Fundamentals of Rietveld Refinement
I. XRD Pattern Calculation and Refinement Parameters

An Introduction to Rietveld Refinement

using

PANalytical X'Pert HighScore Plus v3.0e

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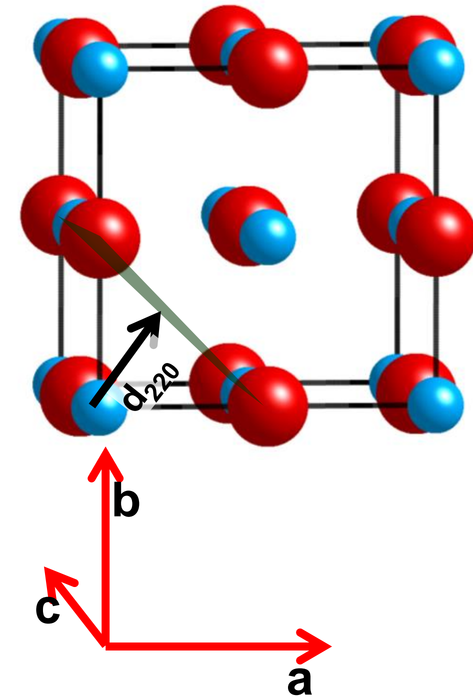
Outline

- Calculating a Diffraction Pattern from a Crystal Structure
- Using HighScore Plus to Simulate a Diffraction Pattern
- Manually Refining a Model to Match Experimental Data

A Brief Re-introduction to Miller Indices

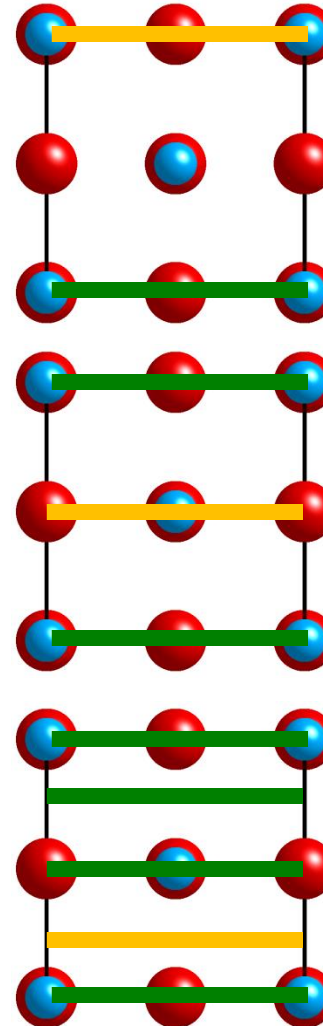
- The Miller indices (hkl) define the reciprocal axial intercepts of a plane of atoms with the unit cell
  - The (hkl) plane of atoms intercepts the unit cell at $\frac{a}{h}$, $\frac{b}{k}$, and $\frac{c}{l}$
  - The (220) plane drawn to the right intercepts the unit cell at ½*a, ½*b, and does not intercept the c-axis.
    - When a plane is parallel to an axis, it is assumed to intercept at ∞; therefore its reciprocal is 0



- The vector $\mathbf{d_{hkl}}$ is drawn from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angle.
  - The direction of d_{hkl} is the crystallographic direction.
  - The crystallographic direction is expressed using [] brackets, such as [220]

A given (hkl) refers to a family of atomic planes, not a single atomic plane

- The Miller indices are determined by using the plane of atoms that is closest to the origin without passing through it.
- The other members of the family of atoms are determined by translating the (hkl) plane of atoms by d_{hkl}
- A family of planes will always have one member that passes through the origin
- Some planes of atoms may belong to more than one family (as illustrated to the right)

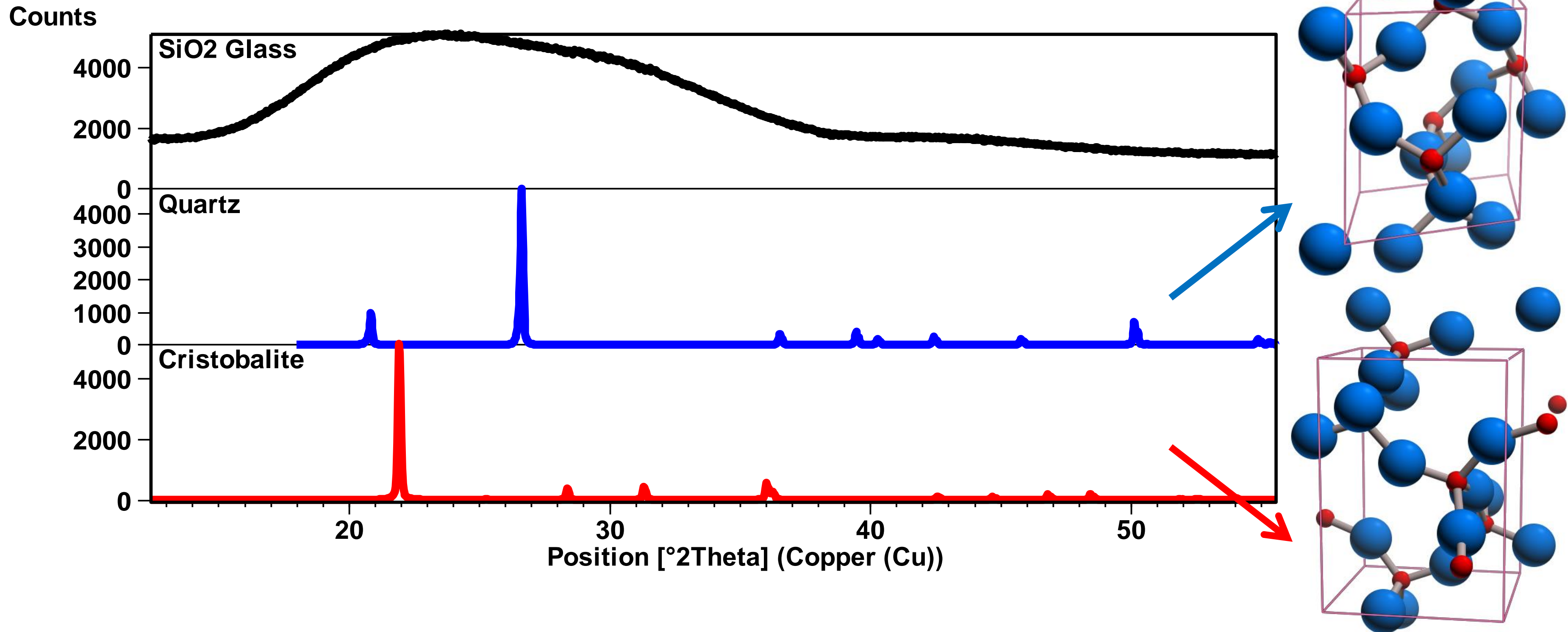


The (100) plane includes two faces of the cubic unit cell. These are produced by drawing the first plane (shaded orange) at the (1,0,0) intercept, and then translating it by [-100].

The (200) plane also includes two faces of the cubic unit cell. These are produced by drawing the first plane (shaded orange) at the (½, 0, 0) intercept, and then translating it by ±[½, 0, 0].

The (400) plane includes members of the (100) and (200) families, as well as the planes at the (¼, 0, 0) and (¾, 0, 0) intercepts. These are produced by drawing the first plane (shaded orange) at the (¼, 0, 0) intercept, and then translating it by ±[n*¼, 0, 0].

The position and intensity of peaks in a diffraction pattern are determined by the crystal structure



- These three phases of SiO_2 are chemically identical.
- Differences in the atomic structure are reflected in the X-ray scattering patterns.

The diffraction peak position is a product of the atomic bond distances in the crystal

Bragg's Law: $\lambda = 2d_{hkl}\sin\theta$

- Bragg's law calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak.
  - In most diffractometers, the X-ray wavelength λ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle 2θ.
  - The lattice parameters of the unit cell are used to calculate d_{hkl}

d_{hkl} is a function of the size and shape of the unit cell

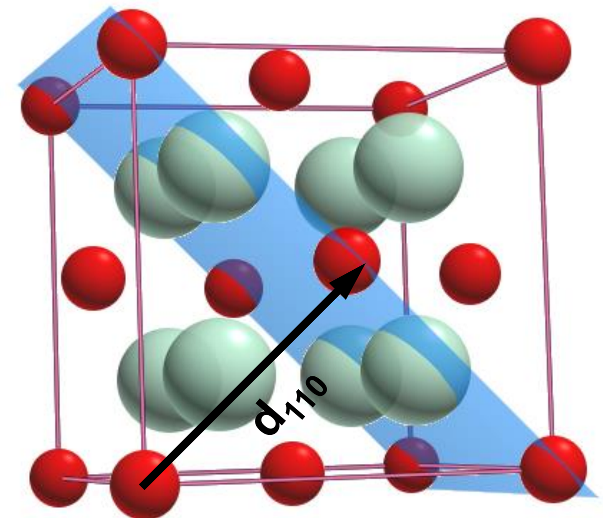
$$d^{*2}_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma + 2hla^*c^*\cos\beta + 2klb^*c^*\cos\alpha$$

- **d_{hkl}*** is the reciprocal of d_{hkl}: $d^{*2}_{hkl} = \frac{1}{d_{hkl}{}^2}$
- **d_{hkl}** is calculated based on the reciprocal space units of the lattice parameters

$$a^* = \frac{bc\sin\alpha}{abc}$$

$$\cos\alpha^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$$

- the diffraction peak position is a product of the average atomic distances in the crystal
- anything that changes the average bond distances (temperature, pressure, etc.) will change d_{hkl} and therefore change the diffraction peak positions



The amplitude of light scattered by a crystal is determined by the arrangement of atoms in the diffracting planes

$$I_{hkl} \propto |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

- The structure factor, F_{khl}, quantifies the amplitude of light scattered by a crystal
  - The patterns of atoms in the unit cell scatters strongly in some directions and weakly in others owing to interference of the wavelets scattered by the atoms
- F_{hkl} sums the result of scattering from all of the atoms in the unit cell to form a diffraction peak from the (hkl) planes of atoms
- The amplitude of scattered light is determined by:
  - where the atoms are on the atomic planes
    - this is expressed by the fractional coordinates x_j y_j z_j
  - what atoms are on the atomic planes
    - the scattering factor f_j quantifies the relative efficiency of scattering at any angle by the group of electrons in each atom
    - N_j is the fraction of every equivalent position that is occupied by atom j

The scattering factor, f, quantifies the efficiency of scattering from a group of electrons in an atom

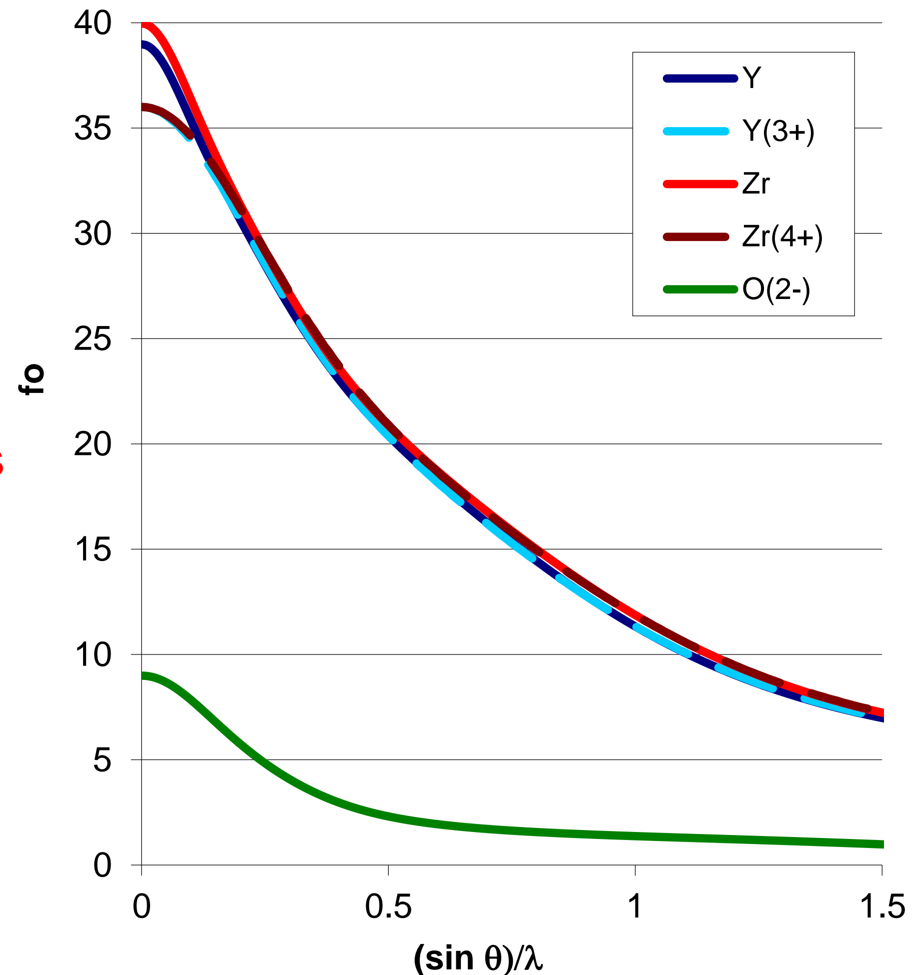
$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

- X-rays are electromagnetic radiation that interact with an electron, which reradiates the X-ray as a spherical wave
- The number of electrons around an atom defines how strongly it will scatter the incident X-ray beam
  - the initial strength of the atomic scattering factor is equal to the number of electrons around the atom
- The scattering factor, f, is a product of several terms describing the interaction of the X-ray with the electrons around an atom

$$|f|^2 = \left(f_0 \exp\left[\frac{-B\sin^2\theta}{\lambda^2}\right] + \Delta f' \right)^2 + \left(\Delta f''\right)^2$$

The atomic scattering factor f_0 can be found using tables or equations determined experimentally or from quantum mechanical approximations

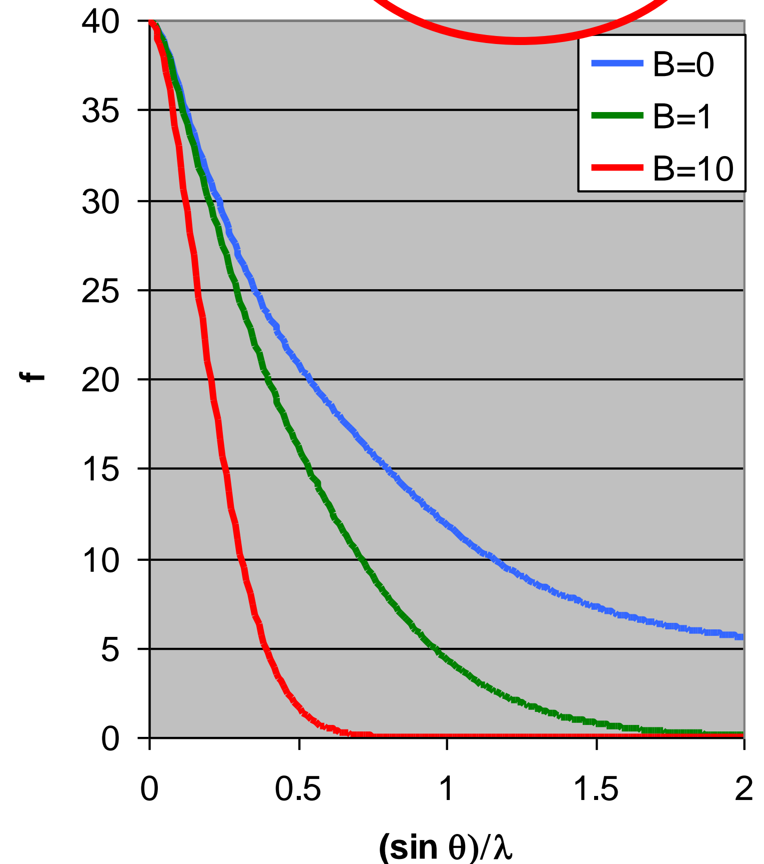
- f_0 at 0° is equal to the number of electrons around the atom
  - Y and Zr are similar, but slightly different, at 0°
  - Zr and Zr^{4+} are slightly different at 0°
  - Y^{3+} and Zr^{4+} are identical at 0°
- the variation with (sin θ)/λ depends on size of atom
  - larger atoms drop off quicker
  - at higher angles, the difference between Y^{3+} and Zr^{4+} is more readily discerned
  - at higher angles, the difference between different oxidation states (eg Zr and Zr^{4+}) is less prominent



Thermal motion of the atom changes the scattering factor

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

- the efficiency of scattering by an atom is reduced because the atom and its electrons are not stationary
  - the atom is vibrating about its equilibrium lattice site
  - the amount of vibration is quantified by the Debye-Waller temperature factor: $B=8\pi^2U^2$
    - U^2 is the mean-square amplitude of the vibration
  - this is for isotropic vibration: sometimes B is broken down into six Bij anistropic terms if the amplitude of vibration is not the same in all directions.
  - aka temperature factor, displacement factor, thermal displacement parameter



Anomalous scattering of X-rays with energies near the absorption edge of the atom changes the scattering factor

$$|f|^2 = \left(f_0 \exp\left[\frac{-B \sin^2\theta}{\lambda^2} \right] + \Delta f' \right)^2 + (\Delta f'')^2$$

- scattering factor has a real and imaginary term
- these terms only matter when the energy of the incident X-ray approaches the ionization energy of atom
  - when the wavelength of the incident X-ray is near the absorption edge of the atom
- anomalous scattering describes how some photons with energy approaching the ionization energy will be scattered out of phase with the majority of photons

With a crystal structure to solve Bragg's Law and F_{hkl}, you can calculate the diffraction pattern from an ideal crystal

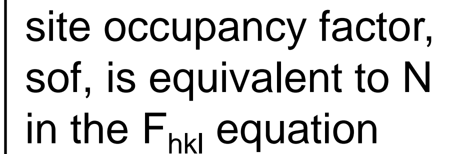
- Ideal powder diffraction patterns can be simulated if you know ...
  - space group symmetry
  - unit cell dimensions
  - atom types
  - relative coordinates of atoms in unit cell
  - atomic site occupancies
  - atomic thermal displacement parameters
- ... for each and every phase in the sample

Where to Get Crystal Structures

- publications
- Commercial Databases
  - ICDD PDF4+ Inorganic
  - Inorganic Crystal Structure Database (ICSD)
  - Linus Pauling File (LPF)
    - this is included in ICDD PDF4+ Inorganic
  - NIST Structural Database (metals, alloys, intermetallics)
  - CCDC Cambridge Structure Database (CSD) (organic materials)
    - Available online http://beta-www.ccdc.cam.ac.uk/pages/Home.aspx
    - MIT Site license available for download from IS&T website
- Free Online Databases
  - Crystallography Open Database http://www.crystallography.net/
  - ICSD- 4% available as demo at http://icsd.ill.eu/icsd/index.html
  - Mincryst http://database.iem.ac.ru/mincryst/index.php
  - American Mineralogist http://www.minsocam.org/MSA/Crystal_Database.html
  - WebMineral http://www.webmineral.com/
  - Protein Data Bank http://www.rcsb.org/pdb/home/home.do
  - Nucleic Acid Database http://ndbserver.rutgers.edu/
  - Database of Zeolite Structures http://www.iza-structure.org/databases/

A Crystal Structure

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



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

Wyckoff Site notation is a shortcut to indicate if the type of site that the atoms occupies in the crystal

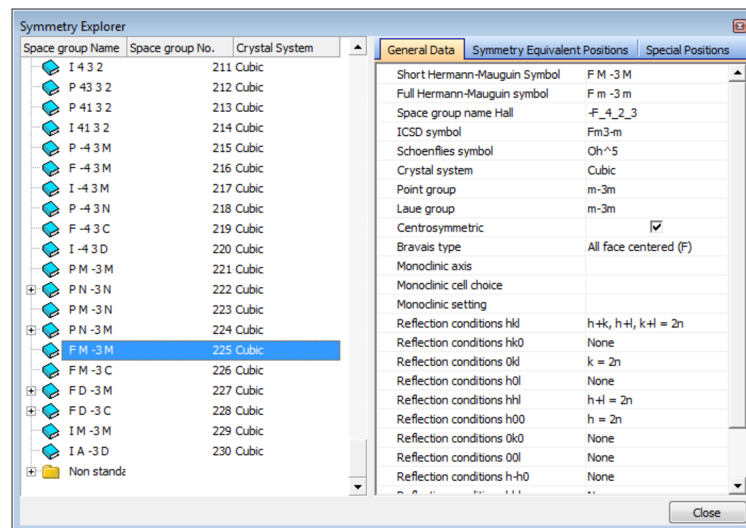
Atom	Wyckoff Site	x	y	z	B_{iso}	sof
Zr	4a	0	0	0	1.14	1
O	8c	0.25	0.25	0.25	2.4	1

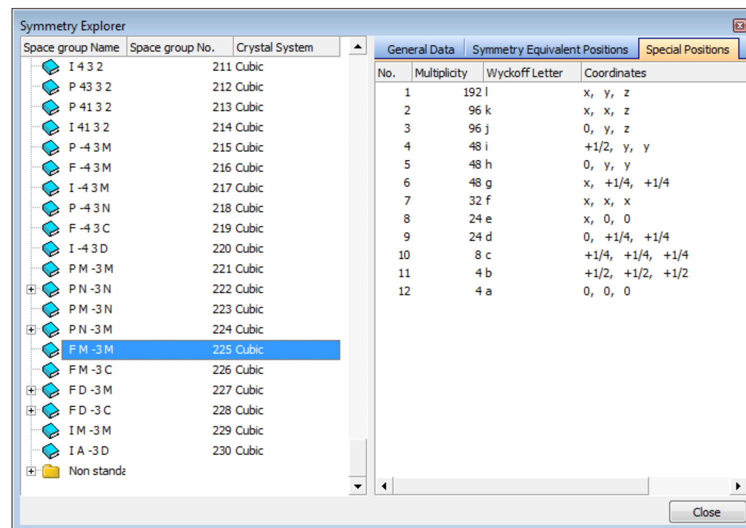
- each letter in the Wyckoff notation specifies a site that sits on a different combination of symmetry elements
  - The Wyckoff site indicates if x, y or z are can change or if they must be fixed to preserve the symmetry of the crystal
  - An element on the 4a site in the Fm-3m space group can only occupy 0,0,0
    - Moving the element to a different position would change the surroundings of the site and would represent a change in the interaction between that atom and its neighbors
  - An element on the 32f site in the Fm-3m space group will occupy x,x,x (indicating that the x, y, and z positions must be the same number)

- the number in the Wyckoff notation indicates the number of atoms put into the unit cell if the atom is on that site
  - 4a- an atom on the a site will populate the unit cell with 4 atoms
  - 8c- an atom on the c site will populate the unit cell with 8 atoms
  - Wyckoff notation gives you a quick way to check if stoichiometry is correctly preserved when you create a crystal structure
  - you can deduce **z**, the number of molecules per unit cell, from the Wyckoff notation (z=4 for ZrO_2)

Retrieve information about space groups using the *Symmetry Explorer* in HighScore Plus

- To use the Symmetry Explorer
  - select the menu *Tools > Symmetry Explorer*
  - In the left pane, select the Space Group you would like to examine
- The entries in the Symmetry Explorer contain information similar to what you would find in the International Tables of Cyrstallography
- The Special Positions tab will show the Wyckoff sites for that space group





The Site Occupancy Factor, sof, indicates what fraction of a site is occupied by a specific atom

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

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

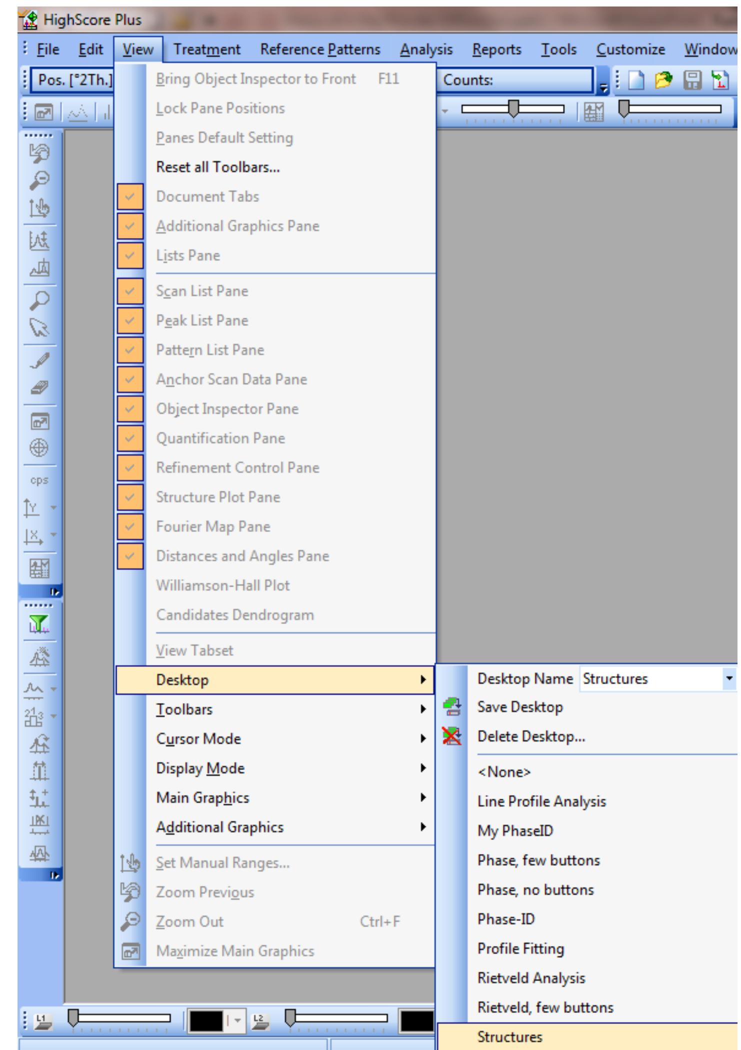
- The sof is N in the structure factor equation
- sof = 1, every equivalent position for xyz is occupied by that atom
- sof < 1, some of the sites are vacant
- two atoms occupying the same site will each have a fractional sof
- remember that the observed XRD pattern is an average of hundreds or thousands of unit cells that make a crystallite

How to manually enter a crystal structure and calculate an ideal X-ray powder diffraction pattern using HighScore Plus

For pattern calculations and Rietveld refinement in HSP, the “Structures” desktop is recommended

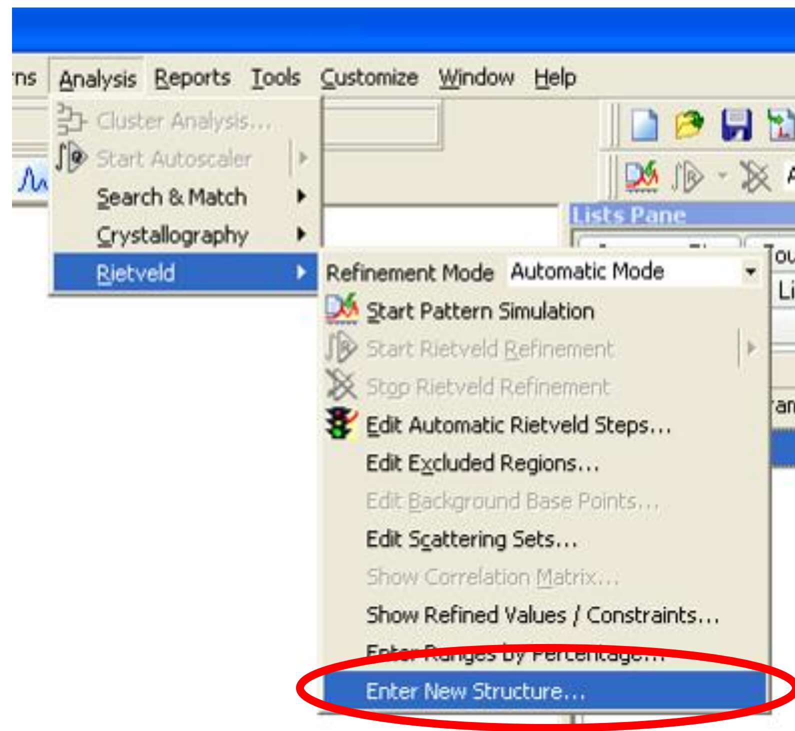
- Desktops can be changed in the menu:
  - *View > Desktops*

- All slides in this tutorial were created with HSP in the “Structures” desktop



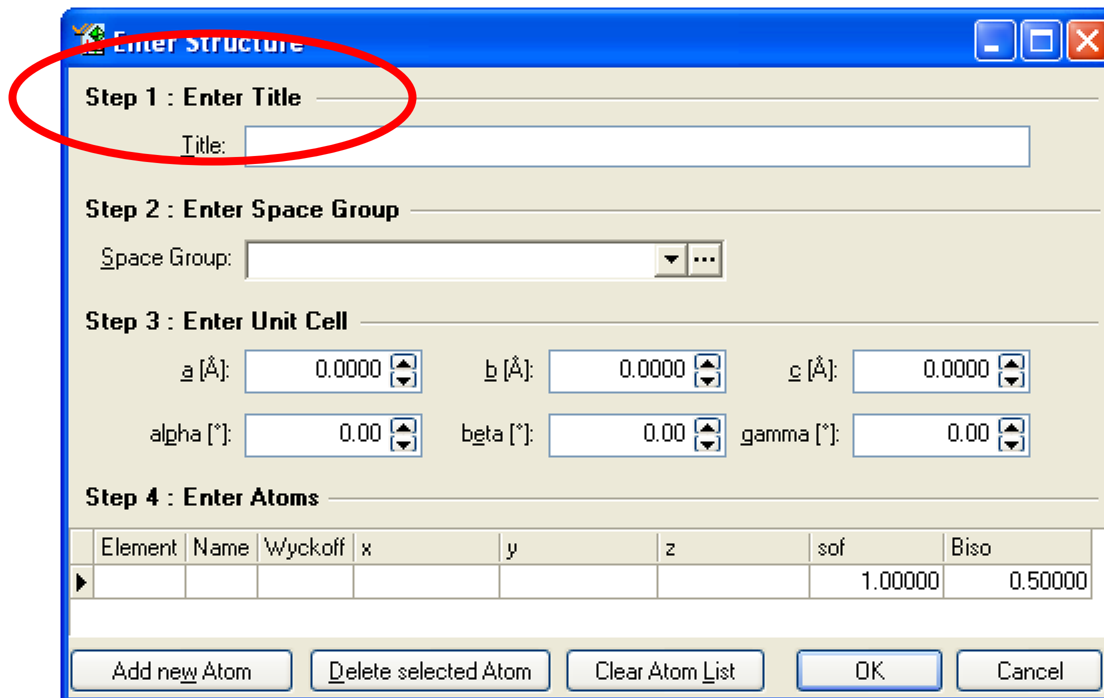
With this crystal structure information, we can build a crystal in HSP

- Start X'Pert HighScore Plus
- Create a New Document *File>New*
- *Analysis>Rietveld>Enter New Structure*



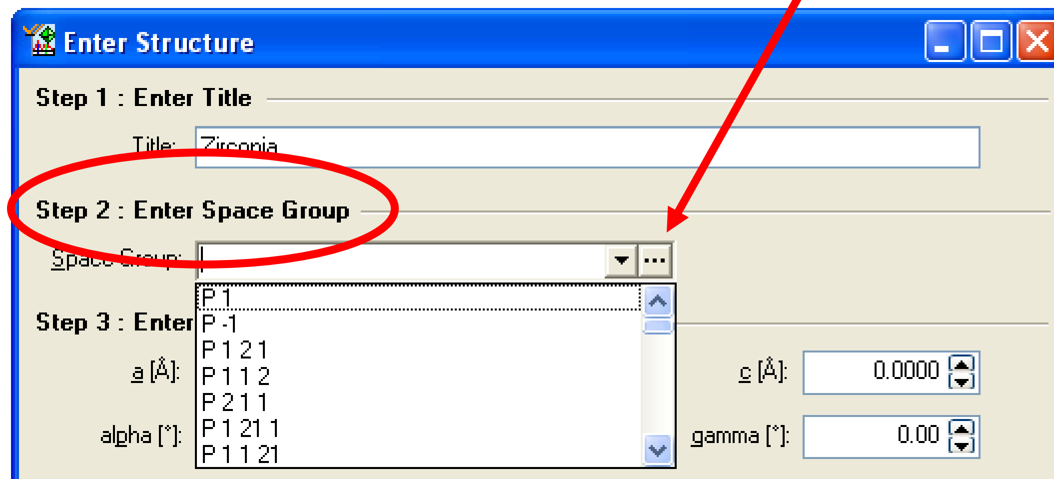
Step 1: Enter Title

- Follow the entry form from top to bottom, via the numbered steps
- The Title can be any name that you want
- In this example, we are creating an entry for *Zirconia*



Step 2: Enter Space Group

- To enter the space group:
  - you can just enter number into the space group field
    - Each space group has a unique number (1 thru 230)
  - You can use the drop-down menu to select a space group
  - You can open the symmetry explorer by clicking on the ... button
- HSP will assume the standard origin and setting unless you use the Symmetry Explorer to select otherwise
- In this example, type 225 for the Fm-3m space group



The symmetry explorer allows you to choose the space group and a specific origin, and to see information about the symmetry elements and special positions

Symmetry Explorer

Space group Name	Space group...	Crystal System
F D -3	203	Cubic
I M -3	204	Cubic
P A -3	205	Cubic
I A -3	206	Cubic
P 4 3 2	207	Cubic
P 42 3 2	208	Cubic
F 4 3 2	209	Cubic
F 41 3 2	210	Cubic
I 4 3 2	211	Cubic
P 43 3 2	212	Cubic
P 41 3 2	213	Cubic
I 41 3 2	214	Cubic
P -4 3 M	215	Cubic
F -4 3 M	216	Cubic
I -4 3 M	217	Cubic
P -4 3 N	218	Cubic
F -4 3 C	219	Cubic
I -4 3 D	220	Cubic
P M -3 M	221	Cubic
P N -3 N	222	Cubic
P M -3 N	223	Cubic
P N -3 M	224	Cubic
F M -3 M	225	Cubic
F M -3 C	226	Cubic
F D -3 M	227	Cubic
F D -3 C	228	Cubic
I M -3 M	229	Cubic

General Data | Symmetry Equivalent Positions | Special Positions

Property	Value
Short Hermann-Mauguin Symbol	F M -3 M
Full Hermann-Mauguin symbol	F m -3 m
Space group name Hall	-F_4_2_3
ICSD symbol	Fm3-m
Schoenflies symbol	Oh^5
Crystal system	Cubic
Point group	m-3m
Laue group	m-3m
Centrosymmetric	✓
Bravais type	All face centered (F)
Monoclinic axis	
Monoclinic cell choice	
Monoclinic setting	
Reflection conditions hkl	h+k, h+l, k+l = 2n
Reflection conditions hk0	None
Reflection conditions 0kl	k = 2n
Reflection conditions h0l	None
Reflection conditions hhl	h+l = 2n
Reflection conditions h00	h = 2n
Reflection conditions 0k0	None
Reflection conditions 00l	None
Reflection conditions h-h0	None
Reflection conditions hhh	None
Internal number	22500
Number of entries in ICSD	1391

OK | Cancel

Step 3: Enter Unit Cell Lattice Parameters

- lattice parameters are automatically constrained by the space group that you chose
  - For example, in a cubic space group: a=b=c, $\alpha=\beta=\gamma=90$
- In this example, a=5.11

Step 2 : Enter Space Group

Space Group: F m -3 m

Step 3 : Enter Unit Cell

a [Å]: 5.1100	b [Å]: 5.1100	c [Å]: 5.1100
alpha [°]: 90.00	beta [°]: 90.00	gamma [°]: 90.00

Step 4 : Enter Atoms

Element	Name	Wyckoff	x	y	z	sof	Biso

Step 4: Enter Atom Information

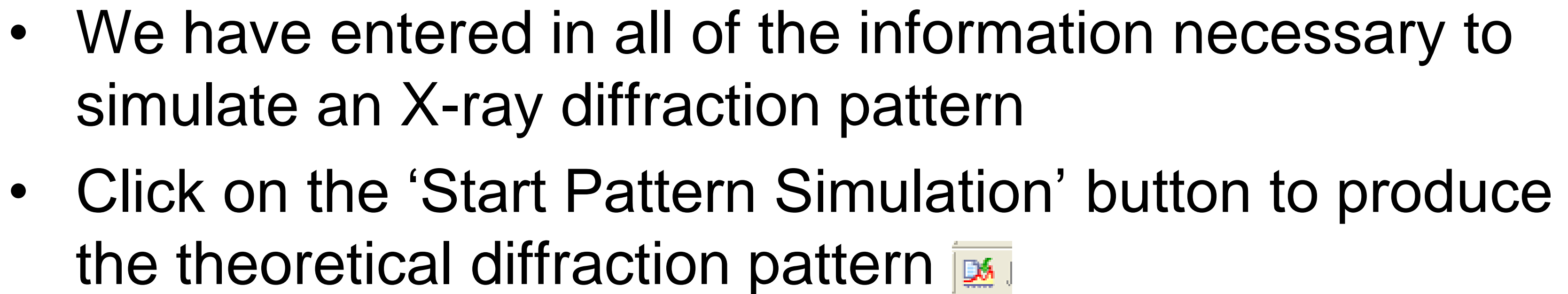
Step 4 : Enter Atoms

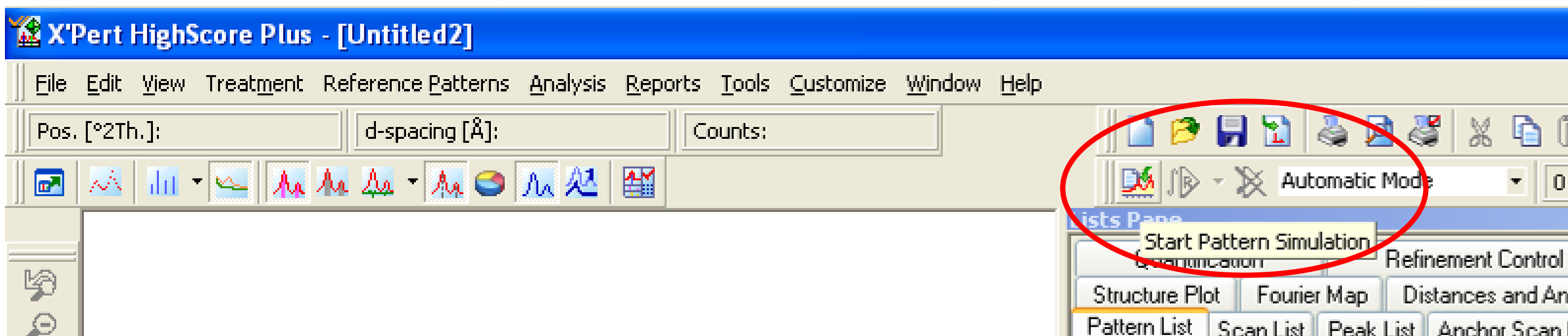
No.	Element	Name	Wyckoff	x	y	z	sof	Biso
1	Zr	Zr	4a	0	0	0	1	1.14
2	O	O	8c	0.25	0.25	0.25	1	2.4

Add new Atom | Delete selected Atom | Clear Atom List | OK | Cancel

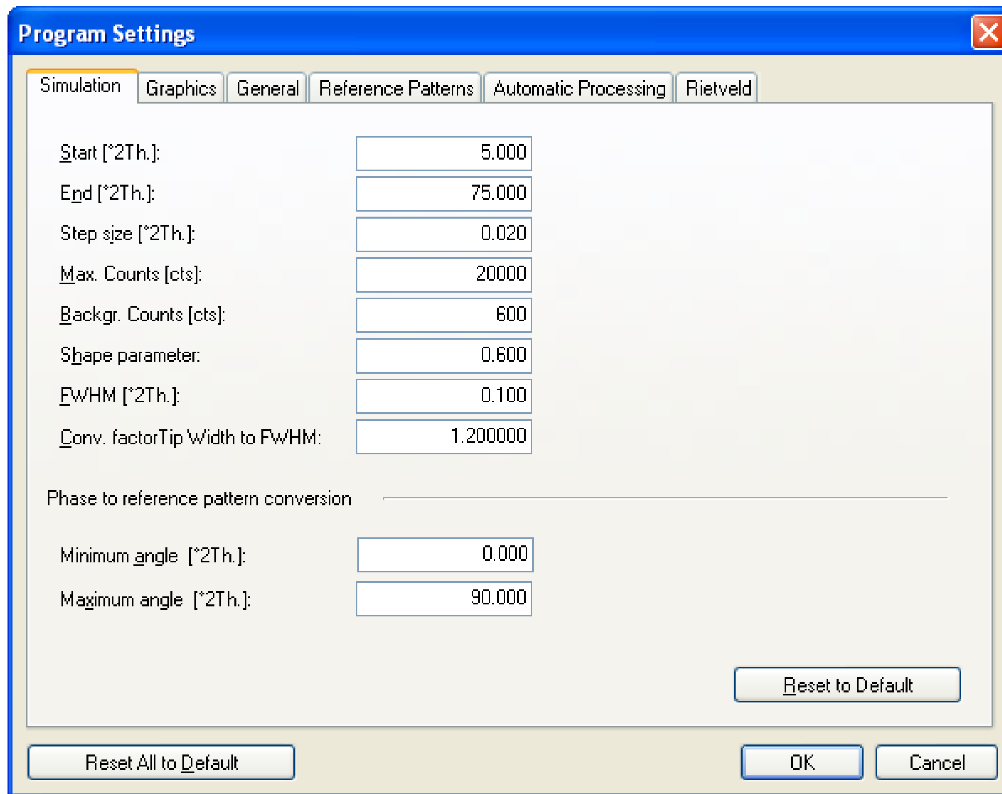
- You can type the element symbol or select from a drop-down menu
  - The element can be an atom or ion (select oxidation state)
    - the use of oxidation states in modifying the scattering factor for an atom is set in *Customize>Program Settings,* in the Rietveld tab
    - by default it is set to “Ignore Oxidation States”
- The name is the element by default, but it can be changed to anything you like (useful if you have the same element on multiple sites)
- Enter the atom positions, sof, and Biso
  - If you enter the Wyckoff site, constrained x, y, and z positions are automatically entered
  - if you enter xyz, the Wyckoff site is automatically assigned
- When finished, click **OK** to create that crystal structure!

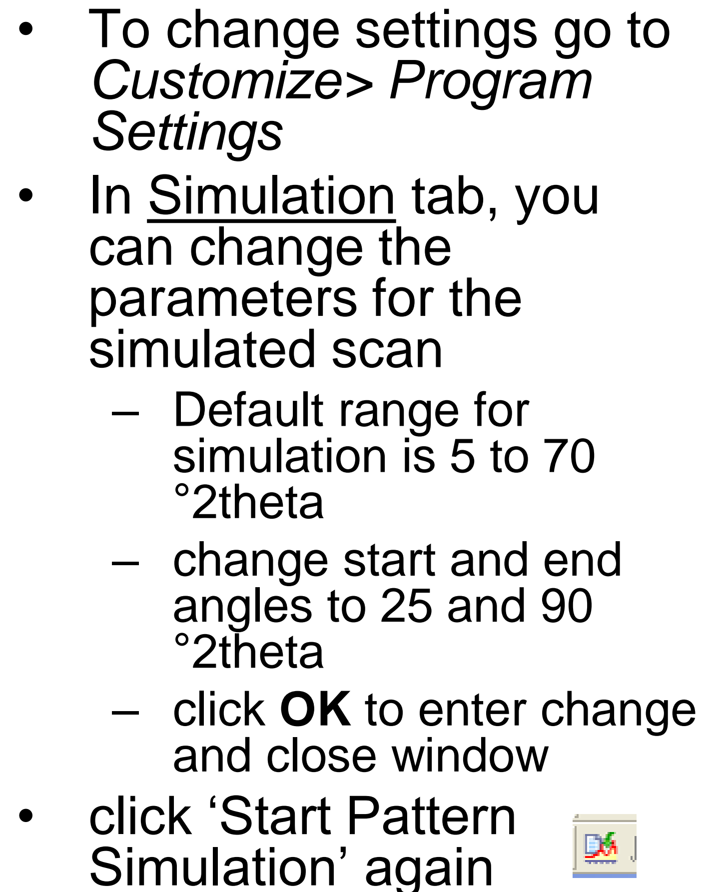
We can now simulate the ideal X-Ray powder diffraction pattern in HSP

- We have entered in all of the information necessary to simulate an X-ray diffraction pattern
- Click on the ‘Start Pattern Simulation’ button to produce the theoretical diffraction pattern 



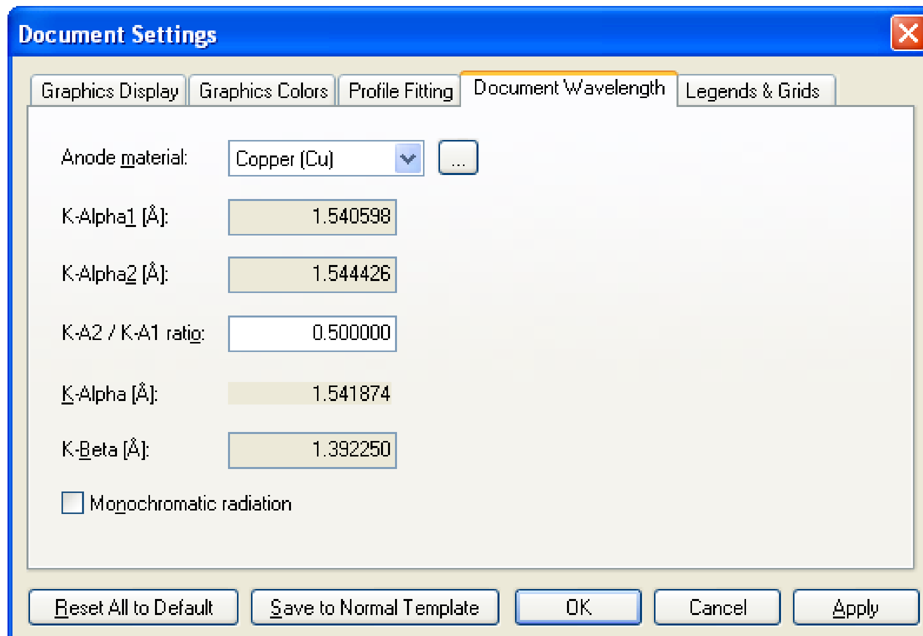
The pattern simulation parameters can be changed in Program Settings





- To change settings go to *Customize> Program Settings*
- In Simulation tab, you can change the parameters for the simulated scan
  - Default range for simulation is 5 to 70 °2theta
  - change start and end angles to 25 and 90 °2theta
  - click **OK** to enter change and close window
- click ‘Start Pattern Simulation’ again

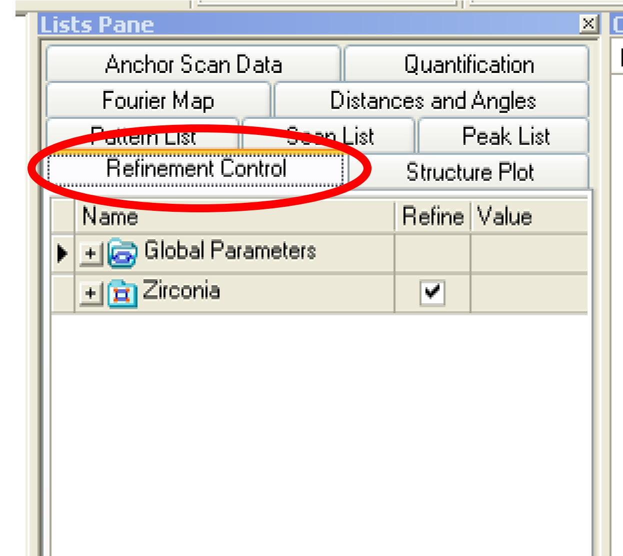
The wavelength of radiation used in the simulation can be changed in Document Settings



- To change settings go to *Customize> Document Settings*
- In Document Wavelength tab, you can change the X-ray source used
  - there is an “Other” option if you used a non-characteristic wavelength, such as at a synchrotron
- click ‘Start Pattern Simulation’ again

Parameters for the crystal structure and the simulation can be accessed in the Refinement Control list

- the parameters for the pattern simulation are shown in the Refinement Control List
- The values for global parameters and each individual crystal structure entered into the simulation are listed in a nested tree format
- You can trim the number of tabs in the Lists Pane in the *View* menu

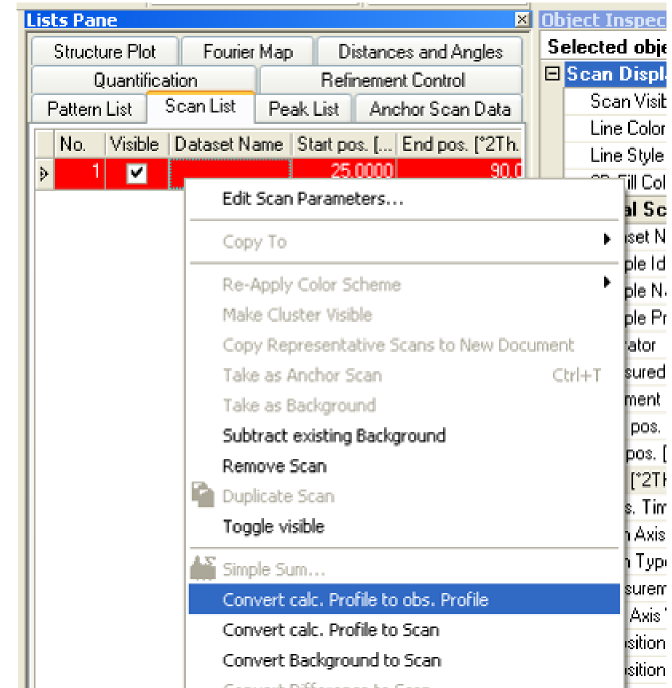


The Object Inspector shows additional details for any object you select in other windows

- If you click on the phase name (eg Zirconia) in Refinement Control list, you will be able to see additional information about that phase in the Object Inspector
  - This includes information such as calculated density, chemical formula, and formula mass
  - You can use these to check that you created the crystal structure correctly
  - You can change details such as the phase name and color of simulated diffraction pattern

We want to keep this pattern as a reference during the next exercises

- Go to Scan List in the Lists Pane
- Right Click on the current scan that is shown in the list (which is the simulated pattern)
- Select “**Convert calc. Profile to obs. Profile**”
- Now the original simulation will remain in the Main Graphics View and we can compare it to new simulations

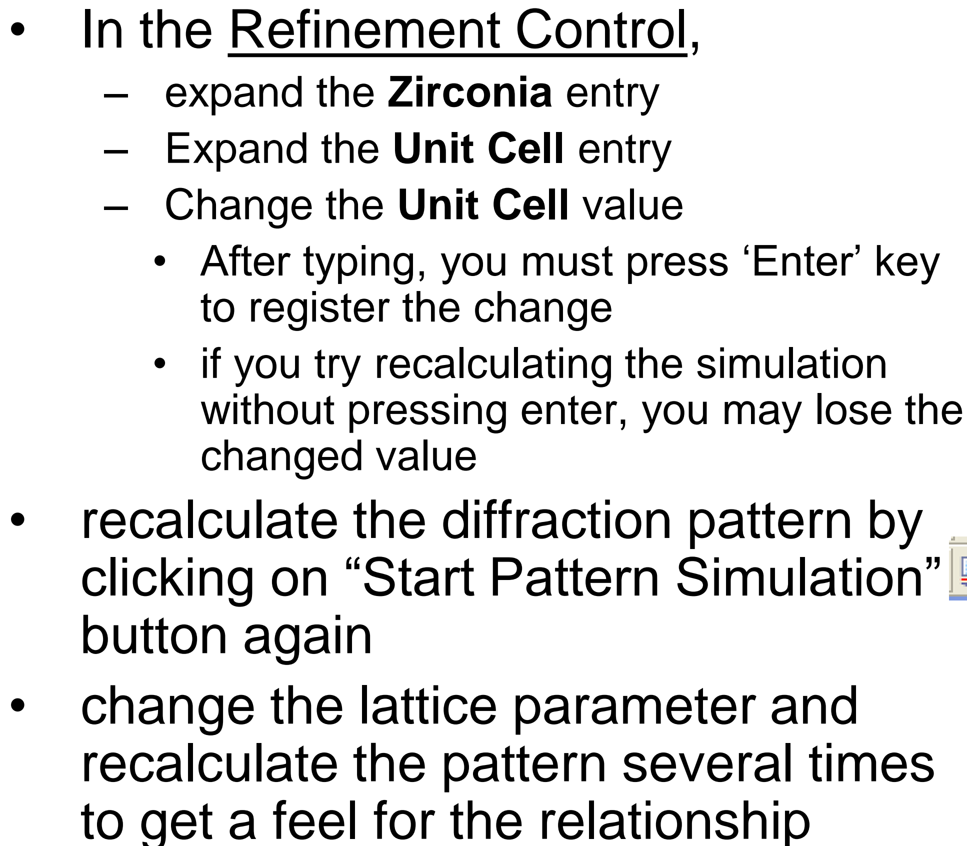


We can change parameters for the crystal structure and observe how they change the diffraction pattern

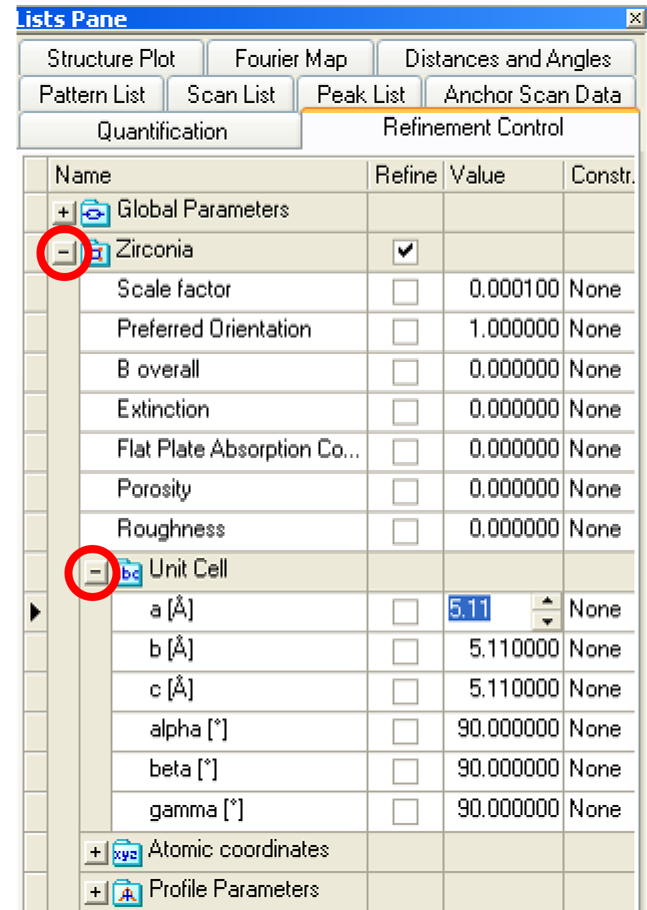
- The unit cell lattice parameters determine where the diffraction peaks are observed
- the peak intensity is determined by
  - what atoms are in the crystal and their positions xyz
  - the site occupancy of the atom
  - the relative scattering strength of the atom, scattering factor, which is a product of the number of electrons around the atom
  - the thermal parameter of the atom

- This is not just useful for these tutorial purposes, but also for anticipating what your real data might look like and for evaluating limits of detection

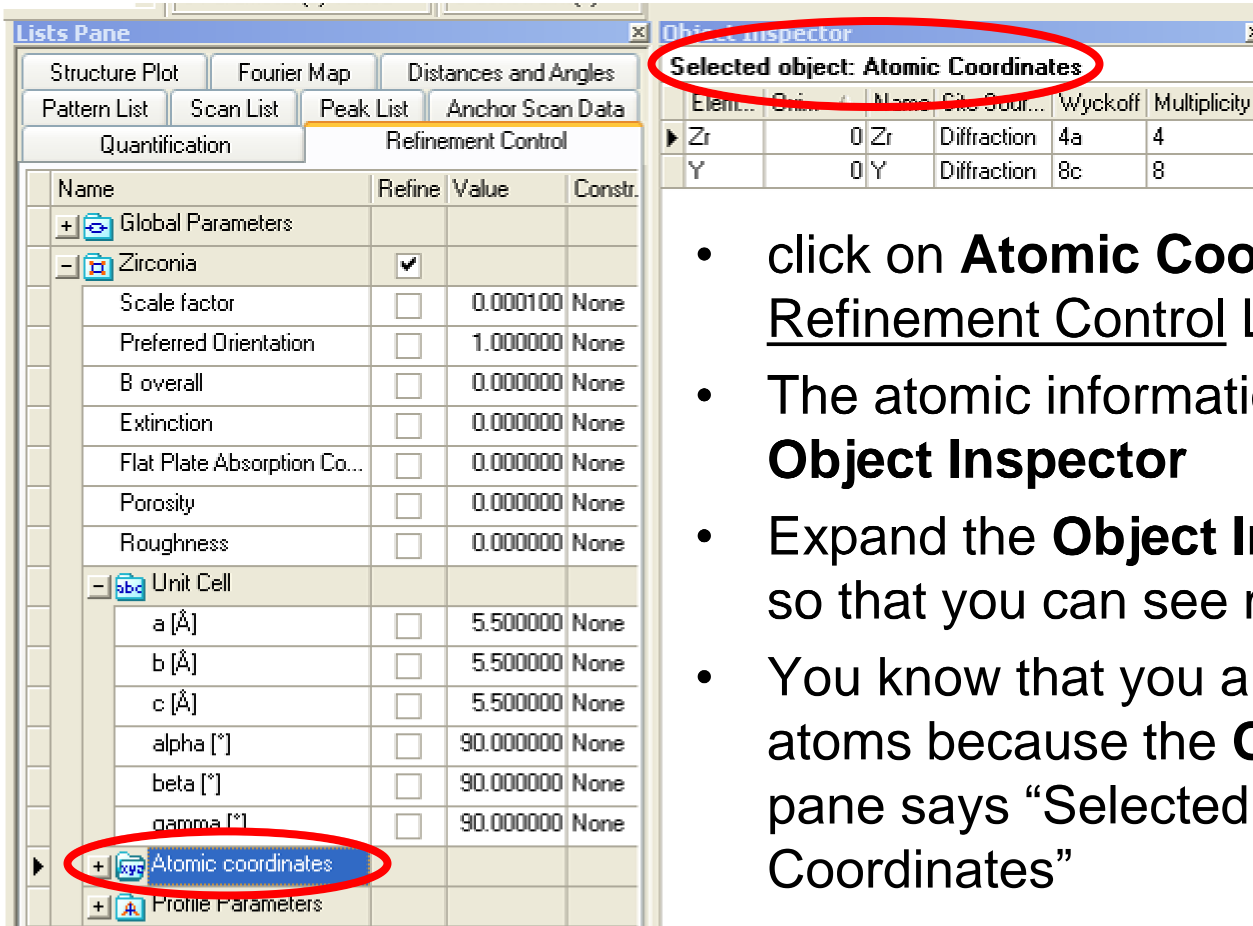
To change values for the simulation



- In the <u>Refinement Control</u>,
  - expand the **Zirconia** entry
  - Expand the **Unit Cell** entry
  - Change the **Unit Cell** value
    - After typing, you must press ‘Enter’ key to register the change
    - if you try recalculating the simulation without pressing enter, you may lose the changed value
- recalculate the diffraction pattern by clicking on “Start Pattern Simulation” button again
- change the lattice parameter and recalculate the pattern several times to get a feel for the relationship



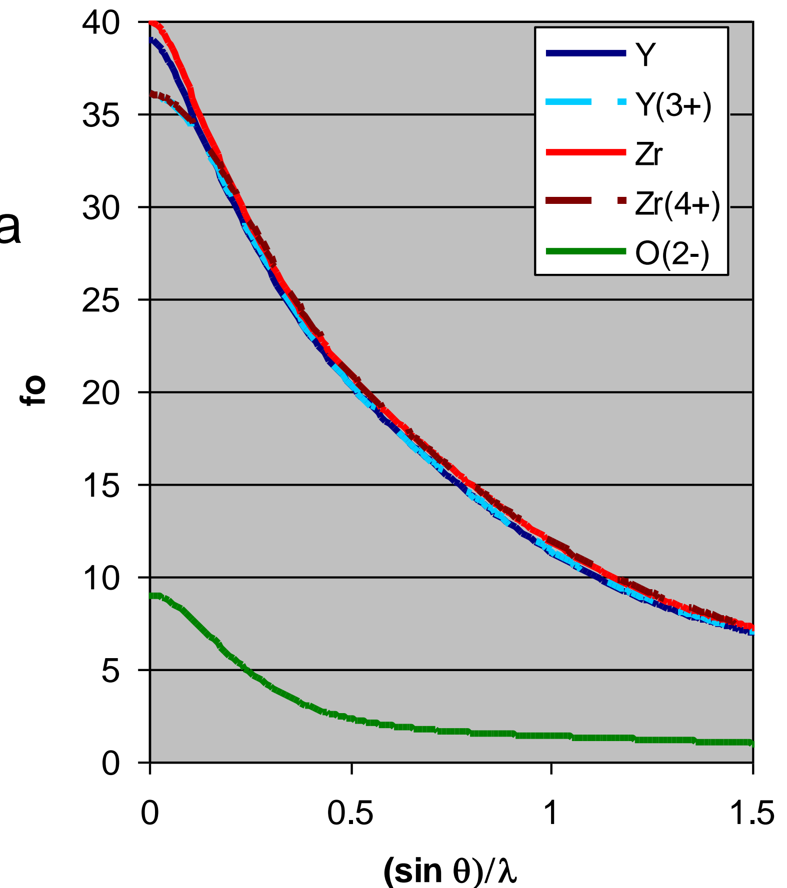
To change atom parameters



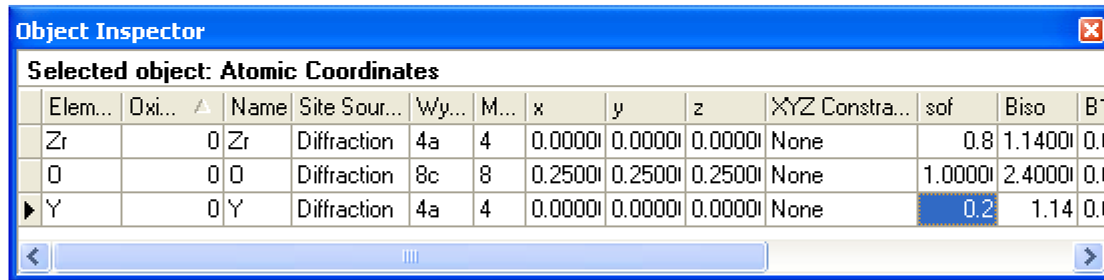
- click on **Atomic Coordinates** in the Refinement Control List
- The atomic information appears in the **Object Inspector**
- Expand the **Object Inspector** window so that you can see more clearly
- You know that you are working with the atoms because the **Object Inspector** pane says “Selected Object: Atomic Coordinates”

Change the Site Occupancies (sof) for the atoms

- Changing the occupancy of Zr has a big effect
  - change the SOF of Zr to 0.5 and recalculate the pattern
- Changing the occupancy of O has a small effect
  - reset the SOF of Zr to 1.0 and change the SOF of O to 0.5, then recalculate the pattern
- Remember, the atomic scattering factor, f_0, is equal to the number of electrons around the atom
  - Zr atoms scatter much more strongly than O, so the XRD diffraction pattern is more sensitive to the Zr atoms



We can predict the change in peak intensities when we dope the sample



Object Inspector

Selected object: Atomic Coordinates

Elem...	Oxi...	Name	Site Sour...	Wy...	M...	x	y	z	XYZ Constra...	sof	Biso	B1
Zr	0	Zr	Diffraction	4a	4	0.0000	0.0000	0.0000	None	0.8	1.1400	0.0
O	0	O	Diffraction	8c	8	0.2500	0.2500	0.2500	None	1.0000	2.4000	0.0
Y	0	Y	Diffraction	4a	4	0.0000	0.0000	0.0000	None	0.2	1.14	0.0

- replace 20% Zr with Y
  - right click on the **Object Inspector** and select "**add new atom**"
  - To create the new atom, type "Y" for the Element
  - tab over to Wyckoff Site and type "4a" and enter
    - this automatically places the atom at 0,0,0
  - make the sof 0.2
  - make the Biso 1.14
  - make the sof for the Zr atom 0.8
  - This means that the 4a site is occupied by 80% Zr and 20%Y
  - recalculate the simulation
    - little change in intensity
- replace 20% Zr with Ce
  - change the atom type of Y to Ce and recalculate the simulation
- how could we quantify amount of Y doping in YSZ?

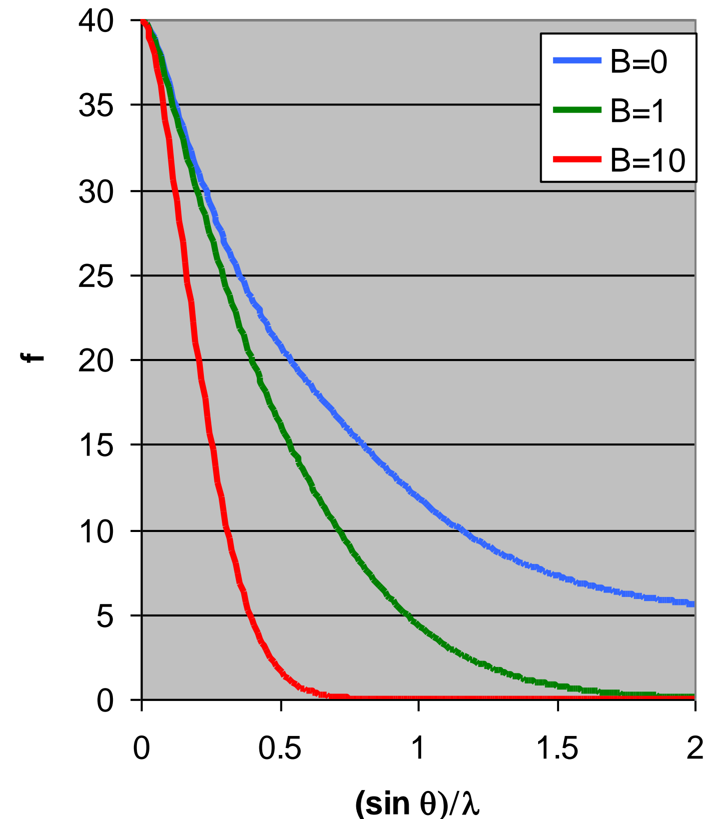
In substitutional doping, peak intensities and/or peak positions may change

- In a substitutionally doped material:
  - peak intensities will change depending on the difference between the number of electrons (and therefore scattering factor **f**) between the original and dopant ion
  - Peak positions will change depending on the difference between the size of the original and dopant ion
    - A difference in ionic radii will produce a change in the average interatomic distances and therefore a change in the unit cell lattice parameter
    - This change cannot be *predicted* by Rietveld modeling; it requires empirical calibration or advanced ab-initio computer simulation.

- Y is significantly larger than Zr
  - The ionic radius for Y is 1.019
  - The ionic radius for Zr is 0.84
  - The relationship between Y content and lattice parameter in YSZ has been empirically determined from known standards
  - The amount of Y in YSZ can be determined by calculating the lattice parameter of the unknown specimen

The thermal parameter, Biso, changes how scattering efficiency changes with as a function of (sin θ)/λ

- change thermal parameter for Zr
  - reset the SOF of Zr to 1 and the SOF of the other 4a atom (Ce or Y) to 0
    - the diffraction pattern will be representative of ZrO_2 with no doping
  - change Biso and recalculate the diffraction pattern
    - change from 1.14 to 2.3
    - change to 5
    - change to 0.1



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

These simulations do not necessarily represent the data that your diffractometer will produce

- There are more factors that contribute to the diffraction pattern that you collect with an instrument

- Some factors are calculated from fundamental equations
  - The simulations automatically account for:
    - multiplicity
    - $K\alpha 2$ radiation
    - Lorentz polarization factor

- Some factors are approximated using empirical formulas
  - The diffraction peak width and shape is a product of the diffractometer optics, sample preparation, and the specimen microstructure
  - Diffraction peak widths and shapes in these simulations have been calculated using default parameters in an empirical formula
    - Some software attempts to model the instrument contribution to peak width and shape using “Fundamental Parameters”. This is not yet implemented in HighScore Plus.

Other Things that effect intensity

$$I_K = S M_K L_K |F_K|^2 P_K A_K E_K$$

- S is an arbitrary scale factor
  - used to adjust the relative contribution of individual phases to the overall diffraction pattern
- M is the multiplicity of the reflection
  - accounts for the fact that some observed diffraction peaks are acutally the product of multiple equivalent planes diffracting at the same position 2theta (for example, (001) (100) (010) etc in cubic)
  - automatically calculated based on the crystal structure
- L is the Lorentz polarization factor
- P is the modification of intensity due to preferred orientation
- A is absorption correction
- E is extinction correction
- F is structure factor, which is the amplitude of scattered light due to the crystal structure (already discussed)

The Lorentz polarization factor corrects for several effects

- The Lorentz factor
  - Different planes remain in the diffracting condition over a different angular range
  - high angle planes remain in the diffracting position longer, increasing their apparent intensity
  - $1/\sin^2\theta\cos\theta$ relationship for Bragg-Brentano
  - varies with geometry of the diffractometer
- Polarization
  - Scattering of light by the atom polarizes the X-rays
  - this causes the scattered intensity to vary as $1+\cos^2(2\theta)/2$
- Monochromator Polarization
  - The monochromator uses diffraction from a crystal to remove unwanted wavelengths of radiation.
  - This diffraction will also polarize the X-ray beam, causing intensity to vary as $\cos^2(2\theta)$
    - POL is the correction factor for the monochromator

    - the correct POL value can be found in HSP Help
      - go to the Help Index, type in POL, and the first option describes the Lorentz polarization factor

$$Lp = \frac{1 + POL\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

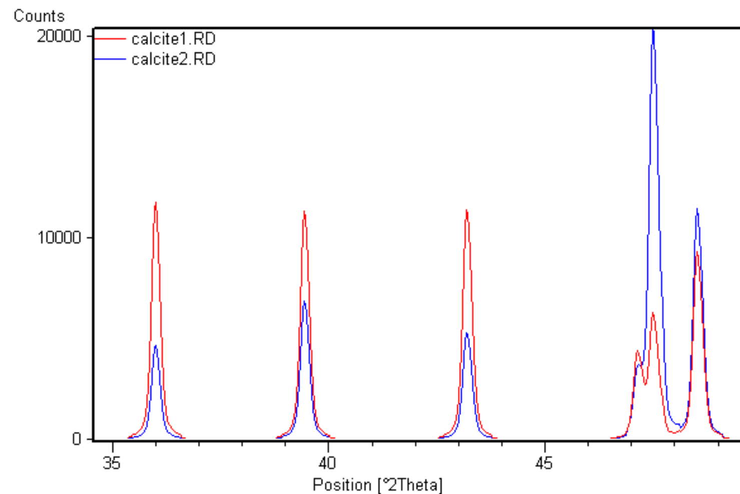
Monochromator	POL
K-beta Filter	1
Cu diffracted beam graphite (point detector)	0.8
Cu X’Celerator	1.25
Cr diffracted beam (point detector)	0.588

Setting the Polarization Correction Coefficient, POL, for your simulation

- in the <u>Refinement Control</u> list, click on Global Parameters
- The Global Parameters will show up in the Object Inspector
- In the "**General Properties**" expansion of the Object Inspector, you can set the **Polarization Correction Coefficient** (POL)

Modeling Preferred Orientation

- The default calculation assumes that there are an equal number of crystallites contributing to every diffraction peak
  - the orientation of the crystallites is random and there are a statistically relevant number of grains
- preferred crystallographic orientation produces a non-random distribution in the orientation of the crystallites
  - the observed diffraction peak intensities will vary systematically



The March distribution function empirically models the preferred orientation effect

- The March distribution function is a model for fitting preferred orientation of cylinder or needle shaped crystals.

$$P_k = \left(r^2 \cos^2 \alpha_k + r^{-1} \sin^2 \alpha_k \right)^{-3/2}$$

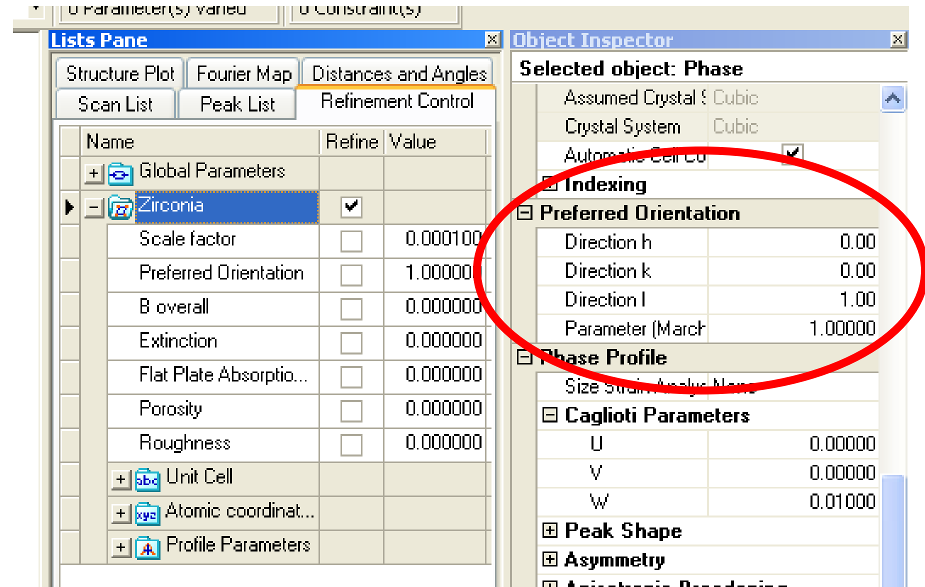
α_k is the angle between the preferred orientation vector and the normal to the planes generating the diffracted peak

r is a refinable parameter in the Rietveld method

- There are other models for Preferred Orientation, such as spherical harmonics
  - The spherical harmonics model will be added in HighScore Plus v4

Modeling Preferred Orientation in HSP

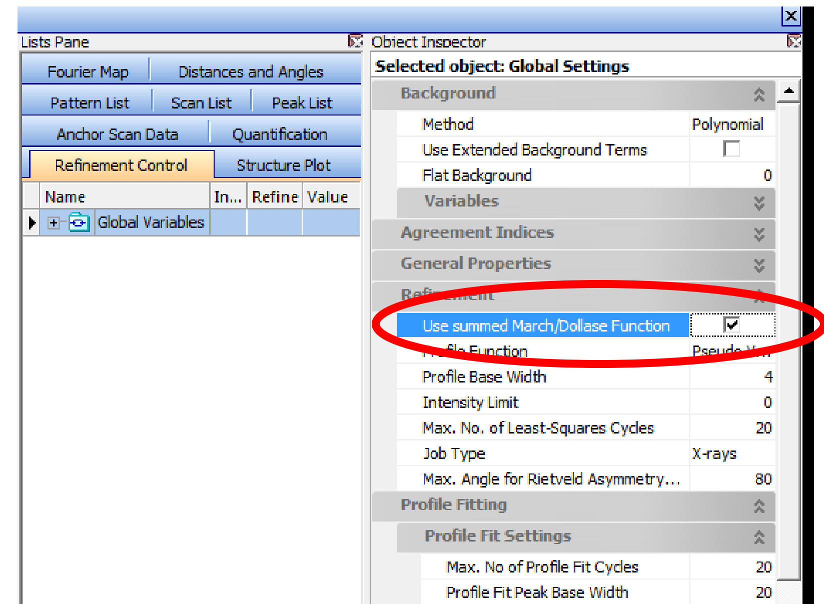
- In the <u>Refinement Control</u> list, click on the phase that has preferred orientation
- In the Object Inspector, expand the **Preferred Orientation** settings
  - set the h,k, and l directions to represent the [hkl] of the preferred orientation



  - set the Preferred Orientation parameter
    - this parameter is found in the Object Inspector as "**Parameter (March/Dollase)**"
    - this parameter is also found in the <u>Refinement Control</u> List as "**Preferred Orientation**"
    - 1 means the orientation of [hkl] is completely random
    - <1 means that the [hkl] direction is the preferred orientation of the crystallites
    - >1 means that the [hkl] direction is preferentially avoided
- recalculate the simulation to observe the change in peak intensities

Modeling Preferred Orientation in HSP

- For high symmetry phases, you should enable the “Summed March/Dollase function”
- In the Refinement Control list, click on Global Parameters
- In the Object Inspector, scroll to the Refinement settings
- Check the option “Use summed March/Dollase function”



Additional Intensity Factors

- Absorption Correction
  - accounts for the transmission and absorption of the X-rays through the irradiated volume of the sample.
  - depends on sample geometry: flat plate or cylindrical
  - depends on the mass absorption coefficient of the sample
    - significant for cylindrical or transmission samples with a high sample absorption
    - significant for a flat plate sample with a low sample absorption
- Extinction Correction
  - Secondary diffraction of scattered X-rays in a large perfect crystal can decrease the observed intensity of the most intense peaks
  - scattering by uppermost grains limits the penetration depth of a majority of X-rays, causing a smaller irradiated volume
  - want “ideally imperfect” crystals– grains with enough mosaicity to limit extinction
  - better to reduce extinction by grinding the powder to a finer size
- These two corrections are rarely used. Caution is advised. Always check to make sure that the correction values are physically meaningful.

We now know how to calculate the diffraction peak intensity, but there a couple of more factors involved in simulating real diffraction data

- The intensity, Y_{ic}, of each individual data point *i* is calculated using the equation:

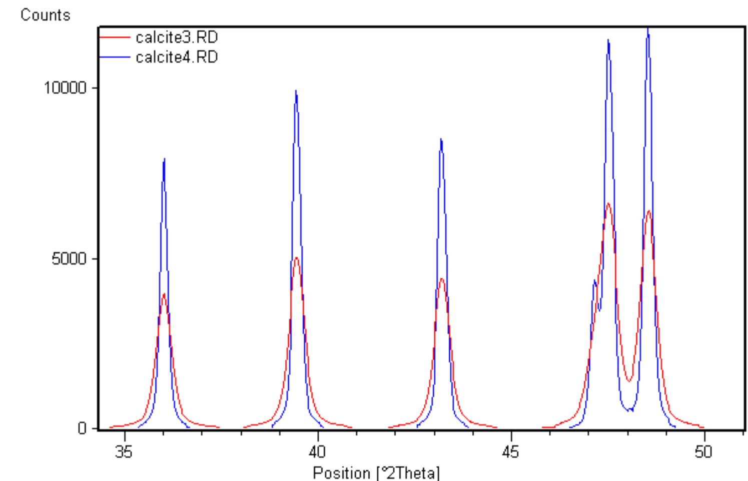
$$Y_{ic} = Y_{ib} + \sum_{k=k1}^{k2} G_{ik} I_k$$

- We already know how to calculate I_K, the intensity of the Bragg diffraction peak k: $I_K = SM_K L_K |F_K|^2 P_K A_K E_K$
- Y_{ib} is the intensity of the background at point *i* in the pattern
- k1 - k2 are the reflections contributing to data point *i* in the pattern
  - sometimes multiple Bragg diffraction peaks overlap, resulting in multiple contributions to the observed intensity at a single data point
- G_{ik} is the peak profile function
  - this describes how the intensity of the diffraction peak is distributed over a range of 2theta rather than at a single point
  - this profile is due to instrument broadening, sample broadening, etc

Diffraction peaks have profiles that must be empirically modeled

- The intensity equation I_k predicts that diffraction peak intensity occurs at a single point 2theta– but in reality the diffraction peak intensity is spread out over a range of 2theta
  - The total area of the diffraction peak profile is the predicted intensity I_k
- Diffractometers contribute a characteristic broadening and shape to the diffraction peak based on their optics and geometry
  - each separate combination of divergence slit apertures, Soller slits, beta filter or monochromators, and detectors will have their own characteristic instrument profile

- Sample attributes also contribute to the diffraction peak shape and width
  - mass absorption coefficient (sample transparency)
  - sample thickness
  - crystallite size
  - microstrain
  - defect concentration



Profile Parameters

- Rietveld refinement assumes that peak profiles vary systematically as a function of 2theta
- Peak profile may also vary according to crystallographic direction [hkl]

Name	Refine	Value
+ Global Parameters		
− Zirconia	☑	
Scale factor	☐	0.000100
Preferred Orientation	☐	1.000000
B overall	☐	0.000000
Extinction	☐	0.000000
Flat Plate Absorption Corre...	☐	0.000000
Porosity	☐	0.000000
Roughness	☐	0.000000
+ Unit Cell		
+ Atomic coordinates		
− Profile Parameters		
U	☐	0.000000
V	☐	0.000000
W	☐	0.010000
Anisotropic Broadening	☐	0.000000
Asymmetry (Rietveld)	☐	0.000000
Peak Shape 1	☐	0.600000
Peak Shape 2	☐	0.000000
Peak Shape 3	☐	0.000000

Peak Width (U, V, W)

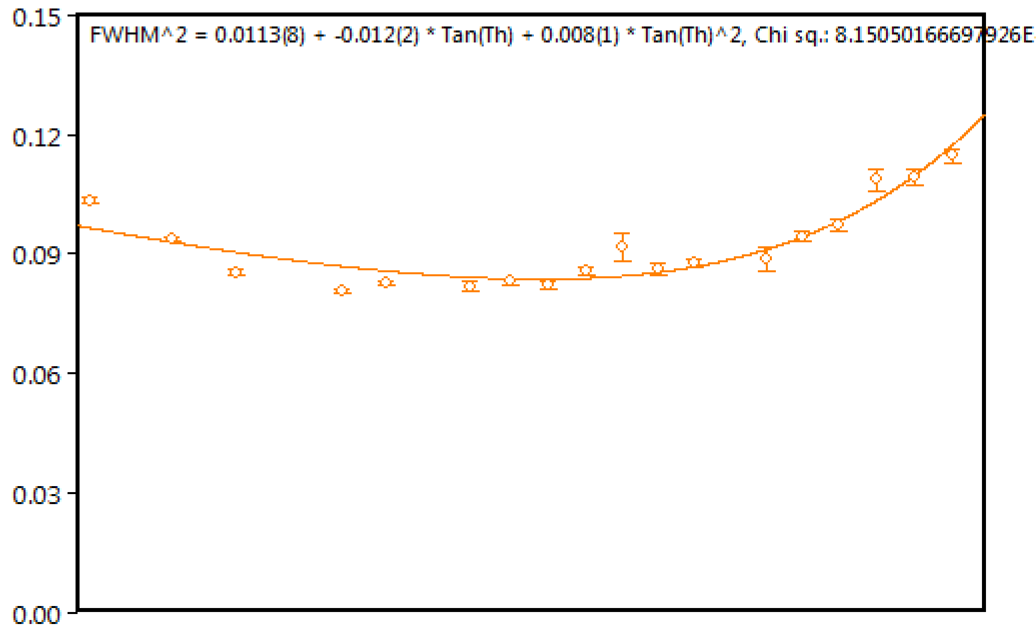
Peak Shape (Asymmetry (Rietveld), Peak Shape 1–3)

The Cagliotti equation describes how peak width varies with 2theta

$$H_k = \left(U \tan^2\theta + V \tan\theta + W\right)^{1/2}$$

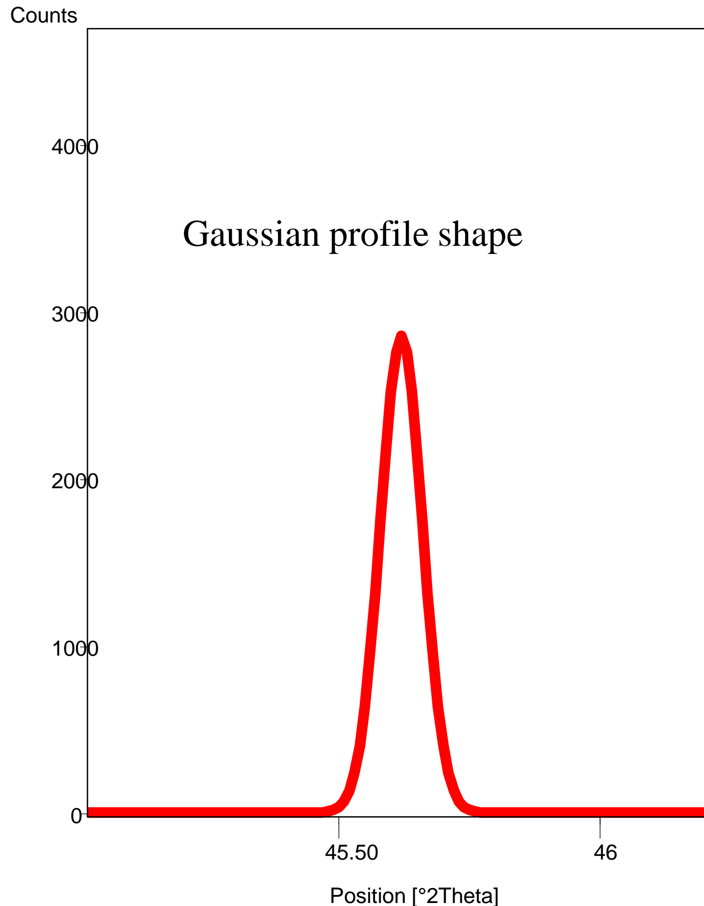
- H_k is the Cagliotti function where U, V and W are refinable parameters
- HSP treats the Cagliotti equation as a convolution between instrument and sample broadening functions
- The change in U and W between an instrument profile standard (eg NIST 640c) and your sample can indicate the amount of nanocrystallite size and microstrain broadening

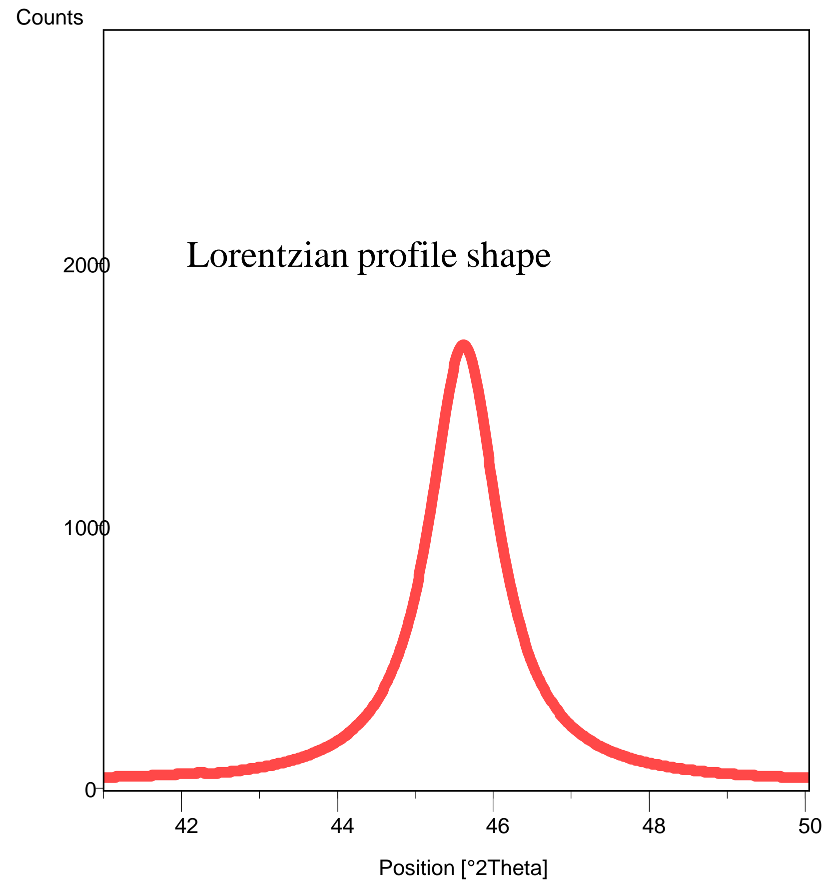
The systematic variation of peak width with 2theta



- For a standard Bragg-Brentano diffractometer
  - U and W will be positive
  - V will be negative
- This trend may vary for data collected with parallel beam, GIXD, and capillary geometries

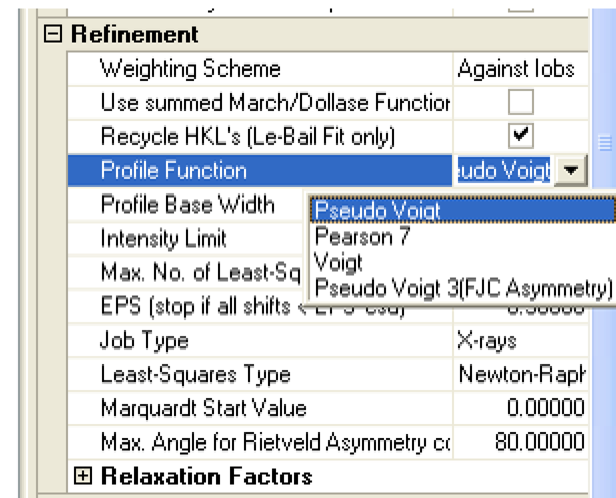
Diffraction Peaks from laboratory diffractometers are a mixture of Gaussian and Lorentzian profiles





Several different functions can be used to describe the mixing of Gaussian and Lorentzian contributions

- The profile function is set in the Object Inspector for Global Parameters (found in Refinement Control list)
  - the same profile function is used for all phases in a single pattern
  - Pseudo Voigt and Pearson VII are the most commonly used
  - Pseudo Voigt
  - Pseudo Voigt with FJC Asymmetry correction
  - Pearson VII
  - Voigt



The Pseudo Voigt equation uses up to 3 parameters to describe Gaussian and Lorentzian components

$$G_{jk} = \gamma \frac{2}{H_k \pi}\left[1 + 4X_{jk}^2\right]^{-1} + \left(1-\gamma\right)\frac{C_1^{1/2}}{H_k \pi^{1/2}} \exp\left[-C_1 X_{jk}^2\right]$$

$$\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_3 \left(2\theta\right)^2$$

- The parameters γ_1, γ_2, and γ_3 are the refinable shape parameters, listed as Peak Shape 1, Peak Shape 2, and Peak Shape 3 in the Refinement Control list
  - Usually Peak Shape 1 is the only one used
- H_k is the Cagliotti peak width function
- C_1 is 4 ln 2
- X_{kj} is $X_{jk} = \frac{\left(2\theta_i - 2\theta_k\right)}{H_k}$

Background can be empirically fit with an equation, manually fit, or evaluated with a blank sample

- refinement of a polynomial function
- refinement using a type I or II Chebyshev polynomial function
- By amorphous sinc function
- linear interpolation between base points
- independent data collection run without the sample in place
  - It is difficult to use this technique effectively– it requires careful evaluation of the validity of the background fit

Lists Pane

Pattern List | Scan List | Peak List | Anchor Scan Data | Quantification
Refinement Control | Structure Plot | Fourier Map | Distances and Angles

Name	Refine	Value	Constr...	Maximum	Minimum	Use Mi.
Global Parameters						
Zero Shift [°2Theta]		0.000000	None	0.000000	0.000000	
Specimen Displacement...		0.000000	None	0.000000	0.000000	
Wavelength [Å]		1.789010	None	0.000000	0.000000	
Background Polyno...						
Flat background		0.000000	None	0.000000	0.000000	
Coefficient 1		0.000000	None	0.000000	0.000000	
Coefficient 2		0.000000	None	0.000000	0.000000	
Coefficient 3		0.000000	None	0.000000	0.000000	
Coefficient 4		0.000000	None	0.000000	0.000000	
1/X Background		0.000000	None	0.000000	0.000000	

Object Inspector

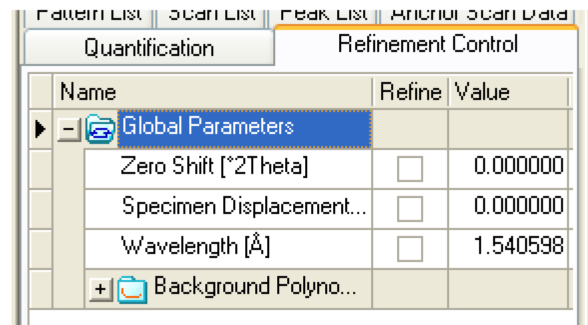
Selected object: Global Parameters

Property	Value
Background	
Method	Polynomial
Use Extended Background Terms	
Flat Background	
Coefficients	
Coefficient 1	
Coefficient 2	
Coefficient 3	
Coefficient 4	0.0000000
1/X Background	0.0000000
Agreement Indices	
R expected	0.00000
R profile	0.00000
Weighted R profile	0.00000
D-statistics	0.00000

Method options: Polynomial; Use available background; Basepoints; Chebyshev I; Chebyshev II; Shifted Chebyshev I; Shifted Chebyshev II

Systematic error in diffraction peak positions can also be calculated

- The systematic error functions are found in Global Parameters
- They apply to all phases in the sample
  - zero shift
  - specimen displacement



The Parameters of a Pattern Simulation

- Global parameters affect the entire sample rather than individual phases
  - Background function
  - Zero Shift
  - Specimen Displacement
  - POL (Lorentz polarization factor)
  - Sample Geometry
  - selecting the Profile Function
- Other parameters are set individually for each phase
  - scale factor
  - preferred orientation (March-Dollase function)
  - unit cell
  - atomic parameters are for each atom in the phase
    - position, SOF, thermal parameter
  - Peak Profile parameters
    - Cagliotti peak width function parameters U,V, and W
    - Profile shape parameters
    - peak asymmetry profile
    - anisotropic broadening function

What is Physically Meaningful?

Wel (1975)

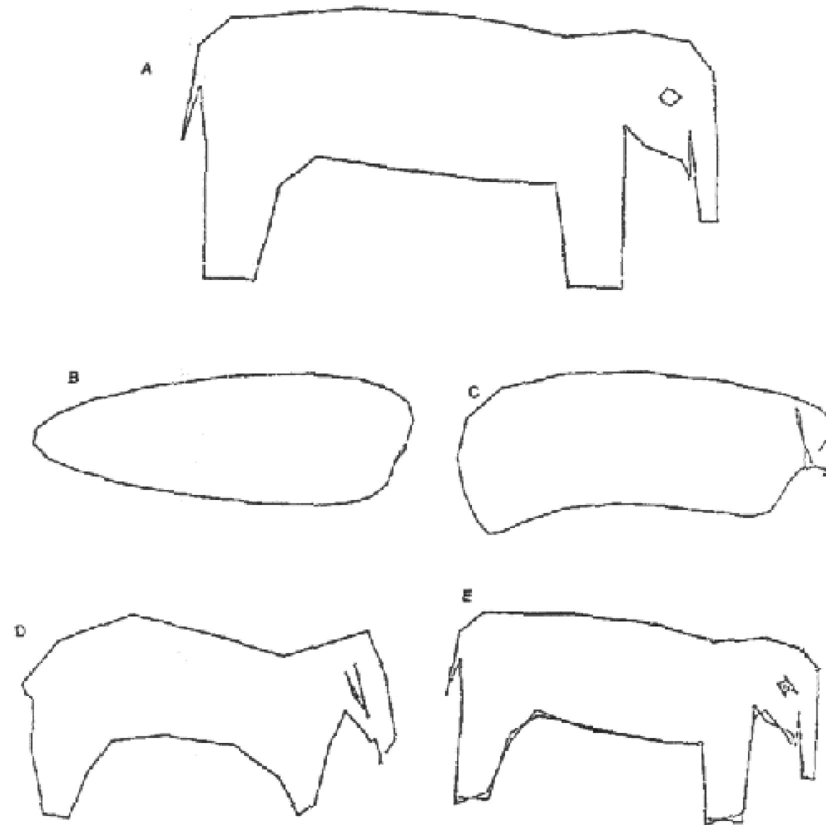


FIGURE 1.2. "How many parameters does does it take to fit an elephant?" was answered by Wel (1975). He started with an idealized drawing (A) defined by 36 points and used least squares Fourier sine series fits of the form $x(t) = \alpha_0 + \sum \alpha_i \sin(it\pi/36)$ and $y(t) = \beta_0 + \sum \beta_i \sin(it\pi/36)$ for $i = 1, \ldots, N$. He examined fits for $K = 5, 10, 20$, and 30 (shown in B–E) and stopped with the fit of a 30 term model. He concluded that the 30-term model "may not satisfy the third-grade art teacher, but would carry most chemical engineers into preliminary design."