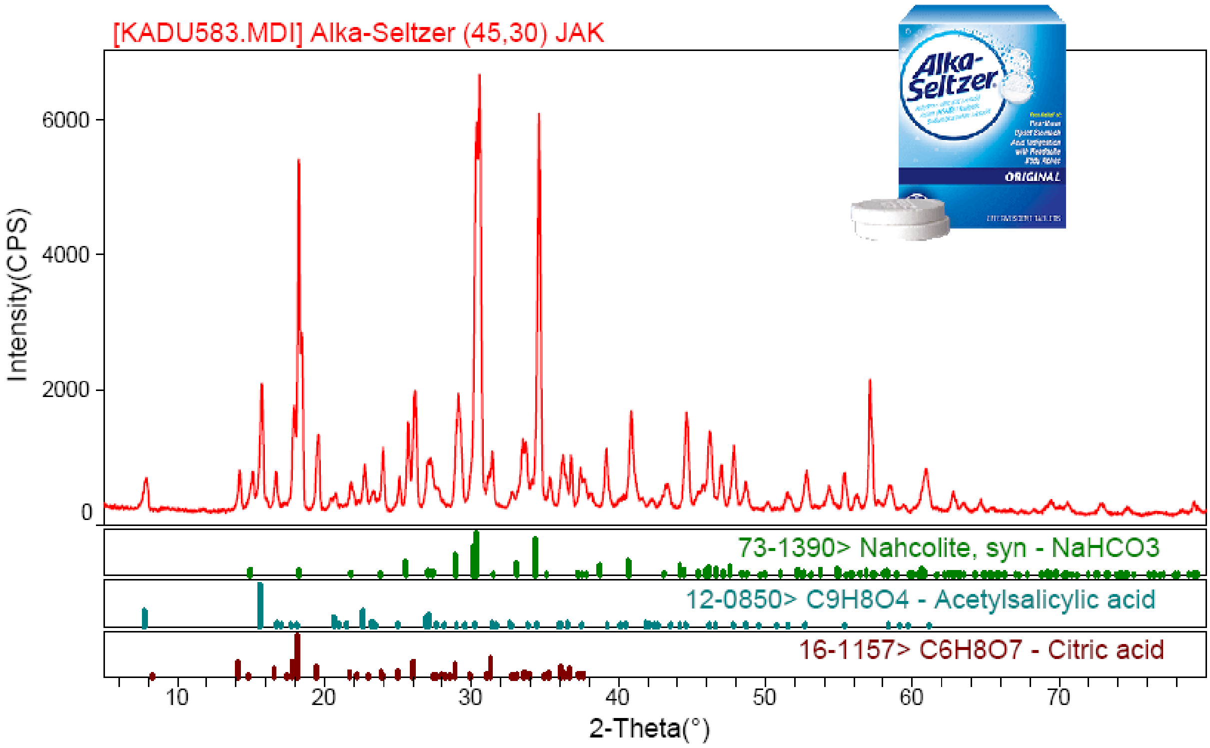




- "powder beats single crystals"
- Structure was correctly determined from powder diffraction data whereas X-ray single crystal results had been in error (← twin)

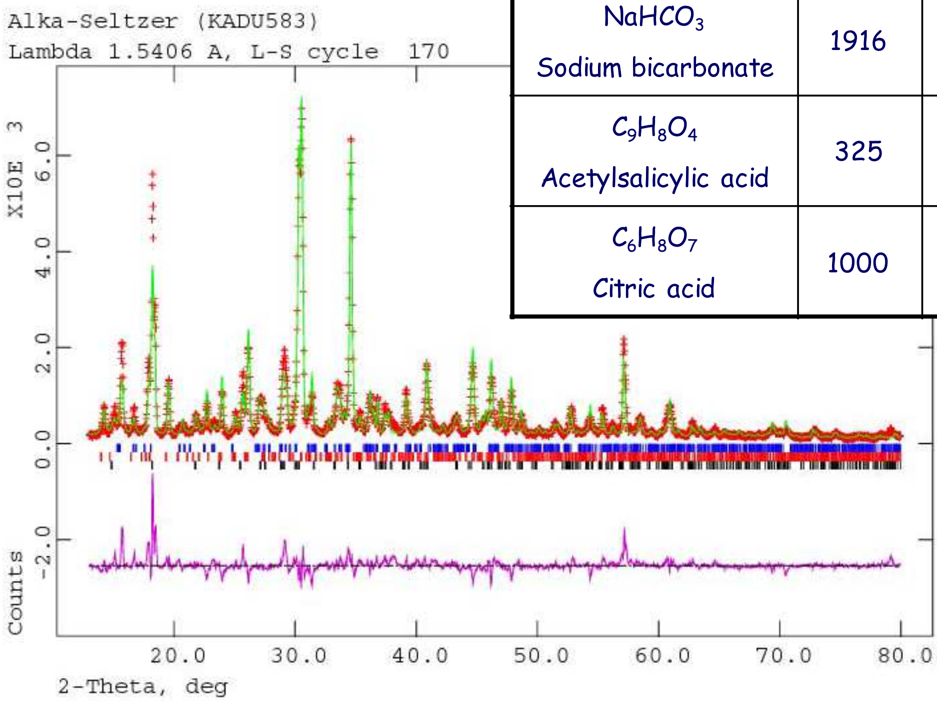
- Variation in the <u>fractional site occupancies</u> for YBCO as a f'n of temp in a 100% oxygen environment. When the occupancies become equal, the orthorhombic symmetry changes to tetragonal.

Example > Alka-Seltzer 1 > phase ID



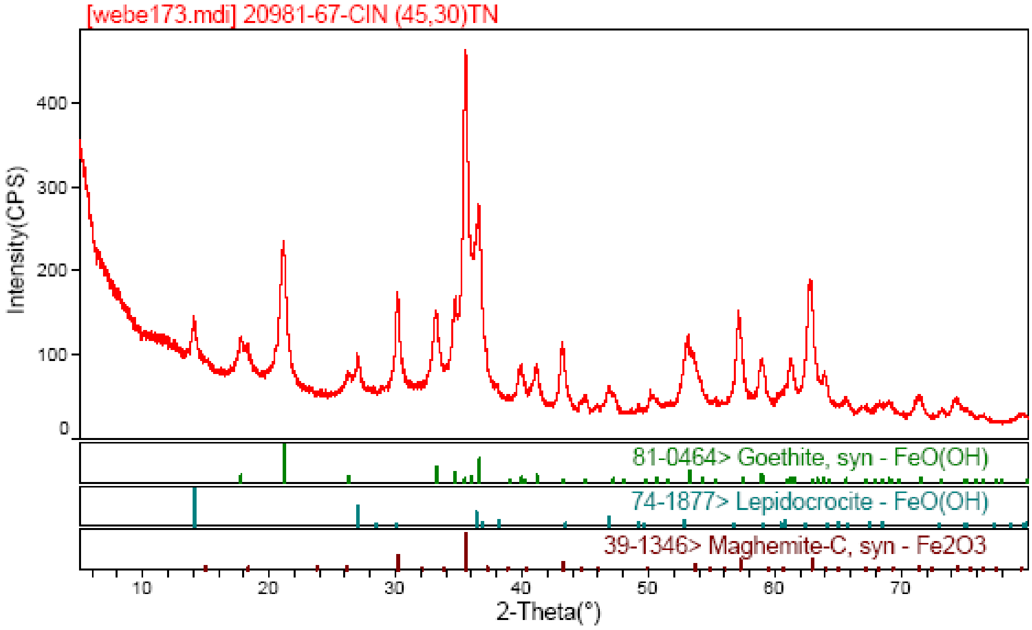
Example > Alka-Seltzer 2 > quant using Rietveld refinement

	on the package		refined
Compound	Amount (mg)	Concentration (wt%)	Concentration (wt%)
$NaHCO_3$ Sodium bicarbonate	1916	59.12	61.4(3)
$C_9H_8O_4$ Acetylsalicylic acid	325	10.03	10.1(2)
$C_6H_8O_7$ Citric acid	1000	30.86	28.5(3)

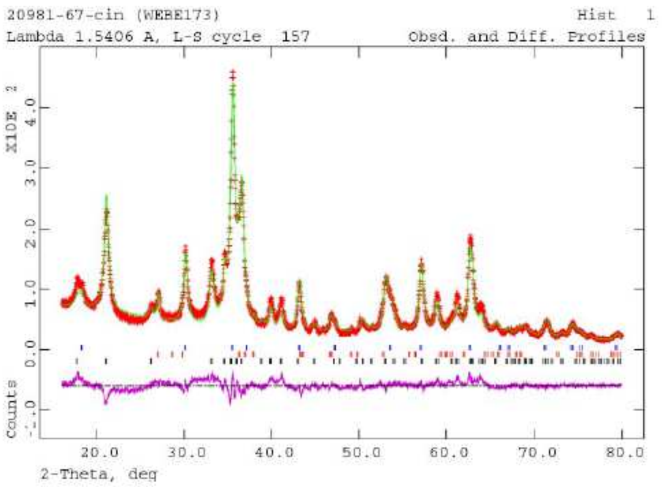


Example > Rust 1

- A rust-colored deposit filtered from the gasoline in one of BP's distribution terminals



Example > Rust 2



phase	Goethite	Lepidocrocite	Maghemite
Wt%	51.4(2)	4.7(2)	43.8(7)
Cell, Å			8.3682(7)
composition	α-FeOOH	γ-FeOOH	Fe2O3
Size, Å	1000	30.86	28.5(3)

Probably some amorphous material is also present

Decreasing the Size of the Problem

Constraints: Use of *a priori* knowledge

- Additional observations or subsidiary relationship can be incorporated into the least-square refinement process
- Constraints (rigorous or hard constraints)
- Restraints (soft constraints)
- Rigid Bodies

Young Chap 10, Pecharsky Chap 7

Constraints, Restraints, Rigid Bodies

- Constraints (rigorous or hard constraints)
  - ✓ Relationships imposed rigorously → relationship **must be** exactly fulfilled
  - ✓ Examples
    - Symmetry constraints placed on atoms in special positions
    - Group constraints where the distances/angles between atoms within a group are fixed and only the orientation of the group as a whole is refined
    - Thermal parameters by atom type, occupancies
- Restraints (soft constraints)
  - ✓ Relationships **imposed approximately**, the degree of approximation is given by a finite weight
  - ✓ Fit is degraded if restraint is not met
  - ✓ Examples - interatomic distances, bond angles, composition
  - ✓ Start strong, then relax
- Rigid Bodies
  - ✓ Assumption that the relative atom positions for a molecule or molecular fragment (e.g. phenyl ring) is known
  - ✓ Define the group (in cartesian coordinates) and define location & orientation (refinable); possible to refine some scaling terms

---

Damping – an aid to convergence

- Apply only part of the calculated shift
- Scale factors and lattice parameters generally well-behaved
- Background terms are highly-correlated (50%)
- Profile coefficients (50%)
- Atom coordinates (OK to 60%)
- Sometimes need to fix parameters (occupancy, U, profiles) at physically-reasonable values

How do you know if a fit is good?

How good is good enough ??????

- ➢ Difference pattern
- ➢ Physical meaning?????
- ➢ Residuals R
  - ✓ R is the quantity that is minimized during least-squares or other fitting procedures
  - ✓ R_{wp} ; is weighted to emphasize intense peaks over background, is more meaningful from a mathematical point of view as the numerator is the residual S being minimized → best function to reflect the progress of the refinement
  - ✓ R_{exp}; estimates the best value R for a data set. is the minimum R_{wp} value reachable using a certain number of refineable parameters. an evaluation of how good the data are.
  - ✓ R_{Bragg}; based on intensities deduced from the model → biased in favor of the model used
- ➢ GOF; Goodness-of-fit (χ^2 ; chi-squared)
  - ✓ is the ratio between the Rwp and Rexp and cannot be lower then 1
  - ✓ A good refinement gives GOF values lower than 2.
  - ✓ The GOF is not a very good index to consider because, with a noisy pattern, it is quite easy to reach a value near 1.
  - ✓ With very high intensities and low noise patterns, it is difficult to reach a value of 2.
  - ✓ The GOF is sensible to model inaccuracies.

Quality of the experiment

A good diffraction fitting, a successful Rietveld analysis, depend strongly on the quality of the experiment:

- ➢ Instrument:
  - ✓ instrument characteristics and assessment
  - ✓ choice of instrument options
- ➢ Collection strategies
  - ✓ Range, step size, collection time, etc.
- ➢ sample
  - ✓ sample size, sample preparation, sample condition

From presentation of Luca Lutterotti

Quality of refinement (1) - residual indices

- Quality is continuously assessed by agreement of the model with the experimental data
- I_K - intensity assigned to the Kth Bragg reflection after refinement
- N = # observations, P = # least square parameters being estimated

$$R_F = \frac{\sum \left| (I_K('obs'))^{1/2} - (I_K(calc))^{1/2} \right|}{\sum (I_K('obs'))^{1/2}}$$

R-structure factor

$$R_B = \frac{\sum \left| I_K('obs') - I_K(calc) \right|}{\sum I_K('obs')}$$

R- Bragg factor

$$R_p = \frac{\sum \left| y_i(obs) - y_i(calc) \right|}{\sum y_i(obs)}$$

R-Pattern (profile)

$$R_{wp} = \left\{ \frac{\sum w_i (y_i(obs) - y_i(calc))^2}{\sum w_i (y_i(obs))^2} \right\}^{1/2}$$

R-weighted pattern

$$S = \left[S_y / (N - P) \right]^{1/2} = R_{wp} / R_e$$

Goodness-of-fit (χ^2 ; chi-squared)

$$R_e = \left[(N - P) / \sum w_i y_{oi} \right]^{1/2}$$

R-expected

Pecharsky, page 521

Quality of refinement (2)

- **Graphical fit**
- Convergence
- Chemical reasonableness
- Distances and angles
- Displacement coefficients
- Bulk composition
- Δ/σ and magnitude of σ
- There is no one measure of the quality of a Rietveld refinement

- Physical/chemical meaning

How do we know when we're finished?

"A Rietveld refinement is never finished, only abandoned" -- P. W. Stephens

Combined Rietveld refinement

Cation site disorder > real materials

- Many real materials do not have just one species on a given crystallographic site
  - $YBa_2Cu_3O_{7-x}$
    - Can have both oxygen and oxygen vacancies on a given site
  - Zeolites, $M_x[Si_{1-x}Al_xO_2]$
    - Extra framework cations M occupy sites that may also have vacancies and water present
    - Al may not be randomly distributed over all available sites
  - $NiFe_2O_4$
    - What is the distribution of Ni and Fe over the tetrahedral and octahedral sites in the spinel?
- It can be difficult to pin down the distribution of species over the available sites

Information from diffraction data

- Bragg scattering provides a measure of the scattering density at a particular crystallographic site.

$$F_k = \sum_{j=1}^{n} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + \ell z_j\right)\right]\exp\left(-B_j \frac{\sin^2\theta}{\lambda^2}\right)$$

$$B_j = 8\pi^2 \left\langle u^2 \right\rangle_j$$

- <u>With one diffraction data set</u>, it can be very difficult/impossible to estimate x_i, n_i and U_i for multiple species on nominally the same site.
  - ✓ typically we assume that the x_i and U_i are the same for all species at nominally the same site --- This may be a gross approximation.
  - ✓ to estimate individual n_i, the species must differ in scattering power, even then more than two species are not easy to handle.
    - Determining Mn/Fe distribution in $MnFe_2O_4$ using neutrons is easy

---

Scattering contrast

- In some cases, lab X-ray data do not generate enough contrast to solve a problem
  - ✓ Ni/Fe distribution and other "neighboring element problems".

- Neutrons may generate the needed contrast.

- More than one data set with different scattering contrast levels may be needed.
  - ✓ Different scattering contrast data set per species on the site.
    - constraints on composition and site occupancy reduce this requirement.
  - ✓ Can get these additional data sets by isotopic substitution and neutron scattering or by <u>resonant x-ray scattering.</u>

Resonant x-ray scattering and isotopic substitution

- Isotopic substitution is very expensive
- Different isotopically substituted samples may not be the same

- Resonant x-ray scattering makes use of the same sample for all measurements
- Reliable resonant scattering factors can be awkward to get
- Absorption and restricted d-spacing range can be a problem with resonant scattering measurements

What are "combined" refinements?

- Traditional "single-crystal" paradigm
  - ✓ collect a set of data → determine a structure

- Complex problems may require more information than can be obtained from a single set of powder diffraction measurements

- Options
  - ✓ give up
  - ✓ use multiple sets of measurements: more observations
  - ✓ build external "knowledge" or assumptions into model

What are “combined” refinements?

- Complex materials often demand diffraction data at more than one scattering contrast level.
- The more data sets you have, the more reliable the result is likely to be
  - ✓ Assumes that you do not introduce systematic errors.
- When combining data from different sources X-ray/neutron, or different energy resonant scattering data sets, be careful.
  - ✓ The lattice constants may not be the same for both data sets; uncorrected absorption may lead to problems.

Why limitations of a single diffraction measurement?

- All a single x-ray diffraction measurement can tell us, is how many electrons are present at an atomic site.
- Example: find amounts of Fe & Ti sharing a site in a perovskite.

  $f_{site} = n_{Fe}f_{Fe}(Q) + n_{Ti}f_{Ti}(Q)$ where $f_{Fe}(Q)/26 \cong f_{Ti}(Q)/22$

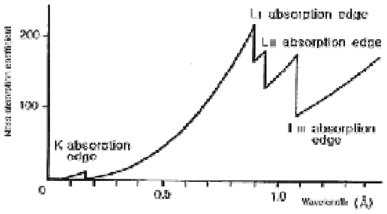
  one observable: f_{site} but two unknowns: n_{Fe} and n_{Ti}
- One approach to solving this: assumptions
  - ✓ Assume no vacancies: $n_{Fe} = 1 - n_{Ti}$
  - ✓ Assume total composition is known: works if only one Fe/Ti site.

Why do multiple X-ray measurements?

- Anomalous Dispersion:
  - ✓ Changing the x-ray wavelength can allow us to “tweak” $f_{Fe}(Q)$ and/or $f_{Ti}(Q)$ near the appropriate absorption edge

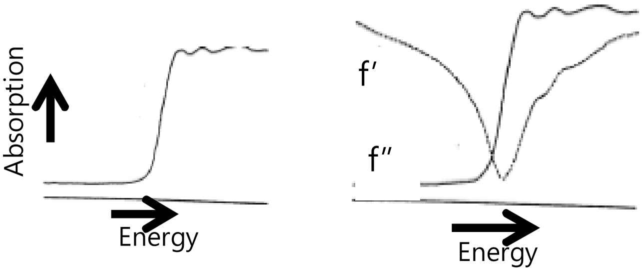
$$|f|^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

$$f(E,Q) = f_o(Q) + f'(E) + if''(E)$$



$$f'(E) = \left(\frac{2}{\pi}\right)\int_0^{\infty}\frac{Ef''(E)}{(E_0^2 - E^2)}dE$$

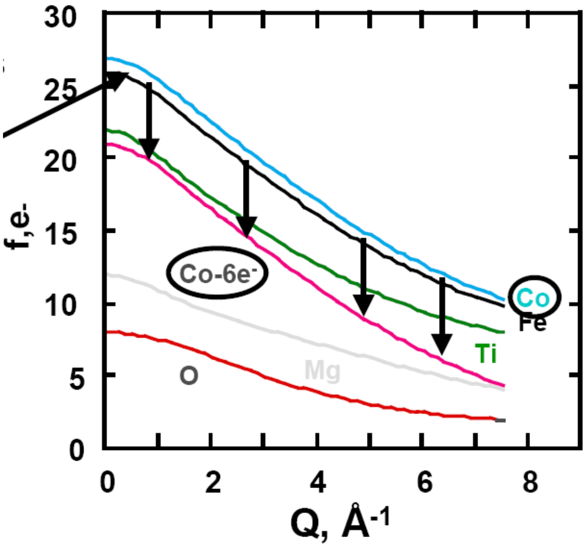
$$f''(E) = \left(\frac{2\pi mc\,\varepsilon_0}{e^2 h}\right)E\mu_a$$



tweak
If you **tweak** something, especially part of someone's body, you hold it between your finger and thumb and twist it or pull it.
If you **tweak** something such as a system or a design, you improve it by making a slight change.

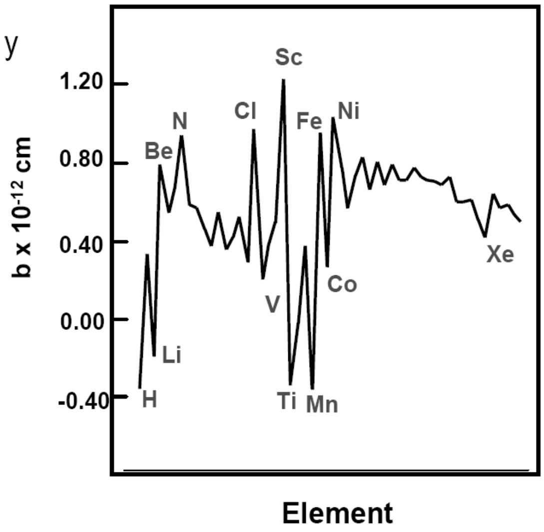
The effect of using a wavelength near an absorption edge

- Co and Fe differ by 1 e′
- Choosing a wavelength just below the Co absorption edge effectively creates a 6 e′ difference in Co X-ray scattering
- Which site V prefer in V-doped FeCo?



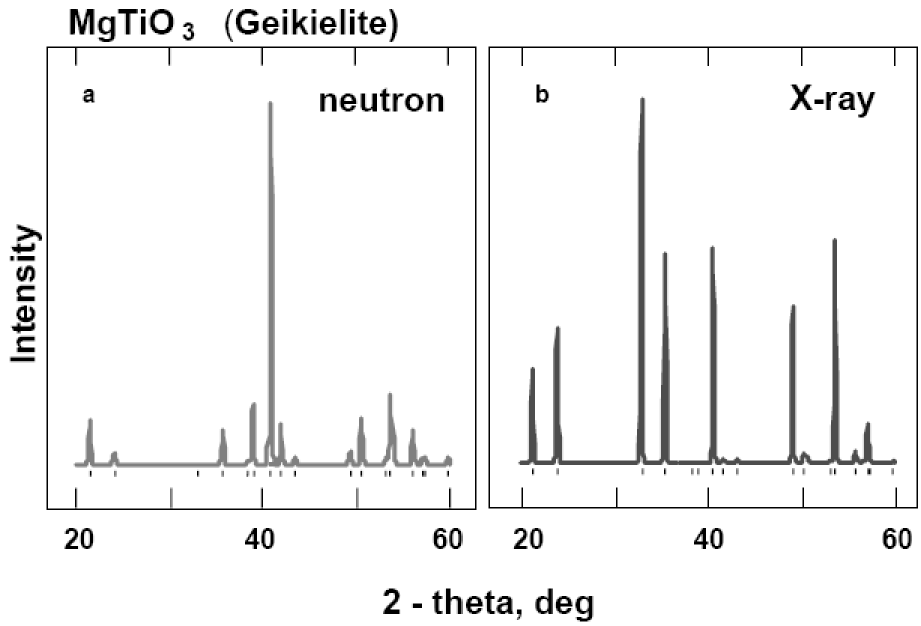
Neutron diffraction has different atomic scattering lengths than x-rays

- Neutron scattering lengths (**b**) vary erratically across periodic table
- Most "light" elements scatter well
- some atoms have "negative" (phase inverted) **b** values
- **b** usually varies by isotope
  - ✓ H (-0.37) vs. D (0.67)
- **b** does not vary with Q: more intense "high angle" scattering
  - ✓ more accurate models
  - ✓ better discrimination of occupancies



Young

X-ray vs. neutron



- X-ray & neutron data - very different pattern of intensities
- Combination → stronger restriction on structure model

Young

Fe & Ti site-sharing example

- With x-ray and neutron information combined:

- $f_{site} = n_{Fe}f_{Fe}(Q) + n_{Ti}f_{Ti}(Q)$ (X-rays)
- $b_{site} = n_{Fe}b_{Fe} + n_{Ti}b_{Ti}$ (neutrons)

- two observables: f_{site} & b_{site} and two unknowns: n_{Fe} & n_{Ti}
- $b_{Fe} = 0.94$, $b_{Ti} = -0.34$ → Fe/Ti contrast is excellent

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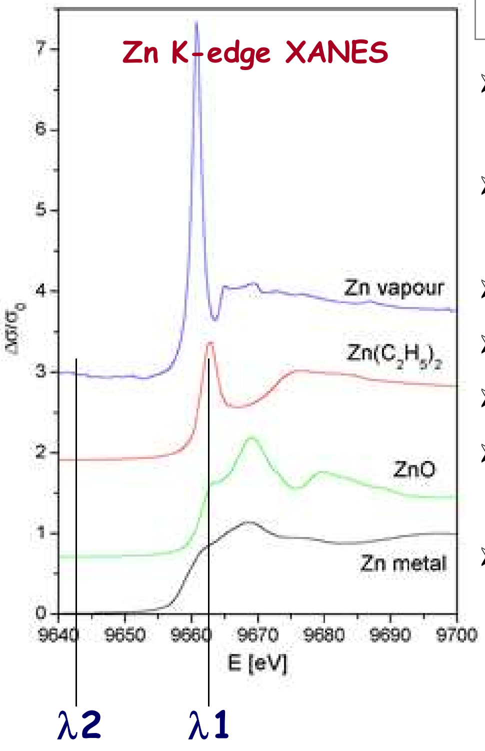
Anomalous scattering



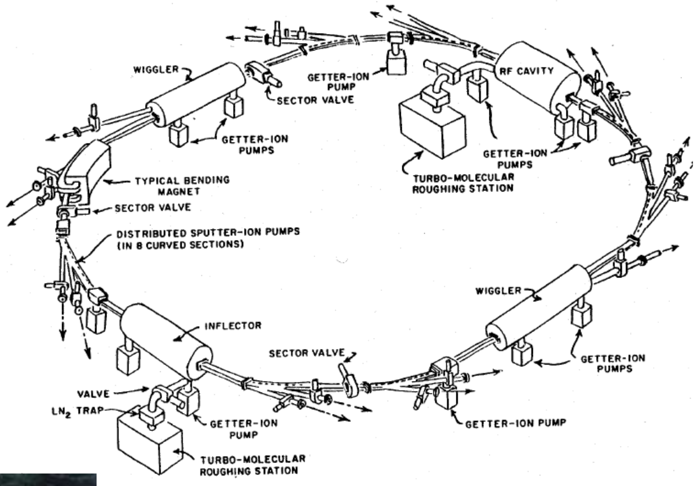
- Atomic scattering factors @ λ1 & λ2 are different → those @ λ1 need to be determined

- Convert X-ray absorption data using optical theorem & Kramers-Kronig dispersion relation
- Integration of I's of Bragg reflections from single crystal
- Determination of I ratios in SAXS experiment
- X-ray interferometry
- Measurement of total reflection curves
- Measurement of index of refraction using prism method
- Collect data @ same wavelength from compound which has same/similar electronic environment and refine atomic scattering factor with other parameters fixed

http://www.p-ng.si/~arcon/xas/xanes/xanes.htm

Synchrotron radiation

- High intensity
- Plane polarized
- Intrinsically collimated
- Wide energy range
- Has well defined time structure



Spring-8, Japan

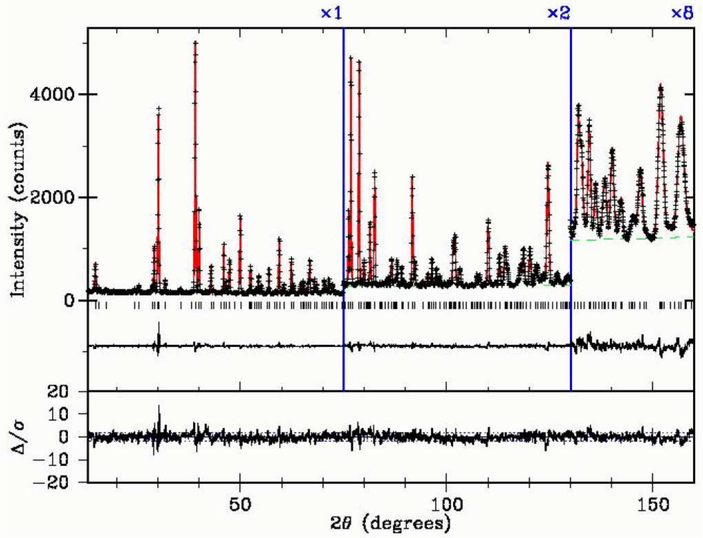
http://www.spring8.or.jp/ja/news_publications/research_highlights/no_36/

Example > X-ray single crystal/Neutron

$KFe_3(D_2VO_2)_3(SO_4)_2$ (Jarosite structure)

- Nice single crystal structure – but no hydrogen site information
- Good powder neutron data, but for vanadium, $b \cong 0$
- Combined refinement was simple

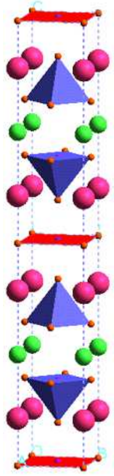
- Removal of each set of data gave virtually no improvement in R-factor for remaining set
- Combined refinement improved X-ray anisotropic U_{ij}'s



Example > Synchrotron/Neutron

cation site disorder of $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_x$

- Synchrotron data collected @ beam line 3B of NSLS, Brookhaven National Laboratory (BNL)
  - ✓ 3 sets collected including one @ Tl edge
- Neutron duffraction data collected @ beamline H1A of the high flux beam reactor (HFBR) at BNL
  - ✓ 1 set collected @ 1.8857A, 2θ = 20° to 152.5° in steps of 0.02°
- Refinement
  - ✓ GSAS distributed in April 1994 was used
  - ✓ Atomic scattering factors of cations were not used from literature when using anomalous scattering

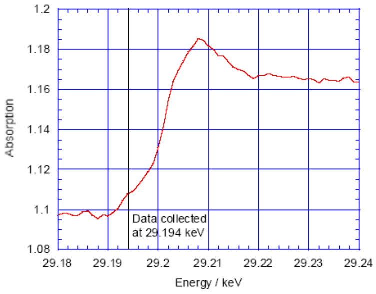


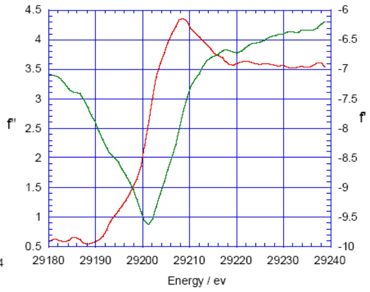
Example > $Cs_8Cd_4Sn_{42}$

- Cd location in the type I clathrate $Cs_8Cd_4Sn_{42}$
  - ✓ Is the Cd randomly distributed over all the available framework sites?
  - ✓ Distribution of Cd affects Seebeck coefficient and thermoelectric performance.
  - ✓ Cd absorbs neutrons.
- Cd (48) and Sn (50) have similar atomic number
  - ✓ essentially indistinguishable by X-ray scattering unless X-rays have energy close to absorption edge
  - ✓ collect data at 80 keV, Cd K-edge and Sn K-edge
    - more good data improves reliability of the results
    - scattering factors estimated from absorption measurements

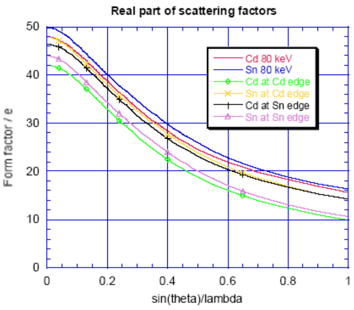
Example > Sn scattering factors, Resonant scattering in $Cs_8Cd_4Sn_{42}$

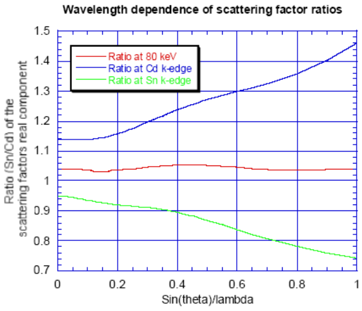
- Anomalous scattering terms calculated from Kramers-Kronig transformation of absorption data





- Selecting X-ray energy close to absorption edge distinguishes Cd from Sn


Real part of scattering factors


Wavelength dependence of scattering factor ratios

Combined refinements > be careful

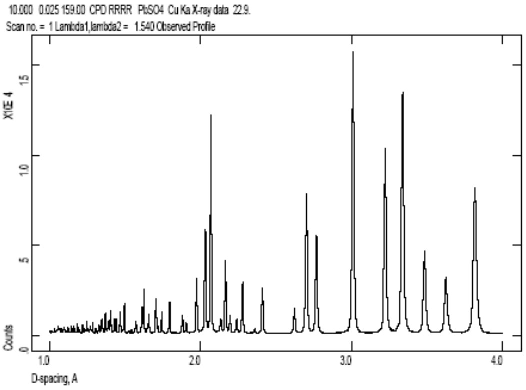
- Are the samples the same?
  - ✓ Beware of single crystals for variable composition phases: specimen may not be representative of bulk material
  - ✓ Surface vs. bulk differences: neutrons sample the entire bulk, while for high-μ materials, X-rays sample the surface

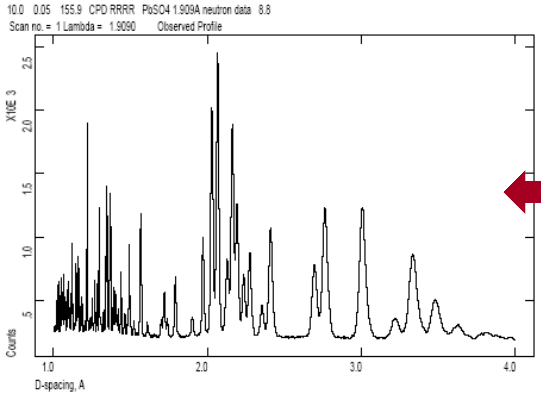
- Incompatible wavelength calibration

- Are the measurement temperatures the same?
  - ✓ Differential thermal expansion for non-cubic materials may result in irreconcilable differences in peak positions

Incompatible data > example $PbSO_4$

- X-ray Diffraction – CuKa Phillips PW1710
  - ✓ Higher resolution
  - ✓ Intensity falloff at small d spacings
  - ✓ Better at resolving small lattice distortions





- Neutron Diffraction - D1a, ILL, λ=1.909 Å
  - ✓ Lower resolution
  - ✓ Much higher intensity at small d-spacings
  - ✓ Better atomic positions/ thermal parameters

Incompatible data > example $PbSO_4$

- Classic failure - $PbSO_4$ Rietveld Round Robin 2 data sets - CuKa X-ray and CW neutron, both excellent but at <u>different temperatures </u>(X-ray at 298K, neutron at 295K?)
- Important experimental controls not followed
  - ✓ Same temperature & Same sample
- Combined Rietveld Refinement not the best
  - ✓ Thermal expansion
  - ✓ Changed atom positions
  - ✓ Changed thermal motion
- Poorer fit than individual refinements - Rwp ~ 2%, high for X-ray data
- Inconsistent results

Testing Constraints

- ➢ If using 2+ data sets: are they consistent with each other?
  - ✓ Try removing individual data sets from the refinement (may need to lock some parameters)
    - Parameter values will change, but changes to Rwp should be fairly small
- ➢ Soft constraints: are the assumptions valid?
  - ✓ Reduce the weights (or increase uncertainties)
    - Parameter values will change, but changes to Rwp should be fairly small
    - What % of total χ^2 comes from constraints? Should be <10-20%
- ➢ Hard constraints: can be hard to test
  - ✓ Try removing them – do the results suggest any conclusions?

- ➢ Be sure to document hard & soft constraints in publications